

**ASSESSING THE POTENTIAL OF MODIFIED RICE HUSK-BASED SILICA  
ADSORBENT FOR THE REMOVAL OF ATRAZINE FROM WASTEWATER**

**BY**

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**DECLARATION**

I, **CWEKE PATRICK** hereby declare that the dissertation titled “*ASSESSING THE POTENTIAL OF MODIFIED RICE HUSK-BASED SILICA ADSORBENT FOR THE REMOVAL OF ATRAZINE FROM WASTEWATER*” is my original work and has not been submitted to any other university.

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## APPROVAL

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## **DEDICATION**

With appreciation, I dedicate this work to my Mother Mrs. Margret Rwoomu for every moral support and unending love that she graced me throughout my studies.

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## LIST OF ABBREVIATION

ANOVA	Analysis of variance
ATR	Attenuated total reflectance
Ce	Equilibrium Concentration
CE	Capillary Electrophoresis
Co	Initial Concentration
df	Degree of freedom
EC	Electrical conductivity
EDS	Energy Dispersive X-ray Spectroscopy
FTIR	Fourier Transform Infra-Red
g	gram
GC	Gas Chromatography
HM	Heavy metals
HPLC	High Performance Liquid Chromatography
HV	High vacuum
LOD	Loss On Drying
M	Mass
mg	Milligram
Mg g <sup>-1</sup>	Milligram per gram
Mg L <sup>-1</sup>	Milligram per litre
mL	Milliliter
MOFs	Metal-organic frameworks
MolL <sup>-1</sup>	Moles per litre
MS	Mass Spectrometry
NaOH	Sodium Hydroxide
NDP	National Development Plan

NMRS	Nuclear Magnetic Resonance spectroscopy
°C	Degrees centigrade
pH	Hydrogen Potential
PPM	Parts per million
PSO	Pseudo-second order
PZC	Point of zero charge
$q_e$	Amount adsorbed at equilibrium
$q_t$	Amount Adsorbed at equilibrium time
RHA	Rice husk adsorbent
SBAC	Sludge-based activated carbon
SDG	Sustainable Development Goals
SS	Sum of squares
SD	Standard Deviation
TDS	Total dissolved solids
UPLC	Ultra-Performance Liquid Chromatography
UV	Ultra-violent
V	Volume
VOC	Volatile organic compounds

## ABSTRACT

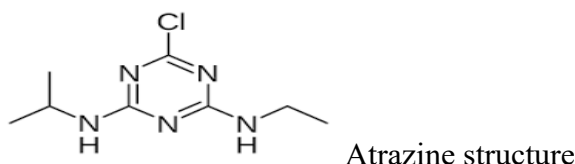
Atrazine (6-chloro-N<sub>2</sub>-ethyl-N<sub>4</sub>-isopropyl-1,3,5-triazine-2,4-diamine) or (2-chloro-4-(ethylamino)-6-(isopropylamino)-1,3,5-triazine) is a very common herbicide used on large scale farming to control weeds by farmers and it must be removed from the wastewater because of the serious harm it causes to the environment and its health risk to human. This research aimed at the use of modified rice husk derived silica adsorbent from waste agricultural biomass for atrazine removal from wastewater. The adsorbent was made by the process of pyrolysis, chemically activated with 7.5% Potassium Hydroxide. The characterisation results by the Scanning Electron Microscopy (SEM) and Fourier Transform Infrared (FTIR) spectroscopy showed that the modified rice husk-based silica adsorbent has good pore structure, oxygen containing functional groups and silica properties. The influence of contact time, adsorbent dosage, initial concentration and pH were investigated by use of a UV-Vis spectroscopy analysis. The adsorption studies were conducted in batch mode, and the results showed that the modified rice husk-based silica adsorbent exhibited high adsorption capacity for atrazine. The adsorption data were fit to several isotherm models such as Langmuir and Freundlich, and kinetic models such as pseudo-first order and pseudo-second-order reactions. The experiments showed that the adsorption process obeyed the Freundlich isotherm and pseudo-second order kinetic model, which means it followed a multi-layer adsorption mechanism and chemisorption which showed sharing of electrons between the adsorbate and the adsorbent. The highest adsorption capacity obtained was 702 mgg<sup>-1</sup>, which is like other reported adsorbents in the literature. The adsorbent was also discovered to be recyclable, suffering only a small decrement in adsorption capacity after five adsorption-desorption cycles. UV-visible spectrophotometer analysis confirmed the efficient removal of atrazine from wastewater using the modified rice husk-based silica adsorbent. In general, this research shows that the modified rice husk-based derived silica adsorbent can be used as a cheap and environmentally friendly material for the removal of atrazine from wastewater.

## CHAPTER ONE

### INTRODUCTION

#### 1.1 Background

Atrazine is a widely used herbicide that controls broadleaf and grassy weeds in crops like corn, sorghum, and sugarcane, it's a synthetic compound, manufactured through chemical processes (It's not naturally occurring). Atrazine belongs to the triazine class of herbicides, Triazines are a group of chemicals that inhibit photosynthesis and are commonly used for weed control in agriculture (Zhang *et al.*, 2004).



Atrazine is a notable example of a widely utilized pesticide in the world for preventing and controlling pre and post-emergence weeds within crops (Jiang *et al.*, 2020). Still even at minimal amounts, atrazine has the potential influence to the endocrine, immune, and central nervous systems (Lin *et al.*, 2019). In particular, atrazine is an extensively used pesticide in agricultural crops such as corn, sorghum, and sugarcane crops additionally, it works well in suppressing weeds (Jiang *et al.*, 2020). Due to its low mobility, lengthy half-life, good chemical stability and strong leaching potential, it is regarded as harmful to aquatic species, plants, and humans (Zhang *et al.*, 2004).

Atrazine is a triazine herbicide with the chemical formula  $C_8H_{14}ClN_5$ . Its mode of action is by inhibiting photosynthesis in plants by binding to the D1 protein in photosystem II, disrupting electron transport and ultimately leading to plant death. It is selective for certain crops like corn, sorghum, and sugarcane, allowing them to grow while controlling (Pathak *et al.* 2022).

broadleaf and grassy weeds. Atrazine can persist in soil and water, leading to potential environmental concerns with high solubility where its moderately soluble in water, which can contribute to its mobility in the environment and atrazine has been linked to potential health and environmental risks, including endocrine disruption and aquatic ecosystem impacts (Mohan *et al.*, 2014). In weeds, atrazine inhibits photosynthesis in weeds by blocking electron transport in photosystem II, ultimately leading to plant death. It's selective for certain crops, allowing them to grow while controlling weed growth (Jiang *et al.*, 2020).

Aquatic life, atrazine can contaminate water bodies through runoff, affecting aquatic organisms. It disrupts the endocrine systems in amphibians and fish, impacting development and reproduction thereby alter community composition and biodiversity in aquatic ecosystems (Zhang *et al.*, 2004). In humans, exposure to atrazine has raised concerns about potential health effects, including the endocrine disruption, potentially affecting reproductive and developmental health (Lin *et al.*, 2019). And in animals, atrazine exposure can lead to reproductive issues such as reduced fertility and altered hormone levels and developmental abnormalities in some species (Lin *et al.*, 2019).

As a result, methods for atrazine removal are required to satisfy environmental quality standards. The low efficiency and high prices of conventional removal techniques are two of their unfavorable traits (Mohan *et al.*, 2014). The popular herbicides, fungicides, and insecticides, fall under the category of pesticides, when used in the field. These chemical occurrences in the soil will be carried off by the rains and end up into non-target areas where they may destroy non-target organisms (such as water living organisms like fish) (Leu *et al.*, 2004). In traditional farming within the world, artificial herbicides are employed globally in farming to manage pests. Herbicides end up on water surface in a dry spell due to improper handling before, during, and after application (Rother, 2018). Additionally, most African nations employ a variety of insecticides. Even some banned pesticides are nevertheless used

because of a lack of control or illicit operations. Statistics for instance, suggest Tanzania and Kenya may still be using most organochlorine pesticides (Olisah *et al.*, 2020). It has been reported that there is a considerable rise in price of herbicides entering Uganda in the previous years (Andersson & Isgren, 2021). Uganda farmers frequently buy pesticides from unofficial, frequently uncertified providers who, in most cases, do not provide instructions on how to handle pesticides properly (Andersson & Isgren, 2021). If pesticide use on agricultural crops is considered, it may not be possible to completely understand pesticide exposure to water bodies. This finding shows, to reduce environmental damage by pesticide usage (material laying and clearing), a more comprehensive understanding of pesticide origin and movement channels are required (Ngabirano & Birungi, 2022).

Utilizing rice husks for the synthesis of silica adsorbents aligns with the principles of green chemistry and sustainability. This approach not only addresses the issue of agricultural waste management but also provides an economical solution for water treatment. The development of efficient adsorbents for atrazine removal could significantly reduce the environmental and health risks associated with pesticide contamination in water sources (Ngabirano & Birungi, 2022). A comprehensive review on the potential of RH and RHA as sources of amorphous silica, the abundance of these materials in rice-producing countries and their applications in ceramics and nanocomposites. However, they emphasize that optimal processing conditions for maximizing silica yield and purity remain inadequately understood. This gap is critical as it influences the applicability of RH/RHA in industrial settings (Rodriguez-Otero *et al.* 2023).

Similarly, Siqueira, (2023) discuss the broader context of agricultural waste fibres, including RH, as raw materials for various industries. They indicate that while agricultural wastes can substitute synthetic fibres, targeted studies on the unique properties of rice husk-derived silica compared to other agricultural residues are lacking. This highlights the necessity for research

that focuses on the specific benefits of rice husk-derived silica in composite materials, particularly for performance enhancements. An alternative, sustainable approach involves utilizing agricultural by-products, such as rice husks, as a source of silica. Rice husks, an abundant agricultural waste, are rich in silica content and provide a cost-effective and eco-friendly raw material for the synthesis of silica adsorbents and rice belongs to the Poaceae family, also known as the grass family (Okoro *et al.*, 2022).

## **1.2 Statement of the problem**

Atrazine is an herbicide used to control and prevent weeds. Its application is widely done in sugar, sorghum, sorghum, maize, and many other plantations across the globe. However, even at low concentrations because of its low mobility, lengthy half-life, high leaching potential, and high chemical stability in soil and flowing rivers, this makes it more detrimental to aquatic species, plants, and humans. In humans, atrazine has a potential influence on the endocrine system by disrupting its functions which involve disruption, interactions with hormone receptors, metabolic enzymes, and transport proteins of cell signaling processes. Nonetheless, farmers continue with its usage due to its efficiency in preventing weeds but the need to safeguard the environment and its inhabitants from this herbicide is fundamental. The available conventional methods used to remove atrazine such as advanced oxidation are often so expensive. Therefore, there is a need for the development of cheaper methods. This study aimed at developing a cheap adsorbent from rice husk for simultaneous cleanup of atrazine from wastewater.

## **1.3 Objectives**

### **1.3.1 General objective**

To assess the potential of modified rice husk – based silica adsorbent for the removal of atrazine from wastewater

### 1.3.2 Specific objectives

- i). To characterize the modified rice husk-based silica adsorbents.
- ii). To evaluate the efficiency of the modified adsorbent for atrazine removal from simulated wastewater.
- iii). To determine the adsorption kinetics of atrazine on the modified rice husk-based silica adsorbents.

### 1.4 Justification of the study

Among the most extensively utilized and long-lasting herbicides in the world is atrazine, also known as 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (Colborn & Short, 1999). The metabolites of atrazine have seriously contaminated groundwater and surface waters through leaching (Bhatti *et al.*, 2022). According to Lasserre *et al.*, (2009), atrazine can have adverse effects on the immunological, endocrine, and central neurological systems. The reproductive systems of frogs, fish, and other species may be dramatically harmed by it, and they may also be dangerous to human health (Langerveld *et al.*, 2009). ATR (Attenuated Total Reflectance) has been found in urine samples, which has confirmed human exposure (Curwin *et al.*, 2007). Interestingly, consumption of more than two cups of unfiltered water per day was linked to a higher chance of irregular menstrual periods in women with elevated ATR levels in the drinking water in Illinois, as compared to women in Vermont (a low ATR-using state) (Cragin *et al.*, 2011). According to Hayes. (2005), atrazine has detrimental effects on the development, metabolism, immune system, and sexual differentiation of fish and frogs. Cragin *et al.*( 2011) conducted a microarray investigation of tadpoles chronically exposed to 400 ppb atrazine from hatching to the peak of metamorphosis to better understand how atrazine interacts with the organism at the level of gene expression (Langerveld *et al.*, 2009).The survival, growth, and development of the larvae were impacted by the atrazine treatment. Both male and female tadpoles had less fat on their bodies.

### **1.5 Significance of the study**

The synthesis and application of a rice husk-based silica adsorbent for atrazine removal directly supports several sustainable development goals (SDGs) through cleaning water and sanitation thereby improving water quality by reducing pollution, eliminating dumping, and minimizing release of hazardous chemicals through using a locally sourced, eco-friendly adsorbent ensures safe removal of atrazine a persistent herbicide contaminant from wastewater, thus contributing to improved water quality.

Through a responsible consumption and production, the modified rice husk-based will substantially reduce waste generation through prevention, reduction, recycling, and reuse. The conversion of rice husk, an agricultural by-product often considered waste, into a high-value adsorbent adds value to biomass resources and promotes a circular economy, also the use of the modified adsorbent will strengthen resilience and adaptive capacity to climate-related hazards. Therefore, the valorisation of rice husks reduces open field burning, a common practice that contributes to greenhouse gas emissions. Utilizing the waste in water treatment supports mitigation of climate impacts. The findings for this research will promote good health and well-being, industry innovation, and infrastructure by substantially reducing the number of deaths and illnesses from hazardous chemicals and air, water, and soil pollution by removing atrazine from drinking and irrigation water, the adsorbent reduces exposure to carcinogenic and endocrine-disrupting chemicals, thereby improving community health and also enhance scientific research and upgrade technological capabilities of industrial sectors through developing low-cost, innovative, and scalable adsorbent technologies builds local scientific and industrial capacity in environmental remediation.

In alignment with Uganda's national development plan IV (NDP IV) Targets (2025-2030), where Uganda's NDP IV focuses on industrialization for inclusive growth, sustainable development, and improved quality of life, this project supports different areas of sustainable

industrialization and environmental stewardship, water resources management and pollution control, the conversion of rice husk waste into value-added silica aligns with NDP IV's emphasis on green manufacturing, waste recycling, and sustainable industrial inputs. NDP IV highlights the importance of pollution control in safeguarding water resources for domestic, agricultural, and industrial use. The application of the modified adsorbent directly addresses the need for affordable, scalable, and locally produced water treatment solutions.

### **1.6 Scope of the study**

The study focused on assessing the potential of modified rice husk-based silica adsorbent for the removal of atrazine from different samples of wastewater. The samples used for this research was spiked wastewater that was used to study the adsorption kinetics of atrazine on the modified rice husk-based silica adsorbent. The samples picked from flowing water streams of Lugazi sugar plantation located in Buikwe district where herbicides are used to control weeds. By use of sterilized and sealable containers, the samples were picked from three (3) different sampling sections, and three (3) samples were picked in each section making nine (9) samples and the three (3) samples in each were combined to make one (1) homogeneous sample in each section thereby making three analytical samples that were analysed and gave positive results of atrazine presence and then used for adsorption capacity determination.

The rice husk used were collected from SWT rice Kampala-ntinda industrial area and two kilograms (2 Kg) of rice husks were collected for experimental purpose. Preparation of the rice husks and carbonation by pyrolysis and base activation were done at Kyambogo University faculty of science laboratory, characterization, SEM-ESD were done in Makerere University laboratories, the FITR and batch adsorption experiments were carried out at Kampala Pharmaceutical Industries (1996) Ltd laboratories. The research study ran for a duration of 12 months (from August 2023 to July 2024).

## CHAPTER TWO

### LITERATURE REVIEW

#### **2.1 Physico-chemical properties of atrazine**

Atrazine is characterized by its chemical stability and hydrophilicity, which complicates its degradation in wastewater. The compound's low volatility and high solubility make it a persistent contaminant in surface and groundwater sources. Studies emphasize the need for advanced treatment methods to mitigate its environmental impact (Nadda *et al.*, 2024). The degradation of atrazine is particularly challenging due to its resistance to conventional wastewater treatment processes, necessitating innovative approaches to enhance removal efficiencies.

##### **2.1.1 Advanced oxidation processes (AOPs)**

A major focus in the literature is the application of advanced oxidation processes (AOPs) for atrazine degradation. Moreira *et al.* (2016) investigated solar photo-Fenton processes, demonstrating that atrazine can be degraded to below detection limits. This method utilizes solar energy to activate Fenton's reagent, producing hydroxyl radicals that effectively break down organic pollutants. The study highlights the importance of optimizing treatment conditions, such as pH and reactant concentrations, to improve degradation rates. Further reinforced the significance of AOPs, specifically ozone-based techniques, in enhancing atrazine removal from wastewater (Liu *et al.* 2021). The combination of ozone and hydrogen peroxide was shown to significantly improve degradation efficiency, underscoring the necessity of understanding the optimal conditions for these reactions. This aligns with the findings of Danfá *et al.* (2021) who explored the use of a highly porous TiO<sub>2</sub> ceramic photocatalyst, which enhanced the photocatalytic activity for atrazine degradation, emphasizing the role of material properties in optimizing wastewater treatment processes.

### **2.1.2 Electrochemical and biological treatment methods**

Electrochemical methods have also been explored as viable solutions for atrazine removal, the developed novel electro-Fenton system that significantly improved degradation rates across various pH levels. The use of sodium tetra-polyphosphate as an electrolyte facilitated the generation of reactive oxygen species, crucial for effective atrazine degradation. This study contributes to the understanding of how electrochemical processes can be optimized to manage atrazine contamination (Moreira *et al.* 2016). In addition to chemical methods, biological treatment approaches are gaining attention. Liu *et al.* (2021) demonstrated the effectiveness of a microbial consortium in biodegrading atrazine in an aquatic environment. The study emphasized the potential of biological systems to effectively treat atrazine, particularly when hydraulic retention times are optimized. This aligns with Ahmad *et al.* (2022) who further explored the role of biological treatments in removing atrazine from wastewater, reinforcing the importance of sustainable methods in managing this persistent contaminant

### **2.2 Ecological Impacts of atrazine**

Research illustrates that atrazine exposure poses serious risks to aquatic ecosystems. A study evaluating the toxicity of atrazine on freshwater fish, specifically *Channa punctatus*, indicated that exposure resulted in significant mortality rates and behavioural changes, which serve as critical indicators of ecological health (Nwani *et al.*, 2010). Furthermore, the study revealed that atrazine induces oxidative stress, evidenced by lipid peroxidation and alterations in antioxidant enzyme activities, which can lead to declines in fish populations and biodiversity (Afzal *et al.*, 2024). This oxidative stress not only disrupts individual health but can also result in cascading effects throughout aquatic food webs. Additionally, atrazine has been identified as one of the most frequently detected pesticides in streams across the United States, indicating widespread environmental exposure (Mueller *et al.*, 2017).

### **2.2.1 Health risks associated with atrazine**

The health risks associated with atrazine exposure, particularly prenatal exposure, have been a subject of concern. Chevrier *et al.* (2011) explored the relationship between urinary biomarkers of atrazine exposure and adverse birth outcomes in a cohort study. Their findings revealed quantifiable levels of atrazine and its metabolites in pregnant women, suggesting potential risks to fetal development. This research highlights a critical gap in understanding the long-term effects of prenatal atrazine exposure on human health. Furthermore, the study by García Espiñeira, (2018) indicated that while atrazine's toxicity has been documented, there remains a scarcity of epidemiological studies examining its effects in human populations, particularly among vulnerable groups such as pregnant women. This gap in the literature calls for more robust epidemiological investigations to elucidate the health effects of atrazine exposure.

The implications of atrazine exposure extend beyond ecological health, posing serious risks to human health through contaminated water supplies and bioaccumulation in the food chain. Research has indicated that atrazine exposure can lead to developmental and genetic alterations in aquatic organisms, with potential implications for human health, particularly through drinking water (He *et al.*, 2019). The endocrine-disruptive properties of atrazine have been well-documented, with studies highlighting its potential to interfere with neuroendocrine and reproductive system development (Chakraborty *et al.*, 2021). Such findings raise alarms regarding the safety of water sources and the potential long-term health effects of atrazine exposure on humans, particularly vulnerable populations such as children. Moreover, the correlation between nitrate contamination in groundwater and atrazine exposure underscores a significant public health concern. Elevated nitrate levels in drinking water can lead to serious health issues, similar to those posed by atrazine (Malik *et al.*, 2025). Both contaminants necessitate comprehensive monitoring and management strategies to ensure safe drinking water for communities.

### **2.2.2 Herbicide contamination in water bodies**

Herbicides, commonly known as weed killers, are substances used to control undesired plants, also known as weeds. Selective herbicides control specific weed species while leaving the desired crops relatively unharmed, while non-selective herbicides sometimes called "total weed killers" kill plants indiscriminately. The combined effects of herbicides, nitrogen fertilizer, and improved cultivars has increased yields per acre of major crops (Thanigaivel *et al.*, 2022). Herbicide contamination of water bodies has emerged as a pressing environmental concern due to its detrimental effects on ecosystems and public health. The widespread use of herbicides in agriculture, coupled with inadequate management practices, has led to significant pesticide residues in surface water and drinking water sources (Thanigaivel *et al.*, 2022). This literature review examines the current understanding of herbicide contamination, its pathways, and the associated health and environmental risks.

### **2.3 Atrazine levels in wastewater across Africa**

Recent studies have focused on the broader context of pharmaceutical and chemical pollutants, including atrazine, in African wastewater systems. Rodrigues *et al.* (2022) emphasize the global trend of pharmaceutical pollution in rivers, suggesting that atrazine, like other active pharmaceutical ingredients, can severely impact aquatic ecosystems. The study indicates that inadequate wastewater treatment facilities in many African countries contribute to elevated levels of these contaminants, including atrazine. Yarkwan, (2023) provide critical insights into wastewater production and treatment across countries, indicating that many African nations face challenges in efficient wastewater treatment. This inefficiency can lead to the accumulation of compounds like atrazine in surface water sources, exacerbating pollution levels. Verlicchi & Grillini, (2020) investigated the impact of wastewater on surface water quality in South Africa, highlighting that various pollutants, including atrazine, are prevalent in treated and untreated wastewater. Their findings underscore the need for more rigorous

monitoring of atrazine levels in wastewater to protect public health and aquatic life. Moodley *et al.* (2016) conducted a study on the occurrence and distribution of pharmaceuticals, including atrazine, in the Msunduzi River in South Africa. They found significant concentrations of atrazine in both wastewater and surface water, raising concerns about its environmental persistence and potential health risks. Aniyikaiye *et al.* (2019) assessed the physico-chemical properties of wastewater from paint industries in Lagos, Nigeria, revealing the presence of various hazardous substances. Although their primary focus was not atrazine, their findings imply the need for comprehensive studies on atrazine levels in industrial effluents, which may contribute to overall contamination.

### **2.3.1 Atrazine contamination in wastewater within Uganda**

Atrazine is commonly detected in agricultural runoff, raising concerns about its presence in wastewater treatment systems. Klammerth, (2011) demonstrated the efficacy of advanced oxidation processes, such as solar photo-Fenton, in degrading atrazine in municipal wastewater treatment plants. Their findings suggest that similar technologies could be adapted for use in Uganda, where wastewater treatment facilities may lack the capacity to effectively remove emerging contaminants like atrazine. Understanding these degradation pathways can inform local practices aimed at mitigating atrazine pollution in urban water bodies.

### **2.3.2 Context of wastewater pollution in Uganda**

Research by Baguma *et al.* (2023) highlights the broader context of pollution in Uganda's water systems, particularly in urban areas like Kampala. Their studies illustrate the presence of various pollutants, including heavy metals and microbial contaminants, in wastewater and sediment. While atrazine was not specifically mentioned, the findings underscore the potential for agricultural runoff to contribute to overall contamination levels. This indicates a pressing need for comprehensive monitoring programs that include atrazine alongside other pollutants, as the cumulative effects of multiple contaminants could pose significant public health risks.

### **2.3.3 Industrial wastewater and Atrazine within Uganda**

The discharge of untreated industrial wastewater is another critical factor influencing atrazine levels in Ugandan water bodies. Research by Baguma *et al.* (2023) emphasizes the lack of wastewater treatment facilities in Kampala, leading to the release of industrial effluents that may contain agricultural chemicals, including atrazine. The absence of regulatory oversight exacerbates this issue, making it essential to establish guidelines for wastewater management that specifically address the risks associated with atrazine and other similar contaminants.

### **2.3.4 Implications for public health**

The implications of atrazine contamination extend beyond environmental concerns to public health risks. Ouattara, (2022) provided insights into the adverse health outcomes associated with atrazine exposure, particularly regarding drinking water quality. Their findings could inform similar studies in Uganda, where atrazine levels in water sources may correlate with health issues in local communities. This connection highlights the need for targeted research on the health impacts of atrazine exposure in Ugandan populations.

## **2.4 Methods for atrazine removal**

### **2.4.1 Adsorption techniques**

Adsorption is noted as a prevalent method for atrazine removal, especially in developing countries where cost-effectiveness is crucial. Akhtar *et al.* (2024) emphasize that adsorption not only serves as a low-cost solution but also presents challenges in commercial applications, such as toxic sludge generation and incomplete removal of atrazine. The adsorption process can be modelled using the Langmuir and Freundlich isotherms, which help characterize the capacity and efficiency of different adsorbents (Sadaiyan *et al.*, 2024). The mechanism of adsorption involves the interaction between atrazine molecules and the adsorbent surface, resulting in either monolayer or multilayer formation of atrazine on the adsorbent. Factors

influencing adsorption efficiency include pH, temperature, and contact time, necessitating optimized operational conditions for enhanced removal (Krzemiński & Popowska, 2020).

#### **2.4.2 Biological methods**

Biological treatment methods have been explored as alternative strategies for atrazine removal. Devi *et al.* (2025) review various biological approaches that leverage microbial activity to degrade atrazine. However, the efficiency of these methods can be inconsistent, and the specific microbial strains capable of effective atrazine degradation are not well-characterized.

#### **2.4.3 Advanced oxidation processes**

Advanced oxidation processes (AOPs), which utilize strong oxidants to break down contaminants, have gained attention for their potential to degrade atrazine effectively. Capodaglio, (2020) discuss both consolidated and new AOPs, noting that while these methods can be effective, they often require high energy inputs and can generate byproducts that may be harmful. The need for comparative studies on operational efficiency and environmental impact remains a knowledge gap.

#### **2.4.4 Innovative sorbents**

Recent studies have highlighted the potential of innovative sorbents, including biomass-based materials, for atrazine removal. These materials not only reduce operational costs but also minimize environmental impacts associated with traditional adsorbents. Belgacem, (2024) suggest that further research should focus on the adsorption capacities of these biomass-based materials and their operational efficiencies compared to conventional sorbents.

Despite the progress in atrazine removal research, several gaps remain unsolved, the commercial viability, while adsorption techniques are promising, issues related to toxic sludge and incomplete removal hinder commercial application. More research is needed to develop adsorbents that minimize sludge production while maximizing removal efficiency.

Biological mechanisms, the specific microbial pathways and strains involved in atrazine degradation are not fully understood. More research is required to characterize these processes and develop targeted biological treatments (Belgacem, 2024).

Comparative studies of AOPs, there is a lack of comprehensive studies comparing the efficiency, costs, and environmental impacts of various AOPs for atrazine removal. Such studies could provide valuable insights for selecting the most appropriate treatment method.

Sorbent characterization, the performance of innovative sorbents, particularly biomass-based materials, needs thorough investigation. Understanding their adsorption mechanisms and operational conditions will be crucial for their integration into wastewater treatment systems.

## **2.5 Herbicides sources, effects, and uses**

Herbicides are a critical component of modern agriculture, designed to control unwanted vegetation and enhance crop yield. However, the environmental and health impacts of toxic herbicides have raised significant concerns in recent years. This literature review synthesizes current research findings regarding various toxic herbicides, their sources, effects on human and environmental health, and their uses. Notably, the review highlights knowledge gaps and suggests directions for future research (de Araújo-Ramos *et al.*, 2021).

### **2.5.1 Sources of herbicides**

Various toxic herbicides originate from different sources. Glyphosate, a widely used herbicide, is primarily found in the formulation of products such as Roundup. Research indicates that glyphosate not only exhibits toxicity to mammals but also enhances the effects of other environmental toxins, raising concerns about its cumulative health effects (de Araújo-Ramos *et al.*, 2021). Similarly, glyphosate-based herbicides (GBHs) have been identified as the most prevalent pesticides used globally, with significant implications for endocrine disruption and cytotoxicity (Agostini *et al.*, 2020). Triclosan (TCS), another toxic compound, is commonly

found in household personal care and consumer products. Its widespread use raises concerns due to its negative effects on both human and animal health, potential for bioaccumulation, and persistence in the environment (Mukherjee *et al.*, 2022).

### **2.5.2 Effects of herbicides**

The adverse effects of toxic herbicides are well-documented across various studies. Glyphosate and GBHs have been linked to a range of health issues, including endocrine disruption, cytotoxicity, and potential associations with modern diseases through mechanisms such as the suppression of cytochrome P450 enzymes (Araújo-Ramos *et al.*, 2021). The consensus statement by Myers *et al.* (2016) emphasizes the growing body of evidence indicating risks associated with glyphosate exposure, suggesting that even low levels of exposure may pose significant health risks. Triclosan's effects include bioaccumulation and persistence, leading to concerns over its long-term impact on ecosystems and human health (Dhillon *et al.*, 2015). The toxicological profile of these compounds necessitates a thorough understanding of their environmental transformations and stability, as indicated by Lead *et al.* (2018), who explored the environmental behavior of silver nanoparticles, which can serve as a parallel for understanding the fate of herbicides in the environment.

### **2.5.3 Use of herbicides**

The application of toxic herbicides is primarily driven by agricultural practices aimed at maximizing crop production. Glyphosate, for instance, is extensively used in various formulations due to its effectiveness in controlling a wide range of weeds, thereby supporting modern agricultural systems (Sang *et al.*, 2021). However, the reliance on such herbicides has led to increased scrutiny and calls for the development of safer alternatives. The prevalence of herbicides such as atrazine also underscores the need for better management practices, as highlighted by Agostini *et al.* (2020) who examined the toxicity, degradation, and analysis of atrazine, indicating its potential long-term effects on the environment and health

#### **2.5.4 Types of herbicides and their mechanisms**

Herbicides can be classified based on their chemical structures and mechanisms of action. The primary categories include pre-emergent and post-emergent herbicides, as well as selective and non-selective herbicides. Pre-emergent herbicides prevent weed seeds from germinating, while post-emergent herbicides target actively growing weeds. Selective herbicides kill specific types of plants, whereas non-selective herbicides affect all plant types (Agostini *et al.*, 2020).

##### **2.5.4.1 Selective herbicides**

Selective herbicides are designed to target specific weed species without harming the crops. Research has shown that the effectiveness of these herbicides relies heavily on their chemical properties and the physiological differences between target weeds and crops. For example, certain selective herbicides exploit metabolic pathways unique to specific weed species, leading to their death while allowing crops to thrive (Agostini *et al.*, 2020).

##### **2.5.4.2 non-selective herbicides**

Non-selective herbicides, such as glyphosate, are used extensively in agriculture due to their broad-spectrum activity. These herbicides work by inhibiting essential biosynthetic pathways in plants, leading to their death. Despite their effectiveness, the widespread use of non-selective herbicides has raised concerns regarding environmental impact and the development of herbicide-resistant weed populations (Agostini *et al.*, 2020).

#### **2.5.5 Recent Advances in herbicide research**

##### **2.5.5.1 Chemical innovations**

Recent studies have focused on developing new herbicide formulations that enhance efficacy and minimize environmental impact. For instance, researchers have explored the use of metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) to create advanced delivery systems for herbicides, improving their selectivity and reducing off-target effects (Alberto *et al.*, 2020). These frameworks can encapsulate herbicides, allowing for controlled

release and targeted application, the exploration of hybrid systems that combine different classes of herbicides has shown promise in overcoming resistance in weed populations.

Table 2.1. Different herbicides and how their target fields of action. (Alberto et al., 2020)

<b>GROUP</b>	<b>PRODUCT</b>	<b>ACTIVE INGREDIENT</b>	<b>CROPS</b>
<b>BURNDOWN</b>			
	Roundup	Glyphosate 360g/L	All Crops
	Roundup Turbo	Glyphosate 450g/L	All Crops
	Glycel	Glyphosate 480 SL	All Crops
	Speed	Glyphosate 70 WG	All Crops
	Tanzaquat	Paraquat 250 SL	All Crops
<b>PREEMERGENT</b>			
	Bullet Sc	Acetachlor 450g/L+ Terbuthylazine 225g/L + Safener 15g/L	Maize
	Integrity	Dimethenamid P 600g/L + Saflufenacil 62.5 G/L	Maize
	Stomp Aqua	Pendimethalin Cs	Maize/Soyabean/Sugarcane/ Wheat/ Potatoes/ Onions
	Frontier Optima	Dimethenamid P 720g/L	Soyabeans/ Tobacco
	Eltachlor	Acetachlor 90ec	Maize / Sugarcane
	Sure Start(DOW)	Acetachlor 41.6% + Flumetsulam 1.3% + Clopyralid 4.27%	Maize
	OPTIL	Kixor (Safluenacil) 178 G/Kg + Imazethopir 500g/Kg	Soyabean
	Broadstrike (DOW)	Flumetsulam 800 G/L WGD	Soyabean
	Sure Shot (DOW)	Acetachlor 41.6% + Flumetsulam 1.3% + Clopyralid 4.27%	Maize
	Tangold	Metalachlor 960g/L	Maize/Soyabean/Tobacco
	Cropzine	Atrazine + Cynazine	Maize
<b>POST EMERGENT</b>			
	Stellar Star	Topramezone 60g/L + Dicamba 150g/L	Maize
	Focus Ultra	Cycloxydim 100 G/L	Soyabean
	Atracel	Atrazien	Maize
	NIC IT	Nicosulfuran	Maize
	EL MCPA	MCPA 40% SL	Wheat/Barley
	Tomoxynil	Bromoxynil 225 G/L+ MCPA 225 G/L	Wheat/Barley
	Basagran	Bentzone	Soyabean / Maize

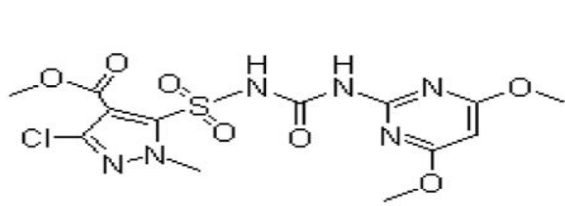
	Hammer	Imazethepir 100 G/L	Soyabean
	Authority	Sulfentrazone	Tobacco /Sugarcane
	Command	Clomazone	Tobacco /Sugarcane
	Elsefan	Fomasefan 250 G/L	Soyabean/Groundnut
	Gallant Super	Haloxypop R Methyl Ester 108 G/L	Soyabean/Groundnut
	Eluron	Duiron	Sugarcane
	Elumuron Super	Chlorimuron + Metribuzin	Sugarcane
	Elsuper	Fenoxypop P Ethyly	Wheat/Barley

### 2.5.5.2 Natural and anthropogenic sources of herbicides

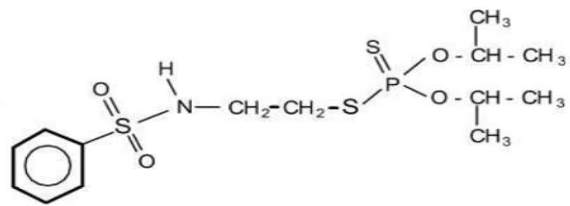
Research indicates that herbicides have both natural and anthropogenic origins. A study by Hooper & Marx, (2018) highlights that natural dust sources account for approximately 75% of global emissions, while anthropogenic sources, primarily linked to agricultural activities, contribute the remaining 25%. This distinction is vital for understanding the broader environmental implications of herbicide use, as the natural background levels can influence the persistence and spread of these chemicals in ecosystems. Pesticides, including herbicides, are primarily derived from chemical ingredients that are synthesized to target specific weeds and pests (Tudi *et al.*, 2021).

### 2.5.5.3 Agricultural practices and waste

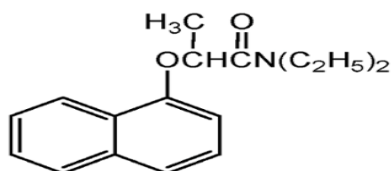
The generation of agricultural waste from cultivation, livestock, and aquaculture is another critical aspect related to herbicide sources. Khatun, (2023) discuss how agricultural waste can potentially be repurposed into useful products, including bio-based materials. However, the improper disposal of such waste can lead to the leaching of herbicides and other agrochemicals into soil and water bodies, thereby posing a risk to environmental and public health, herbicides are utilized not only to protect crops but also to enhance agricultural productivity (Ncube *et al.*, 2022). These dual-purpose underscores the necessity for effective management practices that balance agricultural productivity with environmental sustainability. The emphasis on improving crop yields often leads to increased herbicide application, which may exacerbate the challenges posed by chemical runoff and residue.



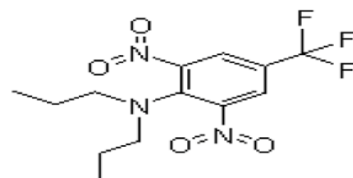
Halosulfuran-methyl



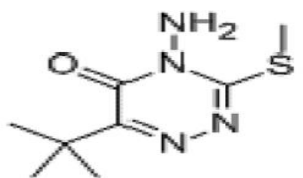
Bensulide



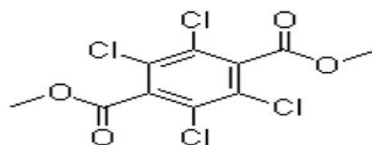
Trifluralin



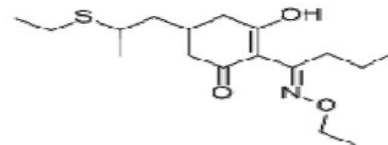
Napropamide



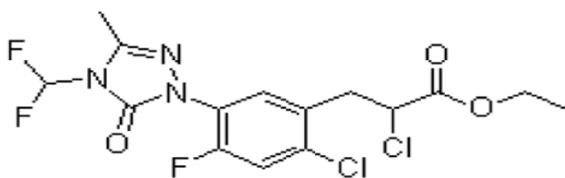
Metribuzin



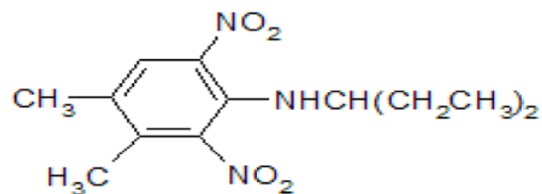
Dacthal



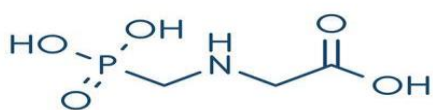
Sethoxydim



Carfentrazone



Pendimethalin



glyphosate

Above are common innovative herbicides used by farmers to increase crop yield.

### 2.5.6 Common herbicides and their occurrence in wastewater with a focus on atrazine

Herbicides, particularly atrazine, have garnered significant attention due to their prevalence in wastewater and potential environmental impacts. Atrazine is a widely used herbicide in agricultural practices, known for its effectiveness in controlling broadleaf and grassy weeds.

Grandclément *et al.*, (2017) however, its presence in aquatic systems raises concerns regarding water quality and ecosystem health. This literature review aims to examine the existing research on the occurrence and removal of common herbicides, with a specific focus on atrazine, in wastewater treatment settings. The research has demonstrated that various micropollutants, including herbicides like atrazine, frequently contaminate aquatic environments due to agricultural runoff and wastewater discharge. Qu *et al.* (2020) conducted a comprehensive review highlighting the widespread presence of micropollutants in aquatic environments, emphasizing the need for effective removal technologies during wastewater treatment processes. The authors noted that conventional treatment methods often fall short in adequately removing these contaminants, which can lead to their accumulation in water bodies. In a related study, Ben *et al.* (2018) examined the occurrence and removal of organic micropollutants in wastewater treatment plants across China. Their findings indicated that atrazine and other herbicides were consistently detected, underscoring the urgent need for improved treatment strategies to mitigate their environmental impact.

#### **2.5.6.1 Pathways of herbicide contamination**

Herbicide contamination of water bodies primarily occurs through several mechanisms such as leaching, runoff, and spray drift. Damalas & Eleftherohorinos, (2011) highlight that these pathways can lead to substantial residues in food and drinking water, posing health risks to consumers. The authors emphasize that occupational exposure to pesticides compounds the risk, particularly for agricultural workers. Furthermore, Thanigaivel *et al.* (2022) identify industrial effluents, fertilizers, and pesticides as primary contributors to drinking water contamination, which can lead to waterborne diseases.

#### **2.5.6.2 Environmental and health impacts of herbicide contamination**

The ecological implications of herbicide contamination are profound. Alengebawy *et al.* (2021) discuss the cumulative effects of heavy metals and pesticides in agricultural soils, noting that

these toxicants not only affect plant health but also pose serious risks to human health through the food chain. Similarly, Pathak *et al.* (2022) report that pesticide concentrations in surface waters often exceed chronic environmental quality standards, indicating significant contamination that threatens both human health and aquatic ecosystems. Cyanobacterial blooms, exacerbated by nutrient runoff that includes herbicides, represent a critical environmental challenge. Soares *et al.* (2021) detail how these blooms can produce highly toxic metabolites, leading to chronic health effects such as cancer in humans. Asiminicesei *et al.* (2024) further elaborate on the severe ecological consequences of cyanotoxin accumulation in water bodies, underscoring the high risk to aquatic organisms and the public health implications stemming from contaminated water sources.

Heinonen Supervisors & Paavilainen-Mäntymäki Jonathan Van Mumford, ( 2022) expand on the notion of environmental pollution through active pharmaceutical ingredients (APIs), asserting that pharmaceutical pollution constitutes a global threat to ecosystems and human health. This emerging concern parallels the issues posed by herbicide contamination, as both pollutants can disrupt aquatic life and compromise drinking water safety. Ocean pollution, which includes herbicide runoff, also poses significant health risks and threatens marine ecosystems. Fontes *et al.* (2023) discuss the various health issues linked to ocean pollutants, emphasizing the need for comprehensive management strategies to mitigate these risks.

#### **2.5.6.3 Removal technologies for herbicide contamination**

The removal of herbicides such as atrazine from wastewater is essential to minimize their ecological risks. Various treatment methods have been explored to enhance the degradation and removal efficiency of these contaminants. Grandclément *et al.* (2017) reviewed the effectiveness of hybrid wastewater treatment processes, noting that integrating advanced technologies can significantly improve the removal of organic micropollutants, including herbicides. The combination of biological and advanced oxidation processes was highlighted

as a promising approach for enhancing degradation rates, Saravanan *et al.* (2021) provided insights into effective methodologies for removing toxic pollutants from wastewater. They emphasized the importance of sustainable treatment options, suggesting that innovative approaches could be implemented to target specific contaminants like atrazine. The review pointed out that while some technologies show promise, the variability in herbicide removal efficiency remains a critical challenge.

### **2.5.7 Overview of analytical techniques**

A variety of modern analytical techniques have shown promise in the determination of herbicide concentrations. Chen *et al.* (2015) reviewed several cutting-edge techniques including Gas Chromatography (GC), High-Performance Liquid Chromatography (HPLC), Ultra-Performance Liquid Chromatography (UPLC), Capillary Electrophoresis (CE) coupled with Mass Spectrometry (MS), and Nuclear Magnetic Resonance (NMR) spectroscopy. These methods offer varying degrees of sensitivity and specificity, making them suitable for different types of herbicides and environmental matrices. Among these, HPLC and UPLC are particularly favored for their ability to separate complex mixtures and provide high-resolution analysis. Furthermore, GC remains a robust choice for volatile herbicides, while CE offers advantages in the analysis of ionic compounds (Chen *et al.*, 2015). The integration of these methods with MS enhances their detection limits, allowing for the quantification of herbicides at trace levels.

#### **2.5.7.1 Emerging techniques**

Recent advancements also include the development of novel biosensors and microfluidic devices. Miranda, (2021) highlighted the utility of an amperometric whole-cell biosensor for quantifying glyphosate and its metabolites in water samples. This approach provides advantages such as rapid response times and the potential for in-field applications. Similarly, Kung *et al.* (2019) explored microfluidic paper-based analytical devices, which present a cost-

effective and portable alternative for herbicide detection. Additionally, Wang *et al.* (2023) introduced a chemiluminescence strategy utilizing porous hydroxy zirconium oxide nanozymes for herbicide analysis. This method enhances the sensitivity of detection and could be particularly useful in monitoring glyphosate levels in agricultural runoff.

#### **2.5.7.2 Importance of removing herbicides from wastewater**

The contamination of water resources by herbicides poses a significant threat to ecological health and human safety. Qu *et al.* (2020) among various contaminants, herbicides like glyphosate are of particular concern due to their widespread use and potential long-term environmental impacts. This literature review synthesizes existing research findings on the importance of removing herbicides from wastewater and the challenges associated with this process, highlighting knowledge gaps associated with high costs and suggesting future research directions (Ukanwa *et al.* 2019) to remove herbicides from wastewater. The presence of herbicides in wastewater can lead to severe ecological consequences. Korte *et al.* (2022) emphasize that the widespread application of glyphosate has resulted in significant environmental contamination, necessitating effective removal strategies due to its high solubility and mobility in water. This underscores the importance of addressing herbicide pollution not only for the immediate health of aquatic ecosystems but also for the long-term sustainability of water resources, the removal of organic pollutants, including herbicides, is vital for maintaining ecological balance and preventing bioaccumulation in the food chain. Wang *et al.* (2017) stress that efficient removal of organic pollutants from wastewater is crucial for ecological and environmental health, indicating that herbicides contribute to the broader category of organic pollutants that require urgent attention.

#### **2.5.7.3 Challenges in herbicide removal**

Despite the recognized importance of herbicide removal, several challenges complicate the treatment process. One of the primary issues is the high operating costs associated with

advanced treatment technologies. Kurniawan *et al.* (2021) highlight the necessity for effective treatment technologies that can manage the increasing urbanization and the associated waste, suggesting that the financial burden of these technologies can be a significant barrier to their implementation, traditional methods often lead to the generation of secondary pollutants, complicating the overall treatment process. Wang *et al.* (2017) note that the release of treated effluent can influence microbial communities and contribute to antibiotic resistance in the environment, indicating that any herbicide removal strategy must also consider broader ecological impacts. The technical limitations related to the solute-solute selectivity in membrane separation technologies further complicate herbicide removal. Bank, (2010) highlight the need for improved techniques in wastewater treatment that can effectively address micropollutants, including herbicides hence this research aim is to use conventional method to address the use of modified rice husk to remove atrazine from wastewater.

## **2.6 Effectiveness of adsorbents in wastewater purification**

### **2.6.1 Novel adsorbents**

The need for effective and sustainable adsorbents has gained increasing attention in the fields of environmental science and engineering (Joseph *et al.*, 2021). Adsorbents play a crucial role in the removal of contaminants from water, air, and other mediums, making advancements in adsorbent materials imperative. Recent developments have focused on the modification of natural materials, such as rice husk-based silica, and the engineering of nanomaterials. This literature review explores recent advancements in these areas, synthesizing findings from various studies while identifying knowledge gaps and potential future research directions.

### **2.6.2 Modified natural materials**

The utilization of modified natural materials has been a focal point in the development of novel adsorbents. Rice husk-based silica has garnered attention for its abundance and sustainability. The transformation of agricultural waste into functional materials not only provides an effective

solution for waste management but also enhances the efficiency of contaminant removal. Recent studies highlight the potential of rice husk-derived silica for adsorbing heavy metals and organic pollutants due to its high surface area and porosity (Ben *et al.*, 2018). While the effectiveness of rice husk-based silica is documented, there remains a gap in understanding the long-term stability and regeneration of these materials. Future research could investigate the reusability of rice husk-derived adsorbents and their performance in real-world conditions, which would provide a more comprehensive understanding of their applications (Ben *et al.*, 2018). Rice husk is used as a source of silica ( $\text{SiO}_2$ ) due to its high silica content (about 15-20% by weight). When burned under controlled conditions, rice husk ash (RHA) is produced, which is rich in amorphous silica. This silica can be extracted and used for various applications, including the synthesis of silica-based adsorbents. Rice husk is abundant, renewable, and inexpensive, making it an attractive biomass resource for producing valuable materials (Ben *et al.*, 2018).

### **2.6.3 Disposal of modified rice husk-based silica adsorbent**

After being used for adsorption processes, the disposal of modified rice husk-based silica adsorbent depends on several factors, including the nature of the adsorbed pollutants and environmental regulations and the possible disposal methods include regeneration and reuse if the adsorbent is not heavily contaminated with hazardous materials, it might be regenerated and reused. Regeneration methods could involve washing, heating, or chemical treatment to remove adsorbed pollutants (Bhatnagar & Sillanpää, 2010). Landfilling can be used if the adsorbent is contaminated with non-hazardous materials, it might be disposed of in landfills designed for industrial waste. Proper landfill management is essential to prevent environmental contamination. Incineration will be done for the adsorbents loaded with organic pollutants; incineration might be an option. This process involves burning the adsorbent at high temperatures, reducing its volume and potentially recovering energy. However, emissions need

to be carefully controlled. Specialized waste treatment is carried out if the adsorbent is contaminated with hazardous or toxic substances, it would require disposal in accordance with hazardous waste regulations. This might involve treatment at specialized facilities equipped to handle such materials and the choice of disposal method depends on the specific application, the nature of the pollutants adsorbed, and local environmental regulations (Okoro *et al.*, 2022).

### **2.6.3.1 Engineered nanomaterials**

Engineered nanomaterials have emerged as a promising class of adsorbents due to their unique properties and enhanced performance. A study by Sadegh *et al.* (2017) discusses the role of various nanomaterials, including magnetic nanoparticles and carbon nanotubes, as effective adsorbents in wastewater treatment. These materials exhibit high adsorption capacities and fast kinetics, making them suitable for the removal of a wide array of contaminants. Despite these advancements, the interaction of dissolved organic matter with engineered nanomaterials is not fully understood. Yu *et al.* (2018) review these interactions, emphasizing the need for more studies to elucidate how natural organic matter affects the adsorption processes of engineered materials. Future research should focus on the environmental implications of these interactions, particularly in complex matrices.

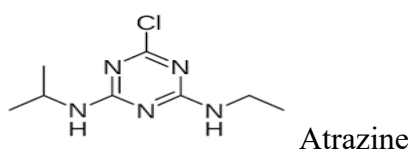
### **2.6.3.2 Advanced fabrication techniques**

The development of advanced fabrication techniques such as microwave-assisted synthesis has accelerated the production of nanomaterials with desirable properties. Grandclément *et al.* (2017) highlight the advantages of rapid assembly processes that enhance the scalability and efficiency of nanomaterial production. This approach could lead to the creation of tailored adsorbents that meet specific environmental challenges. Additionally, electrospinning technologies have been employed to fabricate nanofibrous scaffolds for various applications, including tissue engineering (Bank, 2010). Applying similar techniques to develop adsorbent

materials could enhance their surface area and adsorption capacities, thus improving efficacy in contaminant removal.

## 2.7 Chemical properties and structure of atrazine

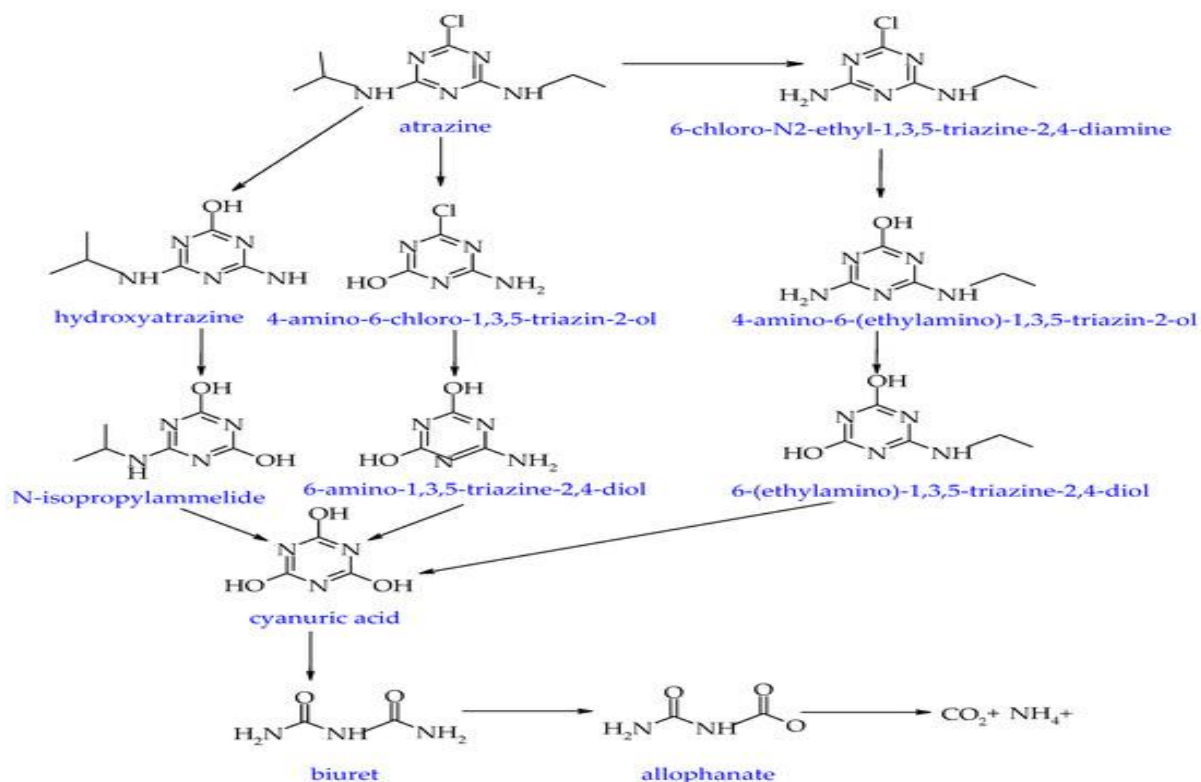
Atrazine, a widely used herbicide, has garnered significant attention due to its chemical properties, environmental persistence, and potential health impacts. Pathak *et al.* (2022) the structural characteristics of atrazine and its various metabolites have implications for its toxicity and degradation pathways. This literature review examines recent findings on atrazine, focusing on its chemical structure, degradation processes, and the associated health risks. Atrazine is a triazine herbicide characterized by its unique chemical structure, which includes a s-triazine ring,  $C_8H_{14}ClN_5$  as its formula and a molecular weight of 215.683. The structure of atrazine facilitates its interaction with various biological systems, leading to its effectiveness as an herbicide. Pathak *et al.* (2022) highlight that the chemical properties of triazines, including atrazine, are essential in understanding their behaviors in environmental and biological contexts. The ability of atrazine to form various metabolites, influenced by environmental conditions, adds complexity to its chemical profile.



### 2.7.1 Degradation mechanisms of atrazine

The degradation of atrazine has been studied extensively to understand its persistence in the environment. Bhatti *et al.* (2022) investigated the enhancement of atrazine degradation through a  $CoFe_2O_4$  activated peroxymonosulfate (PMS) process, revealing significant kinetic improvements and identifying degradation intermediates. This study underscores the importance of exploring advanced oxidation processes for effective atrazine remediation.

Pathak *et al.* (2022) provided a comprehensive review on the toxicity, degradation, and analytical methods associated with atrazine. They noted that the degradation pathways of atrazine can produce various metabolites, some of which may exhibit toxic characteristics. The findings indicate that while atrazine can degrade, the resulting compounds may retain harmful properties, necessitating further investigation into their environmental and health implications.



## 2.8 Adsorbents and there application in environmental remediation

Adsorbents are materials that are used to remove or adsorb substances from a solution or gas.

Adsorbents are classified into different types, including mineral, organic, or biological adsorbents. Val & Tholozan, (2020) adsorbents can be designed and prepared to have specific properties, such as high adsorption capacity, for various applications. The performance of adsorbents depends on factors such as the adsorbent's surface area, particle size, and the interaction between the adsorbent and the target substance. The application of novel adsorbents in environmental remediation has been extensively studied. For instance, Soares *et al.* (2021) report on the effective elimination of environmental pollutants using sorption-reduction and

photocatalytic degradation methods facilitated by nanomaterials. This dual functionality of nanomaterials enhances their applicability in treating complex contaminants, including pharmaceuticals and volatile organic compounds (VOCs). Zou *et al.* (2019) further explore the use of nano-based adsorbents in pharmaceutical contaminant removal, emphasizing the need for comprehensive assessments of these materials in real-world scenarios. While these studies provide valuable insights, there remains a need for standardized methodologies to evaluate the performance and efficiency of various adsorbents across different environments.

## **2.8.1 Concepts in adsorption**

### **2.8.1.1 Adsorption, adsorbent and adsorbate**

Adsorption is the adhesion of particles from a gas, liquid, or dissolved solid to the surface. Adsorbent is the material that provides the surface for adsorption, while the adsorbate is the substance being adsorbed. Various materials have been researched as adsorbents, including activated carbon, metal-organic frameworks (MOFs), and composites. For instance, polydopamine microspheres have been shown to effectively adsorb methylene blue (MB), demonstrating the versatility and efficiency of synthetic adsorbents (Feng *et al.*, 2021). Similarly, a magnesium-based MOF was found to preferentially adsorb hydrocarbons such as propane and propylene, illustrating the importance of molecular interactions (Li *et al.* 2019).

### **2.8.1.2 Adsorption mechanisms of herbicides**

Adsorption mechanisms play a crucial role in understanding how herbicides interact with various surfaces, particularly in environmental contexts. The immobilization of herbicides through adsorption is influenced by several physical and chemical interactions, such as hydrogen bonding, Van der Waals forces, and electrostatic interactions (Agboola & Benson, 2021). This literature review synthesizes recent findings on these interactions, highlighting their significance in enhancing herbicide efficiency while identifying existing knowledge gaps and potential future research directions.

### **2.8.1.3 Fundamental principles of adsorption**

Adsorption is a critical process in various fields, including environmental engineering, catalysis, and materials science. It involves the adhesion of molecules (adsorbates) from a gas, liquid, or dissolved solid to a surface (adsorbent). This review addresses the fundamental principles of adsorption, covering key concepts such as adsorbents, adsorbates, adsorption isotherms, kinetics, and thermodynamics, while integrating recent research findings to highlight advances and knowledge gaps in the field (Omo-Okoro *et al.*, 2018).

## **2.8.2 Mechanisms of Adsorption**

### **2.8.2.1 Van der Waals forces**

Van der Waals forces, characterized by weak attractions between molecules, are pivotal in the adsorption process. Dutta *et al.* (2021) note that these forces, in conjunction with  $\pi$ - $\pi$  stacking and hydrophobic interactions, facilitate the removal of dyes from water, which can be analogous to the adsorption of herbicides. Saad *et al.* (2019) also discusses the role of van der Waals forces in cellulose nanomaterials, highlighting that these forces govern the interactions that underlie various applications, including herbicide formulations.

### **2.8.2.2 Hydrogen bonding**

Hydrogen bonding significantly contributes to the adsorption of herbicides. Silvestrelli & Ambrosetti, (2014) elucidates that hydrogen bonds, along with electrostatic interactions, enhance the stability of complexes formed between herbicides and adsorbent surfaces. This is further supported by Agboola & Benson, (2021) who indicate that hydrogen bonding influences the interactions between micro (nano) plastics and organic chemical contaminants, suggesting similar mechanisms could be at play with herbicides.

### **2.8.2.3 Noncovalent interactions**

The adsorption of herbicides on surfaces can be primarily attributed to noncovalent interactions, which include electrostatic forces, hydrogen bonding, and Van der Waals forces.

Tarn *et al.* (2013) emphasize that these interactions significantly affect the preferential adsorption of cargo onto mesoporous silica nanoparticle surfaces (MSNP) illustrating the importance of understanding these mechanisms in the context of drug delivery systems. Furthermore, Adam *et al.* (2006) identify these interactions as critical in the functionalization of g-C<sub>3</sub>N<sub>4</sub>, affirming their relevance in various applications.

#### **2.8.2.4 Chemical interactions**

##### **2.8.2.4.1 Electrostatic interactions**

Electrostatic interactions, arising from charge differences between herbicides and their surfaces, also play a vital role in adsorption. Leskinen *et al.* (2017) explains that charge transfer during adsorption can significantly impact the binding affinity of proteins to surfaces, which can be extrapolated to herbicide interactions. The presence of charged functional groups on surfaces can either facilitate or hinder herbicide adsorption, depending on the herbicide's charge characteristics.

#### **2.8.3 Rice husks as an adsorbent**

##### **2.8.3.1 Adsorption of atrazine in rice husk biochar**

When biomass is heated in an oxygen-limited atmosphere (pyrolysis), a carbonaceous product called biochar is produced, and the charred byproduct is added to soil as an amendment. This technique for removing atrazine by use of biochar adsorption, takes care of any drawbacks because it is very effective, simple to use, and reasonably priced (Yang *et al.*, 2018). Plant leftovers, which are employed as raw materials, can also find a suitable home through biochar adsorption. (Yang *et al.*, 2018) have also shown the effectiveness of using biochar as adsorbents to adsorb different organic water contaminants. According to Luconi *et al.* (2022), rice husk is a type of biochar that can be used as an alternative to other biochar types that are typically used, such as wood, because it is generated sustainably. 20% of rice is made up of husks, which are

wasted due to their huge volume and sluggish natural absorption into the environment (Abdulrazzaq *et al.*, 2014).

According to earlier research Luconi *et al.* (2022), using rice husk biochar to remove pollutants from an aqueous medium is effective. The raw material source, the pyrolysis situations, and the physical and synthetic features of the biochar all affect how well it removes pesticides from aqueous solutions. Substantial surface area, porosity, polyaromatic structure, and diversity of operative groups are a few of these properties (Ye *et al.*, 2019). Adsorption is one of several processes that may be studied and developed with the use of a mathematical model. Through modeling, one can better comprehend the physical and chemical mechanisms at work in a process and optimize its operating conditions. It is advised to utilize phenomenological models to explain equilibrium and kinetic adsorption since they're more conclusive than empirical models and reveal physically important kinetic parameters (Monte Blanco *et al.*, 2017). Although representative and widely used, the traditional models (pseudo first order and pseudo second order) are less effective in illuminating a clear process (Monte Blanco *et al.*, 2017). The biochar utilized in the study of pseudo first order and pseudo second order was created and supplied by Embrapa Floresta, which is based in the Puerto Rican municipality of Colombo. The materials were made from rice husk that had been dried for 24 hours at 110 °C in an oven. The pyrolysis was carried out in the furnace for one hour at 400 °C and 700 °C at a heating rate of 10 °C min<sup>-1</sup> under low oxygen concentration. According to the procedure suggested by Zhang *et al.* (2004), the two samples were sized and shifted through a 0.075 mm mesh to standard fragments size.

### **2.8.3.2 Application and utilizing rice husk ash in the creation of silica**

According to Hossain *et al.* (2018) another source of silica for ceramics is rice husk/rice husk ash., rice husk adsorbent is the most encouraging trash for producing silica. In several technical applications, such as porcelain and metalwork creations, various materials used in the creation

of optical and electrical equipment, silicon carbide is a crucial component (Okoro *et al.*, 2022). (Hossain *et al.*, 2018) emphasized the production of silicon, nano-SiO<sub>2</sub>, and non-oxide ceramics using silica from RHA, a growth in the market's need for amorphous silica in production of premium cement and concrete for use in marine conditions and bridge construction. Additionally, RHA generated from combustion, it has been suggested to treat with either alkali or acid to enhance silicon concentration to > 99wt% because of the highest need for very pure nano silica for numerous uses in science, rice husk/ash as a substitute supply of silicon for ceramics.

#### **2.8.3.3 Rice husk insulation for fire bricks**

Rice husk has been used in making bricks for higher thermal insulation since it contains pores created when organic materials are burned off during heating. The pores serve as air entrapment, which improves the brick structure's insulating properties and makes it an excellent insulation material (Okoro *et al.*, 2022).

#### **2.8.3.4 Utilizing rice husk to remove heavy metals from aqueous medium**

Due to increased urbanization and industrialization, risky excessive heavy metal toxicity of wastewater is now creating significant environmental problems worldwide. For instance, wastewater containing As<sup>3+</sup>/As<sup>5+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>+</sup>, Cr<sup>3+</sup>/Cr<sup>6+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Hg<sup>+</sup>/Hg<sup>2+</sup>, and Co<sup>2+</sup> is increasingly legitimately or indirectly discharged in water sources, particularly in developing nations (Jiang *et al.*, 2020). Additionally, soil surrounding military installations may contain dangerous metals that could endanger both surface and underground waters (Okoro *et al.*, 2022). These large metal flakes are typically inedible and won't decompose generally effectively collect in living things. Although ingesting small dosages of certain heavy metals are crucial for people due to their value as co-factors or nutrients, unneeded introduction or admittance can be dangerous. Additionally, the existence of heavy metals in industrial effluent can result in a variety of physical and mental problems, including nausea, vomiting, loose

stools, asthma, pneumonia, skin aging, kidney and liver problems, inborn variations from the norm, weight loss, and various tumors (Ray & Shipley, 2015). To remove these heavy metals from polluted soil, a nontoxic, cost-efficient adsorbent must be created. Considering the reason, scientists and researchers have used rice husk in a variety of methods as a substitute material ideal for taking out heavy metals from contaminated soil. In this section, a handful of them are discussed (Srivastava *et al.*, 2021). worked on  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ion adsorption from binary systems utilizing RHA.

According to their research, 6.0 was determined to be the ideal pH for the elimination of the metals in question. The results showed that  $\text{Zn}^{2+}$  Adsorption of ions increased readily than  $\text{Cd}^{2+}$  ions. The combined impact of  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ions on RHA are typically considered to be non-complementary, and it's also discovered that equilibrium metal elimination declined with rise in the quantity of the opposite metal ion. Ahmaruzzaman & Gupta, (2011) has conducted remediation of  $\text{Zn}^{2+}$  and  $\text{Hg}^{2+}$ , a chemically modified carbonaceous sorbent, from the water produced from rice husk. Like this, the heavy metal ions  $\text{Fe}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Cu}^{2+}$  have been removed from the wastewater of electroplating businesses using rice husk. The results showed that this inexpensive adsorbent may be utilized to effectively remove HMs at concentration levels varied from 20 to 60 mg/l. According to Vieira *et al.* (2012), the dosage of inexpensive adsorbent and adsorbent concentration were used to ascertain the extent to which heavy metal ions are removed from aqueous medium.

#### **2.8.3.5 Removing heavy metals from the soil**

The qualities of soil can be improved by using rice husk dust. In an experiment to investigate the consequences of rice husk dust characteristics in soil like hydraulic conductivity, bulk density, total porosity, and particle size distribution and subsequently impacting the maize yield in Abakaliki, South-Eastern Nigeria. According to Amponsem *et al.* (2023) soil amendments should be made using rice husk dust.

## **2.8.4 Synthesis of activated carbon from rice husks**

### **2.8.4.1 Carbonization and activation**

Highly porous carbonaceous materials known as activated carbons have been extensively used as adsorbents, catalysts, and catalyst supports for chemical purification (Zhang *et al.*, 2004). It has been reported that activated carbon is the best material for cleaning aqueous media of organic contaminants. This is because of its wide surface area, strong adsorptive power, and high responsiveness. However, it is not economical to employ activated carbon that is sold commercially. About ten or twenty years ago, researchers started looking for inexpensive activated carbons as a replacement to coal-based activated carbon. Activated carbon that is derived from agricultural wastes or leftovers is known as agricultural-based activated carbon. Activated carbon has been made from a variety of agricultural waste products, including coconut shells, peach pits, rice hulls and husks, fish, peat, wood char, sugar bagasse, and more (Mohan *et al.*, 2014). Selection of the best materials is typically made depending on their presence, low rate of degradation during storage, and simplicity of activation (Torrellas *et al.*, 2015). Carbonization, pyrolysis, and activation (either chemical or physical) are frequently required steps in the production of activated carbons (Zhang *et al.*, 2004). Pyrolyzation refers to the application of heat irreversibly at high temperatures without the presence of oxygen or any halogen. Consequently, organic matter begins to thermally decompose, turning into carbon in the process known as carbonization (Zhang *et al.*, 2004). Activation can be carried out chemically or physically. The amount of carbon in the material is enriched by carbonization, while the pores are widened by activation, increasing the material's porosity (Olorundare *et al.*, 2014).

### **2.8.4.2 Effectiveness of activated carbon**

Activated carbon is well-known for its efficacy in adsorbing volatile organic compounds (VOCs) from gaseous environments. Zou *et al.* (2019) conducted a critical review of activated

carbon-based adsorbents, discussing their advantages in VOC gas adsorption, such as high adsorption capacity and adaptability to various adsorption conditions. The study emphasized the importance of surface modification techniques, which can enhance the adsorption performance of activated carbon for specific pollutants. In addition to VOCs, other contaminants, such as phenolic compounds, have been effectively removed using activated carbon. Liu *et al.* (2020) reported that sludge-based activated carbon (SBAC) demonstrated significant adsorption capacity for phenols, although it was less effective than certain other types of activated carbon (e.g., PICA carbons). This indicates that while traditional adsorbents can be effective, their performance can vary widely depending on the source and treatment of the material.

## **2.8.5 Physical activation**

### **2.8.5.1 Biochar formation by pyrolysis**

Biochar, a stable carbon-rich material produced via pyrolysis, has garnered significant attention for its potential applications in environmental management and agricultural practices. The process of biochar formation involves the thermal decomposition of organic materials under limited oxygen supply and at comparatively low temperatures, typically below 700 °C (Joseph *et al.*, 2021). This literature review aims to synthesize current research findings on biochar production, focusing on the effects of feedstock type, pyrolysis temperature, and the inclusion of additives, while also identifying gaps in knowledge and suggesting future research directions. Biochar, a carbon-rich product derived from biomass pyrolysis, has garnered attention for its potential applications in environmental remediation, particularly in the degradation of organic pollutants and the removal of contaminants from soil and water. The activation of biochar is a pivotal process that enhances its surface area, porosity, and catalytic properties, making it more effective for various applications (Zhang *et al.*, 2004). This literature

review synthesizes recent findings on the mechanisms and methods of biochar activation, highlights knowledge gaps in the current research, and suggests future research directions.

#### **2.8.5.2 The pyrolysis process and feedstock variation**

The pyrolysis of biomass can yield diverse forms of biochar, influenced significantly by both the type of feedstock used and the specific pyrolysis conditions. Tomczyk *et al.* (2020) investigated the physicochemical properties of biochar's derived from three distinct feedstocks wheat straw, poplar wood, and spruce wood. Their findings revealed that varying pyrolysis temperatures (400, 460, and 525 °C) and durations (5 hours for straw and 10 hours for wood) resulted in notable differences in the properties of the resultant biochar's. This highlights the critical role of both feedstock type and thermal treatment in determining the characteristics of biochar. Lian & Xing, (2017) further elucidated that biochar is part of the black carbon continuum, exhibiting variable properties that stem from the interaction of production parameters, including feedstock and pyrolysis conditions. This observation underscores the necessity for a tailored approach in biochar production to optimize its properties for specific applications, particularly in carbon sequestration and soil enhancement.

#### **2.8.5.3 Impact of additives on biochar properties**

The incorporation of minerals and other additives into feedstocks has been explored to enhance biochar properties. Taherymoosavi *et al.* (2018) conducted a study where three minerals were added to rice straw during pyrolysis, revealing that the addition of these minerals could significantly alter the final biochar's characteristics. This finding suggests that further research is warranted into the types of additives that can be incorporated to achieve desirable biochar traits, particularly in terms of nutrient content and pH balance.

#### **2.8.5.4 By-products of pyrolysis (syngas and bio-oil)**

Beyond biochar, the pyrolysis process also generates other valuable products, including syngas and bio-oil. Spokas *et al.* (2012) synthesized the agronomic impacts of biochar, emphasizing its role not only in carbon sequestration but also in enhancing soil fertility and structure. The thermochemical conversion of biomass yields a range of products, and understanding their interactions and potential synergistic effects can inform more effective utilization strategies. This highlights an area for future research focusing on the holistic assessment of all by-products of pyrolysis.

#### **2.8.6 Chemical activation**

##### **2.8.6.1 Acid and base activation of the biochar**

Biochar, a carbon-rich product derived from the pyrolysis of biomass, has gained significant attention for its potential applications in environmental management, particularly in contaminant removal and soil amendment. Olorundare *et al.* (2014) The activation of biochar, through acid or base treatment, can enhance its physicochemical properties and functionality, thereby increasing its efficacy in various applications. This literature review synthesizes recent research findings on the activation of biochar, focusing on its role in contaminant degradation, soil pH adjustment, and nutrient availability. The activation processes of biochar can significantly alter its surface chemistry and porosity. Acid activation has been reported to increase the surface area and introduce functional groups that enhance adsorption properties. Conversely, base activation can increase the content of oxygenated functional groups, which may improve the biochar's reactivity towards contaminants. Wang *et al.* (2017) provide a comprehensive overview of different chemical modification mechanisms, discussing how these alterations in physicochemical properties affect biochar's functionalities and applications.

### **2.8.7 Impact of biochar on soil pH and soil nutrient availability**

Biochar's ability to alter soil pH is critical, especially in acidic soils. Zhang *et al.* (2017) demonstrated that biochar produced at 350°C without activation had a minimal effect on soil pH, while biochar application at high rates significantly increased the soil pH from 4.8 to 6.6, albeit being less effective than traditional agricultural lime (AgLime). This indicates that while biochar can improve soil acidity, its effectiveness can vary based on production conditions and activation methods. Furthermore, Keck, (2024) highlighted the potential of chicken manure biochar as both a liming agent and a nutrient source in acid Appalachian soils, underscoring its dual role in enhancing soil quality.

### **2.8.8 Mechanisms and methods of biochar activation**

#### **2.8.8.1 Gaseous modification**

Gaseous modification involves the treatment of biochar with agents such as steam, carbon dioxide, air, or ozone to enhance its structural properties. This method has been shown to increase the surface area and porosity of biochar, which are crucial for its adsorptive and catalytic capabilities. For instance, Yang *et al.*, (2016) demonstrated that modifications could significantly improve the mercury removal efficiency of magnetic biochar derived from sawdust. Similarly, Wu *et al.* (2023) provided an overview of biochar's effectiveness in removing contaminants, emphasizing the role of gaseous activation in improving performance.

#### **2.8.8.2 Thermal modification**

Thermal modification techniques, including conventional heating and microwave irradiation, also play a crucial role in biochar activation. These methods facilitate the rearrangement of carbon structures and the generation of new active sites. Fu *et al.* (2019) explored the activation of peroxymonosulfate by graphitized hierarchical porous biochar, highlighting the importance of structural characteristics in the degradation of organic pollutants.

### **2.8.8.3 Advanced modification techniques**

Recent advancements in activation techniques, such as ultrasound waves, plasma, and electrochemical methods, offer new avenues for enhancing biochar properties. These innovative approaches have been shown to create defect structures within biochar, significantly impacting its catalytic performance. Ouyang *et al.* (2019) investigated the activation mechanism of peroxymonosulfate by biochar, attributing the efficacy of degradation processes to these defect structures. Additionally, Murtaza *et al.* (2024) emphasized the importance of surface functionalization and heteroatom doping in enhancing biochar's catalytic capabilities.

### **2.8.9 Characterization of activated carbon**

Characterizing activated carbon is crucial to understanding its adsorption capabilities. Various techniques, including scanning electron microscopy and Fourier transform infrared (FTIR) spectroscopy, have been employed to analyze the physical and chemical properties of activated carbon (Val & Tholozan, 2020). These characterization methods, when combined with UV spectrophotometric analysis, can provide comprehensive insights into the surface functional groups and porosity of activated carbon, which influence adsorption performance.

Lafi. (2019) demonstrated that activated carbon with oxygen-containing functional groups had enhanced adsorption properties for Congo Red dye. The study highlights the importance of characterizing activated carbon to tailor its properties for specific adsorption applications. The incorporation of UV spectrophotometry could assist in correlating the chemical structure of activated carbon with its adsorption efficiency.

Sotelo *et al.* (2014) performed competitive adsorption studies of caffeine and diclofenac using activated carbon, emphasizing the complex interactions that can occur in multi-component systems. UV spectrophotometry could be instrumental in distinguishing between the adsorptions of different contaminants, providing a clearer understanding of competitive adsorption phenomena.

### **2.8.9.1 Physical characterization of activated carbon by scanning electron microscopy (SEM)**

Activated carbon is widely recognized for its high adsorption capacity and versatility in environmental applications, particularly in water treatment and pollution control. The characterization of activated carbon is essential for understanding its morphology, surface properties, and interaction mechanisms with various adsorbates. Scanning Electron Microscopy (SEM) has emerged as a critical tool in this characterization process, providing detailed insights into the surface topography and porosity of activated carbon materials. This literature review synthesizes recent studies that utilized SEM for the characterization of activated carbon, highlighting key findings, knowledge gaps, and potential avenues for future research (Mopoung *et al.*, 2015).

### **2.8.9.2 Surface morphology analysis**

Several studies have employed SEM to elucidate the surface morphology of activated carbon derived from various precursors. For instance, Mopoung *et al.* (2015) utilized SEM-EDS to characterize activated carbon prepared from tamarind seed, revealing a porous structure conducive to Fe(III) adsorption. This highlights the importance of precursor selection in determining the structural properties of activated carbon.

Similarly, Ye *et al.* (2019) confirmed the effectiveness of high surface area mesoporous activated carbon derived from bamboo chips through HR-SEM analysis. Their findings demonstrated that the structural features of activated carbon directly influence its adsorption capabilities for organic dyes, underscoring the role of surface morphology in practical applications. Yu *et al.* (2019) showcased the application of SEM in studying fluffy honeycomb-like activated carbon derived from popcorn. Their SEM images indicated well-developed porosity, which significantly enhances the adsorption efficiency for organic dyes. This study illustrates the potential of using agricultural waste as a sustainable precursor for activated carbon production.

### **2.8.9.3 Advanced characterization techniques**

In addition to conventional SEM, several studies have integrated Energy Dispersive X-ray Spectroscopy (EDS) with SEM to provide a comprehensive analysis of activated carbon materials. Mopoung *et al.* (2015) characterized activated carbon derived from *Borassus flabellifer* flowers, utilizing SEM/EDS to assess its potential as an electrode material for supercapacitors. This integrated approach not only revealed surface morphology but also provided elemental composition data critical for evaluating the performance of activated carbon in energy storage applications. Fleker *et al.* (n.d.) also applied SEM to investigate the surface morphology of metal-organic framework/activated carbon composites, emphasizing the enhanced properties imparted by the composite materials. This highlights the versatility of SEM in characterizing not just activated carbon but also its composites, which can significantly affect performance in various applications.

### **2.8.9.4 Chemical characterization and Iodine number**

The iodine number is a crucial parameter in characterizing adsorbents, particularly activated carbon and other porous materials, due to its correlation with the material's surface area and porosity. Budianto *et al.* (2019) Iodine number tests quantify the amount of iodine adsorbed by a given mass of adsorbent, providing insight into its potential effectiveness for various applications, including environmental remediation and chemical separations. This literature review synthesizes recent findings related to the iodine number and its application in adsorption studies, particularly for iodine and related compounds. Mopoung *et al.* (2015) explored the iodine number as part of their characterization of activated carbon derived from tamarind seeds, indicating its importance in determining the adsorptive properties of this material for Fe(III) ions in aqueous solutions. The results highlighted that the iodine number can effectively assess the surface area and porosity, which are critical for adsorption processes. Further applying the iodine number, Xie *et al.* (2021) conducted a similar characterization for activated carbon

derived from coconut leaves. Their findings confirmed that the iodine number is a consistent indicator of the adsorptive capacity of activated carbon across different biomass sources. Zou *et al.* (2019) extended this by examining activated carbon from plantain stems, reinforcing the notion that the iodine number remains a reliable metric in assessing various biomass-derived carbons.

#### **2.8.9.5 Advances in iodine adsorption capacity**

Recent studies have reported significant advancements in the iodine adsorption capacities of various materials, which have implications for their practical applications. For instance, the optimized material iCOF-AB-50 exhibited a static iodine uptake capacity of  $10.21 \text{ g}\cdot\text{g}^{-1}$  Mojoudi *et al.* (2019), showcasing the potential of tailored porous structures for iodine adsorption. Additionally, the Mon-POF was noted for its substantial iodine vapor capture capability, further emphasizing the importance of structural design in enhancing iodine adsorption. Moreover, Solomon *et al.* (2017) documented a remarkable iodine absorption capacity of 639 mg/g for Cu-BTC@PES composite beads, indicating that composite materials could outperform traditional activated carbons. In a similar vein, Xie *et al.* (2021) presented CMP-4, which demonstrated an exceptional iodine capture capacity of 208 wt. %, suggesting that ionic functionalization methods may significantly improve iodine uptake in covalent organic frameworks. Hu *et al.* (2022) reported that Th-SINAP-8 achieved an iodine adsorption capacity of 473 mg/g, further highlighting the effectiveness of macrocyclic arene-based materials for iodine capture. These findings not only underline the diversity of materials available for iodine adsorption but also point to the significant role that chemical structure plays in enhancing adsorption capacities.

#### **2.8.10 Function of Potassium Hydroxide (KOH) in modification process**

In the modification process of rice husk or rice husk ash to produce silica-based adsorbents, potassium hydroxide (KOH) is often used as an activating agent (Azargohar & Dalai, 2008).

KOH serves several purposes which include the activation of surface area which helps to increase the surface area and porosity of the silica material (Saad *et al.*, 2019). This is achieved through the chemical reaction between KOH and the carbon or silica components in the rice husk, which creates more active sites for adsorption. The functionalization on the surface of the silica by introducing functional groups like Siloxane groups (-Si-O-Si-) and Silanol groups (-Si-OH) enhancing its adsorption capacity for specific pollutants or target molecules and also the activation process with KOH leads to the development of a well-defined pore structure, which is crucial for effective adsorption (Zhang *et al.*, 2017).

## **2.9 Factors affecting adsorption efficiency**

Adsorption processes are critical in various environmental applications, particularly in the removal of pollutants from water. This literature review discusses key factors influencing adsorption efficiency, specifically focusing on pH, temperature, herbicide concentration, and adsorbent properties (Liu *et al.*, 2020). Understanding these factors is crucial for optimizing adsorption systems and enhancing pollutant removal efficiency.

### **2.9.1 pH influence on adsorption**

The pH of the solution is a pivotal factor affecting adsorption efficiency. Liu *et al.* (2020) noted that varying pH levels significantly impact the adsorption of dyes using cellulose-based bio adsorbents. Their findings suggest that both low (pH 4-7) and high (pH 8-10) pH conditions influence dye uptake, although the optimal pH for maximum adsorption varies by the type of adsorbent and the pollutant involved Liu *et al.* (2020). Similarly, a study by Belhaj *et al.* (2020) identified an optimal pH of 4.0 for surfactant adsorption, indicating that acidic conditions can enhance adsorption efficiency for specific compounds. Conversely, the impact of pH is not universally beneficial. Chemerys & Baltrėnaitė, (2018) reported that the adsorption of heavy metals and antibiotics also depends on pH but that the optimal range may differ based on the metal ion and the adsorbent used.

### **2.9.2 Temperature effects**

Temperature is another crucial factor that affects adsorption processes. Belhaj *et al.* (2020) both observed that increased temperatures generally enhance adsorption efficiency, likely due to increased kinetic energy that facilitates the interaction between adsorbent surfaces and pollutants. However, the optimal temperature can vary significantly depending on the specific adsorbate and adsorbent properties. For instance, Borges *et al.* (2024) noted a peak adsorption efficiency at 45 °C for certain surfactants, indicating that higher temperatures may not always yield better results for all contaminants. In studies of heavy metals, Chemerys & Baltrėnaitė, (2018) reported variable temperature effects, suggesting that while higher temperatures can enhance adsorption, they may also lead to desorption under some conditions. This indicates a need for more comprehensive studies on the temperature dependence of adsorption across various pollutants and adsorbents.

### **2.9.3 Initial concentration of pollutants**

The initial concentration of the adsorbate is an essential factor influencing adsorption capacity. Research has consistently shown that increased initial pollutant concentrations lead to higher adsorption rates up to a saturation point (Gorzin *et al.*, 2018). Liu *et al.* (2020) also highlighted that varying the initial concentration of dyes significantly affects their removal efficiency, emphasizing the need to optimize initial concentrations for effective adsorption. However, the relationship between initial concentration and adsorption is not linear, and the presence of competing ions or molecules can complicate this relationship. Future research should focus on elucidating these interactions and developing predictive models that can account for varying initial concentrations in complex mixtures.

### **2.9.4 Adsorbent properties**

The characteristics of the adsorbent itself, including its composition, surface area, and functional groups, play a crucial role in determining adsorption efficiency. Biochar and

cellulose-based materials have emerged as promising adsorbents due to their high surface area and functional groups that enhance binding (Chemerys & Baltrėnaitė, 2018). Shanaah *et al.* (2023) explored iron nano-composite materials and found that their unique properties significantly improved atrazine herbicide removal efficiency. However, gaps remain in understanding how adsorbent modifications affect adsorption. For example, research has yet to fully explore the impact of modifying adsorbent surface chemistry on the adsorption of various pollutants under different environmental conditions. Future studies should investigate the structural and chemical modifications of adsorbents to enhance their efficacy.

### **2.10 Adsorption kinetics and isotherms**

Kinetics and isotherms are fundamental aspects of adsorption studies, as they provide insights into the dynamics and equilibrium of the adsorption process. Mabusela, (2021) reviewed various kinetic models applied to lead adsorption using activated carbon, highlighting the significance of understanding these dynamics for optimizing adsorption processes. Their findings emphasize that the choice of kinetic model can greatly influence the interpretation of adsorption data, underscoring the need for precise experimental methodologies, such as UV spectrophotometry, to quantify adsorbate concentrations accurately. Maneerung *et al.* (2016) conducted comprehensive studies on activated carbon derived from biomass gasification, focusing on the adsorption of dyes. Their results demonstrated that both kinetics and thermodynamic parameters are essential for understanding the efficiency of activated carbon in dye removal. The use of UV spectrophotometry in these studies can facilitate real-time monitoring of dye concentration changes, thus providing a more accurate assessment of adsorption kinetics. Jawad *et al.* (2021) investigated KOH-activated carbon for the removal of Methylene Blue, confirming that the Langmuir model provided the best fit for their equilibrium data Khomri *et al.* (2020) explored . This finding aligns with the earlier works and indicates that UV spectrophotometry could be employed to validate these models by accurately

determining the equilibrium concentrations of dyes in solution. The adsorption properties of arginine-modified activated carbon for cationic dye removal, further contributing to the understanding of adsorption kinetics and isotherms, the research indicated that modifications to activated carbon could significantly enhance its adsorption capacity. The integration of UV spectrophotometry in these experiments could improve the reliability of the kinetic and isotherm models proposed (Khomri *et al.* 2020).

### 2.10.1 Adsorption isotherms

Adsorption isotherms describe how the quantity of adsorbate on an adsorbent varies with its concentration in the solution at constant temperature. Common models include Langmuir and Freundlich isotherms. The adsorption of MB onto magnetic beads was well represented by both models, indicating the complexity of adsorption behaviors (Eltaweil *et al.*, 2020). Additionally, the adsorption of phosphates onto brick particles also aligned with the Langmuir isotherm, suggesting a monolayer adsorption process (Eltaweil *et al.*, 2020).

$$\frac{C_e}{q_e} = \frac{1}{Klq_m} + \frac{C_e}{q_m} \dots \dots \dots \text{Langmuir equation}$$

where  $q_m$  is the maximum monolayer adsorption capacity (mg/ g) and  $KL$  is the Langmuir constant (L/mg).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots \dots \dots \text{Freundlich equation}$$

where  $C_0$  is the highest initial concentration of the solute. The  $RL$  value indicates whether the adsorption is unfavourable ( $RL > 1$ ), linear ( $RL = 1$ ), favourable ( $0 < RL < 1$ ), or irreversible ( $RL = 0$ ).

Freundlich isotherm was a formula for describing nonuniform systems, as shown above, where  $K_f$  (mg/g) is the Freundlich constant concerning the adsorption capacity and represents the intensity of adsorption.

### **2.10.2 Adsorption kinetic models**

The study of adsorption kinetics has predominantly focused on various models, notably the pseudo-first-order and pseudo-second-order (PSO) models. Tingting Wu, (2023) highlight that the PSO model is increasingly favored for its ability to accurately fit the rate data of adsorption for a range of compounds, including metal ions and dyes onto cellulose-based materials. This preference for the PSO model is echoed by Jiunn Boon Yong *et al.* (2022) who demonstrate its applicability in the context of biomass-derived activated carbon used for dye adsorption.

In contrast, the pseudo-first-order model, while historically significant, is often inadequate for representing adsorption processes in many cases. This inadequacy calls for further exploration into hybrid models or alternative kinetic frameworks that might better capture complex adsorption behaviors.

### **2.10.3 Influence of material characteristics on kinetics**

The nature of the adsorbent significantly impacts adsorption kinetics. For instance, Jiang Hu *et al.* (2011) studied chromium (vi) adsorption using ethylenediamine-modified chitosan resin, revealing that modifications to the adsorbent can enhance both the kinetics and thermodynamics of the adsorption process. Similarly, Islam *et al.* (2017) investigated NaOH-activated carbon derived from coconut shells and found improvements in the rate of methylene blue adsorption, demonstrating that surface area and chemical properties are critical to kinetic behavior, the work by Pradilla, (2016) on asphaltene adsorption emphasizes that the adsorption process begins in production wells and continues throughout the production chain, highlighting the practical implications of understanding kinetic adsorption in oil and gas industries.

### **2.10.4 Pseudo-first order and Pseudo-second order reactions**

The study of adsorption kinetics is crucial for understanding the behavior of adsorbates on various adsorbents, particularly in environmental and industrial applications. Two primary models are commonly utilized to describe these kinetics: the pseudo-first order and the pseudo-

second order models. This literature review synthesizes existing research focusing on the pseudo-second order model, which has emerged as a predominant framework for modelling adsorption kinetics across various materials and contaminants (Sun *et al.*, 2018).

#### **2.10.4.1 Pseudo-second order kinetics**

The pseudo-second order (PSO) model posits that the rate of adsorption is proportional to the square of the number of unoccupied sites. This model has proven particularly effective in describing the adsorption of a variety of solutes, including metal ions and organic dyes, onto different substrates. Sun *et al.* (2018) emphasized that the adsorption kinetic data for numerous systems align closely with the pseudo-second order model, achieving high correlation coefficients ( $R^2 = 0.99$ ). This suggests that the PSO model provides an accurate representation of adsorption processes, particularly when the adsorption sites are plentiful, and the interactions are primarily between the adsorbate molecules (Sun *et al.*, 2018). Yunusa *et al.* (2021) highlighted the wide applicability of the PSO model, noting its popularity in fitting rate data for metal ions and dyes adsorbed onto cellulose-based materials. This underscores the model's versatility across different adsorbents and contaminants, making it a cornerstone in adsorption studies (Yunusa *et al.*, 2021). Furthermore, Hubbe *et al.* (2019) affirmed that the PSO model is frequently employed to describe adsorption kinetics on cellulosic materials, thereby broadening the understanding of how these materials interact with various pollutants (Hubbe *et al.*, 2019). The research by Feiqiang *et al.* (2018) added to the understanding of the PSO model by analyzing the adsorption of cationic and anionic dyes onto carbonaceous particles. They found that the adsorption of cadmium ions could also be described effectively by the pseudo-second order equation, reinforcing the model's efficacy in heavy metal adsorption scenarios (Feiqiang *et al.*, 2018).

#### 2.10.4.2 Pseudo-first order kinetics

While the pseudo-first order model is also utilized in adsorption studies, it describes processes where the rate of adsorption is directly proportional to the number of unoccupied sites. However, the literature indicates that this model is less frequently suitable for explaining the kinetics of many adsorption systems compared to the pseudo-second order model. Lima *et al.* (2022) noted various systems where both kinetic models were analyzed, but they concluded that the pseudo-second order equation consistently provided a better fit for kinetic data, evidenced by higher R<sup>2</sup> values in most studies. Such findings suggest that the pseudo-first order model may not capture the complexities of adsorption processes as effectively as the pseudo-second order model (Chen *et al.*, 2009).

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \dots \dots \dots \text{pseudo first order model}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots \dots \dots \text{pseudo second order model}$$

where  $q_e$  (mg/g) is the adsorption capacity at equilibrium,  $q_t$  (mg/g) is the adsorption capacity at time  $t$  (min), and  $k_1$  (1/min) and  $k_2$  (g/(mg.min)) are the first- and second-order adsorption rate constants, respectively. The Elovich equation was represented by the following equation

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \dots \dots \dots \text{Elovich equation}$$

where  $\alpha$  (mg/(g min)) and  $\beta$  (mg/g) are the adsorption constants (Lima *et al.*, 2022).

#### 2.10.5 Kinetics of adsorption

Kinetics refers to the rate at which adsorption occurs and is influenced by factors such as contact time, initial concentration, and temperature. The kinetics of MB adsorption was predominantly governed by pseudo-second-order kinetics, indicating that the rate of adsorption was proportional to the square of the number of unoccupied sites (Gorzin *et al.*, 2018). Kinetic studies on the adsorption of Pb(II) onto TiO<sub>2</sub>/MWCNTs also supported this model Edet & Ifelebuegu, (2020) highlighting its applicability across different systems.

### **2.10.6 Synthesis of research findings**

The integration of these studies reveals a comprehensive understanding of adsorption principles. Various adsorbents, including polydopamine microspheres and MOFs, demonstrate the diversity of materials that can enhance adsorption efficiency (Gorzin *et al.*, 2018). The application of adsorption isotherms highlights the importance of selecting appropriate models based on the nature of the adsorbate and the adsorbent. Kinetic studies consistently show that pseudo-second-order kinetics is prevalent, suggesting that chemisorption may play a significant role in many adsorption processes. Furthermore, thermodynamic evaluations provide crucial insights into the feasibility and energy dynamics of adsorption (Edet & Ifelebuegu, 2020).

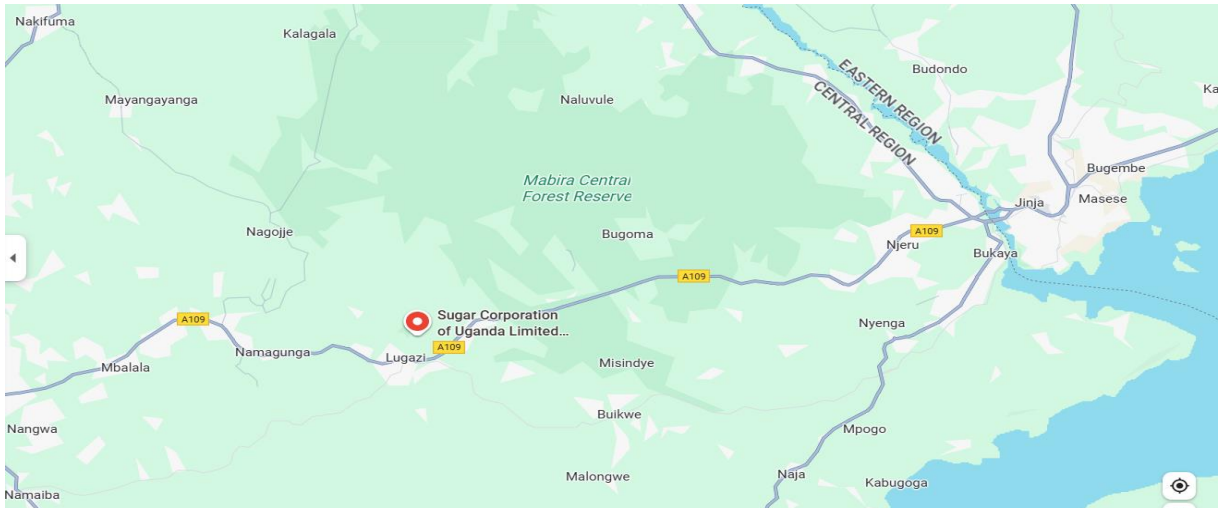
### **2.11 The role of ultraviolet spectrophotometry in adsorption studies using activated carbon**

The application of activated carbon in adsorption processes has garnered significant attention due to its efficiency in removing various contaminants from aqueous solutions. This literature review explores the integration of ultraviolet (UV) spectrophotometry in studying adsorption phenomena involving activated carbon (Wang *et al.*, 2017). Specifically, it synthesizes research findings related to adsorption kinetics, isotherms, and the characterization of activated carbon, while identifying gaps in the existing literature and suggesting potential future research directions.

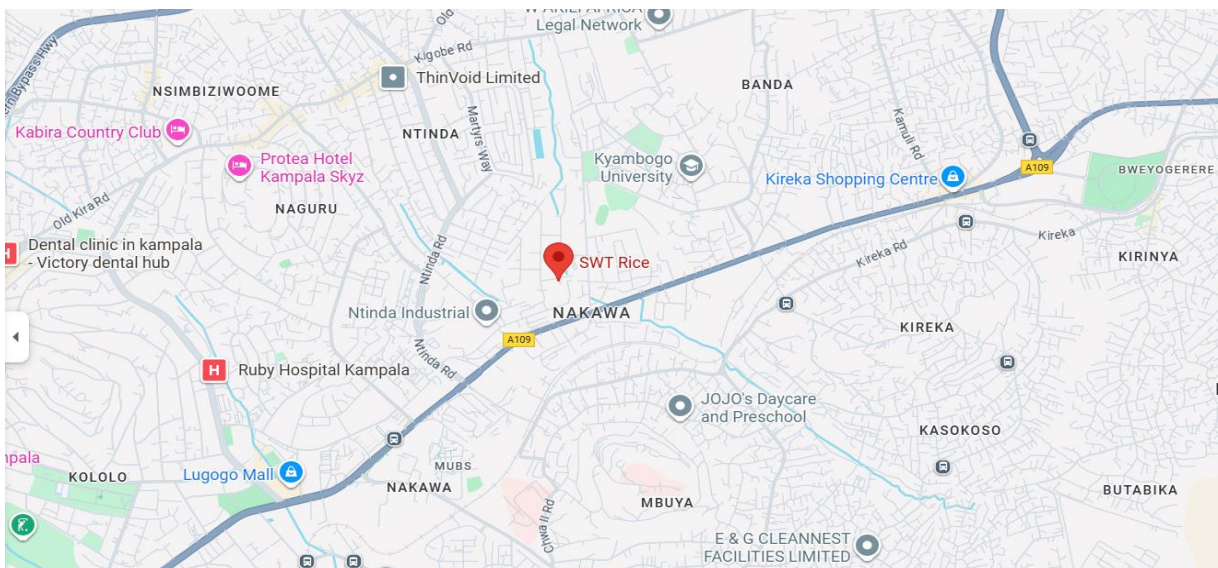
## CHAPTER THREE

### MATERIALS AND METHODS

Map showing different locations of sample collection that were used for practical experimental application in the laboratory.



Map showing the location of Lugazi in Buikwe district in the central region, Uganda, on the map of Uganda with exact geographical coordinates, latitude and longitude-0.3739085, 32.9381321.



Map showing the geographical location of Pakistan long grain factory rice in Ntinda-Kampala industrial area

### 3.1 Materials

The materials that were used were used in this dissertation were rice husk, analytical grade chemicals, spiked water samples and wastewater samples from Lugazi streams.

## **3.2 Methods**

### **3.2.1 Collection of rice husk**

The rice husk was obtained from Pakistan long grain rice factory located at Plot M566, SWT Close, Ntinda Industrial Area, Kampala, Uganda. The specific GPS coordinates for the location are approximately 0.3399° N latitude and 32.6215° E longitude

### **3.2.2 Preparation of modified rice husk adsorbent from rice husks**

Rice husk (1.5 kg) was weighed using a standard calibrated weighing scale. Following this, the rice husk underwent a thorough cleansing process with distilled water to take out all fragments of dirt, after which it was air-dried to reduce moisture content by up to 35%. Subsequently, the cleaned rice husk was subjected to combustion in a pyrolizer at 800 °C for a duration of 3 hours, resulting in the production of carbon biomass. The carbon biomass was then finely ground and sieved through an 18-micron sieve with necessary adjustments made (Zhang *et al.*, 2004). The rice husk biochar obtained was chemically activated using a 7.5% solution of Potassium Hydroxide (KOH) in a ratio of 1:3 (Activator: Adsorbent). The resulting mixture was neutralized using 0.05 M hydrochloric acid to achieve a neutral pH, and the activated adsorbent was subsequently dried at 100 °C in an oven according to standard procedures (Olorundare *et al.*, 2014).

### **3.2.3 Composition studies of the modified rice husk adsorbent**

Rice husk adsorbent is studied using Fourier Transform Infrared Spectroscopy (FTIR) to determine its chemical makeup and groups. By measuring the absorption of infrared light at various wavelengths, FTIR provides a spectrum that depicts the chemical fingerprint of the material and aids in the recognition of the functional groups found in rice husk. The Iodine Index Number is used to assess the porosity of the rice husk adsorbent. This index is a common way to evaluate the surface area and porosity of the material; it quantifies the quantity of iodine

absorbed by the adsorbent. More porosity and surface area are indicated by a higher iodine number, and these properties are essential for effective adsorption.

### 3.2.3.1 Proximate analysis of the modified rice husk-based silica adsorbent

Proximate analysis is used to evaluate the modified rice husk adsorbent's physical characteristics. Determining the quantity of moisture, ash, volatile matter, and fixed carbon is usually part of this examination. These characteristics shed light on the material's overall suitability as an adsorbent as well as its stability and composition.

### 3.2.3.2 Moisture content

The temperature of an automatic moisture balance analyzer (Shimadzu) was set at 105 °C. The modified rice husk-based silica adsorbent which weighed 15.061 g was put in a petri dish on to an automatic moisture analyzer and then covered with the top cover of the moisture analyzer. The instrument automatically started and then stopped after all the moisture had dried out of the sample (*British Pharmacopeia 2024*).

A printout was automatically printed out showing all results of analysis.

$$\text{Moisture Content} = \frac{\text{Wet Mass (g)} - \text{Dry Mass (g)}}{\text{Wet Mass (g)}} \times 100\% \dots\dots\dots (1)$$

### 3.2.3.3 Volatile matter

The adsorbent was heated in a Loss on drying (LOD) bottle at 105 °C for 3 hours in a hot air oven to determine the volatile matter. 1.0 g of the adsorbent was accurately weighed in a pre-weighed LOD bottle (the bottle plus the sample was weighed) and put in an oven which was maintained at 105 °C. After three (3) hours the bottle and the sample were removed, cooled, weighed and placed in a desiccator. The calculation of the volatile substance used the equation below (*British Pharmacopeia 2024*).

Wt. of LOD bottle = A

Wt. of LOD bottle + Sample = B

Wt. of LOD bottle + Sample after drying = C

$$\%Volatile\ Matter = \frac{(B-C)}{(B-A)} \times 100 \dots\dots\dots (2)$$

### 3.2.3.4 Ash content

The adsorbent was heated at 600 °C for 1 hour to determine the amount of ash present. 1 g of the activated carbon was weighed in a silica crucible, 1ml of concentrated sulphuric acid was added and then heated at 100 °C to remove the fume. When the fume was gone, it was put in the furnace which was maintained at 600 °C. the crucible plus the ash was then weighed. From the result, the percentage (%) of the moisture, volatile matter, and ash content was subtracted from 100% to evaluate/calculate the fixed adsorbent content (*British Pharmacopeia 2024*).

Wt. of crucible =A

Wt. of crucible + Sample = B

Wt. of crucible + Ash = C

$$\%Ash = \frac{(C-A)}{(B-A)} \times 100\% \dots\dots\dots (3)$$

### 3.2.3.5 Morphology study of the rice husk modified adsorbent

An electron microscopy (SEM) was utilized to scan the representation of the adsorbent, and a high-vacuum setting (HV) was set to track the adsorbent at an increased voltage of 20 kV by use of secondary electron detector of an electron microscope.

## 3.2.4 Chemical properties of the modified rice husk adsorbent

### 3.2.4.1 Determination of the pzc of the modified rice husk-based silica adsorbent

The Point of zero charge and known as pzc of the adsorbent was ascertained by varying the concentration of potential metric concentration of sodium chloride. The hinderance of the negative and positive charge to the active points of the modified adsorbent was seen. The different concentrations of 0.001 M, 0.01M and 0.1 M of Sodium Chloride solution were mixed with 2 g of the modified rice husk-based silica adsorbent for 24 hours was then evaluated (*Liu et al., 2020*).

Sodium Chloride of 0.001 M, 0.01 M and 0.1 M concentration were prepared. The pH of each concentration of Sodium Chloride were adjusted to 4, 4.5, 5.5, 6.5, 7, 7.5, 8.5, and 9 by using 0.5 M HCl and 0.5 M NaOH. The modified rice husk-based silica adsorbent of 2.0 g was added to each pH-adjusted 20 ml solution, sealed, and were kept in a state of balance for 24 hours. After equilibration, the final pH of the solution was measured, the final pH values were then plotted against the initial pH values for each concentration of NaCl. The PZC was determined from the point where the curve of final pH versus initial pH intersects the line where the final pH equals the initial pH is the PZC value (Liu *et al.*, 2020).

#### **3.2.4.2 Chemical group and composition of the modified rice husk adsorbent**

The infrared absorption spectrum of the sample was obtained by using an FTIR machine, the ATR crystal (Attenuated Total Reflectance) and the tip of the plunger were cleaned to ensure that there was not any dirt or any crystal substance with tissue paper. An amount of 0.001 g of the adsorbent was put on the ATR crystal in the center and the clamp arm was pressed by resolving it from the top to lock. The sample was scanned by clicking on sample scan and the Spectrum of the adsorbent appeared on the monitor showing details of the chemical groups and the composition of the adsorbent (using Bruker FTIR) (Budianto *et al.*, 2019).

#### **3.2.5 Calculating the surface area of the modified rice husk adsorbent using iodine index number**

**Sample preparation for surface area test**, the modified adsorbent was dried for an hour in an oven at 125 °C using an open petri dish and then cooled at room temperature in a desiccator.

##### **Reagents preparation procedure for modified rice husks surface area test**

**Sodium thiosulfate,  $\text{Na}_2\text{S}_2\text{O}_3$ ,  $0.1 \text{ molL}^{-1}$** , 25 g of sodium thiosulphate was dissolved in water; 0.2 g of sodium carbonate was added then topped to the mark in 1000 mL volumetric flask (*British Pharmacopeia*)

**Iodine solution,  $\text{I}_2$ ,  $0.05 \text{ molL}^{-1}$** , 12.7 g of Iodine and 20 g of Potassium iodide was dissolved in water and diluted to 1000 mL with water.

**Standardization of Sodium Thiosulfate, 0.1molL<sup>-1</sup>**, 210 mg of potassium dichromate was added in conical flask containing 100 ml of water, 3.0 g of potassium iodide, 2.0 g of sodium carbonate and 5 ml of hydrochloric acid were dissolved together. The resulting solution was titrated with sodium thiosulphate in the burette, and the exact molarity was ascertained using equation (4) (*British Pharmacopeia 2024*).

$$M = \frac{\text{Mass of potassium dichromate}}{\text{Titre Volume}} \times 49.04 \text{ (reaction equation)} \dots\dots\dots (4)$$

**Standardization of Iodine solution, (I<sub>2</sub>), 0.05 molL<sup>-1</sup>**, to 10 mL of the iodine solution, 1 mL of dilute acetic acid and 40 mL of water was added and then titrated with 0.1 M sodium thiosulphate, and the end point was determined using starch solution as an indicator.

**Blank Iodine determination**, 50 mL of 0.05 molL<sup>-1</sup> I<sub>2</sub> solution was pipetted into the titration beaker, it was then titrated against the standardized solution of 0.1 molL<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, using starch solution as an indicator.

**Surface area sample titration**, 50 mL of 0.05 molL<sup>-1</sup> I<sub>2</sub> solution was pipetted into the titration beaker containing 0.5 g of the adsorbent, it was then titrated against the standardized solution of 0.1 molL<sup>-1</sup> Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>, using starch solution as an indicator.

**3.2.5.1 Calculation of surface area**, Iodine adsorption was acquired by measuring the titration's volume between Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> and I<sub>2</sub>. Iodine (mgg<sup>-1</sup>) index number was computed using the equation (5).

$$\text{Adsorbed Iodine } \left(\frac{mg}{g}\right) = (v1 - v2) \times 12.69 \times \frac{2}{W} \dots\dots\dots (5)$$

where; V<sub>titrate</sub>: I<sub>2</sub> volume that combined with adsorbent (5ml), V stands for volume of natrium thiosulphate(ml), n for sodium thiosulphate solution concentration, and W for the weight (g) of the modified adsorbent utilized (*British Pharmacopeia 2024*).

### 3.2.6 Determination of adsorption capacity and efficiency of the modified rice husk adsorbent using simulated wastewater

#### 3.2.6.1 Adsorption capacity of the modified rice husk adsorbent

0.20 g of the modified adsorbent and 100 mL of wastewater simulated with atrazine solution of a specific concentration of  $18.5 \text{ mgL}^{-1}$  was mixed well in 250 mL conical flask by sonication at an rpm of 150 at  $30 \text{ }^\circ\text{C}$  for adsorption capacity test. The beginning pH was maintained at 9 and the adsorbent was then carefully filtered from the wastewater simulated with atrazine and kept for Adsorbent re-use test. The filtrate was used for the adsorption capacity test.

The quantity of atrazine present in wastewater was determined using a UV-Vis Spectrophotometer at 235 nm wavelength and the equilibrium adsorption capacity was computed utilizing the formula defined in equation (6)

$$q_e = \frac{(C_0 - C_e)V}{m} \dots\dots\dots (6)$$

where,  $C_0$  is the initial concentration of atrazine in wastewater in ( $\text{mgL}^{-1}$ ) at time  $t = 0$ ;  $C_e$  is the concentration of atrazine in ( $\text{mgL}^{-1}$ ) at time  $t$ ;  $V$  is the total suspension volume, and  $m$  = the mass of the adsorbent (g) according to (Ojemaye *et al.*, 2017).

#### 3.2.6.2 Adsorption efficiency of the modified rice husk adsorbent

100 ml of  $18.5 \text{ mg}\cdot\text{L}^{-1}$  of wastewater containing atrazine was put in 6 different conical flasks and each was mixed with 0.2 g of the adsorbent. The mixture was left intact for 25, 55, 85, 115, 145 and 175 min independently.

The atrazine concentration remaining in wastewater was established utilizing the UV- visible Spectrophotometer machine at 235 nm wavelength. From the experiments, adsorption efficiency of the adsorbent was computed using the equation (7).

$$\text{Adsorption efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \dots\dots\dots (7)$$

where;  $C_0$  and  $C_e$  ( $\text{mg}\cdot\text{L}^{-1}$ ) are the beginning and steady state concentrations reaction of atrazine in wastewater (Zbair *et al.*, 2019).

### **3.2.6.3 Optimal operation conditions of the modified rice husk adsorbent using simulated wastewater**

It involved the study of different parameters like contact time, pH effect, adsorbent dosage, atrazine's initial concentration's impact on the efficiency of the adsorbent when it was used during the adsorption experimental procedures.

#### **3.2.6.3.1 pH's impact on the modified rice husk adsorbent**

The pH impact was investigated by varying the pH of the initial concentration of atrazine in wastewater ( $18.5 \text{ mgL}^{-1}$ ) from 2, 3, 4, 5 and 6 using a constant adsorbent dosage of 0.2 g in each of the five solutions.

#### **3.2.6.3.2 Contact time's impact on the modified rice husk adsorbent**

The tests were performed across various contact periods of 15, 30, 60, 90, and 120 minutes. The initial concentration of atrazine in wastewater was  $18.5 \text{ mgL}^{-1}$  using 100 ml in each conical flask at a pH of 9 at  $25^\circ\text{C}$ , the dose of the adsorbent used was 0.2 g.

#### **3.2.6.3.3 The impact of the modified rice husk adsorbent's dosage**

The adsorbent dosage that was used ranged from 0.2 g, 0.4 g, 0.6 g, 0.8 g and 1.0 g at a pH of 9, at  $25^\circ\text{C}$ , and the initial concentration of atrazine in wastewater was  $18.5 \text{ mgL}^{-1}$ , each containing 100 ml.

#### **3.2.6.3.4 Impact of initial concentration of atrazine in wastewater on the modified rice husk**

Impact of initial concentration of atrazine was conducted by setting the following conditions; 0.2 g of adsorbent was weighed. The initial concentration of atrazine in wastewater varied from  $3.7 \text{ mgL}^{-1}$ ,  $7.4 \text{ mgL}^{-1}$ ,  $11.1 \text{ mgL}^{-1}$ ,  $14.8 \text{ mgL}^{-1}$  and  $18.5 \text{ mgL}^{-1}$ , using 100 ml of each solution.

### 3.2.7 Re-use of the modified rice husk adsorbent using simulated wastewater

The performance of the regenerated adsorbent was explored by mixing 0.18 g of the modified adsorbent from the adsorption capacity test with 18.5 mgL<sup>-1</sup> wastewater containing atrazine. The initial concentration was taken and then the blend was agitated at 150 rpm at a pH of 9 for 45 minutes. The quantity of atrazine present in wastewater was measured at a wavelength of 235 nm using a UV-vis Spectrophotometer, and the equilibrium adsorption capacity was computed utilizing the subsequent equation (8) (Collivignarelli *et al.*, 2019).

$$q_e = \frac{(C_o - C_e)V}{m} \dots\dots\dots (8)$$

### 3.2.8 Adsorption experiment on wastewater sample from Lugazi streams

The tests were performed at various contact time intervals of 15, 30 and 60 minutes, after identifying the pH and the beginning concentration of atrazine of the picked sample of wastewater from Lugazi flowing streams, the amount of the adsorbent used was 20 mg carried out at 25 °C.

### 3.2.9 Kinetics of atrazine in simulated wastewater adsorption using modified rice husk adsorbent

The kinetic studies were conducted using 0.02 g of the modified adsorbent, with various contact times of 10, 30, 60, 90, and 120 minutes. With a concentration of 9.25 mgL<sup>-1</sup> and the Elovich, the pseudo-first-order, the pseudo-second-order and the intraparticle diffusion kinetic models were employed to investigate the mechanisms behind atrazine adsorption onto the modified adsorbent, the pseudo-first-order and pseudo-second-order equations (9) (Liu *et al.*, 2020)

Pseudo-first-order equation

$$\log(q_e - qt) = \log q_e - \frac{k_1}{2.303} t \dots\dots\dots (9)$$

Pseudo-second-order equation

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots \dots \dots (10)$$

Therefore;  $q_e$  ( $\text{mgg}^{-1}$ ) = capacity for adsorption of the adsorbent at equilibrium,  $q_t$  ( $\text{mgg}^{-1}$ ) = adsorption capability at time  $t$  (min), and  $k_1$  and  $k_2$  ( $\text{gmg}^{-1} \cdot \text{min}$ ) are the first- and second-order adsorption rate constants (Gorzin & Bahri Rasht Abadi, 2018). Equation (11) illustrates how the Elovich equation works (Lima *et al.*, 2022).

$$qt = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \dots \dots \dots (11)$$

Therefore;  $\alpha$  and  $\beta$  in ( $\text{mgg}^{-1}$ ) are the adsorption constants.

Diffusion within interparticle was done by Weber-Morris kinetic model as expressed in the equation (12).

$$qt = \frac{k_i t^{1/2}}{2} \dots \dots \dots (12)$$

$k_i$  in ( $\text{g}(\text{mg min}^{-1/2})^{-1}$ ) = adsorption constant as per (Jin *et al.*, 2014).

### 3.2.10 Simulated wastewater with atrazine adsorption isotherm mechanism

Isotherm models' applicability was carried out by adding 100 mL each of wastewater containing atrazine of different concentrations of  $3.7 \text{ mgL}^{-1}$ ,  $7.4 \text{ mgL}^{-1}$ ,  $11.1 \text{ mgL}^{-1}$ ,  $14.8 \text{ mgL}^{-1}$  and  $18.5 \text{ mgL}^{-1}$  in five conical flasks each containing 0.02 g adsorbent

At contact time of 1 hour, the adsorption potential of the adsorbent was established by Langmuir and Freundlich isotherms. The Langmuir isotherm model presupposed that sorption took place in a particular uniform position and equation (13) provides the model.

$$\frac{C_e}{q_e} = \frac{1}{Klq_m} + \frac{C_e}{q_m} \dots \dots \dots (13)$$

$K_L$  = Langmuir constant, and  $q_m$  = the highest monolayer adsorption capacity in milligrams per gram.  $R_L$  = distance between objects or coefficient of separation was used to demonstrate whether the adsorption procedure was favorable by using the expression (14) (Cao *et al.*, 2009).

$$R_L = \frac{1}{1 + K_L C_0} \dots \dots \dots (14)$$

$C_0$  = highest initial concentration of the solute,  $R_L$  = is the value which indicates whether the adsorption is unfavorable when  $R_L > 1$ , linear when  $R_L = 1$ , favorable when  $0 < R_L < 1$  and irreversible when  $R_L = 0$ . To describe nonuniform systems, the Freundlich isotherm will be used in equation (15) (Feiqiang *et al.*, 2018).

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \dots \dots \dots (15)$$

$K_f$  (mg/g) = Freundlich constant measures adsorption intensity and the capacity of adsorption

### 3.3 Data analysis

Statistical was analysed using ANOVA and micro soft excel. Descriptive statistics including means, sums and standard deviation was determined and used to report the concentrations of different parameters as mean  $\pm$  standard deviation (SD). The means of pH effect, effect of initial concentration, analysis of variance (ANOVA) was used to compare the adsorption capacity, adsorption efficiency, adsorption isotherm, adsorption kinetics, effect of adsorbent dosage, adsorbent re-use, effect of contact time, and adsorption efficiency of Lugazi wastewater samples.

## CHAPTER FOUR

### RESULTS AND DISCUSSION

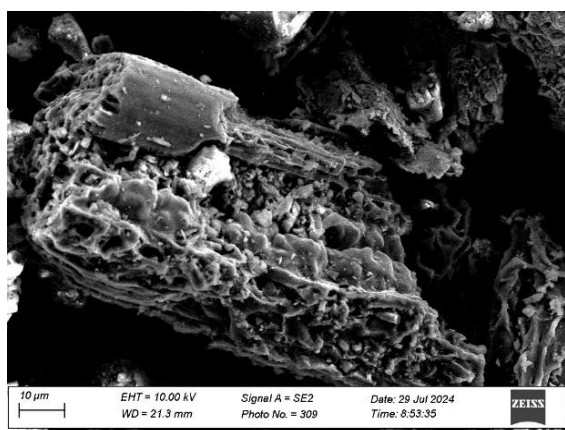
#### 4.1 Characterization of the modified rice husk-based silica adsorbent

The characterization of the modified rice husk-based silica adsorbent was done by both physical characterization and chemical characterization.

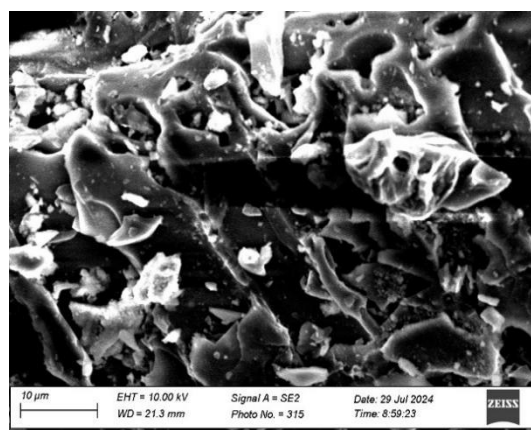
#### 4.2 Physical characterization

##### 4.2.1 Structural morphology of the modified rice husk-silica based adsorbent

After the electron microscope scan, high-resolution obtained were shown the surface morphology of the modified rice husk-based silica adsorbent as seen in Fig.4.1. A and B below.



**Figure (A)**



**Figure (B)**

Fig.4.1: Structures of the modified rice husk-based silica adsorbent

A is the scanning electron microscope structure of the modified rice husk-based silica adsorbent structure and B is the SEM structure of the modified rice husk-based silica adsorbent interior pore appearance of figure A.

##### 4.2.2 Pore structure in image analysis

The pores structures of the modified rice husk-based silica adsorbent were intensively studied to distinguish between distinct kinds of pores, such as macropores, mesopores, and micropores distributions pore size were ascertained, the total pore volume, and specific surface area through quantitative analysis was determined (Adam *et al.*, 2006). These are crucial factors that affect the

material's adsorption capacity performance. Particle size distribution, homogeneity of the modified rice husk-based silica adsorbent particles was studied by examining the particle size distribution seen in the pictures. To guarantee consistent adsorption and filtration behavior's, it was essential to comprehend the distribution of particle sizes (Adam *et al.*, 2006). Surface roughness and flaws, the reactivity and adsorption kinetics of a material were influenced by surface roughness and flaws. To find surface imperfections, fissures, or contaminants that can impair the material's performance during adsorption experimental studies, the pictures were carefully examined to have a standard modified adsorbent (Güçbilmez *et al.*, 2023).

Comparison and interpretation, to match the structural properties and observable morphology of the modified rice husk-based silica adsorbent were established to get the ideal requirements of the modified rice husk-based silica adsorbent in comparison with other carbon materials. However, in water treatment applications, for instance, a large specific surface area and a well-defined pore structure are desirable for effective pollutant adsorption. The thorough morphological analysis of modified rice husk-based silica adsorbent conducted with an electron microscope technique offers priceless insights into the structure-property correlations of the material, facilitating well-informed decision-making for maximizing its performance in a variety of applications in this study (Borges *et al.*, 2024).

#### 4.2.3 SEM-EDS characterization results of the synthesized adsorbents.

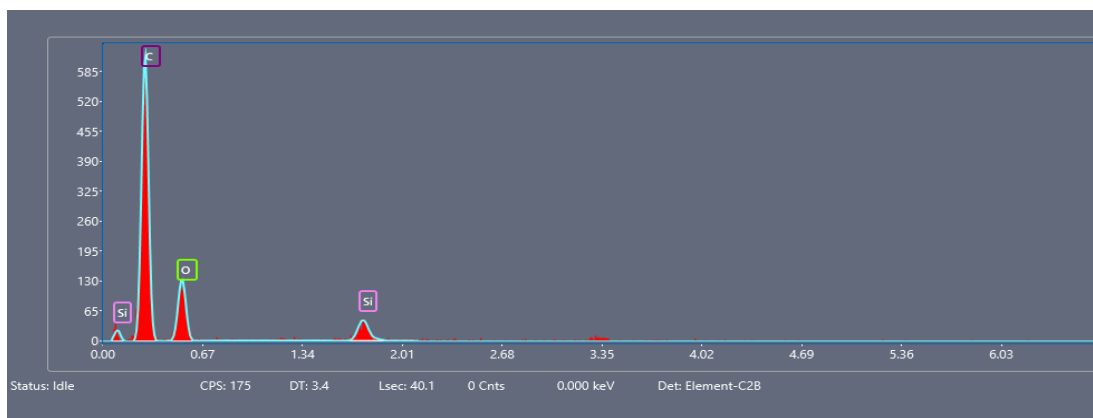


Fig.4.2: An EDS results for the modified rice husk-based silica adsorbent.

SEM (Scanning Electron Microscopy) gave the morphological details of the adsorbent surface, and the EDS (Energy Dispersive X-ray Spectroscopy) provided the elemental composition of the sample by detecting characteristic X-ray signals emitted when the material was bombarded with an electron beam and the peaks correspond to specific elements present in the sample. From the spectrum above, the main peaks are labelled as Si (Silicon) detected at  $\sim 1.74$  keV, represents the silica backbone ( $\text{SiO}_2$ ) derived from rice husks which confirms the successful extraction and presence of silica (Feng *et al.*, 2021).

The Oxygen peak at  $\sim 0.52$  keV is present due to Si-O bonds in the silica framework ( $\text{SiO}_2$ ), indicates the oxidized form of silicon rather than elemental Si. The Carbon is a strong peak near  $\sim 0.27$  keV which is from the residual carbonaceous matter in rice husk and other minor peaks may be due to impurities or trace elements from rice husks. The dominant peaks of Si and O confirm that the synthesized material is silica rich. The C peak suggests residual organic matter from rice husk carbon, the very low intensity of other elemental peaks shows that the synthesized adsorbent was relatively pure silica with little contamination from other elements (Güçbilmez *et al.*, 2023). The high Si and O content confirms a silica network (Si-O-Si, Si-OH), provided active binding sites for adsorption and the presence of carbon enhanced surface reactivity by introducing functional groups that interacted with atrazine organic pollutants like atrazine. Therefore, the Limited foreign element interference ensured that adsorption is dominated by silica's intrinsic functional groups, improving reproducibility and the SEM-EDS analysis confirms that the modified rice husk-based adsorbent is mainly composed of silica, carbon and Oxygen. This composition is consistent with rice husk-derived silica and suggests successful synthesis. The dominance of silica-related peaks proved the efficiency of the modification process in extracting and retaining silica as the major component, making the material suitable for adsorption applications in wastewater treatment (Adam *et al.*, 2006).

Table.4.1: Elemental composition of the modified rice husk-based silica adsorbent.

Element	Line	Weight %	Atomic %	Error %	Net Int.	R	A	F
C K	K	81.34	86.02	8.51	86.57	0.9445	0.5132	1.0000
O K	K	16.24	12.89	14.68	19.21	0.9530	0.2543	1.0000
Si K	K	2.41	1.09	11.37	9.09	0.9706	0.9204	1.0047

#### 4.2.4 Moisture content

The moisture content of the synthesized modified rice husk-based silica adsorbent was found to be low and within the desirable range for functional adsorbents. The recorded value of 10.30 % indicates that the adsorbent retains minimal physically bound water. The low moisture content demonstrates the effectiveness of the thermal and chemical treatment processes used in the synthesis of the silica adsorbent (Tomczyk *et al.*, 2020). This suggests that most of the structural water, loosely bound to organic matter in raw rice husks, has been removed. The small fraction of retained moisture corresponds to hydroxyl groups  $\text{OH}^-$  and silanol groups  $\text{Si-OH}$  that remain bound to the silica framework, which are crucial for adsorption (Tomczyk *et al.*, 2020). This moisture level is considered optimal because too high moisture content could block pores, reducing adsorption efficiency and too low moisture content could reduce the presence of active  $\text{OH}^-$  groups necessary for pollutant interaction.

The low moisture ensured that the adsorbent can be stored for longer periods without agglomeration, microbial growth, or loss of structural integrity as the retained hydroxyl groups at this moisture level serve as active sites for hydrogen bonding and electrostatic interaction with atrazine. A reduced moisture level made the adsorbent lighter, free-flowing, and easier to dose during experimental procedures and this confirmed a successful modification (Kapile, 2024). The measured moisture content of the modified rice husk-based silica adsorbent confirms that the material possesses excellent physicochemical stability and retains the right balance of structural water and hydroxyl functionality. This result validates the modification

procedure and highlights the potential of rice husk-derived silica as a promising low-cost adsorbent for wastewater treatment applications (Tomczyk *et al.*, 2020).



Fig.4.3: automatic print out of the amount of moisture content that was in the modified rice husk-based silica adsorbent.

#### 4.2.5 Volatile matter

The volatile matter content of the rice husk was found to be moderately low after thermal treatment, indicating that most organic fractions (cellulose, hemicellulose, lignin, oils, and resins) had been effectively decomposed. A low volatile matter percentage signifies a stable, inorganic-rich material with minimal interference from organic residues ( Yang *et al.*, 2016). The reduction in volatile matter compared to raw rice husk highlights the effectiveness of the carbonization process used during synthesis. Lower volatile matter means fewer carbonaceous impurities in the final silica product, it improves the thermal stability of the adsorbent, making it more durable under varying adsorption-desorption cycles. And it also ensured a cleaner surface functional group (Si-O-Si, Si-OH), which were essential for atrazine binding (Spokas *et al.*, 2012).

Table.4.2: Percentage wight of volatile matter results from calculations.

weight before drying (A) g	weight after drying (B) g	(A-B) g	% weight of volatile Matter
1.0006	0.9111	0.0895	8.94

#### 4.2.6 Ash content

The measured ash content of the rice husk sample was found to be 18 %, which is consistent with rice husks being a silica-rich agricultural waste. The elevated ash content indicates a high concentration of inorganic minerals, particularly silica (SiO<sub>2</sub>), which forms the backbone of the adsorbent material (Amran *et al.*, 2021). The result confirmed that rice husk is an excellent precursor for silica extraction since the ash fraction represents the potential yield of amorphous silica after controlled burning and modification. High ash content signified greater recovery of silica, reducing reliance on synthetic silica sources and this ensured cost-effectiveness and sustainability of the adsorbent production process (Amran *et al.*, 2021).

The mass of the residue was then measured and compared to the mass of the original sample in order to determine the amount of ash content and the limits are between 4-6% (Budianto *et al.*, 2019).

Table.4.3: Ash content calculation.

<b>weight before drying (A) g</b>	<b>weight after drying (B) g</b>	<b>(A-B) g</b>	<b>% Ash content</b>
13	10.64	2.36	18.2

#### 4.3 Chemical characterization

In this study characterization was based on the identification of the chemical behavior of the modified rice hush-based silica adsorbent. The Fourier Transform Infrared Spectroscopy (FTIR) was used for chemical group and composition studies of the modified adsorbent. The point of zero charge and the surface porosity were also determined (Hamid *et al.*, 2020).

##### 4.3.1 Composition and chemical group of the modified rice husk-based silica adsorbent

The Reference Spectra of the activate carbon (blue) and query spectrum (red) are identical hence the query spectrum has the same characters as those of the activated carbon as shown fig.4.4:

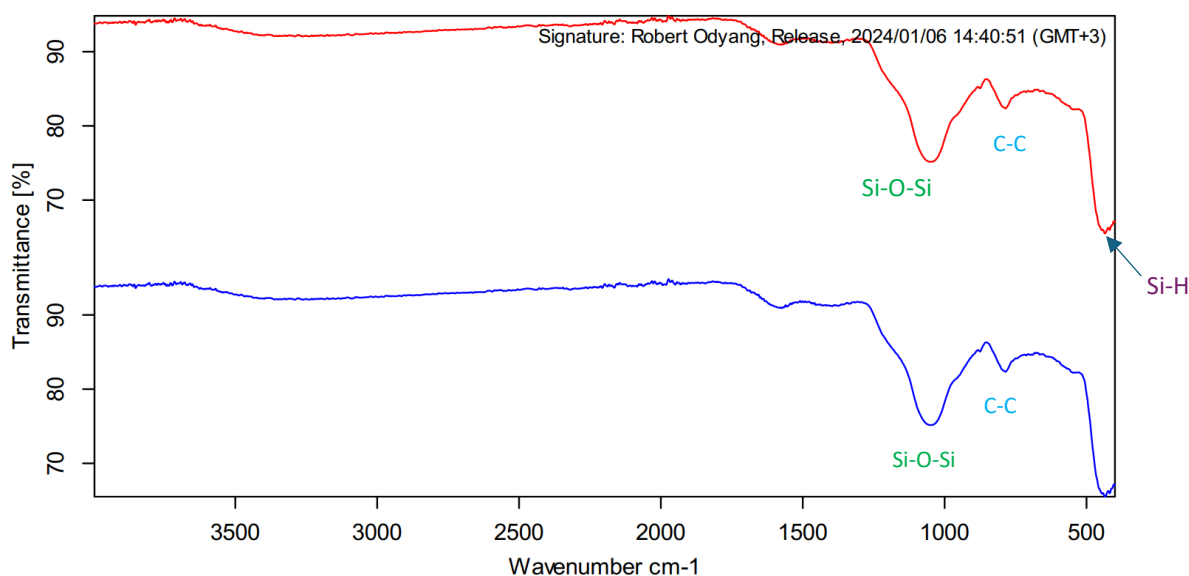


Fig.4.3: FTIR spectrum of rice husk-based silica adsorbent was identical to activated carbon sample before adsorption.

The FTIR spectra represent the functional groups, and bonding characteristics present in the materials. By comparing the two spectra, the red one of the *standard carbon* and the blue of the *modified rice husk silica*, we can identify how the rice husk silica has been modified and how it differs from pure carbon. The broad peak around  $3400\text{-}3200\text{ cm}^{-1}$ , red (carbon) is very weak or nearly absent, the blue (modified silica) the broad band is present (Hamid *et al.*, 2020).

The O-H stretching vibrations from surface hydroxyl groups ( $\text{-OH}$ ) and adsorbed water molecules. This is a characteristic feature of silica due to silanol groups ( $\text{Si-OH}$ ) and the absence of this peak in standard carbon indicates hydrophobicity and lack of hydroxyl-rich surface. The region around  $2920\text{-}2850\text{ cm}^{-1}$ , the red (carbon) pronounced peaks visible while the blue (Silica) has a much pronounced as red. The C-H stretching vibrations of aliphatic groups ( $\text{-CH}_2$  and  $\text{-CH}_3$ ) are detected mainly in carbon due to organic residues and the reduced intensity in silica indicates successful removal of organic matter during modification (Saad *et al.*, 2019). The band at  $\sim 1630\text{-}1650\text{ cm}^{-1}$ , the red (carbon) is defined and broad while the blue (silica) is more defined. The H-O-H bending vibrations of molecular water stretching in carbon are stronger in silica due to water adsorbed on the highly porous structure (Hamid *et al.*, 2020).

The strong band around 1080-1000  $\text{cm}^{-1}$ , the red (carbon) and the blue (silica) have very strong and sharp bands. The asymmetric stretching of Si-O-Si (siloxane linkages) is the fingerprint region of silica and confirms the formation of silica network in rice husk-derived material. The peaks around 800-780  $\text{cm}^{-1}$ , the red (carbon) and the blue (silica) have distinct peak hence symmetric stretching vibration of Si-O-Si, and it confirms the presence of a structured silica framework. The peak around 460-470  $\text{cm}^{-1}$ , red (carbon) and the blue (silica) have a strong absorption band hence bending vibration of Si-O bonds, this low-wavenumber feature is typical of silica-based materials (Saad *et al.*, 2019). The modified rice husk-based silica (blue spectrum) and the carbon (red spectrum) displays strong Si-O-Si stretching (1080  $\text{cm}^{-1}$ , 800  $\text{cm}^{-1}$ , 460  $\text{cm}^{-1}$ ) confirming silica network. Broad O-H band ( $\sim 3400 \text{ cm}^{-1}$ ) presence of surface hydroxyl groups, important for adsorption. The water bending band ( $\sim 1630 \text{ cm}^{-1}$ ) was due to hydrophilicity and porous silica structure. The spectrum shows successful removal of organic content and enrichment in silica functional groups (Torrellas *et al.*, 2015).

#### **4.3.2 Point of no charge**

The pH level at which the modified rice husk-based silica adsorbent material's surface charge becomes neutral is known as the point of zero charge, or PZC. At this pH, there is a net zero surface charge because there is an equal number of positively charged (protons) and negatively charged (hydroxyl groups or other functional groups) sites on the surface. The findings of identifying an activated rice husk adsorbent's point of zero charge are explained here (Egirani *et al.*, 2021). The surface of the modified rice husk-based silica adsorbent has a net positive charge at low pH levels because surface functional groups have been protonated, which occurs before the adsorbent reaches the PZC. The surface charge gradually decreases as pH rises and eventually reaches zero at the PZC. Because the surface functional groups have deprotonated, the surface becomes negatively charged beyond the PZC (Egirani *et al.*, 2021).

When it comes to the modified rice husk-based silica adsorbent's ability to remove atrazine from wastewater, the PZC has a substantial impact on both its capacity and efficacy. Gaining an understanding of the PZC facilitates the optimization of pH settings for adsorption processes, hence improving atrazine removal.

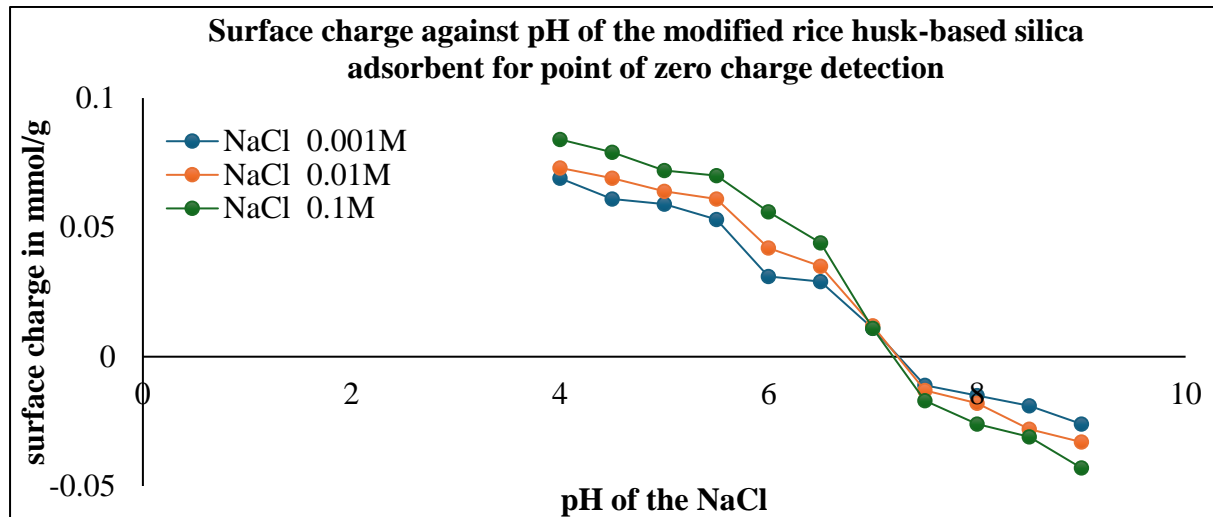


Fig.4.5: A plot of surface charge against the pH of the modified rice husk-based silica adsorbent for detecting the Point of Zero Charge.

Understanding the PZC offers valuable perspectives on the adsorption mechanism of the silica adsorbent derived from modified rice husk-based silica adsorbent. This mechanism entails the electrostatic interactions between charged species in the solution and the surface functional groups of the modified adsorbent that have opposing charges (Egirani *et al.*, 2021).

#### 4.3.3 Surface area of the modified rice husk adsorbent

The porosity of the modified rice husk-based silica adsorbent was determined by Iodine Index Number by calculating the volume of the remaining Iodine that was not adsorbed by the adsorbent after mixing both the Iodine and the modified rice husk-based silica adsorbent. From the formula below the surface area was calculated basing on the volume of iodine adsorbed by the adsorbent (Egirani *et al.*, 2021).

$$\text{Adsorbed Iodine} \left( \frac{\text{mg}}{\text{g}} \right) = (v_1 - v_2) \times 12.69 \times 2/w$$

From the titration, the titre values were  $V_1 = 48.95$ ,  $V_2 = 34.86$  and the weight (W) of the adsorbent used was = 0.50 g

Table.4.4: Surface porosity of the adsorbent as per adsorbed quantity of iodine.

Titre volume		weight (w)		
V1	V2	V1-V2	(g)	adsorbed Iodine(mg/g)
48.95	34.86	14.09	0.5	715.21

From the calculation, 715.21 mg/g is the mass of the Iodine that is adsorbed at the surface of the modified rice husk-based silica adsorbent. The significance of higher mass of iodine that is adsorbed by the modified adsorbent reflects high pore volume of the adsorbent and, hence, a higher adsorption capacity level for the purpose of removing atrazine from wastewater (Vieira *et al.*, 2012).

#### 4.4 Adsorption capacity of the modified rice husk-based silica adsorbent

To assess the modified rice husk-based silica adsorbent's capability for adsorption, its efficacy in filtering waste from wastewater was measured. The formula was used in the calculations to obtain the adsorption capacity. From the experimental values that were used,  $C_0$ ,  $C_e$  and the volume were 1.421 mg/L, 0.017 mg/L and 100 mL respectively and as shown in appendix I (Okoro *et al.*, 2022).

Equilibrium adsorption capacity ( $q_e$ ) experiment(3) = 702 mg/g, the results demonstrate that the modified rice husk-based silica adsorbents has excellent pore characteristics, and its good surface area contributed to its high affinity for the removal of atrazine from wastewater. The computation above yielded a large equilibrium capacity ( $q_e$ ) value of 702 mL/g, indicating that the adsorbent's surface had a large number of active sites that made it easy for atrazine to be adsorbed from wastewater (Ojemaye *et al.*, 2017).

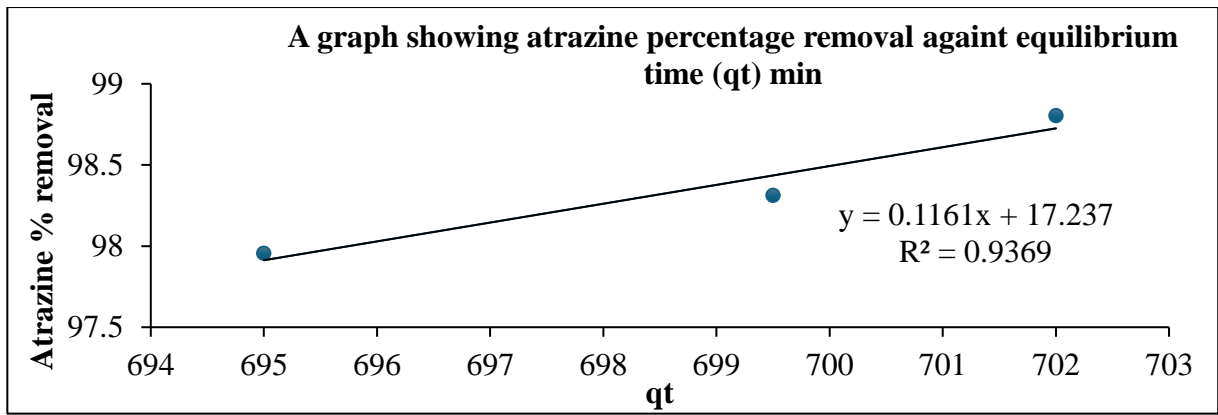


Figure.4.6: Percentage removal of atrazine versus the equilibrium adsorption capacity of the rice husk-base silica adsorbent with a concentration of 18.5 mg/L, pH of 9, adsorbent dosage of 0.2 g and at a contact time of 30 minutes (Okoro *et al.*, 2022).

#### 4.5 Re-use of the modified rice husk-based silica adsorbent

To evaluate the re-adsorption capabilities of the modified rice husk-based silica adsorbent for the removal of atrazine from wastewater, it was reused. Although the efficiency is poor, the results show that the adsorbent's active sites continue to interact with atrazine. This suggests that some of the active sites may have been lost during washing since the adsorbent's mass was different (Srivastava *et al.*, 2021) as presented in appendix II and Fig.4.7.

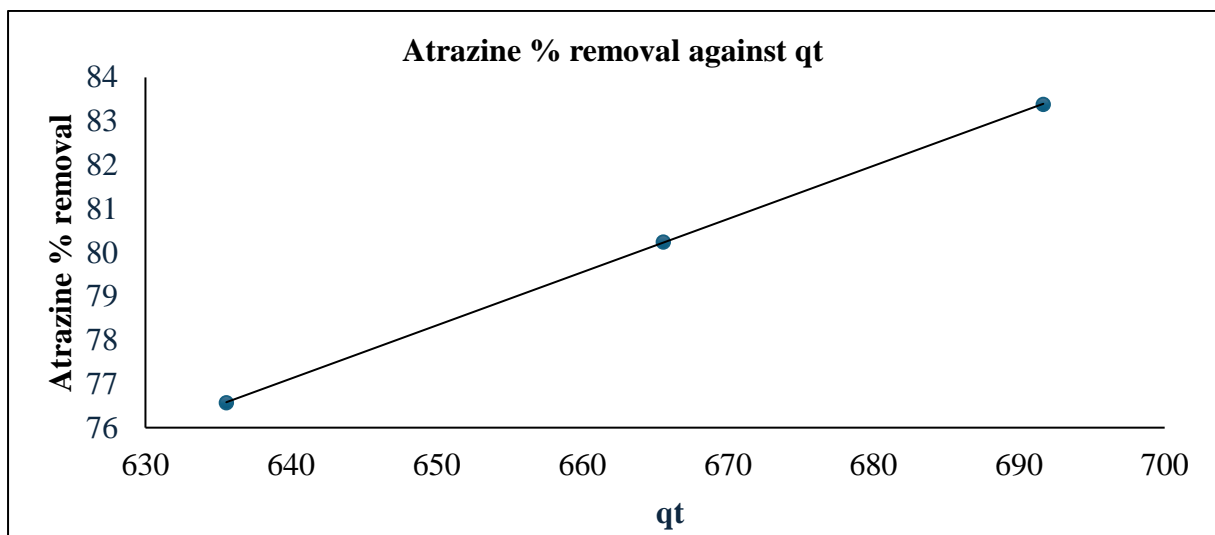


Fig.4.7: Rate of atrazine adsorption from wastewater against equilibrium adsorption at 45 minutes, pH of 9, concentration of 18.5 mg/L and mass of 0.18 g of re-used adsorbent.

#### 4.6 Adsorption efficiency of the modified rice husk-based silica adsorbent

Experiments on the length of contact time were used to determine the adsorption efficiency and convenience of use of the modified rice husk-based silica adsorbent. Atrazine was gradually adsorbed from wastewater, as the illustrated in fig.4.8. The results of the experiment were recorded for up to 55 minutes, during which time the maximum adsorption of 86.30% was achieved (Okoro *et al.*, 2022). The adsorbent dosage was 0.2 g, pH was 9, the concentration was 18.5 mg/L, and different contact times were tried. The highest yield was obtained after 55 minutes, indicating that efficiency rose with the duration of interaction and that the occupation of active sites across the surface area was used to maximize efficiency with the contact time (Zbair *et al.*, 2019).

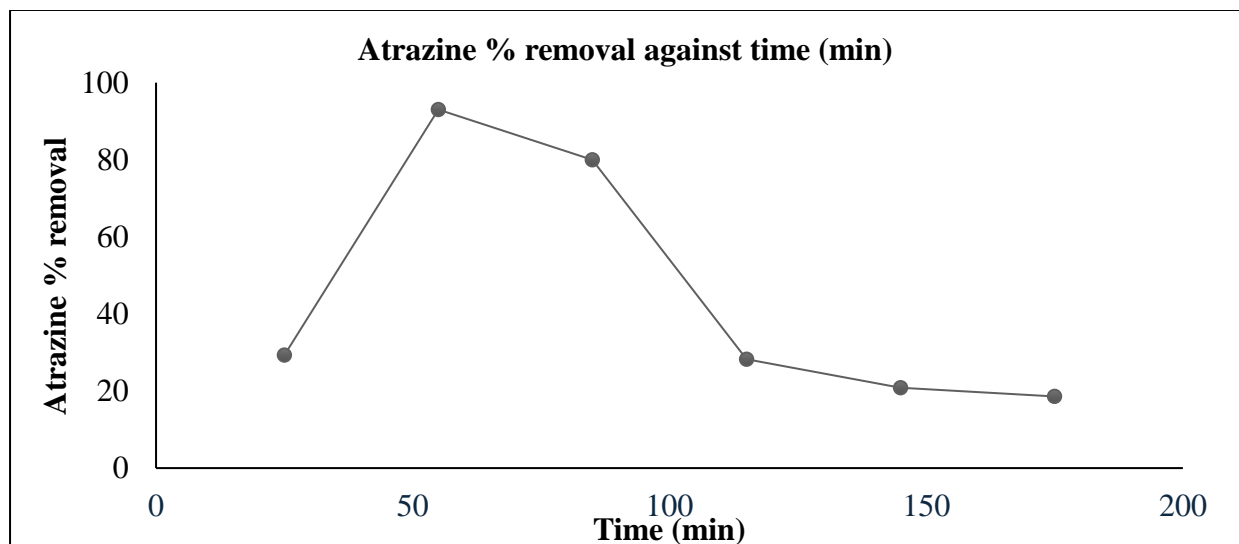


Fig.4.8: Percentage removal of atrazine by the modified adsorbent against time (mins).

From the 55 minutes, the detection was no longer for atrazine because of either its concentration was incredibly low in solution to be detected or because of competition of the active site with the adsorbent which was excess in the solution (Yang *et al.*, 2018). Thus, because of active site competition, it caused the interferences at the UV detector since the detection and absorbance were no longer for atrazine.

#### **4.7 Adsorption studies to investigate the optimum operation conditions of the modified rice husk-based silica adsorbent**

The modified rice husk-based silica adsorbent was subjected to different parameters during these experimental investigations to determine the ideal operating conditions under which the modified adsorbent adsorbs atrazine from wastewater the best. The effects of pH, contact time, adsorbent dose, and the starting concentration of atrazine were the parameters that differed (Cao *et al.*, 2009).

##### **4.7.1 pH's impact on the modified rice husk-based silica adsorbent**

Atrazine adsorption from wastewater was found in the pH range under investigation. The surface charge of the modified rice husk-based silica was influenced by the pH of the solution. The surface charge of the modified rice husk-based silica adsorbent can be positive or negative at different pH values, and this charge influences the atrazine ions' repulsion from the solution. As a result of its effects on the presence of other ions or molecules in the solution that compete with the atrazine adsorption sites on the modified rice husk-based silica adsorbent, pH influences the chemical reactions between atrazine and functional groups on the surface of the adsorbent. Depending on the pH, these reactions can either enhance or hinder the adsorption of atrazine onto the adsorbent (Jiang *et al.*, 2020)

As observed from Fig.4.9, the optimal pH of 9 was best for atrazine adsorption onto the modified rice husk-based silica adsorbent with a yield of 93.2%. Therefore, pH significantly influences the adsorption of atrazine using modified rice husk-based silica adsorbent by affecting the surface charge of the adsorbent. However, the high concentration of hydrogen ions in the acidic range hindered atrazine uptake, and as the level of hydrogen ions increased, atrazine adsorption gradually increased with pH. The adsorption in solution depends on pH. There was a notable increase in atrazine adsorption at pH = 9 because the hydroxonium ion level was sufficient to counteract the hydrogen ions as shown in Fig. 4.8 (Franco *et al.*, 2017)

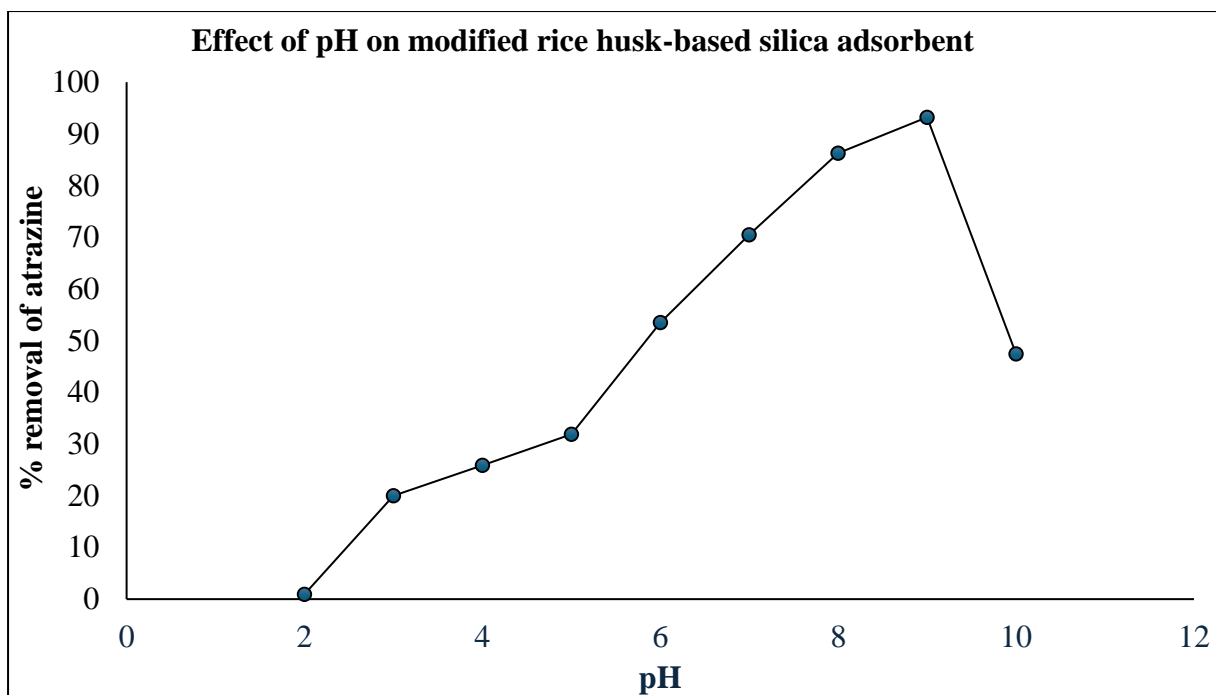


Fig.4.9: Percentage of atrazine removal against pH for modified rice husk-based silica adsorbent. At a contact time of 40 minutes, concentration of 15.50 mg/L of atrazine and an adsorbent dosage of 0.2 g. A rise in pH facilitates atrazine's attraction to various reactive functional groups of the adsorbent by deprotonating the active carbon sites (Franco *et al.*, 2017). This enhances the negative charge that leads to electrostatically induced bonding. Atrazine was more effectively removed from solution because of better hydroxylation and decreased protonation. The removal of atrazine was impeded by the pH drop. Atrazine's removal from wastewater was hampered by competition between it and hydronium for reactive sites (Jiang *et al.*, 2020).

#### 4.7.2 Contact time's impact on the modified rice husk-based silica adsorbent

The experimental data in Fig.4.10 below depict the impact of contact time on atrazine and the modified rice husk-based silica adsorbent. They provide valuable insights about the adsorption behaviors of modified rice husk-based silica adsorbent and its effectiveness in removing atrazine from wastewater (Gorzin & Bahri Rasht Abadi, 2018).

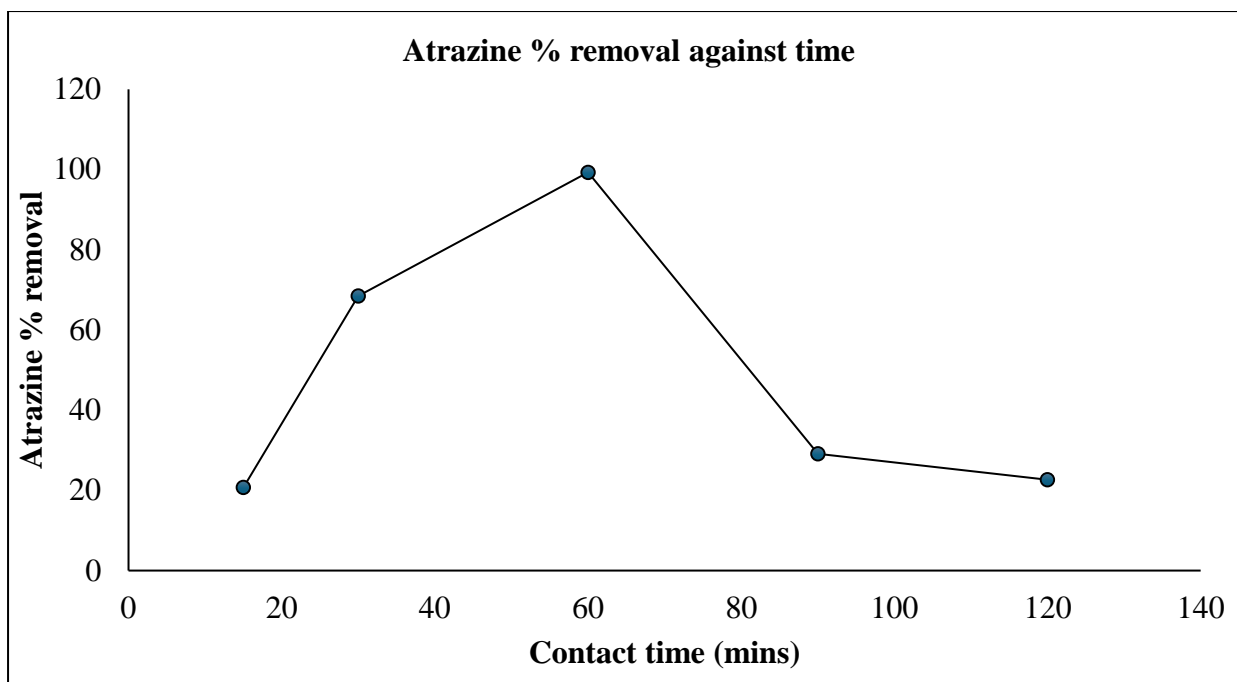


Fig.4.10: Atrazine percentage removal against time (mins).

The modified rice husk-based silica adsorbent rapidly adsorbs atrazine upon contact, demonstrating the material's high adsorption capacity. Fig.4.10 shows a steady, steep decline in the concentration of atrazine from wastewater over time, with a yield of 99.3% at the 60-minute mark (Bertsch & Fischer, 2020). Following the graph's initial, a sharp rise, there was a steady decline that indicated the lack of active sites (David Kowanga *et al.*, 2016). This decline could also have been caused by the adsorbent's interference because atrazine's low concentration prevents it from being detected by UV light. The initial concentration used was 18.5 mg/L with a pH of 9 and 0.2 g of adsorbent (Güçbilmez *et al.*, 2023).

#### 4.7.3 The impact of the modified rice husk-based silica adsorbent's dosage

The amount of atrazine in wastewater noticeably decreases as the adsorbent dosage is increased. The steep decline suggests that atrazine is removed from wastewater more effectively at higher doses of the modified rice husk-based silica adsorbent. This is due to more modified silica adsorbent derived from rice husks that increased surface area and improved the adsorption capacity, resulting in more active sites (Ponnusami *et al.*, 2007).

The rate at which the atrazine concentration dropped decreased with an increase in the dosage of the modified rice husk-based silica adsorbent. This indicates that atrazine removal efficiency may reach a point of diminishing returns, beyond which adding more modified rice husk-based silica adsorbent won't yield appreciable improvements. This is because more adsorbent has little effect on the process once the surface area that is available for adsorption becomes saturated (Yadav *et al.*, 2021). A plateau eventually occurs, as shown in the graph, where additional increases in the dosage of the adsorbent have little to no effect on the atrazine concentration. This suggests that the modified rice husk-based silica adsorbent has utilized all its adsorption capacity. There is currently no more atrazine concentration reduction that can be achieved by adding more adsorbent saturated (Yadav *et al.*, 2021).

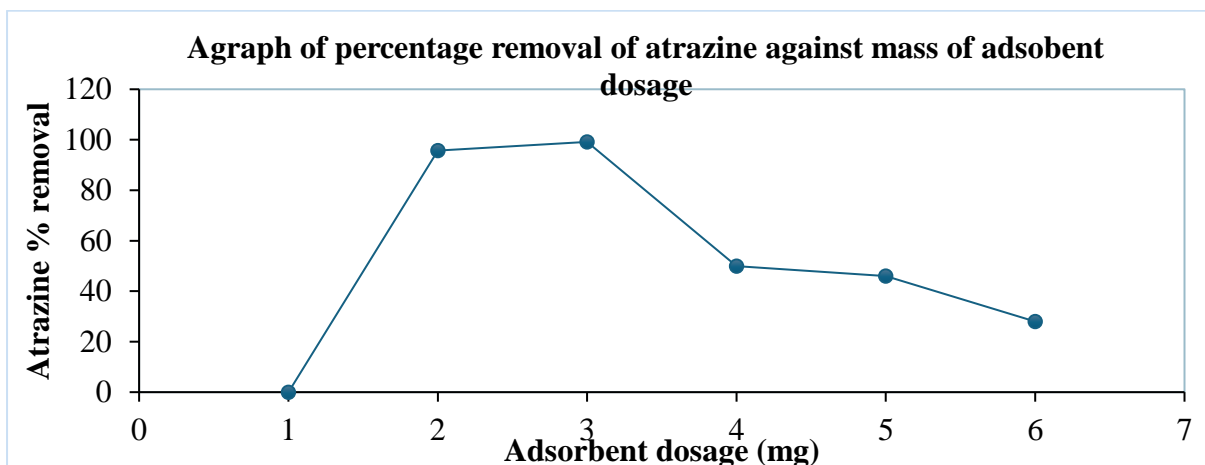


Fig.4.11: Rate at which atrazine was removed on varying the modified adsorbent dosage.

The graph above helps identify the optimal dosage of the modified rice husk-based silica adsorbent for atrazine adsorbent. At this point, the greatest atrazine removal efficiency can be attained without wasting any extra adsorbent. It is usually detected shortly before the plateau phase, which is the point at which the rate of atrazine concentration declines noticeably (Ponnusami *et al.*, 2007). It is imperative to comprehend the effects of adsorbent dosage because exceeding the recommended dosage of modified rice husk-based silica adsorbent wastes resources and raises treatment costs. As a result, the graph assists in figuring out the

most economical dosage of a modified rice husk-based silica adsorbent for the removal of atrazine. The optimum dose of 0.3 g registered high percentage removal of 99.16%, concentration of 18.5 mg/L, contact time of 30 minutes and pH of 9 (Gorzin & Bahri Rasht Abadi, 2018).

#### 4.7.4 Impact of initial concentration of atrazine in wastewater on the modified rice husk-based silica adsorbent

A significant long-term decrease in atrazine concentration at lower starting concentrations. This suggests that atrazine can be effectively removed from wastewater with low initial contamination levels using a modified rice husk-based silica adsorbent. The initial adsorption rate is usually rapid because there are more available adsorption sites on the modified rice husk-based silica adsorbent surface than there are in the solution (Dutta *et al.*, 2021). The graph indicates a longer time to reach equilibrium as the initial atrazine concentration rises. This is due to the fact that increased atrazine concentrations increase competition for adsorption sites on the surface of the modified rice husk-based silica adsorbent. As a result, the modified rice husk-based silica adsorbent gradually saturates with atrazine, taking longer for it to reach its maximum adsorption capacity (Ponnusami *et al.*, 2007).

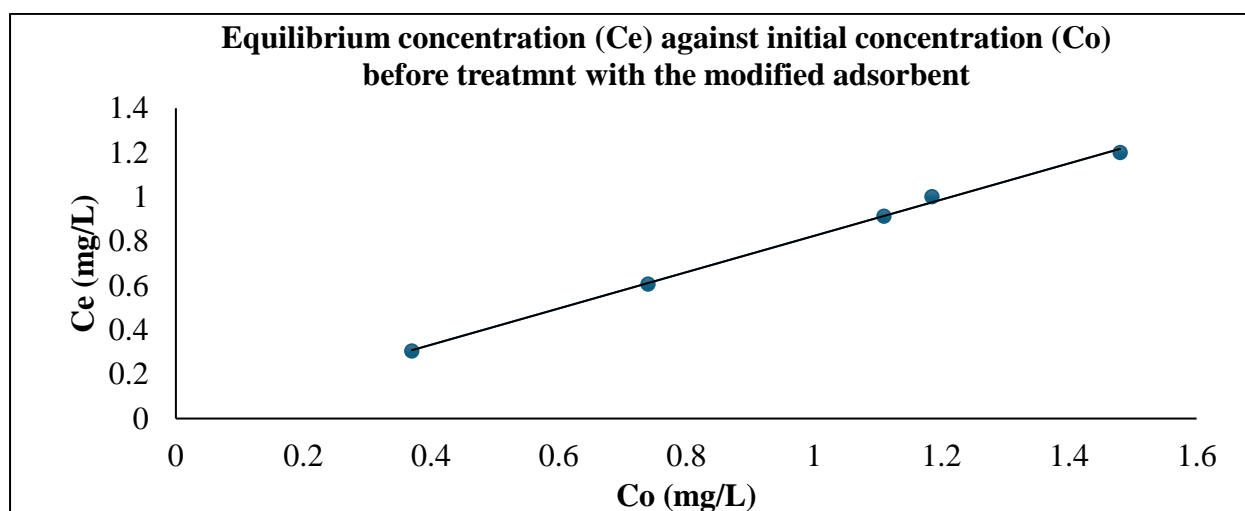


Fig.4.12: Equilibrium concentration against initial concentration before treatment with the modified adsorbent.

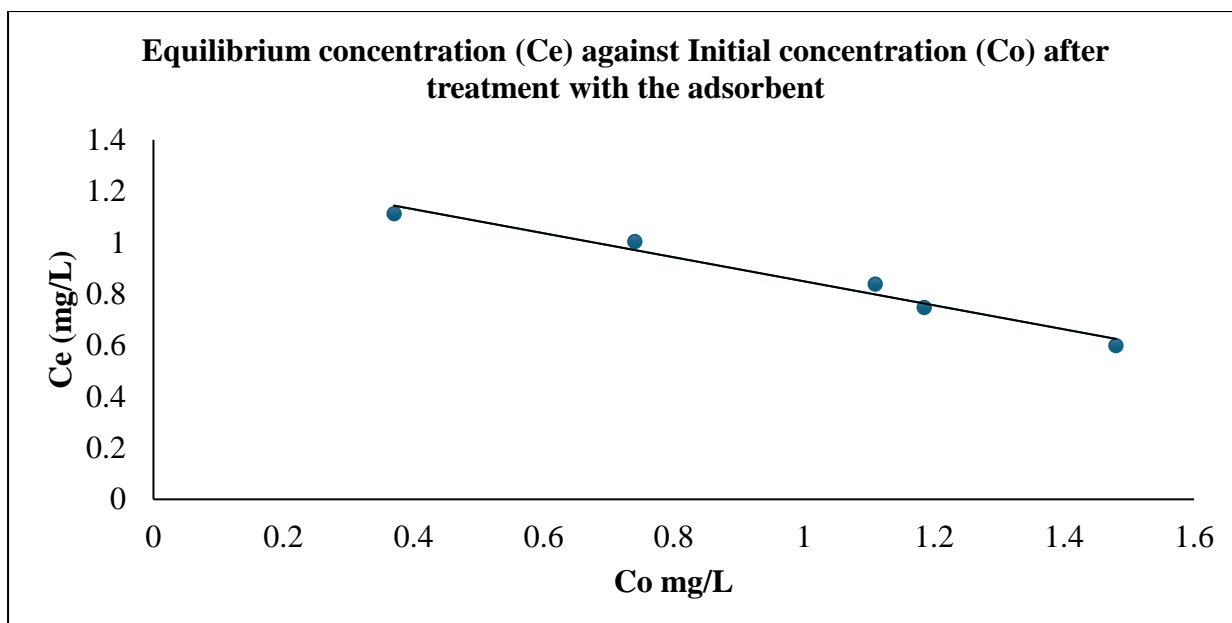


Fig.4.13: Equilibrium concentration against the initial concentration after treatment with the modified rice husk-based silica adsorbent (Lima *et al.*, 2022).

The graph indicates a steeper decline in atrazine concentration over time at higher initial concentrations than at lower concentrations. This implies that as the initial contamination level rises, modified rice husk-silica adsorbent loses effectiveness at removing atrazine, eventually reaching a point where additional increases in the initial concentration yield diminishing returns in terms of atrazine removal efficiency (Ponnusami *et al.*, 2007). The graph shows the concentration at which the modified rice husk-based silica adsorbent's ability to adsorb atrazine significantly decreases. This threshold concentration is the point at which the concentration of atrazine in the solution overwhelms the modified rice husk-based silica adsorbent, resulting in decreased adsorption efficiency and an extended equilibrium time (Dutta *et al.*, 2021).

#### 4.8 Physiochemical properties of wastewater sample from Lugazi stream

The wastewater samples were collected thrice from three(3) different sampling points (A1, A2, A3). Different physico-chemical parameters were measured, and the results presented in the table

4.5

Table 4.5: Physico-chemical properties of wastewater sample from Lugazi flowing streams using Anova analysis.

**Anova: single factor analysis**

<b>SUMMARY</b>						
<i>Groups</i>	<i>Count</i>	<i>Sum</i>	<i>Average</i>	<i>Variance</i>		
pH	12	72.23	6.019167	0.026008		
Turbidity	12	1072.8	89.4	81.9		
TDS	12	1335.8	111.3167	4.534242		
Salinity	12	0.3	0.025	2.73E-05		
EC	12	2671.7	222.6417	27.24629		
Temperature	12	300.5	25.04167	0.289924		

<b>ANOVA</b>						
<i>Source of Variation</i>	<i>SS</i>	<i>df</i>	<i>MS</i>	<i>F</i>	<i>P-value</i>	<i>F crit</i>
Between groups	434357.7	5	86871.53	4572.327	2.14E-82	2.353809
Within groups	1253.961	66	18.99942			
Total	435611.6	71				

The first part of Anova table gives the summery pH, turbidity, total dissolved solids (TDS), salinity, electrical conductivity (EC), and temperature are the six wastewater parameters that were subjected to an Analysis of Variance (ANOVA) as shown in table 4.5. This is a detailed analysis of the findings. The figures shown summarize the central tendency or average and dispersion /variance of each parameter, giving a snapshot of the data's distribution for each group. The second part of Anova table gives a detailed summery description from the groups and their source of variation.

**4.8.1 Source of variation between group**

The sources of variation between groups are sum of squares (SS) = 434357.7, the degrees of freedom (df) = 5, the mean square (MS) = 86871.53, the F = 4572.327, the P-value = 2.14E-82 and the critical f-value (F crit) = 2.353809.

#### **4.8.2 The source of variance within groups**

The variance within the groups that are analyzed are the Sum of Squares (SS) = 1253.96, the degrees of freedom (df) = 66 and the Mean Square (Ms) = 18.999.

#### **4.8.3 The source of variation in the total**

The variance within the total analyzed are sum of squares (SS) = 435611.6 and the degrees of freedom (df) = 71.

#### **4.8.4 Analysis and interpretation of results from Anova**

##### **4.8.4.1 The sum of squares (SS)**

The sum of squares (SS) between groups = 434357.7, this measures the variability between the means of different groups parameters. From the figure 434357.7 calculated by Anova, it implies that there are significant differences between group means. The sum of squares (SS) within groups = 1253.961, this measures the variability within each group. Since figure 1253.961 is a lower value, this implies that the data points within each group are similar. The total sum of squares (SS) = 435611.6 which is the overall variability in the dataset from analysis of variance.

##### **4.8.4.2 The degrees of freedom (df)**

The df between groups = 5 was got by subtracting one (1) from the number of groups. There are six groups (parameters), therefore  $df = 6 - 1 = 5$ . The df within groups = 66 was calculated by observing the total number of observations less the number of groups therefore  $df = 72 - 6 = 66$ . The total df = 71 is got by subtracting one (1) from the total number of observations therefore total  $df = 72 - 1 = 71$ .

##### **4.8.4.3 The mean square (MS)**

The mean square between groups = 86871.53, was calculated by dividing the sum of squares (SS) between groups with its df ( $434357.7 / 5$ ) which represents the average variability between

groups. The mean square within groups = 18.999 and it is calculated by dividing the sum of squares within the groups by its df (1253.961 / 66), it represents the average variability within each group.

#### **4.8.4.4 The F-statistic = 4572.327**

The F-statistic is the ratio of the mean square between groups to the mean square within groups (86871.53 / 18.999). The F-value is high which clearly indicate that the variability between group means is much larger than the variability within groups, implying that there are significant differences between the group means.

#### **4.8.4.5 The P-value = 2.14E-82**

The occurrence of observing such an extreme F-value if all the group means were equal (null hypothesis) if they were true. A much smaller P-value  $< 0.05$  leads to rejecting the null hypothesis, implying that there are significant differences between the group means.

#### **4.8.4.6 F crit = 2.353809**

From the analysis of variance, the critical value of F at a chosen significance level was 0.05. The calculated F-value 4572.327 is greater than the critical F-value 2.353809. Therefore, the null hypothesis is rejected. The means of the six wastewater parameters differ statistically and significantly, according to the results of the ANOVA analysis. This indicates that rather than within each group, the variance in the data is caused by variations between the group means in the specified parameters. Practically speaking, this implies that the means of at least one parameter diverge noticeably from the others, emphasizing the significance of considering each parameter independently when analyzing the quality of wastewater.

#### **4.8.5 Adsorption experiments on wastewater sample from Lugazi streams**

Upon treatment of the wastewater from Lugazi sugar plantation stream with the modified rice husk, there was significant drop of atrazine concentration from the wastewater as shown in Fig. 4.14.

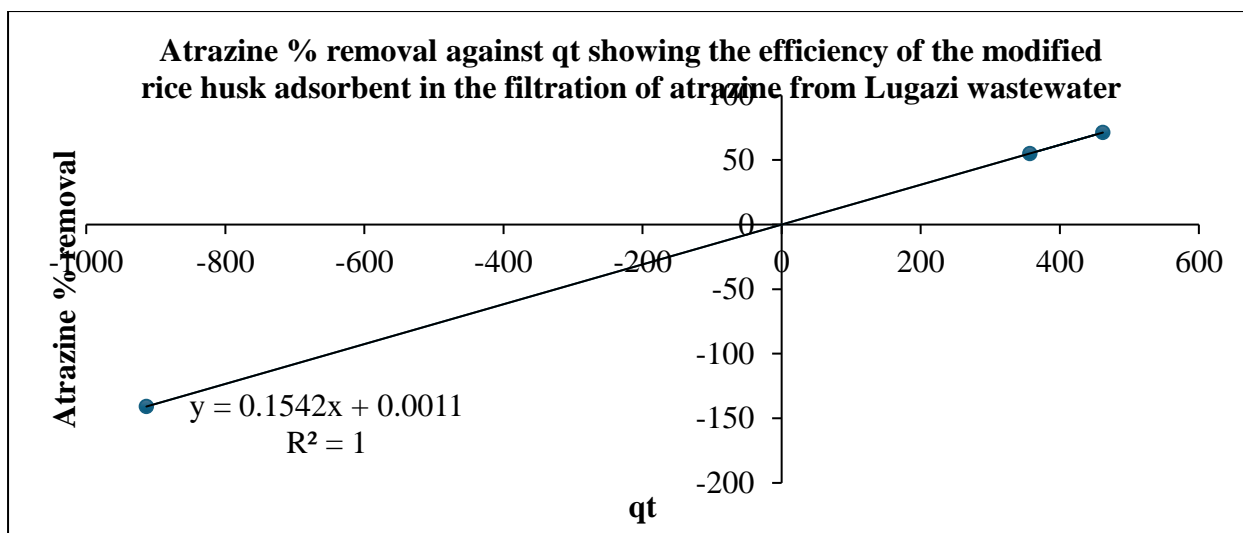


Figure.4.14: A plot of atrazine percentage removal against equilibrium concentration at a given contact time (mins).

Maximum adsorption was achieved at a contact time of 30 minutes with a percentage yield of 71.24%. Adsorption of atrazine from Lugazi sugar plantation streams increased with increased interaction against time. Therefore, with increase in contact time, more adsorption is achieved as the active sites of the modified rice husk-based silica adsorbent interact freely with the atrazine present in the wastewater. There was a significant drop at the 60-minute due to interference during absorbance by the UV-visible spectrophotometer due to high concentration of the modified adsorbent as compared to the concentration of atrazine that could not be detected due to its low concentration (Okoro *et al.*, 2022).

Atrazine, a persistent herbicide, is efficiently removed from wastewater through adsorption onto modified and natural adsorbents. The removal efficiency is significantly influenced by key physico-chemical parameters of wastewater. A positive understanding of these parameters helped to optimize operational conditions, ensures maximum removal efficiency, and guided the sustainable application of adsorption technologies. During adsorption total dissolved solids (TDS), provided a realistic condition of natural wastewater, ensuring that the adsorbent's performance was tested under competitive conditions (Okoro *et al.*, 2022). This enhances the robustness and reliability of the adsorbent in real applications and after adsorption, the TDS

measures helped to confirm the reduction of dissolved impurities, demonstrating both atrazine uptake and improvement in wastewater quality (Ukanwa *et al.*, 2019). During adsorption, salinity modified the ionic strength, which enhanced electrostatic interactions on the adsorbent surface functional groups, this helped in tuning adsorption behaviour for atrazine.

After adsorption, salinity ensured that adsorption has not only removed atrazine but also maintained ionic balance for reuse. Turbidity provides suspended solids that can act synergistically with the adsorbent, sometimes offering additional surfaces for atrazine binding. After adsorption, a decrease in turbidity after treatment confirms particle removal and supports the dual benefit of adsorbing atrazine and clarifying the wastewater (Val & Tholozan, 2020). During adsorption, the electrical conductivity (EC) reflected the ionic content of the solution, helping to evaluate the competitive adsorption effects. This ensured that adsorbents remain selective and efficient even in mineral-rich waters. After adsorption, a reduction in electrical conductivity was an indicator of removal of ionic species along with atrazine, reflecting a broader purification effect (Yang *et al.*, 2018).

The temperature influenced the reaction kinetics and adsorption equilibria. A slight temperature rise enhanced diffusion of atrazine molecules, leading to faster attainment of equilibrium. After adsorption, stable temperatures ensure reproducibility and scalability of the process, which is important for industrial applications. Physico-chemical parameters such as TDS, salinity, turbidity, EC, conductivity, and temperature play a constructive role in shaping the efficiency of atrazine removal from wastewater during and after adsorption. While they introduce complexity, their proper monitoring and management allow for optimized adsorption conditions, improved water quality, and increased confidence in the practical application of adsorbents. The positive interaction between these parameters and the adsorption process ensured that, treated wastewater is not only free of atrazine but also exhibits improved physico-chemical quality, aligning with environmental and public health standards (Grandclément *et al.*, 2017).

#### 4.9 Kinetics of atrazine in simulated wastewater using modified rice husk adsorbent

The adsorption kinetics of atrazine on modified rice husk-based silica adsorbent is presented in Fig.4.15. To fit the experimental data, pseudo-first order and pseudo-second order equations were applied. The corresponding Fig contain the computed values for  $q_e$ ,  $k_1$ ,  $k_2$ , and the correlation coefficient ( $R^2$ ) (Sarathchandran *et al.*, 2021).

##### 4.9.1 Pseudo first order kinetic model

The pseudo-first-order model used to plot the experimental data indicates that there is no linear relationship between time ( $t$ ) and the natural logarithm of the atrazine adsorbed by the modified rice husk-based silica adsorbent ( $\ln(q_e - qt)$ ). Rather, the data points show a non-linear relationship and substantially depart from the predicted linear trend (Chen *et al.*, 2009). The lack of a good fit indicates that the modified rice husk-silica adsorbent does not adhere to pseudo first-order kinetics, which states that the rate of adsorption is directly proportional to the adsorbate concentration (Sun *et al.*, 2018).

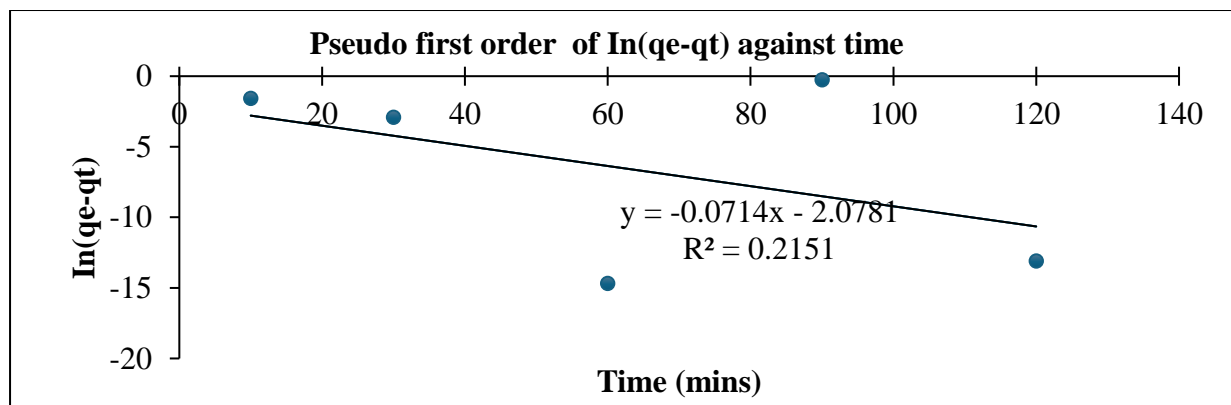


Fig.4.15: Represents Pseudo first order, the graph is not passing through all the dots, the experimental value of  $q_e$  and that if  $q_e$  calculated are not close to each other and the value of  $R^2$  is 0.2308 which is not close to 1 (one). The adsorption kinetics are not well described by the discrepancy in the rate constants ( $k$ ) derived from the pseudo-first-order model (Sun *et al.*, 2018). The computed value of  $k$  deviates considerably from the experimental findings, suggesting that the atrazine adsorption onto the modified rice husk-based silica adsorbent cannot be adequately described by the pseudo-first-order model. The non-compliance of the

adsorption mechanism with the pseudo-first-order model suggests that atrazine is more effectively adsorbed onto the modified rice husk-based silica adsorbent by other adsorption mechanisms, such as intra-particle diffusion or chemisorption (Liu *et al.*, 2020).

#### 4.9.2 Pseudo second order kinetic model

To ascertain whether strong interaction or chemisorption occurred during the adsorption process between the adsorbent (modified rice husk-based silica adsorbent) and the adsorbate (atrazine), a pseudo-second-order model was utilized. The model's experimental data, which is shown below, indicates that the modified rice husk-based silica adsorbent is effective at removing atrazine from wastewater (Jin *et al.*, 2014). The maximum amount of atrazine that was adsorbed onto the adsorbent at equilibrium is represented by the equilibrium adsorption capacity, or Equilibrium Adsorption Capacity( $q_e$ ) of the pseudo-second-order model. The amount,  $q_t$ , which represents the amount of atrazine adsorbed at time  $t$ , was found by intercepting the linear plot of  $t/q_t$  against  $t$  (Ding *et al.*, 2014). An understanding of the kinetics of the adsorption process can be gained from the Rate Constants ( $k$ ) that are obtained by fitting the experimental data to the pseudo-second-order model. Higher rate constant values indicate faster adsorption kinetics, indicating a high affinity of the modified rice husk-based silica adsorbent for atrazine as shown in fig.4.15 below (Islam *et al.*, 2017).

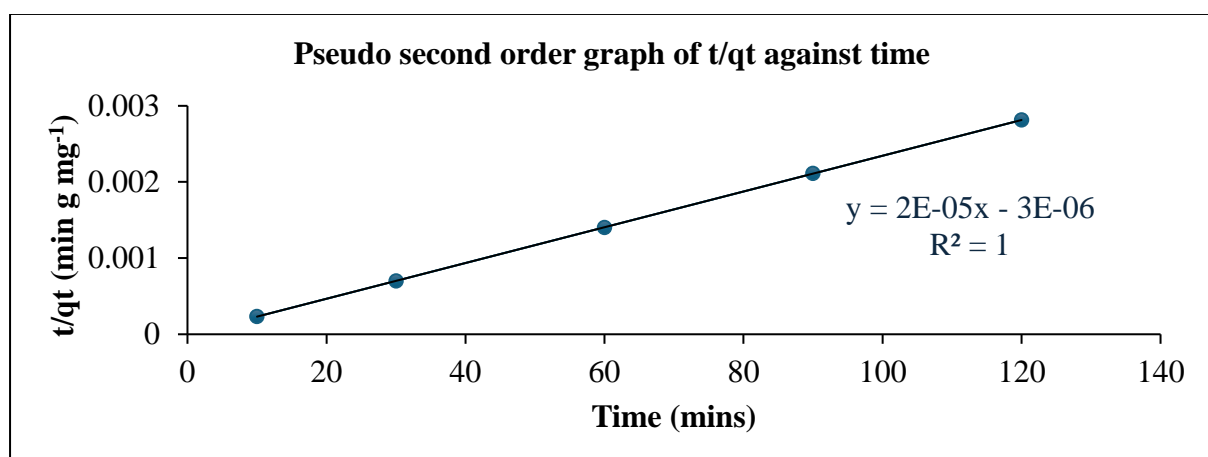


Fig.4.15: The graph above is a plot of pseudo second order model.

The  $R^2$  value of the modified rice husk-based silica adsorbent for pseudo-second-order model is 1(one) which is higher than that of the pseudo-first-order model. This showed that the rate-limiting step is chemical adsorption, and that the reaction rate was proportionate to the number of active sites of the modified rice husk-based silica adsorbent surface (Jin *et al.*, 2014). The pseudo-second-order model's adsorption mechanism postulates that chemisorption, the sharing, or exchange of electrons between the adsorbate and the adsorbent is the rate-limiting step in the adsorption process. Consequently, the effective implementation of this model implies that atrazine adsorption onto the modified rice husk-based silica adsorbent was significantly influenced by chemical interactions (Islam *et al.*, 2017).

From the plot of the graph above,  $\frac{t}{qt}$  Vs  $t$ ,  $Slope = \frac{1}{qt}$  and  $intercept = \frac{1}{k_2 q_e^2}$

$q_e$  and  $q_t$  = amount of atrazine adsorbed at equilibrium and equilibrium time  $t$ (min) respectively.  $K_2$  = Pseud second order equilibrium constant (Chen *et al.*, 2009). The pseudo-second-order reaction isotherm can offer important insights into the kinetics and mechanism of the adsorption process as well as the effectiveness of the adsorbent in removing atrazine from wastewater. The results of applying this isotherm to the atrazine adsorption onto the modified rice husk-based silica adsorbent are displayed in Fig.4.15.

#### **4.9.3 Elovich kinetic model**

The premise is that the rate of atrazine adsorption decreases exponentially as the amount of atrazine adsorbed increases because the number of adsorption sites increases exponentially with adsorption, an indicator of multilayer adsorption (Lima *et al.*, 2022). This model aids in the prediction of the mass and surface diffusion, activation, and deactivation energy of the modified rice husk-based silica adsorbent as it adsorbs the atrazine from wastewater (Liu *et al.*, 2020).

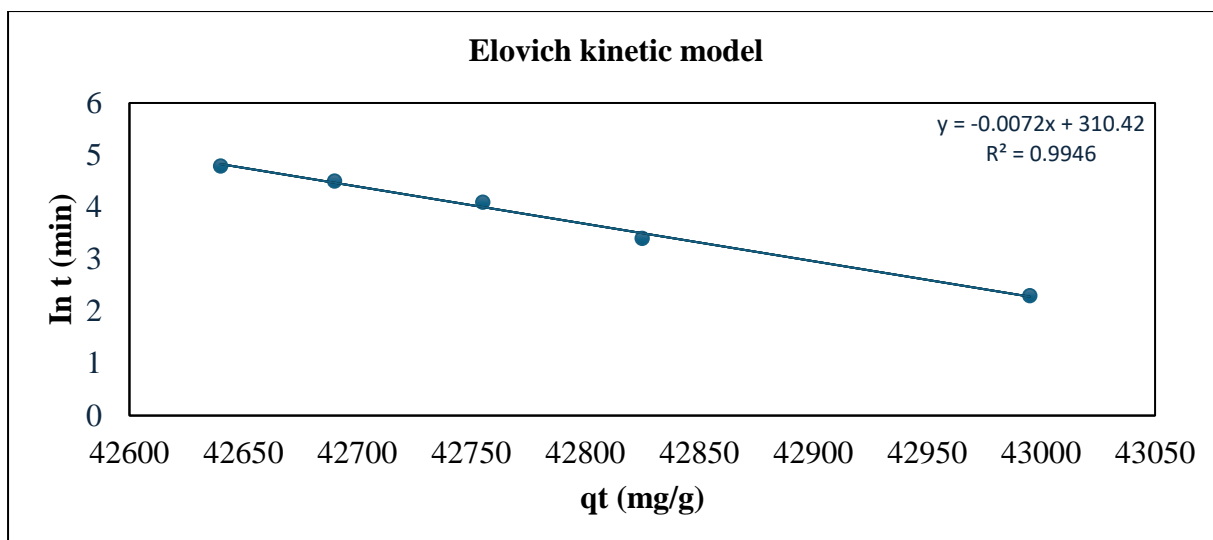


Fig.4.16: A graph of  $\ln t$  (min) against  $qt$  which made it possible to identify whether chemisorption was taking place on the adsorbent's heterogeneous surface.

The equation  $qt = \alpha \ln(t) + \beta$ , where  $\alpha$  and  $\beta$  are the Elovich constants, describes the Elovich kinetic model. The initial rate of surface covering by atrazine molecules is represented by the parameter  $\alpha$ , whilst the extent of surface coverage or the adsorbent's adsorption capacity is indicated by the value  $\beta$ . From the equations,  $Slope = 1/\alpha$ ,  $intercept = 1/\alpha \ln(\alpha\beta)$ , (Lima *et al.*, 2022). According to the foregoing findings, atrazine's adsorbate-adsorbent interaction did not have a significant effect on the surface of the modified rice husk-based silica adsorbent. This resulted from either the unique chemical characteristics of atrazine or the makeup of the surface functional groups on the modified adsorbent (Lima *et al.*, 2022).

The Elovich model presupposes monolayer adsorption, in which the adsorbent surface creates only one layer of adsorbate molecules. The adsorption kinetics have not been satisfactorily represented by the Elovich model since a multilayer adsorption took place. Atrazine may have faced competition from other compounds in the wastewater for adsorption sites on the modified rice husk-based silica adsorbent. This competition may cause the atrazine adsorption kinetics to change and depart from the Elovich model ( Yang *et al.*, 2018). Diffusion limitation during Elovich kinetic models presupposes rapid mass transfer between the liquid phase and the adsorbent surface, yet adsorption kinetics may be impacted if diffusion was sluggish inside the

liquid phase or inside the adsorbent's porous structure. The adsorption kinetics of the modified rice husk-based silica adsorbent did not follow the Elovich model, which requires a uniform surface, because the surface is heterogeneous, with varying types of active sites or surface energies (Lima *et al.*, 2022).

#### 4.9.4 Linear intra-particle diffusion model

Plotting the experimental results in accordance with the linear intra-particle diffusion model reveals a linear relationship between the atrazine adsorbed ( $q_t$ ) and the square root of time ( $t^{0.5}$ ).

A distinct stage of the adsorption process is represented by each line in Fig.4.17.

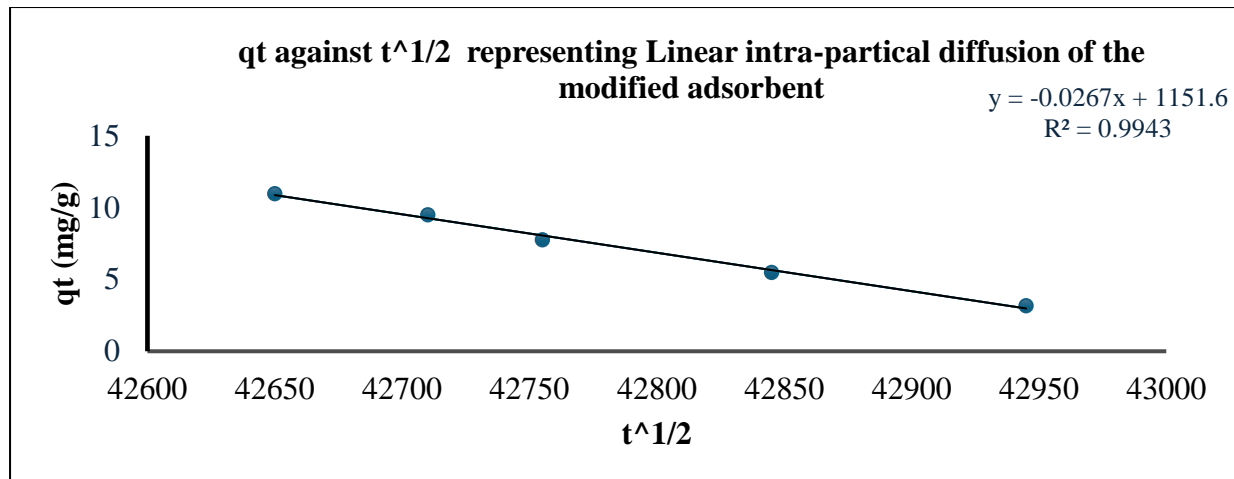


Fig.4.17: Linear intra-particle diffusion

The information regarding the rate of intra-particle diffusion is given by the slopes above. Whereas a lower slope denotes slower diffusion, a steeper slope indicates faster intra-particle diffusion (Fathy *et al.*, 2020). The modified rice husk-silica adsorbent surface was next to a stationary layer of solution, and the intercept of the linear curve tells how thick that layer was. A thicker boundary layer, which denotes a slower mass transfer from the solution to the adsorbent surface, is suggested by a higher intercept (Fuhrmann *et al.*, 2019). The plot's degree of linearity can shed light on the adsorption mechanism. Plotting linear segments with little deviation indicates that the adsorption process's rate-limiting stage is intra-particle diffusion. Adherence to the intra-particle diffusion reaction that is linear isotherm indicates that atrazine adsorption onto

the modified rice husk-based silica adsorbent is largely dependent on intra-particle diffusion (Fathy *et al.*, 2020).

#### **4.10 Adsorption isotherm mechanism for simulated wastewater**

##### **4.10.1 Freundlich adsorption isotherm mechanism**

Adsorption onto heterogeneous surfaces, such the modified rice husk-based silica adsorbent, can be described by the Freundlich isotherm and below are experimental data after atrazine's interactions with the modified adsorbent (Luconi *et al.*, 2022). The adsorption of atrazine onto the modified rice husk-based silica adsorbent was a multi-layer adsorption process with heterogeneous adsorption energies, according to the experimental results to the Freundlich model. Adsorption onto several sites on the adsorbent surface with different energies is taken into consideration by the Freundlich model (Luconi *et al.*, 2022).

The Freundlich plot below illustrates the distribution of adsorption energies across the adsorbent surface and reflects the assumption made by the Freundlich model that there is surface heterogeneity, i.e., that not all adsorption sites on the modified rice husk-based silica adsorbent have the same affinity for atrazine molecules (Feiqiang *et al.*, 2018). The adsorption of atrazine onto the modified rice husk-based silica adsorbent appears to have involved heterogeneous adsorption behavior, which can be explained by a model that considers varying adsorption energies and surface affinities, according to the compliance with the Freundlich adsorption isotherm mechanism (Vieira *et al.*, 2012). Understanding the adsorption mechanism, maximizing process variables, and creating effective adsorption systems for the removal of atrazine from wastewater treatment applications can all benefit from this knowledge (Borges *et al.*, 2024).

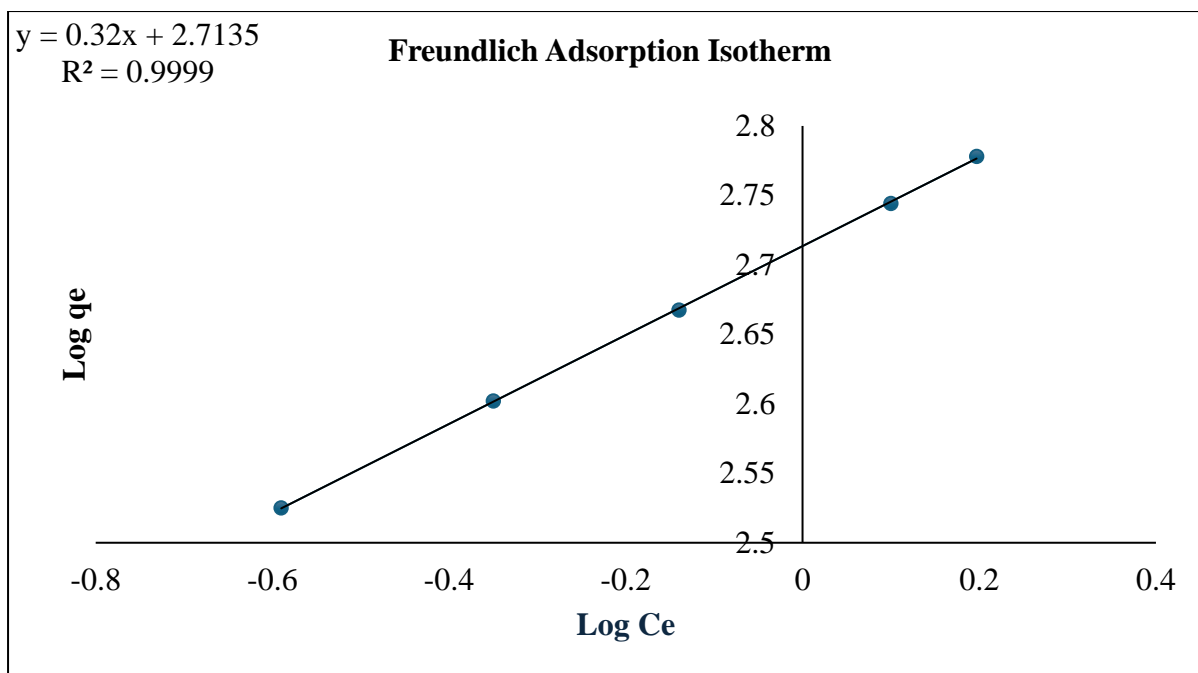


Fig.4.18: Log  $q_e$  against log  $C_e$  showing Freundlich's adsorption isotherm. The  $R^2$  value is 0.8015 as shown in the figure above.

#### 4.10.2 Langmuir adsorption isotherm mechanism

According to Langmuir, adsorption happens on a homogenous surface by monolayer adsorption, which does not include interactions between adsorbed species and uniform adsorption energies on the adsorbent's surface (Jin *et al.*, 2014). The experimental data did not exhibit a linear relationship between the equilibrium concentration of atrazine in the solution ( $C_e$ ) and the amount of atrazine adsorbed ( $q_e$ ), when plotted in accordance with the Langmuir adsorption isotherm (Vieira *et al.*, 2012). The adsorption process may not have followed the Langmuir model's presumptions, which call for monolayer adsorption on a homogenous surface with no interactions between adsorbed molecules, based on Fig.4.18. The atrazine adsorption mechanism onto the modified rice husk-based silica adsorbent is more complex than monolayer adsorption on a homogenous surface, as evidenced by the failure to comply with the Langmuir model (Masoumi *et al.*, 2016).

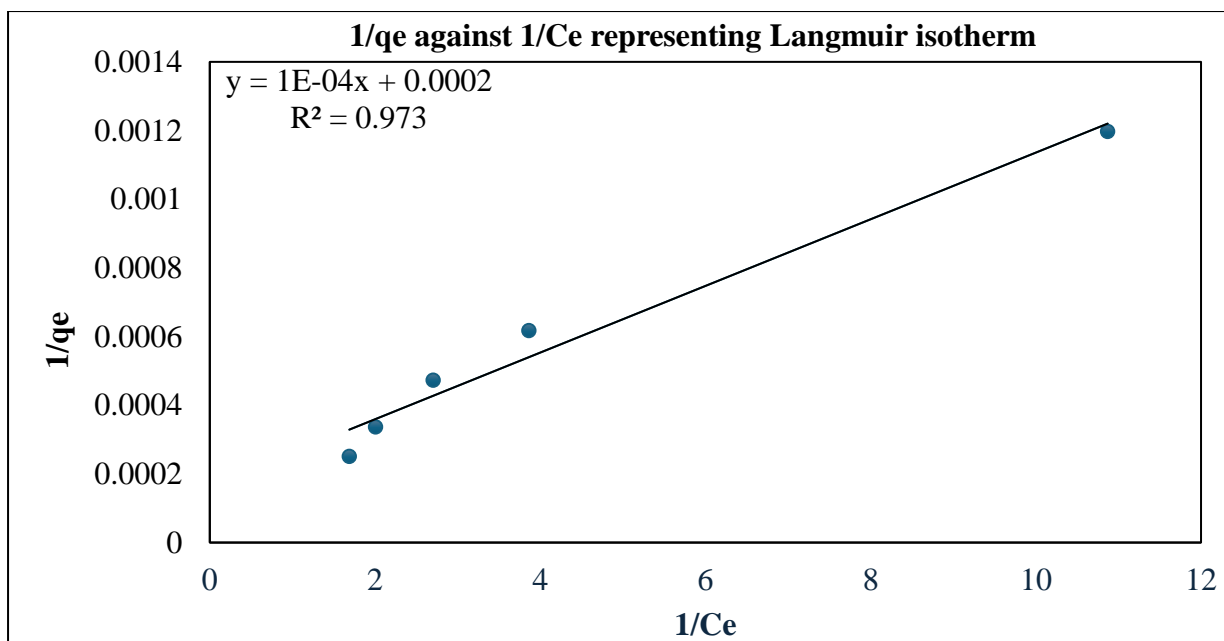


Fig.4.19: The result suggested that mononuclear adsorption was not favorable for the modified rice husk-based silica adsorbent as it possesses a low specific surface area as shown in the graph as its  $R^2$  value of 0.1396, the adsorption isotherm could only be explained by the Freundlich model, which also showed that atrazine sorption could be explained as chemisorption on a heterogeneous surface because it produced a larger  $R^2$  value for all the adsorbents (Cao *et al.*, 2009). Furthermore, a lower  $1/n$  and bigger  $K_F$  values of the modified rice husk-based silica adsorbent suggest a higher adsorption capacity, intensity, and affinity for atrazine (Masoumi *et al.*, 2016)..

## CHAPTER FIVE

### CONCLUSIONS AND RECOMMENDATIONS

#### 5.1 Conclusions

This study successfully achieved its objectives, leading to significant findings in the field of environmental remediation as summarized. The synthesis of modified rice husk-based silica adsorbents was successfully carried out using a KOH activation process. Characterization of the adsorbents revealed that the modification process significantly enhanced the surface area, porosity, and density of functional groups, particularly silanol groups (-Si-OH), C-O and Siloxane groups (-Si-O-Si-) which are crucial for adsorption. The modified adsorbents exhibited improved physicochemical properties compared to unmodified rice husk ash, making them suitable for adsorption applications.

The modified rice husk-based silica adsorbents demonstrated high adsorption capacity and efficiency for atrazine removal from simulated wastewater. Batch adsorption experiments showed that the adsorbents could effectively remove atrazine from aqueous solutions, with adsorption capacities influenced by factors such as initial atrazine concentration, adsorbent dosage, pH, and contact time. The adsorption data fitted well to kinetic and isotherm models, indicating a complex adsorption mechanism involving both physisorption and chemisorption.

Efficiency in real-world application of the modified adsorbent for atrazine removal from flowing streams at the Lugazi sugar plantation yielded promising results. The adsorbent efficiently reduced atrazine concentrations in the stream water, demonstrating its potential for practical environmental remediation. This finding highlights the feasibility of using agricultural waste-derived materials for mitigating pesticide pollution in water bodies.

Optimization studies revealed that the efficiency of atrazine removal by the modified adsorbent was influenced by several factors, including adsorbent dosage, pH, and contact time. The

optimal conditions for maximum atrazine removal were determined, providing valuable insights for scaling up the adsorption process. Kinetic studies showed that the adsorption of atrazine onto the modified adsorbent followed pseudo-second-order kinetics, indicating that chemisorption played a significant role in the adsorption process.

Therefore, this study demonstrated the potential of modified rice husk-based silica adsorbents for effective removal of atrazine from wastewater. The synthesis of these adsorbents not only provides a sustainable solution for managing agricultural waste but also contributes to environmental remediation efforts. The findings of this research can be applied to develop cost-effective and efficient technologies for removing pesticides from water bodies, thereby protecting both human health and the environment.

## **5.2 Recommendations**

Based on the findings of this dissertation, the following recommendations are proposed for future research and practical applications.

On optimization of KOH concentration, further studies should be carried out to investigate the effect of varying KOH concentrations on the surface properties and adsorption capacity of the modified rice husk-based silica adsorbents. This could lead to the development of adsorbents with even higher efficiency for atrazine removal.

Competitive adsorption studies should be experimentally conducted to assess the adsorbent's selectivity for atrazine in the presence of other pesticides or contaminants commonly found in agricultural runoff for efficiency and adsorption capacity assessment, and scaling up adsorption process in pilot-scale studies should be conducted to evaluate the feasibility and efficiency of using the modified adsorbent for atrazine removal in larger volumes of water.

Long-term field studies should be done to perform long-term field studies to assess the durability and sustained performance of the modified adsorbent in removing atrazine from flowing streams, considering factors like seasonal variations and potential adsorbent degradation. Integration with existing water treatment systems to explore the potential for integrating the modified adsorbent into existing water treatment systems used in agricultural areas to enhance their capability to remove pesticide residues.

Developing and validating models that can predict the adsorption behavior of atrazine onto the modified adsorbent under various operating conditions. This would aid in optimizing the design and operation of adsorption systems. Regeneration and reuse studies should be investigated to determine the potential for regenerating and reusing the modified adsorbent to assess its economic viability and sustainability for large-scale applications.

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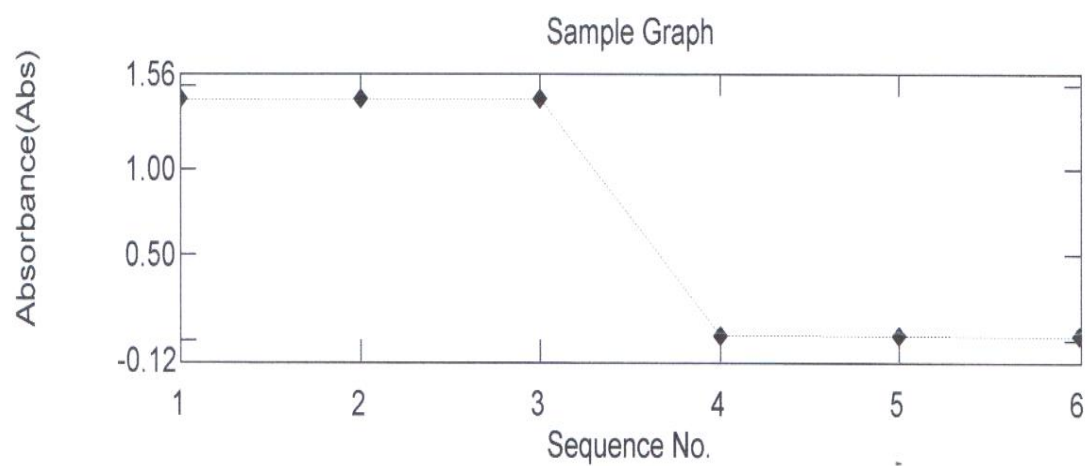
<https://doi.org/10.1016/j.cej.2004.06.011>

Zou, W., Gao, B., Sik, Y., & Dong, L. (2019). Chemosphere Integrated adsorption and photocatalytic degradation of volatile organic compounds ( VOCs ) using carbon-based nanocomposites : A critical review. *Chemosphere*, 218, 845–859.

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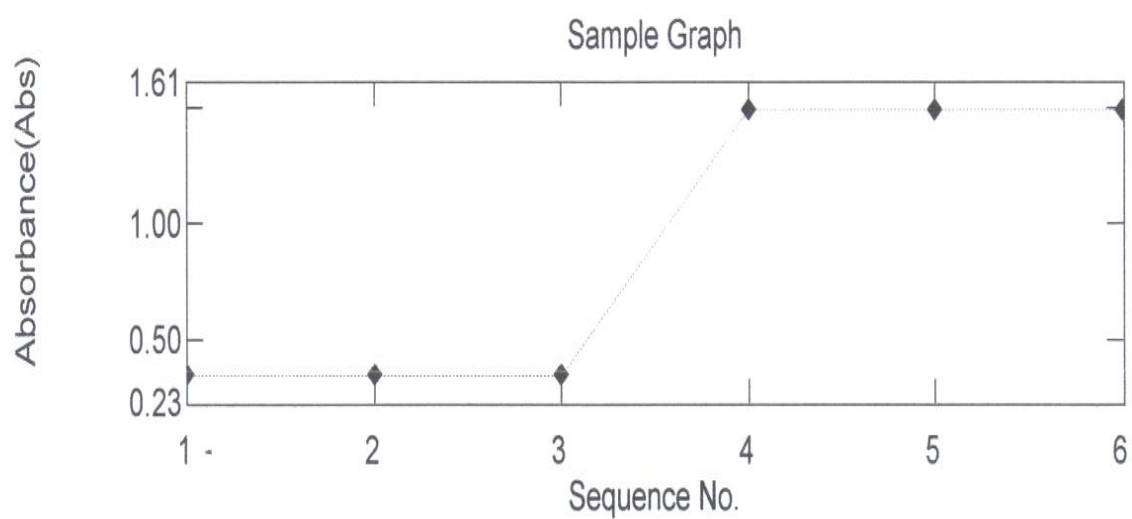
## APPENDICES

Appendix I showing the adsorption capacity test of the modified rice husk-base silica adsorbent and its spectrum.



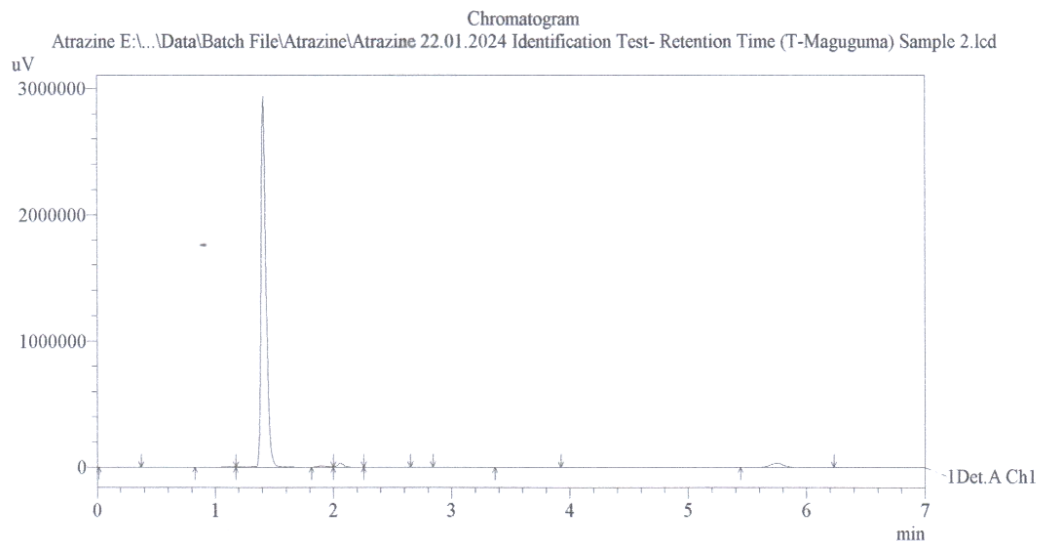
	Sample ID	WL235.0	Comments
1	Initial Concentration	1.419	
2	Initial Concentration	1.423	
3	Initial Concentration	1.421	
4	Final Concentration	0.029	
5	Final Concentration	0.024	
6	Final Concentration	0.017	

Appendix II showing adsorbent re-use test of the modified rice husk-base silica adsorbent



	Sample ID	WL235.0	Comments
1	Final Concentration	0.350	
2	Final Concentration	0.350	
3	Final Concentration	0.348	
4	Initial Concentration	1.494	
5	Initial Concentration	1.493	
6	Initial Concentration	1.493	

Appendix III showing the spectrum identification of atrazine in Maguguba sample that contain pure atrazine using an HPLC machine.

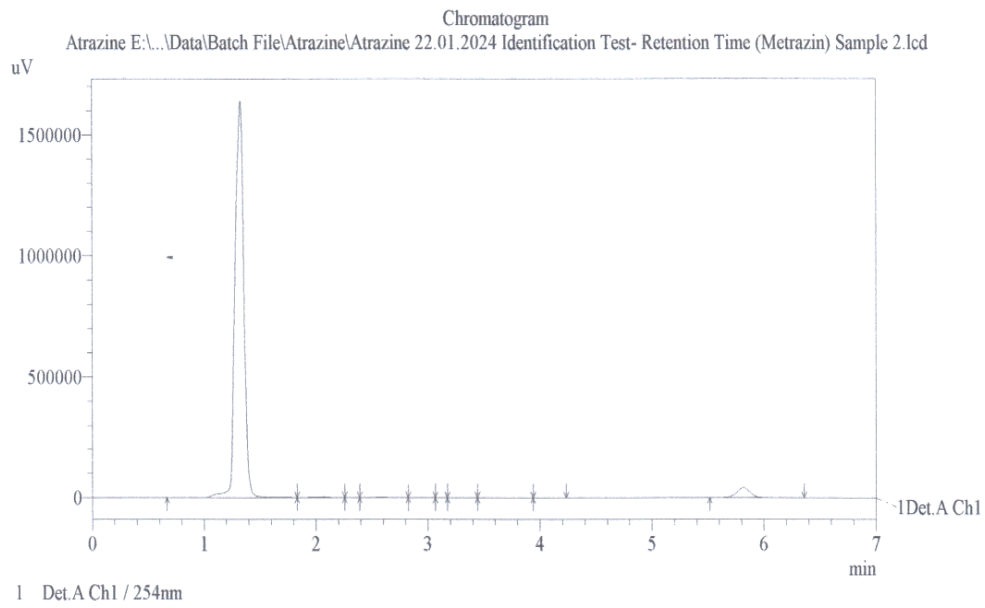


PeakTable

Detector A Ch1 254nm

Peak#	Name	Ret. Time	Area	Theoretical Plate#
1		0.156	5269	5.512
2		1.100	29610	50.795
3		1.404	8551765	4359.363
4		1.899	67954	1853.040
5		2.056	129246	4831.728
6		2.353	7203	4107.690
7		3.492	2384	9461.101
8		5.743	266833	10152.389
Total			9060264	

Appendix IV showing the spectrum identification of atrazine in Metrazine sample mixture using an HPLC machine.



PeakTable

Detector A Ch1 254nm

Peak#	Name	Ret. Time	Area	Theoretical Plate#
1		1.325	8937150	1186.247
2		2.062	29827	3013.467
3		2.302	4726	97.545
4		2.577	22821	4634.783
5		2.896	7050	556.277
6		3.108	2486	0.000
7		3.241	5582	40.067
8		3.522	6967	481.195
9		4.043	2138	5464.011
10		5.813	345750	10031.381
Total			9364496	