Synthesis and Characterization of MgO Loaded Corncob Bio Char Adsorbent for The Removal of Phosphate Ion from Wastewater

Ayalew Tamrat Derseh

A Thesis Submitted To

The Department of Chemical Engineering

School of Mechanical, Chemical, and Materials Engineering

Presented in Partial Fulfillment of the Requirement for The Degree of Master's in Chemical Engineering

Office of Graduate Studies

Adama Science and Technology University

October, 2023

Adama, Ethiopia

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Advisor: Alemu Gizaw (PhD)

Co-Advisor: P. Selvakumar (PhD)

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DECLARATION

I hereby declare that this Master Thesis entitled **"Synthesis and Characterization of MgO Loaded Corncob Bio Char Adsorbent for the Removal of Phosphate Ion from Wastewater**" is my own work. That is, it has not been submitted for the award of any academic degree, diploma, or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

Ayalew Tamrat _____ _____

Name of student Signature Date

RECOMMENDATION

We, the advisors of this thesis, hereby certify that we have read the revised version of the thesis entitled **"Synthesis and Characterization of MgO Loaded Corncob Bio Char Adsorbent for the Removal of Phosphate Ion from Wastewater**" prepared under our guidance by Ayalew Tamrat Derseh submitted in partial fulfillment of the requirements for the degree of Masters of Science in Chemical Engineering. Therefore, we recommend the submission of the revised version of the thesis to the department following the applicable procedures.

Alemu Gizaw (PhD)		13-11-2023
Major Advisor	Signature	Date
P. Selvakumar (PhD)		
Co-advisor	Signature	Date

APPROVAL PAGE

We, the advisors of the thesis entitled **"Synthesis and Characterization of MgO Loaded Corncob Bio Char Adsorbent for the Removal of Phosphate Ion from Wastewater**" and developed by Ayalew Tamrat Derseh, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

Alemu Gizaw (PhD)	_____	13-11-2023
Major Advisor	Signature	Date
P. Selvakumar (PhD)	_____	_____
Co-advisor	Signature	Date

We, the undersigned, members of the Board of Examiners of the thesis by Ayalew Tamrat Derseh have read and evaluated the thesis entitled **"**Synthesis and Characterization of MgO Loaded Corncob Bio Char Adsorbent for the Removal of Phosphate Ion from Wastewater**"** and examined the candidate during the open defence. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Chemical Engineering.

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Finally, approval and acceptance of the thesis is contingent upon submission of its final Copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

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LIST OF ABBREVATIONS

ACF	Activated Carbon Fibers
ASTU	Adama Science and Technology University
BC	Bio char
BET	Brunauer- Emmette-Teller
CC	Corncob
DTA	Derivative Thermal Analysis
EBC	European Bio Char Certificate
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full Width at Half Maximum
HTC	Hydrothermal Carbonization
K_L	Energy of Adsorption
MgO	Magnesium Oxide
N/A	Not applicable / Not available
NBC	Nutrient-enriched bio char
OFAT	One Factor at a time
PV	Pore Volume
PZC	pH at point of zero charge
R_L	Separation factor
SA	Surface Area
TDS	Total Dissolved Solids
TGA	Thermo-gravimetric Analysis
UV-Vis	UV-Visible spectroscopy
WWTP	Wastewater Treatment Plants
XRD	X-ray Diffraction

ABSTRACTS

Nutrients mainly phosphorus exist with water excessively uncontrollable, leads to eutrophication problem, which has an adverse impact on the social, economical, and ecological values of water bodies. Hence, mitigation technology like adsorption is highly recommended for application. In this study, MgO modified corncob bio char adsorbent was prepared for the adsorption removal of phosphate from wastewater. Hence, the aim of this work was synthesis and characterization of MgO loaded corncob bio char adsorbent for the removal of phosphate ion from wastewater. FTIR, TGA, XRD, and BET were used to characterize the specific functional groups, thermal stability, crystalline structure, and specific surface area of the synthesized adsorbent. The BET specific surface area of MgO loaded corncob bio char before and after adsorption were determined to be 26.94 m^2/g and 19.32 m^2/g respectively. Moreover, the optimization effects of adsorption parameters namely pH, adsorbent dose, initial phosphate concentration and contact time have been carried out. The adsorption process of MgO-CB for phosphate proceeded relatively fast in the first 50 minute and basically tended to equilibrium around 60 minute. The result was confirmed that 89 % of phosphate ion was removed from wastewater at optimum 60 minute, 0.5 g adsorbent dose, the pH level of 9, and 5 mg/L of initial phosphate concentration. Furthermore, the adsorption models like equilibrium isotherm, and kinetics were conducted. The adsorption isotherm data were best fitted to the Langmuir (R^2 = 0.98) with a maximum adsorption capacity of 26.12 mg/g implied that the adsorption process was dominated by chemisorption. In addition, the result of the kinetic model proved that pseudo-second-order provided a good description of the experimental data with a maximum R^2 of 0.97. The coexisting ions such as NO_3^- and SO_4^{2-} were observed significantly impacted phosphate adsorption. The removal efficiency of 69.29 % of phosphate ion was found after five cycles of the adsorption/desorption cycles, which indicated wonderful reusability of the adsorbent. The results were illustrated that MgO loaded corncob bio char adsorbent was an excellent adsorbent for the removal of phosphate ions.

Keywords: *Adsorption; Bio char; Corncob; MgO loaded/Modified; Phosphate removal; Wastewater*

CHAPTER ONE

1. INTRODUCTION

1.1. Background

Phosphate is an essential ingredient for the growth of plants, animals, and the proper functioning of ecosystems (Cumming et al., 2015). Phosphate is discharged to surface water from different sources such as agricultural applications, industries, sanitary, and other human activities (Younes et al., 2019). Phosphorus (P) is a macro element that is necessary for the growth of plants and algae, but its overabundance as phosphate (PO_4^{3-}) in aquatic ecosystems can cause eutrophication, which may deteriorate the water quality (Bektaş et al., 2021). The growth and development of plants depend on the indispensable and irreplaceable nutrient known as phosphate. But because of the quick depletion of phosphorus sources, the rising need for fertilizer in the agricultural sector, and the detrimental effects it has on the environment in water bodies (eutrophication), it has emerged as an urgent concern and aquatic species may suffer as a result of high phosphate levels causing algal blooms and a decrease in dissolved oxygen in water bodies (Arbelaez Breton et al., 2021). Human activities such as animal manure, fertilizer application in soil or discharge of industrial, domestic and agricultural water are responsible for the enrichment of surface waters with phosphate loadings (S. Kumar & Jain, 2013). As a result, phosphate removal from Wastewater is a crucial environmental responsibility thus the threat to the environment from phosphate runoff from both point and non-point sources is significant (Y. Yao et al., 2011). High levels of phosphate can encourage an excessive amount of photosynthetic aquatic microbe production in natural water bodies, which ultimately contributes to the eutrophication of many freshwater and estuary coast habitats (Adelagun et al., 2021). The world faces an increasing number of global threats and environmental problems, such as climate change, scarcity of water and water pollution as a result climate change concerns are among the most recent risks, so they are anticipated to influence agricultural water demands as well as water supply (Y. Yao et al., 2011). Thus, it is crucial to create methods that effectively remove phosphate from aqueous solutions before releasing them into runoff and natural water bodies (Zhangh et al., 2010). For phosphate removal, a variety of physical, chemical, and biological treatment techniques have been used (Bunce et al., 2018). Yet, because water quality has a significant impact on the phosphate removal ratio, biological processes are unstable but chemical methods, frequently use a lot of chemicals and still have to deal with expenses, issues associated with processing, disposing of, and neutralizing the effluent (Ahmed et al., 2022). Reverse osmosis and electro dialysis are two

examples of physical treatments that have been shown to be either ineffective or prohibitively expensive (Lichtfouse et al., 2022). The adsorption technique is a potential method for phosphate removal compared to the methods listed above (Mekonnen et al., 2020). The continual discharge of various organic and inorganic contaminants, including dyes, heavy metals, surfactants, medicines, pesticides, and personal care items from industry and municipalities into water bodies is causing the world's water supplies to deteriorate (Rahman et al., 2021).Because of the potential harm to ecosystems that these chemicals' unchecked release could cause (Bogusz et al., 2019). The use of readily accessible and inexpensive materials in various treatment processes has the potential to reduce overall treatment costs while improving process effectiveness in order to make more effective and affordable methods for cleaning up contaminated water, there are still obstacles to overcome (Mustafa et al., 2022). The task can be completed using material removal techniques and technology in a variety of ways for the use of bio char (BC) for environmental management is one such strategy (Akgül et al., 2019). BC is a carbonaceous substance produced by the pyrolysis of biomass and stands out as a sustainable substance thus, it has lately been employed as a sorbent material to remove contaminants like inorganic species, organics, or pesticides because of its qualities, which are similar to activated carbon (AC) (Akgül et al., 2019).

Inorganic pollutants such as heavy metals (C. Wang et al., 2022), and organic contaminants such as dyes (Aragaw & Bogale, 2021). Eutrophication has emerged as a severe danger to aquatic ecosystems in recent decades due to the quick expansion of industry, intensification of agriculture, and increased water production in both phosphorus (P) and nitrogen (N), perhaps to a lesser extent, are crucial nutrients for plant growth, and the trophic status of aquatic environments is influenced by their aqueous concentrations (Goloran et al., 2022). Of these two elements, phosphorus has long been considered to be the most significant in terms of nutrition, and plant growth can be influenced by regulating the quantity of dissolved phosphorus (Dodds & Smith, 2016). Therefore, it has been regarded as the main nutrient contributing to the eutrophication of reservoirs and lakes (Bennett & Lee, 2020). Today's world faces a serious environmental issue called water eutrophication, which happens when phosphorus concentrations rise above a range of 0.003 to 0.8 g/L (Nobaharan et al., 2021).

Currently, one of the most critical problems facing humanity is environmental pollution and the most significant environmental issues that arise in stagnant water basins is eutrophication. Phosphorus has been identified as a fundamental component in eutrophication, which results in the plentiful growth of aquatic plants, the growth of algae, some of which are harmful, and the maintenance of the balance of aquatic species (Dodds & Smith, 2016).

1.2. Statement of the Problem

Large amounts of hazardous waste are being discharged into rivers and other water bodies as a result of the rapid developments of the agricultural, industrial, commercial, hospital, and healthcare sectors. The rate of water contamination is rising in Ethiopia as a result of increased industry, primarily contaminants discharge from industries. The improvement in agricultural productivity that allowed food production to increase to keep up with the tripling of the human population was one of the incredible achievements of the twentieth century (Mekuria, 2018). The rate and scope of eutrophication have increased due to an increase in agricultural and industrial activity of intensity brought on by the rise in the human population. As a result of human activities, nutrient over enrichment or eutrophication of freshwater and marine ecosystems is expanding quickly (Malone & Newton, 2020). In the lowlands of Ilubabor (Baro and Gillo), the lake Tana area (marshy stretches of the Blue Nile or Abbay river near its exit with Lake Tana), and the Rift Valley in Ethiopia, the growth of water hyacinth has become a treat (Awash river, Koka dam and lake Ziway) (Minychl et al., 2020). The primary rivers that drain into Lake Tana are experiencing an increase in phosphorus flux, and the lake's average dissolved phosphorus concentration is 0.2 mg P/L (Kebedew et al., 2020). It has an impact on hydroelectric systems' mechanical integrity, water flow, recreational usage of aquatic systems, and navigation. Also, it contributes to the rapid spread of dangerous diseases in tropical nations which causes significant changes in the animal and plant groups that live in freshwater habitats. Low income earners cannot afford the available water treatment techniques. This makes a lot of people susceptible to diseases caused by microorganisms that are found in water, such as cholera, typhoid, and amoeba, which requires a lot of money to treat. Therefore, to solve this problem utilization of an appropriate removal technique is crucial by producing low cost, effective, and capacitive MgO modified corncob bio char adsorbent for the removal of phosphate, since phosphate ion contamination in wastewater can lead to eutrophication and water quality degradation. In this study MgO modified corncob bio char adsorbent was synthesised and characterized for the removal of phosphate ion from wastewater in order to reduce the above mentioned problems and necessitating the development of efficient adsorbent materials.

1.3. Objectives of the Study

1.3.1. General Objective

The overall objective of this study was synthesis and characterization of MgO loaded corncob bio char adsorbent for the removal of phosphate ion from wastewater.

1.3.2. Specific Objectives

The specific objectives are:

- To synthesize and characterize corncob bio char adsorbent by using different analytical instruments (i.e. XRD, FT-IR, BET, TGA and point of zero charge analysis).
- To investigate the effects of pH, adsorbent dosage, contact time and initial phosphate concentration in removal efficiency of phosphate ion from wastewater.
- To examine the best equilibrium isotherm model, and adsorption kinetics model by using batch adsorption experimental data that represents the nutrient removal process.
- To investigate the effect of competing ions.
- To examine adsorption regeneration in phosphate removal process.
- To determine the performance evaluation of the adsorbent using real wastewater.

1.4. Scope of the Study

This study focuses on the removal efficiency and capacity of bio char which is produced from waste biomass (i.e. corncob) on the removal of phosphate ion from Wastewater. Adsorption is a complex process, in which different variables such as pH, contact time, initial phosphate concentration, and adsorbent dosage might have varying effects on the removal efficiency of different adsorbents and pollutants. Hence, the factors would be analytically determined by using one factor at a time (OFAT) for the efficiency of the system. In this study the effect of several influencing factors such as adsorbent dosage, pH, contact time, and initial phosphate concentration on the adsorption capacity and the removal efficiency of corncob bio char adsorbent for adsorption in relation to phosphate removal was investigated. And it is characterized by Fourier Transform Infrared Spectroscopy (FT-IR), X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), Thermo-gravimetric analysis (TGA), point of zero charge analysis (pHpzc), and its application for removal of phosphate ion from wastewater to reduce eutrophication.

1.5. Significance of the Study

This study has great significance in terms of introducing an alternative form of nutrient removal adsorbent by producing MgO modified bio char from corncobs, which are locally available, abundant with no economic value it also contributes to ongoing research endeavours in the area of resource-oriented solid waste and wastewater management. In the process of environmental remediation, such as the removal of phosphates from aqueous solution, environmental pollution is currently one of the most significant problems facing humanity. Therefore, MgO loaded corncob bio char adsorbent is more preferred because they are able to react longer, disperse better, and

reach locations further than bigger particles. Waste valorisation is demonstrated by turning waste corncob into a value-added adsorbent because it has a high surface area, porous, non-toxic to the environment, and has several significant implications including environmental remediation and sustainable resource utilization. Corncobs can be converted into a usable substance with applications in water treatment rather than being disposed of as waste, which will decrease waste production and encourage the concepts of the circular economy and cost-effective treatment. The use of MgO as a modifier enhances the adsorption capacity and efficiency of corncob bio char for the removal of phosphate ion. This modification increases the active sites available for adsorption and improves the affinity compared to conventional treatment methods such as chemical precipitation or membrane filtration, which could potentially result in lower operational costs and easier access to phosphate ion removal. Flexibility in application (the development of a versatile adsorbent, which provides flexibility in its application for phosphate ion and can be used in various water treatment settings, including industrial settings), potential for regeneration (assessing the regeneration potential of the adsorbent as it allows for multiple cycles of use, thus regenerated effectively, reduces the need for frequent replacement and disposal, and makes it more environmentally friendly and economically viable). Since stagnant water bodies are where eutrophication of the water bodies occurs, phosphorus has been identified as a key factor contributing to eutrophication. Eutrophication causes a variety of aquatic plants to develop, algae to grow, some of which are toxic, and it disturbs the balance of the organisms already living in the water. As a result, this study made adsorbents for water treatment using materials that were readily available locally, thereby reducing the environmental pollution caused by this waste and to investigate the effectiveness of MgO modified corncob bio char as an adsorbent for phosphate removal and to optimize the modification process to achieve maximum adsorption capacity and efficiency.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Water Pollution

Water pollution is increasing due to the different factors such as population growth, urbanization, industrialization, etc., which is a major concern in worldwide (Guignard et al., 2017). It refers to the contamination of water bodies, such as rivers, lakes, groundwater, and oceans, by harmful substances or pollutants are introduced into water sources leading to adverse effects on aquatic ecosystems, human health, and the environment as a whole (Yenihan et al., 2023). Water is considered polluted if some substances or conditions are present to such a degree that the water cannot be used for a specific purpose and to be the presence of excessive amounts of hazards (pollutants) in water in such a way that it is no long suitable for drinking, bathing, cooking, or other uses. Environmental pollutants can cause various diseases, neurological problems, and cancer (Chirwa et al., 2021). The wastes generated by industries are released into the water bodies, atmosphere, and soil, contributing to the pollution of soil, water, and air (Mallin & Cahoon et al., 2020). Pollution results in adverse effects on the entire ecosystem, especially on human life and most pollutants that pose a threat to the environment originate from industry (Amer et al., 2021). Industrial wastewater, which consists of organic and inorganic substances, is toxic to humans and must therefore be threated before it can be released into the environment (Belete et al., 2019; Manzar et al., 2018). Water pollution is a complex issue that requires ongoing efforts from governments, industries, communities, and individuals to protect and preserve water resources for the benefits of both ecosystems and human well-being (Nobaharan et al., 2021). Depending on the nature of the industrial, agricultural, and municipal, wastewater releasing operations, different contaminants may be present in the wastewater and the various kinds of water pollution can be divided into inorganic, organic, and biological categories (Fones et al., 2020). Heavily toxic and cancer causing heavy metals and non-metals are the most prevalent inorganic water contaminants (Mustafa et al., 2022). Nitrates, sulphates, phosphates, chlorides, fluorides, and oxalates are some substances that can be extremely dangerous and also pesticides, such as insecticides, herbicides, and fungicides, as well as phenols, poly chlorinated biphenyls, halogenated aromatic hydrocarbons, formaldehyde, poly brominated biphenyls, biphenyls, detergents, soap, oils, and greases, are some harmful organic pollutants. So, the dissolved phosphates either it can be sink into the soil and be taken up by growing plants or leach into water bodies to taken up by algae and other photosynthetic organisms (Comber et al., 2013 ; Zubair et al., 2017). The excessive

phosphate loss from land causes eutrophication of waterbodies which manifests in algal blooms and consequently water quality degradation and fish deaths (Yuan et al., 2018).

2.2. Phosphorus in Water

Phosphorus is an essential nutrient for plant and animal growth and is naturally present in water bodies such as rivers, lakes, streams, and oceans. However, excessive levels of phosphorus in water can lead to water pollution and have detrimental effects on aquatic ecosystems (Dey et al., 2021). It can be found in water in different forms, including dissolved phosphates (inorganic phosphorus compounds) and particulate forms (such as organic matter or sediment bound phosphorus) (Ibrahim & Bsharat, 2018). According to (P. Kumar et al., 2010) dissolved phosphorus are the most bioavailable and readily used by aquatic organisms. Phosphorus in water plays a vital role in supporting aquatic ecosystems and the growth of aquatic plants and algae and it is a necessary nutrient for primary production in the process by which plants and algae convert sunlight, nutrients, and carbon dioxide into organic matter through photosynthesis, however when phosphorus concentrations are too high, it can cause eutrophication, which is the excessive growth of algae and plants this over growth can negatively impact water quality, deplete oxygen levels and harm aquatic organisms (Dodds & Smith, 2016).

2.3. Sources of Phosphorus

The two main sources of phosphorus in water are natural and through anthropogenic activities (Omar et al., 2020). Natural source includes leaching of phosphate from rock deposits, decomposition of organic matter, biological processes and anthropogenic activities include use of detergent, deforestation and land disturbance, agricultural runoff, storm water runoff, wastewater discharge and industrial effluents (Mohammed et al., 2020). Phosphates added to surface water by a variety of means, humans add phosphates to water through industrial and agricultural wastes (Letshwenyo , 2021). Phosphates are a component of DNA, RNA, ATP and phospholipids complex compounds fundamental to cells and elemental phosphorus first isolated from human urine, and bone ash, which are an important early sources of phosphorus. Phosphate mines contain fossils because phosphate is present in the fossilized deposits of animal remains and excreta thus, low levels of phosphate are an important limit to growth a number of plant ecosystems. Fertilizers contain high levels of phosphates and will enter the water by means of runoff and soil erosion, this will lead to even more phosphates being washed out of the soil and into the water and it can also come from the excrement of animals living in or near the water (Asmellash & Ayele, 2022). The

use of fertilizers (phosphates) by farmers increases on daily basis due to the increasing demands for agricultural products (Michael et al., 2017).

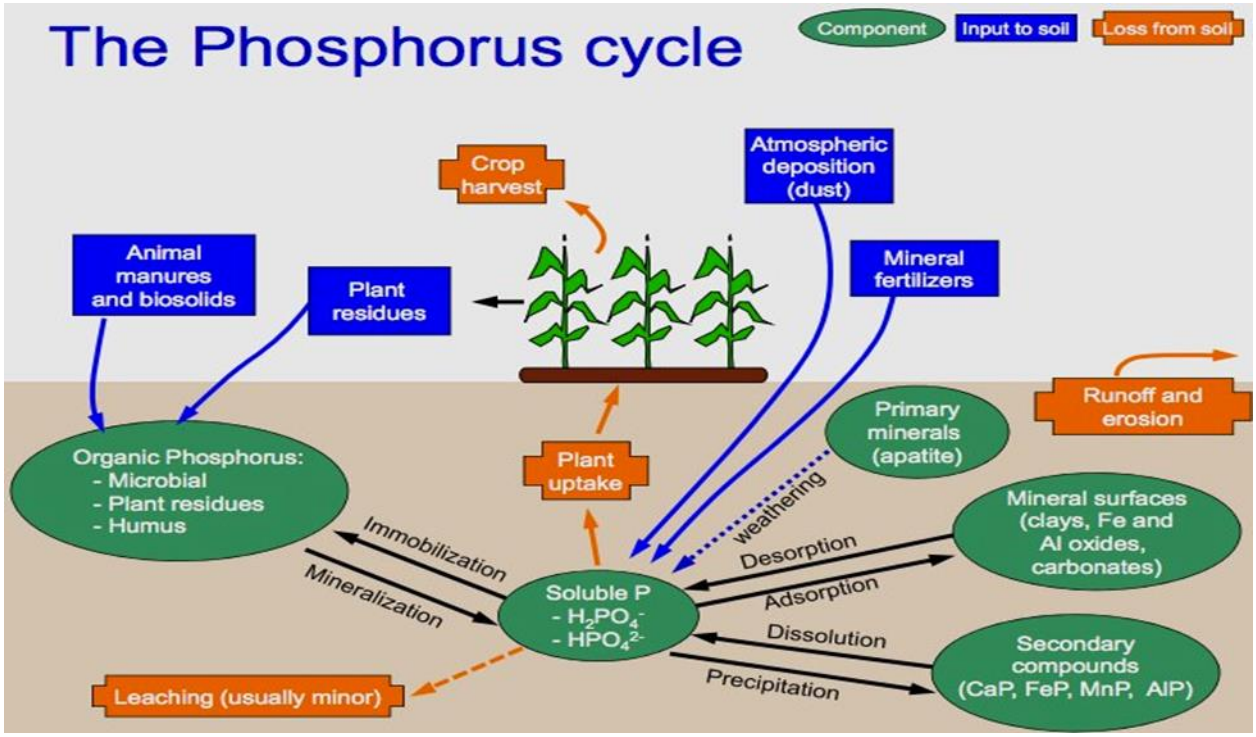

Figure 2. 1: Phosphorus cycle showing the transport (input and uptake) of phosphorus between the terrestrial and aquatic ecosystems (Mukherjee et al., 2015).

2.4. Effects of Excess Phosphorus in Water

Excess phosphorus in water bodies can have various effects on both human health and the environment.

Table 2. 1: Effects of excess phosphorus in water both human and environment (Msimbira et al., 2017).

	Water borne disease	Excessive phosphorus can contribute to the growth of harmful algal blooms (HABs) in water bodies. Some types of algae in these blooms can produce toxins called cyanotoxins, which causes gastrointestinal problems, skin rashes, respiratory irritation, and, in severe cases, liver toxicity or neurotoxicity.
Effects on human health	Drinking Water Contamination	High levels of phosphorus in water sources can impact the quality of drinking water supplies. This have been associated with adverse health effects, including an increased risk of cancer and reproductive issues.

	Recreational Hazards	Excessive phosphorus can lead to the growth of harmful algal blooms in recreational water bodies. Can cause skin irritations, eye irritation, respiratory problems, and gastrointestinal issues in humans.
	Eutrophication	When phosphorus enters lakes, rivers, or coastal areas, it stimulates the excessive growth of algae and aquatic plants. This overgrowth can lead to oxygen depletion in the water, creating hypoxic or anoxic conditions. As a result, fish and other aquatic organisms may suffer from reduced oxygen levels, leading to fish kills and disruptions in the food web.
Effects on the Environment	Harm to Aquatic Life	High levels of phosphorus can result in the proliferation of algae and aquatic plants, which can block sunlight from reaching the deeper layers of water. This reduces the availability of light for submerged aquatic vegetation, affecting their growth and disrupting habitats for fish and other organisms.
	Loss of Biodiversity	Eutrophication caused by excess phosphorus can lead to a decline in biodiversity in affected water bodies.
	Altered Water Quality	Excessive phosphorus can degrade water quality by causing increased turbidity and reducing clarity. Algal blooms can give water a greenish appearance and produce foul odours, making it aesthetically unpleasing and affecting recreational activities.

2.4.1. Eutrophication

The process of eutrophication occurs when a body of water receives an excessive amount of nutrients, which promotes the rapid growth of low-complexity plant life. Since it frequently leads to the degradation of water quality and the reduction of dissolved oxygen in water bodies, it has seen as a severe environmental hazard in which eutrophic waters have the potential to eventually turn into "dead zones" that cannot sustain life (Watler K., 2016) . The term "eutrophication" is more commonly associated with human activity, where the artificial introduction of plant fertilizers has resulted in alterations to local communities and a decline in the quality of water in many freshwater systems (W. Dodds , 2018). For instance, lake Tana, lake Hayq, big and small Akaki rivers which, has (12 - 10.5 mg/L) of phosphate (Eshetu et al., 2014).

Phosphorus and nitrogen enhance the growth of algal blooms in the water bodies (such as rivers, lakes and seas), which reduce light penetration and available oxygen in the water bodies, reduced growth of submerged aquatic vegetation and benthic organisms this phenomenon is known as eutrophication (Rahman et al., 2014a). Eutrophic water bodies contain dead zones in which water from such water bodies may cause outbreaks of diarrheal diseases or poisoning of cattle and poultry (Frumin et al., 2015). Therefore, it is obligatory to remove nitrogen and phosphorus from Wastewaters before discharging it into the water bodies to create healthy, pollution-free environment (Berkessa et al., 2020).

2.4.1.1. Effects of Eutrophication

Numerous writers have summarized the main effects of aquatic eutrophication, which are complicated (Smith et al., 2018). In general, accelerated eutrophication of surface water causes issues with its use for fisheries (due to blooming and food web change), recreation, industry, or drinking water, because of the increased growth of undesirable algae/ cyanobacteria and aquatic weeds and oxygen shortages (Kumdu, 2018). Eutrophication reduces water clarity, affects taste and odour, interferes with water supply filtration, poses health risks to animals, including humans, shifts the composition of fish species towards undesirable species, and increases the likelihood of fish kills and also depletes dissolved oxygen in the water column (Malone, 2020).

2.4.1.2. Effects of Eutrophication on Biodiversity

Following eutrophication, water hyacinth, one of the top ten notorious invasive aquatic weeds worldwide, could develop in aquatic ecosystems (Abeyou et al., 2020). The weed grows in dense, interlocking mats that impede light penetration down the water column, limit the amount of light that native macrophytes and algae may receive, and compete with them for resources (such as nutrients) (Twongo et al., 2017). Accordingly, as trophic status increases, a zooplankton community frequently transitions from macro to micro zooplankton (Karabin et al., 2018; Park and Marshall 2020). For instance, in highly eutrophic habitats, rotifers predominated the overall zooplankton biomass (Zhao et al., 2017; Mohammed et al 2018). Rotifers are a varied and quantitatively dominant zooplankton in Lake Ziway and Lake Koka (Dagne 2017, Degefu et al., 2021). Additionally, the weed prevents tilapia and other fish species from accessing their breeding, nursing, and feeding grounds, which may reduce the overall catchability of fish by up to 45 % (Kateregga and Sterner 2017). Water hyacinth has quickly grown to cover almost 50,000 acres in Lake Tana (Anteneh et al., 2018). In the same ecosystem, (Zelalem et al., 2015) found that areas with water hyacinth infestations had lower phytoplankton species richness than sites without

infestations. A water hyacinth-infested habitat in Lake Tana had an extremely low dissolved oxygen saturation (18.18 % or 2 mg/L), which made aerobic living challenging and may have an impact on biodiversity (Gezie et al., 2021).

2.5. Phosphate Removal Methods

Phosphate removal refers to the process of reducing and eliminating phosphate ions from water and wastewater. High concentrations of phosphate can lead to eutrophication, which is the excessive growth of algae and aquatic plants in water bodies. Phosphate removal methods aim to reduce phosphate concentrations to acceptable levels, minimizing the negative impacts on water quality and aquatic ecosystems. It is a critical step in water and wastewater treatment to ensure compliance with environmental regulations, protect water resources, and maintain ecosystem health by effectively removing phosphates. Various treatment methods can be employed, such as chemical processes, biological processes, adsorption, ion exchange, membrane filtration (i.e. reverse osmosis), and electro dialysis.

Table 2. 2: Comparison of phosphate removal technologies (Zeng & Yang, 2015).

Technologies	Characteristics
Adsorption	- Requires high TDs disposal - Requires saturation adsorbent disposal - pH and temperature effects are important - Post – treatment is not commonly required - Removal efficiency differs with various adsorbents - Medium operational costs
Reverse Osmosis	- pH and temperature effects are not important - Post – treatment is required due to the corrosivity product water - > 95% efficiency can be achieved - high operational cost
Ion exchange	- Requires waste brine disposal - pH and temperature effects are not important - Post – treatment is required due to the corrosivity of product water - Approximate 90% of efficiency can be achieved - High operational cost

Electro dialysis	- Requires lesser acid dosages
	- Higher water recovery rates
	- Requires waste disposal
	- Requires pre-treatment systems and close monitoring
	- High operational cost
Chemical process	- No waste disposal is required
	- pH and temperature effect are important
	- Post-treatment is required due to the product of byproduct
	- Maximum efficiency >60-70%
	- High operational cost
Biological process	- Requires biomass waste disposal
	- Temperature effect is important (low limit of operation 2-6 °C)
	- Post-treatment is required due to microorganisms
	- Medium operational costs

2.6. Adsorption

Adsorption is regarded as a reliable and affordable technique for removing pollutants from wastewaters and it is a surface phenomenon in which characterized by chemical species (adsorbate) from its vapour or liquid solution phase onto or near the surface of solid (adsorbent). Adsorption is a phenomenon of an increase in the concentration of any substance or molecule on the surface of a solid or liquid (Madelene et al., 2018). The substance which gets adsorbed or deposited is called adsorbate, while the substance on which adsorption/deposition takes place is called adsorbent. The presence of excess surface occurs when the attractive energy of a substance with the solid surface that is adhesive work is higher than that of cohesive energy of the substance (Chiou et al., 2013). Adsorption is the mass transfer operation of solute (adsorbate) exists in a fluid phase to the surface of solid phase (adsorbent) due to the existent of high molecular interaction between them and it is a process of the interface in which a film of adsorbates is created on the surface of the adsorbents material so, it is the result of surface energy (Machado et al., 2020). Adsorption is commonly employed as a polishing step to remove organic and inorganic contaminants in water and water treatment. The surface area or active sites, the lack of selectivity, and the adsorption kinetics usually limits the efficiency of conventional adsorbents (Qu et al., 2021). Adsorption is a term used to describe the metal or organic substances in solution attached to a solid adsorbent at low, medium, and high coverage (Al-anber, 2011). It is as a separation

process and widely applied in our manufacturing economy for daily life so it's process takes advantages of the ability of a particular solid to preferentially concentrate a particular substance in a solution (gas or liquid) on the surface (Battas et al., 2019). Therefore, the required purpose of purification or separation can be achieved by contacting the fluid with such a solid. It can happen at the gas-liquid, gas-solid, liquid-liquid, or liquid-solid interfaces between two phases (Bouaidi et al., 2022). Solid surfaces have unique electrical and spatial characteristics that make them active, energetic places capable of interacting with solutes. Since adsorption is a surface-based process, the quality of adsorbents is significantly influenced by the surface area.

In nature, adsorption can be divided into two types: physical (physisorption) and chemical (chemisorption). Intermolecular forces in physical adsorption are not particularly strong and the exchange or transfer of electrons is not permitted and the interacting species always keep their uniqueness as a result (Aly et al., 2020).

Chemisorption frequently takes place at high temperatures typically correlated with the activation energy since it includes chemical bonding. Additionally, because the adsorbed molecules are localized, they are unable to move freely to the surface. Table 2.3 Comparison of physical and chemical adsorption. Generally, adsorption can occur at any interface that is either gas-solid interface or liquid-solid interface (Abdalla et al., 2020).

Table 2. 3: The difference between chemical and physical adsorption (Peng et al., 2017).

Parameters	Chemical Adsorption	Physical Adsorption
Force of Attraction	Strong attraction forces or chemical bond such as ionic bonds	Weak inter particle bond as van der Waal forces
Temperature	Higher heat of adsorption	Low heat of adsorption
Compound formation	Surface compounds are formed in chemisorption	No new compounds are formed in this phenomenon
Amount of heat required	Heat of adsorption is high (40-400 KJ mol^{-1})	Heat of adsorption is low (20-40 KJ mol^{-1})
Energy required	Activation energy is required	It doesn't require activation energy
Occurrence	It is specific in nature	It is not specific in nature
Electron transfer	electron transfer leading to bond formation between sorbate and surface	Not involve electron transfer, although polarization of sorbate may occur.

Adsorption layer	Monolayer only	Monolayer or multilayer
Adsorption Kinetics	Activated, may be slow and irreversible	Rapid, non - activated and fully reversible
Adsorption sites	Site specific, adsorbed molecule are fixed at specific site	Not site specific, the adsorbed molecules are free to cover the entire surface

It is clear that an integrated treatment system, which includes many aspects like available space for the building of treatment facilities, waste disposal restrictions, desired finished water quality, capital and operating expenses, encompasses the adsorption process (Orbeci et al., 2018). Achieving the ideal operating conditions for low-cost, high efficiency is implied by all of these factors (Grassi et al., 2022). The capacity to reverse the process, low cost, high availability, profitability, versatility in design and operation are all significant advantages of adsorption (Abbas et al., 2014). Electrostatic interaction (attraction between opposite charges), ligands and ion combination, and binding to surfaces are some of the adsorption methods or principles that remove pollutants from contaminated areas or water streams (Oanamari et al., 2018). As shown in Figure 2.7 there are five adsorptive removal mechanisms: chemical diffusion between adsorbent and adsorbate, surface precipitation, redox reactions, and ion exchange, which is primarily due to the presence of hydroxyl/OH functional groups. The adsorption process allows for design flexibility and frequently result in high-quality treated effluent and the same crucial characteristics, such as high internal volume accessibility to various component targets, high surface area, especially internal surface area, pore size distributions, and pore nature all have a significant impact on the type of adsorption process (Iwuozor & Ighalo, 2021).

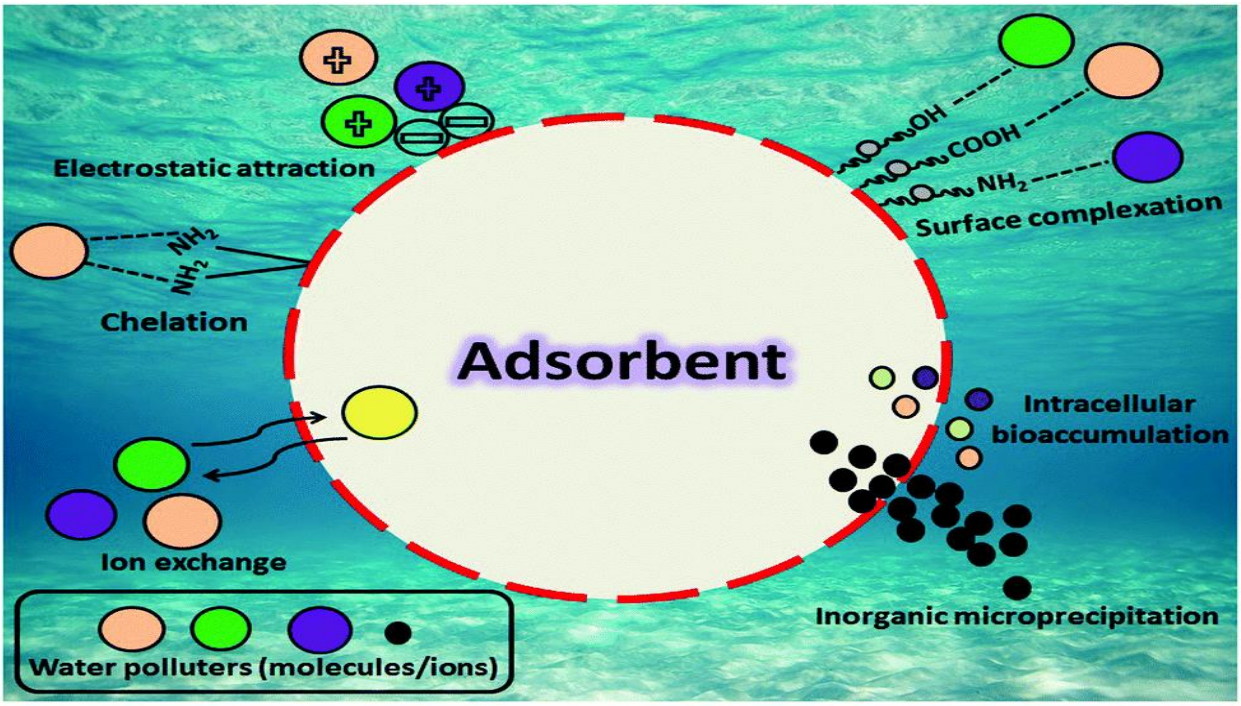

Figure 2. 2: Various mechanisms occurring in the adsorption process (Ambaye et al., 2021).

Table 2. 4: Adsorption capacity, models (kinetics and isotherm), and adsorption optimum conditions of selective phosphate adsorbents comparative study.

Adsorbent	Adsorption capacity	Kinetic models	Isotherm models	pH	C_o (mg/L)	t (min)	Reference
$La(OH)_3$ modified nut bio char	148.11	PSO	Langmuir	6	-	20	(Jia et al., 2020)
Calcium based bio char	83.95	PSO	Langmuir	7.5	10.3	-	(Qin et al., 2022)
Salt based bio char	118	PSO	Langmuir	7-9	318	140	(Xu et al., 2019)
Rice straw derived	50	PSO	Freundlich	-	50	100	(Huang et al., 2022)
Egg shell modified bio char	460	PSO	Langmuir	5-13	120	40	(Sun et al., 2022)

Mg-laden bio char	344	PSO	Freundlich	8	40	90	(Jiang et al., 2018)
Pg-bio char	102.4	PSO	Freundlich	6	100	400	(Wang et al., 2020)
Natural pumice	167.37	PFO	Langmuir	5	60	70	(Battas et al., 2019)
Local clay	27.77	PSO	Langmuir	9	210	110	(Yang et al., 2017)
Chitosan	8.25	PSO	Langmuir	7	130	50	

2.6.1. Mechanisms of Adsorption

The adsorption mechanism is the primary determinant of the adsorption kinetics, energy, capacity, thermodynamics and it is significantly influenced by the kind, charge, and molecular makeup of the adsorbent (Madelene et al., 2018). Several adsorption mechanisms can be observed in the same adsorption system, and the adsorption mechanism also varies with pH. Several mechanisms, such as ion exchange, electrostatic interactions, ligand exchange, precipitation, Lewis acid-base interaction, inner sphere complexation, outer sphere complexation, and others, have been used to explain adsorbents (Aboud et al., 2021). The diffusion of adsorbed water on the surface sites of the adsorbent molecules in a liquid film is known as the second film diffusion and a pore diffusion of intra-particle diffusion of adsorbed water in the adsorbent's spaces occurs on the third. Last but not least, the adsorption of adsorbed water on the adsorbent's inner surface (Kaushal et al, 2017).

In the context of adsorption, the main challenge is to choose the most promising adsorbent types, primarily in terms of low cost, high capacity (often expressed as qmax values), high adsorption rates, high selectivity, and fast kinetic adsorption mechanism(s), especially at interfaces where adsorbents/adsorbates interactions take place (Crini et al., 2019).

2.6.1.1. Ion exchange

Ion exchange is an adsorption phenomenon which is reversible, stoichiometric, and electrostatic. It is used to replace an ion in the aqueous phase with an ion from the resin phase in water treatment applications (Cristina et al., 2018). In this process, the ions on the surface of the adsorbent are replaced by adsorbate ions, for example, demineralization of water, in which cations are replaced by H^+, and anions are replaced by OH^- (Grassi et al., 2021). The counter-ion connected is a cation if the functional group is negative and in aqueous phase, the counter-ion can exchange with another counter-ion if it is positive and is an anion (Aboud et al., 2021). The exchanger must have an open network structure, either organic or inorganic, which carries the ions and which allows ions to pass

through it and it is related to ion replacement, in which a phosphate ion replaces an ion from the structure of the BC, according to (Almanassra et al., 2020). An example of phosphate removal using an ion exchange process is iron oxide-modified BCs (Carmignano et al., 2021). Ion exchange technology is technically simpler than other common methods, and has the advantage of being able to efficiently remove even trace impurities from the solution, enabling high processing power, high removal efficiency, and high-speed kinetics. Reversible processes and low energy requirements are the most important advantages of this method. This method can reduce organic and inorganic pollutants by about 95 %, but if the water contains oil or grease, pre-treatment may be required (Ince, 2019).

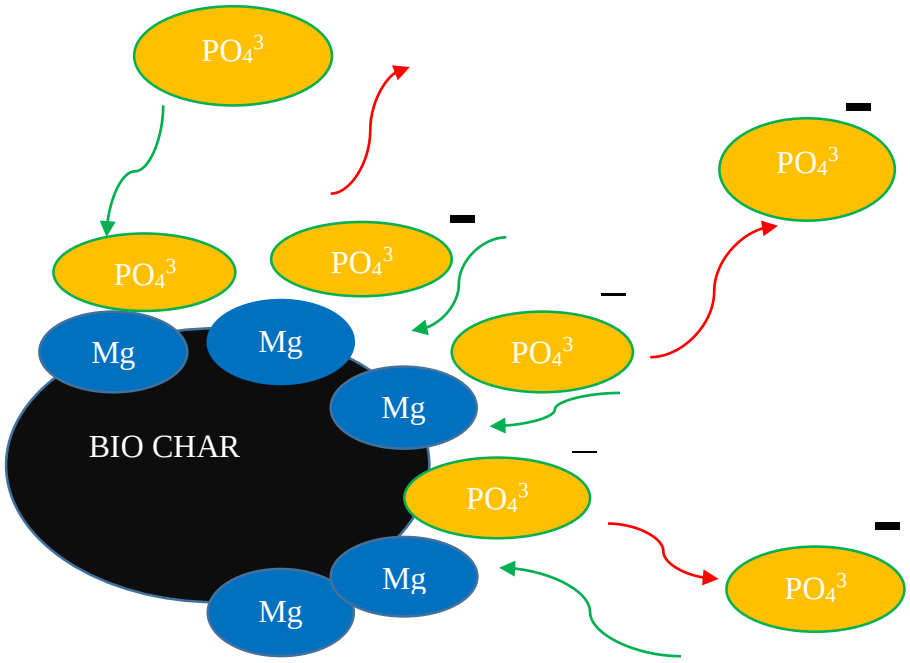

Figure 2. 3: Representation of ion exchange between Mg^{2+} ion and phosphate (PO_4^{3-}) ion.

2.6.1.2. Electrostatic Attraction

The electrostatic force of long-range interaction between electrostatic adsorption in aqueous solution with differently charged particles or uncharged particles is known as electrostatic attraction (B. Wang et al., 2020). The majority of studies show that electrostatic interactions govern how well the phosphate binds to BCs thus, on BC, a carbon-based adsorbent, phosphate ions have a negative surface charge and dissociate with pH (Almanassra et al., 2020). The electrostatic mechanism is employed in both chemical and physical adsorption processes. Electrostatic interactions are thought of as simple and reversible adsorption events when compared to other mechanisms (Bogusz et al., 2019). Strong electrostatic adsorption occurs in chemisorption, which is when the functional groups of the adsorbent and adsorbate are connected to one another by their opposite charges. In physisorption, the attraction is caused by a weak electrostatic force, a weak

Vander Waals force, or both and ionic bond formation is fundamentally based on electrostatic interactions. Anion and cation interact to produce the chemical bond known as an ionic bond in which the complete transfer of one or more electrons results in the formation of an ionic bond between two oppositely charged ions, which is the electrostatic force of attraction takes place. Electrostatic repulsion and attraction are two types of electrostatic interaction, with the same charge expressing attraction and heterogeneous charge exhibiting repulsion. When researching electrostatic interactions, pH and the point of zero charge are both crucial variables (Abbas et al., 2018). In this study, related information on the point zero charge has been mentioned.

2.6.1.3. Ligand Exchange

The metal atom requires the donation of ligands or neutral molecules with electron pairs in order to form a coordinating covalent bond. According to reports ion replacement is connected to the adsorption mechanism through ligand exchange, for instance, when phosphate groups replace hydroxide groups (Yang et al., 2021). Higher phosphate ion binding to BC than ion exchange is caused by the development of inner sphere complexes in conjunction with phosphate adsorption via ligand exchange (Bogusz et al., 2019). Protonated anions can be adsorbed onto a negatively charged surface once their protons are split apart and Surface hydroxyls then react with this to create water molecules, which can then be easily replaced by the anions. However, it has now been contested that the protonated anion had a part in this pathway as a proton donor (Rajan et al., 2018). Because the pH dependency of anion adsorption may be explained by the protonation-proton dissociation processes of the hydroxylated mineral surfaces alone (Stum et al., 2014).

2.6.1.4. Precipitation

Precipitation is the process of changing a dissolved substance from a super-saturated solution to an insoluble solid in an aqueous solution. Precipitate refers to the produced solid when the phosphate concentration is greater than the solubility, low soluble phosphate salts precipitate. According to the thermodynamic solubility principle, it can also happen at lower concentrations when the finite volume next to the adsorbent mineral surface is oversaturated with phosphate (Li et al., 2016). By drying aqueous salt solutions and adding a base, the precipitation method is a quick and straight forward way to create metal hydroxides thus, particles that have been produced are easily aggregatable and the control of the preparation process is challenging but using this technique, it was possible to create a wide range of metal hydroxides that were both crystalline and amorphous in character (Guo et al., 2021). The materials contain porous structures and irregular, rough surfaces, as shown by X-ray diffraction analysis and scanning electron microscopy

through a variety of chemical reactions in solution, small-scale materials with a homogeneous chemical composition can be produced (Liao et al., 2016).

2.6.1.5. Lewis Acid-Base Interaction

The adsorption of phosphate onto carbon-based adsorbents was likewise governed by the Lewis acid-base interaction. When exposed to high H^+ ion concentrations in acidic conditions, the changed element on the adsorbent protonates, turning it into a weak acid and acting as an electron acceptor. Under acidic conditions, the phosphate ions serve as electron donors and are regarded as weak bases. When the environment is alkaline, this behaviour is reversed. When interacting with the elements affixed to the carbon adsorbents, phosphate ions are acting as an electron donor and acceptor. The modified ACF is an example of phosphate adsorption through Lewis acid-base interactions (Ferral-Pérez et al., 2020). At lower pH values, metal active sites become protonated and changed into Lewis acids, which act as electron acceptors because there are too many hydrogen ions in the solution and Lewis base is formed from the electron donors known as phosphate anions (Aboud et al., 2021). When the pH is alkaline, both the phosphate species and the negatively charged metal active sites undergo deprotonation. As a result, the Lewis acid is created by the phosphate anions and the Lewis base is created by the metal active sites. This shows that the phosphate anions and metal active sites have interactions with Lewis acids and bases as well as electron donors and acceptors. When a phosphate molecule approaches the metallic centre, the cluster surface releases one H_2O group, allowing an acid-base Lewis interaction to result in a mono-dentate complex. It's possible that this mono-dentate complex will continue to target neighbouring, unreacted H_2O/OH species and transform into a bidentate complex (Acelas et al., 2015).

2.6.3. Factors Affecting Adsorption

Adsorption is not a uniform process, and a number of variables influence how effective it is. The characteristics of water also significantly affect the overall removal efficiency, in addition to the adsorbent's physical characteristics. In an adsorptive system, the performance of the adsorbent is significantly influenced by the solution parameters. Many variables, including pH, adsorbent dosage, contact time, and the initial ion concentration of the adsorbate, have been the subject of scientific study. The most important characteristics of the feed solution and the adsorbents are reviewed below.

pH of Solution

The pH of the solution affects the degree of adsorption, as the distribution of the surface charge of the adsorbent is likely to change and this is due to the composition of the raw material and the activation technology, so the degree of adsorption is different depending on the functional group of the adsorbate (Gualin et al., 2023). The pH of the solution controls the electrostatic interactions between the adsorbent and the adsorbate so the study of adsorption is very much depending on pH of the solution. Generally, the oxides surface exhibits a surface charge, which is dependent on the pH of a solution and all oxides have a well-defined pH at which this change is zero (Lifang et al., 2023). The pH of the solution is found to be very effective in deciding the amount of adsorption especially if the solid adsorbent is prone to surface alternation due to changes in the hydrogen concentrations, large variation have been found with metal, metal oxides and metal hydroxides as adsorbents.

The dissociation, phosphate species concentration, chemical state of binding sites, and affinity of phosphate species towards binding sites are all influenced by the pH value of the solution. The pH profiles can be used to identify the adsorption mechanism, improve the process, and choose the best eluting agents. Thus, attempts have been made to determine the ideal pH levels in different AWs-PO_4^{3-} adsorption systems (Bernal et al., 2017). Depending on the pH of the solution (pK_1 = 2.15, pK_2 = 7.20, pK_3 = 12.33), phosphate can exist in aqueous environments as various ionic species such as monovalent $H_2PO_4^{-l}$, divalent HPO_4^{2-}, and trivalent PO_4^{3-} ions (Pokhrel et al., 2019). As a result, depending on the pH level of the aquatic medium, the dominating phosphate species can change thus,$H_2PO_4^-$ and HPO_4^{2-} species dominated in the pH range of 4 to 9 (Pokhrel et al., 2019). However, at pH_4, the dominating species $H_2PO_4^-$ undergoes protonation to form H_3PO_4, which is thought to replace the neutral water molecules that are loaded onto AWs by hydrated metal ions. Due to the low affinity of these neutral species for the binding site, the removal of phosphate from the solution at low pH was inadequate so, similar to this, HPO_4^{2-} and PO_4^{3-} species dominated at pH > 9 (Kishore et al., 2023).

Initial Concentration

The initial concentration of phosphate in a solution can have a significant effect on the adsorption capacity and efficiency of the adsorbent materials for phosphate removal (Fazy,M.A., et al., 2020). When the initial concentration of phosphate is low, the adsorption capacity of the adsorbent material is usually not fully utilized. This means that there are still a significant number of unoccupied adsorption sites on the surface of the adsorbent material that can be utilized to adsorb more phosphate ions (Wang, J., et al., 2019). As the initial concentration of phosphate increases, the number of available adsorption sites decreases, and the competition for these sites among the

phosphate ions increases. This can result in a decrease in the adsorption capacity of the adsorbent material and a decrease in the removal efficiency of phosphate (Huang et al., 2023).

Adsorbent Dosage

When it comes to phosphate adsorption, adsorbent dosage is crucial or very important. The complete attachment of the anion to the adsorbent is the result of an interaction between the phosphate and the adsorbent, as demonstrated by studies using modest dosages of adsorbents (Nguyen et al., 2020). According to theory (Zhang et al., 2018), the amount of adsorbent needed to remove phosphates is directly proportional to that amount. Phosphate is absorbed at a rate that increases with the amount of adsorbent used. The active surface area and active site for the adsorption of phosphate from the solution, however, might be reduced in the presence of an excessive amount of adsorbent due to particle aggregation, which lowers the adsorption rate (Nguyen et al., 2020). When the phosphate concentration is maintained at a steady level and the active site is not completely occupied, increased active sites on adsorbents may result in excessive locations (Trinh et al., 2020).

The sorbent-sorbate equilibrium of an adsorption system is significantly impacted by the dosage of the adsorbent as well. Due to the availability of additional sorption sites, the application of a higher adsorbent dosage improved the removal effectiveness of organic and inorganic contaminants (Guo Hua et al., 2022). However, when the dosing rate is too high, the bio char's ability to adsorb can be reduced. As a result, the adsorption layers may overlap, protecting the absorbent surface's active sites that are still present (Bouaidi et al., 2022). According to every scientific study, phosphorus adsorption rose with rising adsorbent dose up to a certain point, after which it stayed constant. One straightforward reason for this is that more binding sites are created in the solution by adding more adsorbent.

Adsorption Capacity

The adsorbent's capacity is a significant criterion since it establishes the quantity of adsorbent needed to quantitatively remove a certain amount of metal ions from a solution. According to their size, level of hydration, and binding constant with the adsorbent, different metal ions have different adsorption capacities. The following equation could be used to get the adsorption capacity:

$$Q_e = \frac{(C_o - C_e) \times V}{M} \quad \text{.....2.1}$$

where, C_e and C_o (mg/L) are the equilibrium and initial concentrations of PO_4^{3-} ions in an aqueous solution, V (L) is the volume of the aqueous P solution, and M (g) is the mass of the corncob bio

char adsorbent, Q_e (adsorption capacity) is the amount of adsorbed PO_4^{3-} ions at equilibrium (mg/g) (Tewhibo, 2019).

Contact Time

The adsorption of phosphate is greatly affected by contact time for a specific dosage or initial concentration of the adsorbent, the contact time offers information on the adsorption kinetics of the adsorbate. The main goal of determining contact time is to determine the minimal amount of time needed for adsorbents to optimally adsorb the phosphate ions until an equilibrium state between the adsorbed and desorbed phosphates is reached. This aids in understanding the rate of phosphate adsorption onto the adsorbents' surfaces as well as the effectiveness of the adsorbent. (Iftekher et al., 2018). According to (Zhang et al., 2020), the type of adsorbent, initial phosphate concentration, adsorption temperature, and degree of mixing all affect the equilibrium time.

The adsorption is more fully accomplished the longer the contact time. In order to gain insight into the settlement process, it is crucial to know the contact time needed to accomplish the settlement. Additionally, it details the minimal amount of time needed for significant adsorption to take place as well as any potential adsorbent diffusion control mechanisms (Batool et al., 2018). According to the literature review, longer contact durations result in higher removal efficiency, this is because the solid and liquid are in contact for a longer period of time, allowing for improved interaction between the medium and the adsorbate (Nabhan et al., 2019). To determine the equilibrium time at 150 rpm, 100 mL of the test solution containing 5 mg/L PO_4^{3-} in a dose of 0.5 g MgO modified corncob bio char is adsorbed in a 500 mL plastic bottle by changing the contact time from 0 minutes to 90 minutes and stirring the mixture. The findings demonstrated that the efficiency of phosphate removal increased over time, maximum at 60 minutes, and subsequently stabilized (Waktole et al., 2019)

Competing Ions

Adsorption selectivity affects how well phosphate ion is removed from the solution. Real water samples always contain a variety of aqueous components that could compete for adsorption sites and hinder an adsorbent's capacity to remove phosphate (Chen et al. 2015;Zhang et al. 2017). Sulphate's, carbonates, nitrates, chlorides, and fluorides are inorganic ions that may be found in actual water (Zhang et al., 2018). Several researchers have looked into how different anions in water could affect the effectiveness of adsorption. These anions could potentially interfere with the process. According to (N. T. Nguyen, 2015) the presence of cations such Ca^{2+}, Mg^{2+}, Cu^{2+},

Fe^{2+}, and Zn^{2+} facilitate the process while anions like Cl^-, SO_4^{2-}, NO_3^-, and CO_3^{2-} did not exhibit any significant influence. The phosphorus adsorption was hardly affected by the anions of Cl^-, NO_3^-, and SO_4^{2-}. However, a study by (X. Zhang et al., 2020) indicated that SO_4^{2-} and CO_3^{2-} had a detrimental effect on the uptake of phosphate and the delicate nature of the adsorption process, particularly when competing ions are present. By adding 10 M of NaCl to the 5 mg/L phosphate solutions in different vessels, the impact of the common coexisting anions, sulphate (SO_4^{2-}), chloride (Cl^-), carbonate (CO_3^{2-}), and nitrate (NO_3^-), was studied.

2.7. Adsorption Isotherm Models

The relationship between the equilibrium amount of adsorbed adsorbate and the remaining adsorbate in the solution is defined by the adsorption isotherm model (Overah, 2020). Isotherm refers to the relationship between the equilibrium adsorbate concentrations in the liquid-phase and the equilibrium adsorption amount on the solid-phase at a certain temperature. In most cases, practicing static adsorption in a batch system might yield the necessary information for determining the adsorption isotherm (Zhang et al., 2018). As a result, a graph of the equilibrium adsorbed amount vs the equilibrium concentration may be made. These must be understood in order to develop and optimize an adsorption system as well as compare the efficacy of various adsorbent materials under various operational situations. Therefore, an accurate mathematical description of the equilibrium isotherm, preferably based on a correct sorption mechanism, is essential to the effective design of sorption systems (Ho et al., 2002). We can model the equilibrium adsorption data by the isotherms, and investigate the adsorption information, such as the adsorption mechanisms, the maximum adsorption capacity, as well as the properties of adsorbents by the isotherms (J. Wang & Guo, 2020). According to the paper, studied by (Berkessa et al., 2019) adsorption isotherm can be described as a curve that explains the phenomenon governing the retention (release) or mobility of a substance to a solid at constant temperature and pH in an aqueous porous medium or aquatic environment.

Adsorption isotherm gives an idea about relation between the adsorbate and the extent of adsorbate adsorbed on the surface of adsorbent at fixed temperature (Mor et al., 2016). The adsorption equilibrium has been continuously clarified by the isotherm equations such that their parameters demonstrate the surface characteristics and affinity of the adsorbent toward the adsorbate (Ghadiri et al., 2017). The most often used models for analysing the adsorption behaviour of the adsorbents are Langmuir, Freundlich and Temkin isotherms (Chahkandi et al., 2021).

2.7.1. Langmuir Isotherm Model

Langmuir isotherm decides the adsorption of ions on the surface of the adsorbent on the monolayer and comparable destinations on the surface (Mor et al., 2016). According to Langmuir isotherm, assumptions can be taken based on adsorption that occurs at specific homogeneous sites within the adsorbent (Nsami & Mbadcam, 2013). The basic assumptions of Langmuir adsorption isotherm model are: - (i) Monolayer adsorption: adsorbate molecules are not sited in another adsorbate molecule on top. (ii) Homogeneous surface, (iii) Each adsorption sites are equivalent, and (iv) There are no interactions between adsorbate molecules on adjacent sites. Langmuir isotherm can be expressed as:

$$q_e = \frac{q_{max} K_L C_e}{1+K_L C_e} \quad \text{.....2.2}$$

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad \text{.....2.3}$$

$$\frac{1}{q_e} = \frac{1}{q_{max} K_L} \times \frac{1}{C_e} + \frac{1}{q_{max}} \quad \text{.....2.4}$$

where, q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L), while q_{max} and K_L are constants related to adsorption capacity and energy of adsorption, respectively. In addition, a dimensionless constant, commonly known as separation factor (R_L) defined by Webber and Chakkravorti, is presented in the equations below:

$$R_L = \frac{1}{1+K_L C_o} \quad \text{.....2.5}$$

where, K_L (L/mg) refers to the Langmuir constant and C_o is the adsorbate initial concentration (mg/L). The computed R_L value suggests the adsorption nature to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$) (Foo & Hameed, 2010).

2.7.2. Freundlich Isotherm Model

Freundlich isotherm is based on the idea that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent and is relevant for both monolayer (chemisorption) and multilayer (physisorption). The Freundlich isotherm is an empirical equation employed to describe the heterogeneous system. This isotherm is not only limited to the formation of monolayers but also the first known relationships to explain non-ideal reversible adsorption. This empirical model can be applied to non-uniform surface adsorption heat and non-uniform distribution of affinity and multi-layer adsorption. At present, Freundlich isotherm is universally applied in varied systems especially for organic synthesis or considerably interactive species on triggered carbon and molecular sieves.

The slope ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, as its value gets closer to zero. Whereas, $\frac{1}{n}$ value below unity implies a chemisorption process and $\frac{1}{n}$ above one is indicative of collaborative adsorption. Freundlich isotherm summarized according to the equation below:

$$Q_e = K_f C_e^{\frac{1}{n}} \quad \text{.....2.6}$$

The linear form of Eq.2.6 is:

$$\ln Q_e = \ln K_f + (\frac{1}{n}) \ln C_e \quad \text{.....2.7}$$

where, Q_e is the quantity of adsorbate adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration (mg/L), K_f denotes the adsorption capacity ((mg/g)(L/mg)$^{1/n}$), and $\frac{1}{n}$ denotes the Freundlich intensity factor and surface heterogeneity, which indicates an adsorption process is feasible (Chahkandi et al., 2021).

2.7.3. Temkin Isotherm Model

The Temkin isotherm model can be used to analyse the effects of indirect adsorbate/adsorbate interactions on the adsorption process. It is also believed that as surface coverage increases, all molecules in the layer's heat of adsorption decreases linearly (Ayawei et al., 2017). This isotherm includes a feature that specifically considers adsorbent-adsorbate interactions by ignoring the extremely low and high concentrations. The model assumes that the heat of adsorption (function of temperature) of all molecules within the layer would decrease linearly rather than logarithmically with coverage (Olalekan et al., 2012). The equation for the Temkin isotherm model typically represented as:

$$Q_e = B \ln (A_T * C_e) \quad \text{.....2.8}$$

The following equation provides the Temkin isotherm model in linear form.

$$Q_e = B \ln A_T + B \ln C_e \quad \text{.....2.9}$$

where, Q_e is equilibrium adsorption capacity (mg/g), B is constant related to heat of adsorption = RT/b, b is Temkin constant (J/mole), R is universal gas constant (8.314J/mole, K), T is absolute temperature (K), A_T is Temkin isotherm constant (L/mg), here a higher value of "B" indicates the stronger interaction and higher heat of adsorption and also the adsorption process is favourable and vice versa.

2.8. Adsorption Kinetic Studies

Adsorption kinetics reflects the evolution of the adsorption process as a function of time. This is an important parameter to consider when choosing an adsorbent. Several models have been developed that describe the diffusion of solutes on the surface of particles and within pores (such as film distribution models, intra-particle diffusion models, out-of-particle diffusion models, and pore diffusion models). In the case of phosphate removal, simplified models such as pseudo-first-order kinetics and pseudo-secondary kinetics were common (Battas et al., 2019). Analysing the rate of adsorption, adsorption mechanism, and rate-limiting processes is made easier by the concept of sorption kinetics (Chahkandi et al., 2021).

Kinetics explains solute take-up rates additionally characterize the residence time of the adsorbate at the solid-liquid interface. Kinetic modelling was used to investigate the adsorption mechanism and potential velocity control processes (Ghadiri et al., 2017)**.** The most common methods for phosphate removal is pseudo first order, pseudo second order and intra-particle diffusion kinetics model can be express as shown below.

2.8.1. Pseudo First-Order Kinetics Model

Pseudo first-order kinetics model is one of the most widely used rate equation to describe the adsorption of adsorbate from the liquid phase. Pseudo first- order kinetics is a commonly used model to describe the adsorption kinetics of pollutants onto adsorbent materials. The model assumes that the rate-limiting step is the adsorption of the pollutant the surface of the adsorbent, and that the number of available adsorption sites decreases as the adsorbent becomes saturated. Pseudo first-order kinetic model as given by Lagergren for liquid-solid phase adsorption that is expressed (Yifru Waktole Berkessa et al., 2019).

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad \text{.....2.10}$$

where, q_e (mg/g) and q_t (mg/g) are the amounts of phosphate adsorbed on the adsorbent at equilibrium and at any time t, respectively, and k_1 (min^{-1}) is the rate constant of the first-order adsorption. After integration and applying boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at time = t, the integrated form should be:

$$\ln (q_e - q_t) = \ln q_e - k_1 \times t \quad \text{.....2.11}$$

The plot of ln (q_e – q_t) versus t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

2.8.2. Pseudo Second-Order Kinetics Model

The pseudo-second order kinetic model is another commonly used model to describe the adsorption kinetics of pollutants onto adsorbent materials such as the corncob bio char. The pseudo-second-order kinetic model can be expressed as the following equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad \text{.....2.12}$$

where, k_2 (g/mg min) is the rate constant of the second-order equation, q_e (mg/g) is the maximum adsorption capacity, and q_t (mg/g) is the amount of adsorbate adsorbed at time t (min). After integration:

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{t}{q_e} \quad \text{.....2.13}$$

If pseudo-second order kinetics are applicable, the plot of $\frac{t}{q_t}$ against t should give a linear relationship, from which q_e and K_2 can be determined from the slope and intercept of the plot of $\frac{t}{q_t}$ versus t, respectively.

2.8.3. Intra- particle Diffusion

The intra-particle diffusion model states that if intra-particle diffusion is involved in the adsorption process, the plot of the square root of time ($t^{1/2}$) vs Q_t should be linear. Furthermore, in a multi-step adsorption process, two or more slopes may appear if these lines pass through the origin when the intra-particle diffusion is the rate-determining step (Pan et al., 2017). To determine whether particle diffusion was a rate-limiting step or not during the adsorption of phosphate onto MgO-loaded corncob bio char, an intra-particle diffusion model based on the theory advanced by Weber and Morris was applied. The mathematical equation for intra-particle diffusion model is given in Equation below;

$$Q_t = K_p t^{\frac{1}{2}} + C \quad \text{.....2.14}$$

where, Q_t is the amount of phosphate adsorbed (mg/g) at a given time t (min) and K_p (mg/g $min^{1/2}$) is the intra-particle diffusion rate constant and C is intercept. The Kp and C value were obtained from plotting of $t^{1/2}$ versus Q_t.

2.9. Bio chars

Bio char is an organic porous material produced as a result of the thermochemical conversion or thermal decomposition of biomass in an oxygen-restricted environment. It is a newly developed

approach for environmental restoration that is currently being tried in a variety of scenarios. Due to its physicochemical characteristics, including its high surface area and cation exchange capacity, it is a solid and carbon-rich substance that can be utilized as an adsorbent agent (Seleiman et al., 2021). By heating organic, carbon-based materials at high temperatures (200–900 °C) without any oxygen, black carbon in the form of bio char is produced (Ogonek, 2016). Bio char is typically made from agricultural waste, water-treatment algae, or wood by products like sawdust, husks, and cherry stones. In the past, bio char has been used to increase agricultural output and soil fertility in infertile or low-fertility areas (Adeyemi & Idowu, 2017). Recent studies have demonstrated that bio char can be used to enhance soil, remove contaminants from the soil and water, boost agricultural fertility, and lower greenhouse gas emissions (Osman et al., 2022). Traditional slash and burn techniques are substantially worse than bio char, which is produced from waste biological matter under controlled conditions and then applied to agricultural soils since it is much more economically possible (Qayyum et al., 2015). Due to its numerous potential environmental applications and advantages, bio char, a cheap adsorbent, is currently gaining more attention. A number of recent studies suggest that bio char made from agricultural waste has a strong ability to bind chemical contaminants in water, including heavy metals and organic contaminants, despite the majority of current bio char studies being concentrated on bio char land application as a simple and affordable way to sequester carbon and increase fertility (M. Zhang et al., 2020). Bio char is a stable carbon-rich substance that exhibits great potential to handle water/wastewater impurities (Adeyemi & Idowu, 2017).

2.9.1. Bio char production

Bio char is created by heating carbon-based materials like maize stalks, sawdust, or other organic waste under oxygen-limited or non-existent conditions and it is produced by heating biomass in the total or partial absence of oxygen (Adeyemi & Idowu, 2017). Pyrolysis is the most common technology employed to produce bio char, and also occurs in the early stages of the combustion and gasification processes besides bio char, bio-oil and gas can be collected from modern pyrolysers (Alagha et al., 2020). These could be refined to a range of chemicals and/or used as sources of renewable energy if derived from sustainably produced biomass thus pyrolysis and hydrothermal carbonization are common manufacturing processes that involve heating raw materials at high pressures and temperatures (Boguta et al., 2020). The most popular methods for making bio char from different types of biomass are shown in Figure 2.3, and the type of bio char that is created as a result of pyrolysis depends on a variety of variables, including the pre-treatment

of the biomass, the type of reactor, its dimensions, the pressure, and the amount of time it spends inside the reactor (Oktor & Yenihan, 2023).

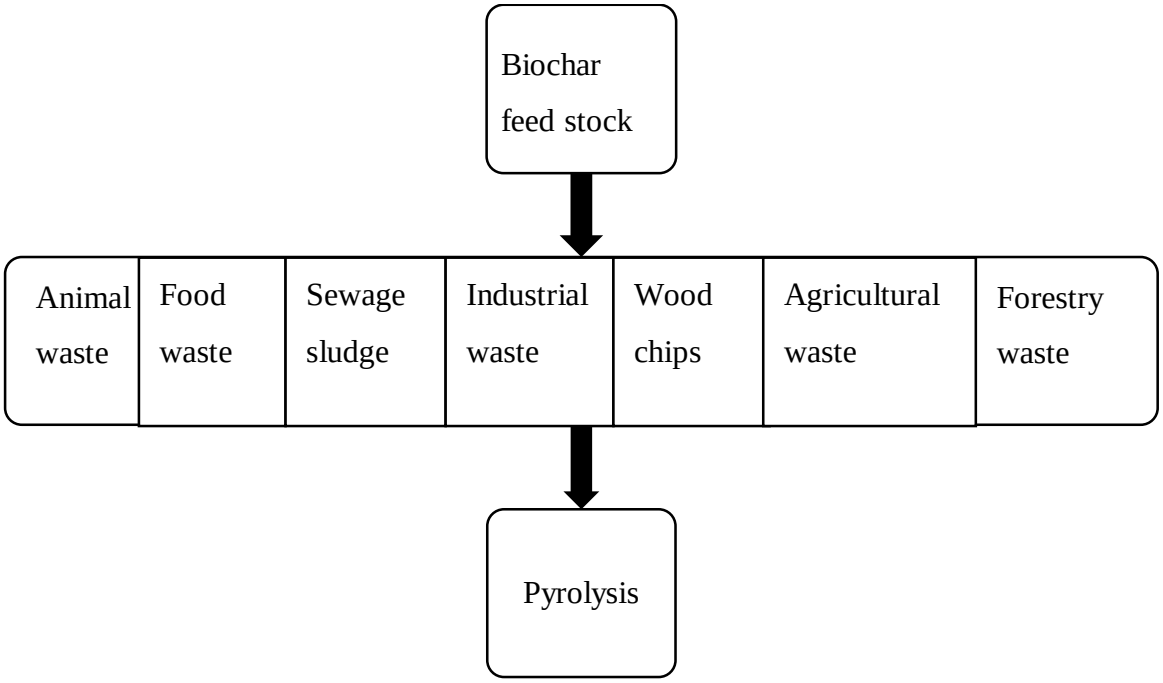

Figure 2. 4: Schematic representation of the bio char production process flow diagram.

The yields and compositions of bio char are influenced by a number of production factors, such as the biomass composition, the reaction conditions, and the recovery of the finished products (Tripathi et al., 2016). Bio chars can be modified for specific uses, such as the adsorption of heavy metals, nutrients, or inorganic pollutants, using some industrial pre-treatment techniques (Venkatesh et al., 2022).

Table 2. 5: Bio char produced and their effects on bio char characteristics.

Bio char produced	Effect on bio char	Reference
Magnetic bio char	Decreased SA, PV High number of micro-pores Separated from solution easily	(Zhou et al., 2018)
Alkali	Alkaline bio char Greatly increased SA, cation exchange capacity	(Huff et al., 2018)
Zero-Valent Iron bio char	Greatly reduced PV, SA Greatly increased pore size	(Xu et al., 2020)

MgO-bio char	MgO-bio char nanocomposites formed	(Venkatesh et al., 2022)
Acid-Modified bio char	Increased monolayer adsorption capacity, Introduction of carboxyl groups, , Increased or decreased SA, PV	(Mopoung et al., 2015)

2.9.1.1. Pyrolysis

In the absence of oxygen, pyrolysis is the thermal degradation of biomass to yield a mixture of condensable liquids (bio-oil), gases, and solid residue (bio char) (Shariff et al., 2016). The three primary categories of pyrolysis are slow pyrolysis, fast pyrolysis, and flash pyrolysis (Chemerys & Baltrėnaitė, 2016). Operating factors including temperature, heating rate, and holding duration can be used to distinguish between each class. For slow pyrolysis, the reaction temperature is between 300 ℃ and 700 ℃, for flash pyrolysis, it is between 400 ℃ and 650 ℃, and for fast pyrolysis, it is beyond 550 ℃ (Rattanaphaiboon et al., 2022). A slow heating rate of between 10 ℃ min^{-1} and 20 ℃ min^{-1} is used for slow pyrolysis. While slow pyrolysis occurs at significantly lower heating rates, fast pyrolysis occurs at substantially higher heating rates (G. Wang et al., 2020). According to (Shariff et al., 2016), fast pyrolysis can be finished in as little as two seconds while slow pyrolysis requires a long holding period of at least 30 minutes to several hours for the feedstock to fully pyrolyze. While slow pyrolysis generates the most charcoal and gas while producing the least amount of liquid, fast and flash pyrolysis yield higher amounts of liquid with shorter holding durations (Mustafa et al., 2022). The proportions of bio char, syngas, and bio oil produced may vary depending on the production factors (temperature, residence time) Table 2.7 and feedstock composition. The pyrolysis temperature is a critical parameter in the pyrolysis process that can be manipulated to control the yield and properties of the resulting products depending on the intended application. Thus, the products that produced from pyrolysis was described on the figure above and to realize it as shown below on Figure 2.5. Pyrolysis was carried out at temperatures of 300, 450 and 600 ℃ in a muffle furnace with a residence time of 90 min at the desired temperature in the presence of N_2 gas.

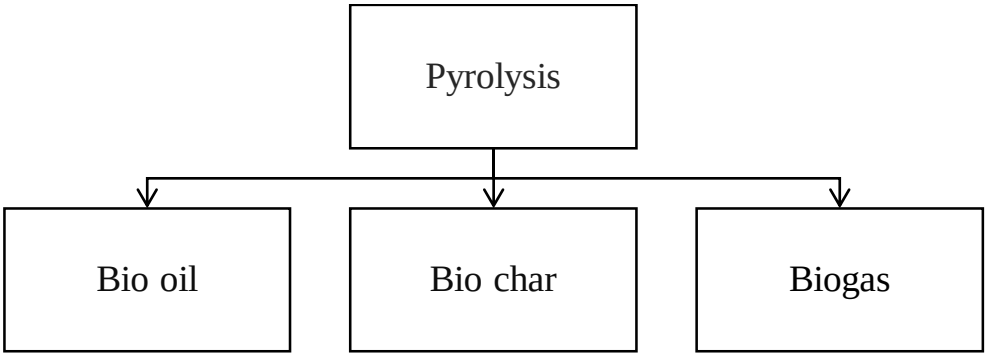

Figure 2. 5: Diagram representation of pyrolysis products from different biomass.

Table 2. 6: Production methods of bio chars based on (Pyrolysis Variations) (Ogonek, et al., 2021).

Process	Temperature	Residence time	Bio-oil (%)	Bio char (%)	Syngas (%)
Fast	~500 °C 400-600	1-2s	75 (25 water)	12	13
Intermediate	~500 °C 400-600	10-20s	50 (50 water)	25	25
Slow	~500 °C 350-800	5 min – days	30 (70 water)	35 20-40	35
Gasification	>750 °C	5-20s	5 tar (5 water)	~10	85
HTC	180-250	1-12h	N/A	30-60	N/A

2.9.1.2. Hydrothermal Carbonization (HTC)

HTC is one of the most appealing thermochemical conversion processes utilized to create materials with high energy densities. This technique allows for high conversion efficiency of biomass into a carbonaceous material with reasonably high yield at low operation temperature and is ideally suited to wet feedstock (Ahmed et al., 2022). HTC involves heating biomass in the presence of a liquid to temperatures between 180 and 300 °C the pressures between 2 and 10 MPa for a number of hours (Daniel et al., 2015). According to (Bol et al., 2018), HTC is regarded as a practical method for converting biomass into porous materials with a lot of functional groups that contain oxygen and are effective in adsorbing pollutants from Wastewater. Similar to the biomass to liquid process, hydrothermal carbonization enables the use of practically all of the carbon present in biomass for the production of fuel. The subject of biomass conversion to biofuel has been around for a while, but it has recently undergone new development in Germany (Maniscalco et al.,

2020). It involves moderate temperatures and pressures over an aqueous solutions of biomass in a dilute acid for several hours and the resulting matter reportedly captures 100 % of the carbon in a "bio coal" powder that could provide feed source for soil amendment (similar to bio char) and further studies in an economic nanomaterial production (Maniscalco et al., 2020).

2.9.1.3. Gasification

By converting biomass or other organic waste into a gas mixture called "syngas" (85 %), which contains H_2, CO, CO_2, and likely tiny hydrocarbons like CH_4, a solid char (10 %), and a liquid phase called "tar" (5 %), gasification is a thermochemical process (Almanassra et al., 2020). Tar and char are examples of gasification's undesirable by-products in which char produced by biomass gasification processes has a wide variety of various qualities depending on the kind of feedstock, reactor architecture, gasifying agent, and gasification temperature (Panwar et al., 2019). Carbonaceous materials derived from biomass or fossil fuels can be converted into gases by a process called gasification. The major fractions produced include nitrogen (N_2), carbon monoxide (CO), hydrogen (H_2), and carbon dioxide (CO_2). However, high temperature solid oxide fuel cells are capable of accepting mixtures of H_2,CO,CO_2, steam, and methane without any additional processing or reforming (Mansur et al., 2020). In order to produce clean gas from potentially problematic feedstock material, several gasification procedures try to refine out caustic ash components like chloride and potassium. Currently, electricity is produced on industrial scales by gasifying fossil fuels. Pollutants like SO_x and NO_x can be produced in lower quantities by gasification than by burning (Drissi & Mouats, 2018).

2.9.1.4. Torrefaction

Torrefaction is a typical thermal pre-treatment procedure that enhances the physicochemical and thermochemical properties of biomass by allowing for the homogenization and solidification of the biomass's energy content. It frequently occurs slowly, at atmospheric pressure, between 200 and 300 °C, without oxygen or with very little oxygen (Salehi et al., 2022). It is the primary process used to produce biofuel (Bunce et al., 2018), whereas pyrolysis is the primary method used to produce charcoal for both waste water and water depollution. Due to the lower temperatures used during the thermal process, torrefaction char may have more functional groups containing oxygen than charcoal (Adeyemi & Idowu, 2017). It creates a product that is relatively dry, which lessens or completely eliminates the possibility of organic breakdown and a significant source of energy is biomass (Tumuluru et al., 2021). In comparison to the biomass they are made from, pellets or briquettes have a higher density, less moisture, and are more stable in storage (Amer et al., 2021).

2.9.2. Modification of Bio char

Modification of bio char can involve physical, chemical, or biological methods but physical modifications may include changes in particle size, surface area, or pore structure, while chemical modifications may involve the addition of functional groups or the removal of impurities (Panwar et al., 2019). Bio char is being modified in an effort to enhance its capacity to remove pollutants. The adsorption capacity of bio char can typically be increased through the modification of metal oxide and metal salts, acid-base reactions, composite synthesis, and ball milling (Chemerys et al., 2016). The modified bio char has a higher adsorption capacity due to its significant anion exchange capacity, precipitation, and electrostatic attraction (Baltrėnaitė et al., 2018). This modification uses magnesium, iron, aluminium, and manganese as the metals (Valeria et al., 2016).

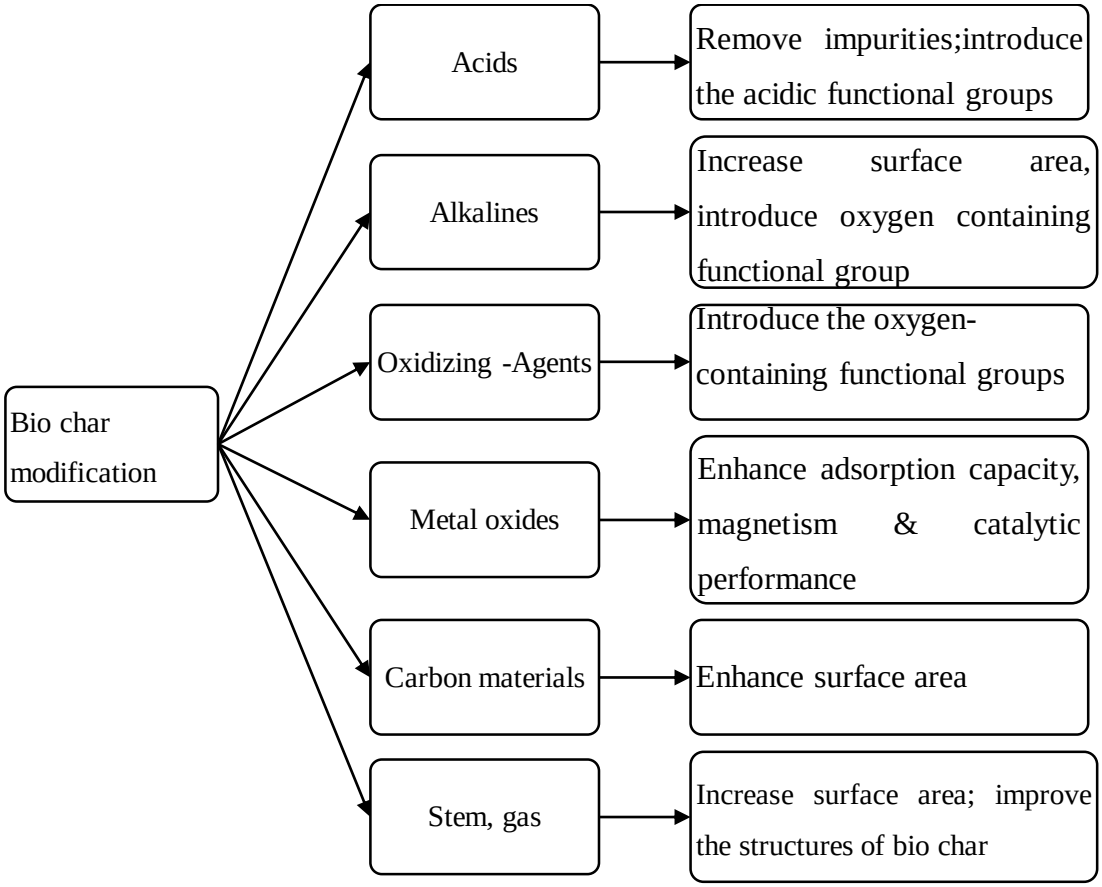

Figure 2. 6: Representation of different agents of bio char modification and their applications.

Table 2. 7: PO_4^{3-} adsorption capacities demonstrated in various studies.

BC feedstock	Pyrolysis method	Activation/modification	P adsorption capacity (mg g^{-1})	Reference

Corncob	Pyrolysis	MgO/CaO	326.63	(Yousef et al., 2020)
Bamboo	Pyrolysis	Mg/Al or Mg/Fe loaded	172	(Zhong et al., 2019)
Cotton wood	Pyrolysis	Mg/Al or Mg/Fe loaded	410	(Veetil et al., 2017)
Cotton stalks	Chemical precipitation	Treated with $MgCl_2$ before pyrolysis	129.90	(Lichtfouse et al., 2022)
Water hyacinth	Pyrolysis	Fe_3O_4 and Fe_2O_3	3.2	(Adelagun et al., 2021)
Wood chips	Pyrolysis	Fe $(OH)_3$	5.07	(Zhong et al., 2019)
Tea waste	Pyrolysis	MgO	~100	(P. Kumar et al., 2010)
Rape straw	Chemical precipitation	MnO_x ($KMnO_4$)	24	(Rahman et al., 2021)
Grape husk	Pyrolysis	Mg-Al	30	(Bian et al., 2022)
Wheat straw	Pyrolysis	Al	64.1	(Yang et al., 2021)

2.9.3. Environmental Application of Bio char

A carbon-rich, fine-grained residue called bio char can be created using either outdated methods (such covering burnt biomass with dirt and letting it smoulder) or cutting-edge contemporary biomass pyrolysis procedures. Many environmental advantages of bio char include carbon capture, reduced global warming, improved soil quality, and pollutant elimination (Panwar et al., 2019). Various kinds of biomass, including agricultural wastes (Mustafa et al., 2022), forestry residues and sewage sludge (X. Zhang et al., 2020), can be used as a feedstock for pyrolysis to create charcoal. In the agricultural field, the use of bio char as a soil amendment has shown promising results, so various bio char types and preparation methods are being researched in an effort to create the most efficient bio char that can boost soil fertility, porosity, and nutrient availability, among other things (Li et al., 2016). Transformation to bio char has multiple benefits and is be used as a soil amendment to improve fertility and crop production as well as a method for carbon sequestration (Wang et al., 2016a), organic contaminant degradation (Luo et al., 2023) and protection against nutrient leaching (Chen et al., 2021). Due to these sources, bio char is less expensive than activated carbon, which requires labour-intensive activation processes (Hagemann et al., 2018).

2.9.3.1. Bio char as Soil Conditioner

Applying untreated bio char had a positive impact on soil fertility in some poor soils (mostly in the tropics). They include the soil's increased ability to store water, aeration of the soil, and the release of nutrients via increasing the pH-value of the soil (Msimbira & Smith, 2020). Fresh bio char may, in fact, absorb nutrients from the soil and hinder plant growth, at least in the short and medium term. Due to these factors, bio char should only be employed in temperate areas after being initially enriched with nutrients and after the char surfaces have undergone microbial oxidation (Rasse et al., 2022). The biomass that is going to be composted needs to have 10–30% bio char (by volume) added can be combined with organic wastes like wool, molasses, ash, slurry, and pomace to create organic carbon-based fertilizers since it acts as a carrier for plant nutrients (Alkharabsheh et al., 2021). The widest application of bio char is for soil remediation because its extensive pore structure generates a huge surface area that contains functional O-groups and a high cation exchange capacity (Zhang et al., 2022). Therefore, bio char has also been used for adsorption of plant nutrition's such as NH_4^+, Ca_2^+, and K^+ (Peng et al., 2021). However, bio char possesses a net negative surface charge and provides only a limited capacity to adsorb, phosphate ($H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}) and nitrate (NO_3^-) anions. In addition, the presence of SO_4^{2-} and CO_3^{2-} in coastal and saline-alkaline soils prevents further adsorption (Graber et al., 2012). Adsorption of phosphate and nitrate from aqueous solution onto bio char can be negatively affected by phenolic, carboxyl, and hydroxyl functional groups (Chen et al., 2011). In particular, surface modification with metal oxides that have high-phosphate-affinity (MgO) increase anion binding sites (Zhang et al., 2012). The use of MgO-modified bio char for phosphate removal and retention have been performed but only on a small scale using water or pot experiments and not under field conditions (Li et al., 2017). Because soil is a heterogeneous system, the more complex saline-alkaline conditions where competing effects of soluble ions are higher as compared to neutral soil conditions have still not been tested in the field.

2.9.3.2. Bio char for Water Treatment

Being an effective adsorbent, bio char holds potential for low-cost water treatment, yet it has been marketed as a soil supplement. As a porous, bio-stable, and readily available substance, bio char has drawn interest as a potential replacement for adsorbents like activated carbon and zeolite. Its use in anaerobic digestion is also progressively expanding and the use of bio char to extract and concentrate the nutrients could solve present issues with the storage of large amounts of digestate and other waste liquids as well as resolve environmental issues with applying large amounts of liquid fertilizer to the soil (Gupta et al., 2017).

2.9.3.3. Bio char for Nutrient Removal

Recently, research has concentrated on using bio char to remove nutrients. Because it has the advantages of improving soil and being produced cheaply, nutrient-enriched bio char can be used directly in soil as opposed to activated carbon and zeolite (Rattanaphaiboon et al., 2022). Also, this will help with the treatment of biomass waste, particularly in developing nations where the uncontrolled burning of biomass waste increases the risk of air pollution and fires (Ferronato, 2019). In order to remove nutrients while producing nutrient-enriched material (NBC) fertilizer, charcoal may be a desirable adsorbent (Shi et al., 2021).

2.9.4. Future Perspectives and Environmental Concern of Bio char

In regard to water depollution, bio char is a renewable resource that has a lot of promise to address a number of environmental problems. Although bio char has a great capacity for adsorbing a variety of pollutants, a clear knowledge of the various mechanisms driving the adsorption process is still lacking (Salehi et al., 2022). The stability of the bio char was also found usually decreased after several cycles when the bio char is used as a support for catalyst due to the variation in the carbon structure of the bio char and its stability generally depends on the nature of the starting feedstock and on the experimental conditions used during its thermal conversion (Quispe et al., 2022).

2.9.4.1. Future Perspectives

Bio char is a unique renewable resource, which has a significant potential to address several environmental issues we have been encountering in recent years including remediation of pollutants in soil, water, and gaseous media (Adilah et al., 2016). This could be synergistically improving soil, water, air quality, carbon sequestration, and greenhouse gas emissions mitigation. Since the bio char quality and the performance varies significantly depending on feedstock types and pyrolysis conditions, future progress in bio char (Ojedokun & Bello, 2017). The future perspectives for the application of bio char are promising and include the following:

A. Sustainable agriculture: Bio char has shown great potential as a soil amendment to improve soil fertility, water retention, enhance water holding capacity, and crop yields. In the future, bio char may become a widely used tool in sustainable agriculture, particularly in areas with degraded soils or low agricultural productivity.
B. Climate change mitigation: Bio char has the potential to sequester carbon in the soil for hundreds or even thousands of years, reducing greenhouse gas emissions and mitigating

climate change. In the future, bio char may become an important tool in climate change mitigation efforts.

C. Renewable energy: Bio char can be produced from a variety of organic waste streams and can be used as a source of renewable energy through combustion or gasification. In the future, bio char may become an important component of sustainable energy systems.
D. Waste management: Bio char can be made from a variety of organic waste streams, reducing the amount of waste sent to landfills and reducing greenhouse gas emissions from waste decomposition. In the future, bio char may become an important tool in waste reduction and management efforts.

Table 2. 8: Advantages and disadvantages of bio char (Salehi et al., 2022).

Advantages	Disadvantages
Soil improvement	Feed stock availability and sustainability
Carbon sequestration	Energy intensive production
Nutrient retention	Lack of standardization
Soil moisture management	Cost and infrastructure
Contaminant remediation	Relatively complex process control
Complete destruction of pathogens	High operational temperatures
Low space requirement for continuous processes	Need for flue gas treatment
Co-treatment with other waste fractions	Little to no experience at scale
Storage, transport and disposal of outputs	Nitrogen is largely lost to the vapour phase

Finally, most of the literatures studied earlier concerns, when the phosphorus concentration was above 2 mg/L but in this study the phosphorus concentration both below and above the prescribed number or 2 mg/L in order to monitoring and managing phosphorus levels in water bodies, since it is essential to maintain water quality, preserve ecosystem health and prevent the detrimental effects of phosphorus pollution by producing an adsorbent from locally available or agricultural waste corncob. When people used corncob as energy source it creates smog and that is difficult for elder peoples' eye. So, it is so important to produce corncob adsorbent for the removal of phosphate from water.

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Chemicals, Reagents and Equipment's

The main raw material that was used to generate MgO modified corncob bio char adsorbent during the experimental work was corncob from the agricultural waste of Awash Melkassa Agricultural Research Centre in Oromia regional state (Oromia, Ethiopia). Analytical grade chemicals such as sodium hydroxide (NaOH, 99.0%), magnesium oxide (MgO, 96-100.5%), sodium nitrate ($NaNO_3$), hydrochloric acid (HCl, 35-37%), nitric acid (HNO_3, 37%), sulphuric acid (H_2SO_4, 98%), acetone (C_3H_6O, 99.5%), ethanol (C_2H_6O or C_2H_5OH, 96%), ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$, 98%), L-ascorbic acid ($C_6H_8O_6$, 99%), tap water and distilled water were used to synthesis MgO loaded corncob bio char adsorbent. To produce synthetic phosphate containing wastewater, Potassium dihydrogen phosphate (KH_2PO_4, 98-101%) was used as a precursor during in this experimental work. All the above mentioned chemicals were found from Chemical Engineering department of chemical store except MgO that was purchased from Kirkos, chemical store. The diluted solution of HCl, (HNO_3, 69-72%) and NaOH used to adjust the pH of the solution that were prepared. The reagent was synthesized from ammonium molybdate tetrahydrate by using L-ascorbic acid as a reducing agent to form ammonium molybdate blue. Equipment's that were used for experimental work includes; digital electronic balance, magnetic stirrer, electronic grinding machine, spatula, test tube, ball mill, conical flask, Erlenmeyer flask, aluminium foil (high thickness), digital pH meter, beaker, SX-2,5-10 box type resistance furnace, centrifuge, mortar and pestle, funnel, water bath, measuring cylinder, dropper, syringe, gloves, beaker, Clifton oven (RS 232), desiccator, volumetric flask, petri dish, filter paper (Whatman,15.0 cm), vacuum pump, and various mesh size sieves (i.e.35 mesh and 60 mesh sizes which is 0.5 mm and 0.25 mm respectively).

3.2. Bio char Preparation

Bio char producing materials corncob, first sun dried, cut into small pieces, then ground and passed through a 0.5 mm sieve by using 0.25 mm size sieve as a reference. The powder was inserted into crucibles and then converted into bio char throw slow pyrolysis in a SX-2,5-10 box type resistance furnace under an anoxic condition at 450 °C for 1.5 hours with a heating rate of 10 °C min^{-1} (Adekanye et al., 2022). The produced bio char was allowed to cool to ambient temperature inside the furnace following the experiment. After the cooling stage, bio char samples were washed with

distilled (de-ionized) water for several times until it becomes the pH stabilizes or neutralizes and again washed with acetone or alcohol. Finally filtered the washed bio char by using vacuum pump and shaking with distilled (de-ionized) water and then decanting the water. The washed bio char was dried in an oven at 105 °C for 24 hours and stored under desiccation at room temperature until use it.

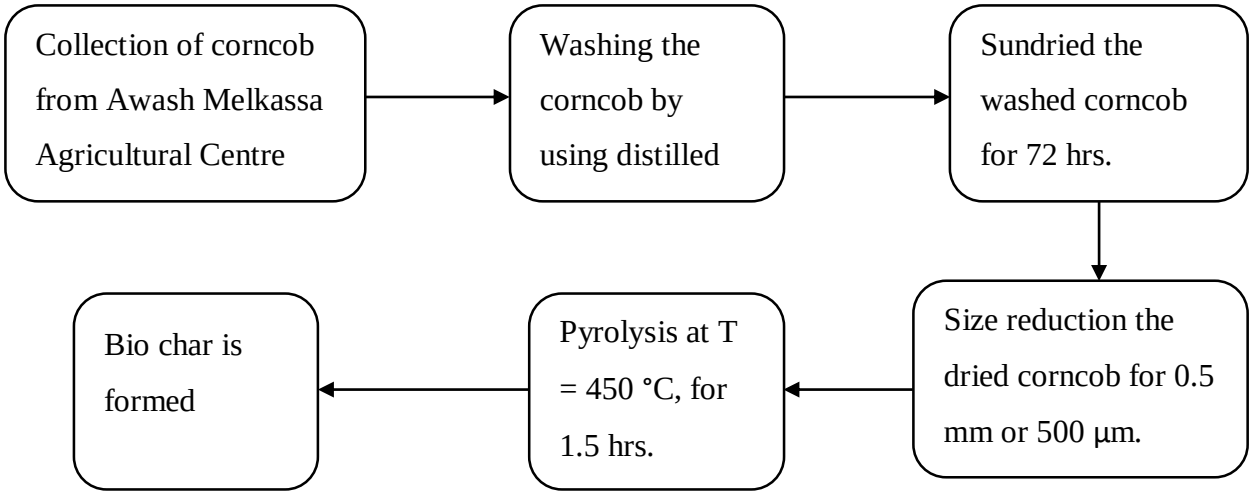

Figure 3. 1: Experimental frame work of corncob bio char synthesis.

After the bio char is produced MgO loaded corncob bio char can be synthesized

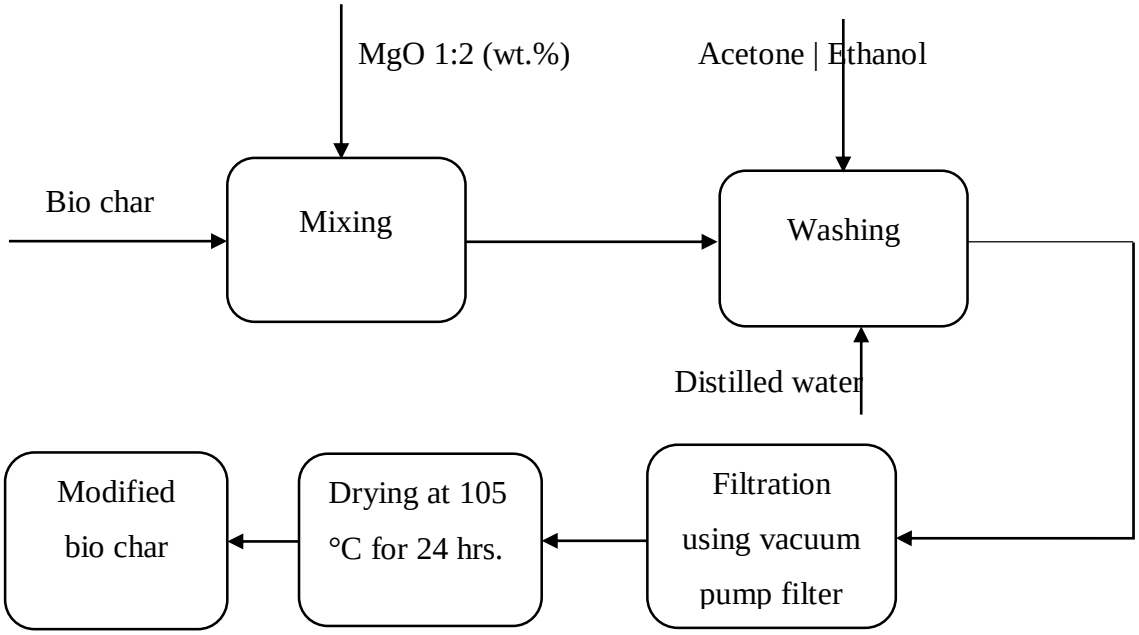

Figure 3. 2: Experimental frame work of MgO modified corncob bio char synthesize.

3.3. The pH at point of zero charges

To identify the working pH value for adsorption studies the point of zero charge was determined before optimization of pH. 40 mL of 0.1 M $NaNO_3$ solutions were taken in ten conical flasks with

pH range of 3-12 by 1 pH increment and the pH was adjusted by using 0.1 M HCl and 0.1 M NaOH. Then, 0.5 g of MgO modified corncob bio char powder was added to each solution and vibrated by using water bath as a mechanical shaker at a speed of 150 rpm for 24 hrs. Then, the adsorbent was separated from the solutions by using filter paper and vacuum pump. After equilibrium achieved the final pH of each sample was measured by using pH meter. Then, the change in pH (ΔpH) was calculated (ΔpH = final pH – initial pH). Finally, to determine the pH at PZC, the graph of change in pH vs. final pH could be plotted.

An aliquot of 40 mL of 0.1 M $NaNO_3^-$ is added in ten different Erlenmeyer flasks & set different pH values from (3-12) of the solution with 0.1 M of HCl and NaOH

Add 5 g of the bio char in each flask

Shake the flasks at a speed of 150 rpm on a water bath at 25 °C for 24 hrs.

After equilibrium filter the sample by using vacuum pump

Record the pH values of the filtrate accordingly

Figure 3. 3: Point of zero charge analysis.

3.4. Phosphate Ion (PO_4^{3-}) Adsorption Study

3.4.1. Stock Solution Preparation

Adsorption of PO_4^{3-} onto corncob bio char was carried out in a series of batch process or batch experiments and stock solution of PO_4^{3-} was prepared by dissolving a known mass of analytical reagent grade Potassium dihydrogen phosphate (KH_2PO_4) in one litre of distilled water to achieve the concentration of 1000 mg/L. Other samples for all experiments were prepared by diluting the stock solution to the predetermined concentration. A number of parameters such as the initial concentration of phosphate, adsorbent dosage, contact time and pH effect of the process were studied and also those variables affecting the removal of phosphate ion were varied widely in order to optimize the removal of the ion in the process. The experiments were performed in several 500 mL and 1000 mL plastic bottles, each including a different amount of phosphate solution (i.e., primary stock solution and secondary stock solution) and the solution pH was adjusted by using the addition of 0.1 M NaOH and HCl but the reagent was prepared by using ammonium molybdate blue method which is by measuring 1.25 g of ammonium molybdate tetra hydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$), 2.5 mL of concentrated H_2SO_4 in 100 mL of distilled water and 1 g of L-ascorbic acid ($C_6H_8O_6$) in 100 mL of distilled water was mixed together.

3.5. Material Characterization Techniques

3.5.1. X-ray Diffraction (XRD)

X-ray diffraction (XRD) has been widely used techniques for the characterization of materials, including the identification of crystal structures, phase composition, crystalline grain size, and lattice parameters. It is one of the most considerably used techniques for characterization and the

crystalline size, crystalline structure, miller indices and space group present in a synthesized corncob bio char and MgO modified corncob bio char adsorbent were characterized using an X-ray diffractometer (XRD-700, Shimadzu Co., Japan). A Cu target for generating a Cu Kα radiation (λ = 0.154056 nm) was used as the incident X-ray beam at an accelerating voltage of 40 kV and a current of 30 mA. The powder samples were mounted on a flat XRD plate and scanned in the range 10º to 85º at room temperature in the continuous scan speed 3°/min. The crystal structure, phase purity of corncob bio char and MgO modified corncob bio char adsorbent powder were studied from the XRD pattern obtained in the step scanning mode in the same 2θ range. The step size and the time per step were 0.02° and 0.40 sec respectively. The average particles size are calculated by using Scherrer equation (Abraha, 2015).

$$D = \frac{K.\lambda}{\beta Cos\theta} \quad \text{.....3.1}$$

where, D is crystalline size, K = (0.94) is a Scherrer constant, λ = is the wavelength of the x-ray, θ is Bragg angle of corresponding diffraction peak and β is full width at half maximum (FWHM)

$$n\lambda = 2dsin\theta \text{.....3.2}$$

where, n (an integer) is the "order" of reflection, λ is the wavelength of the incident X-rays, d is the inter-planar spacing of the crystal and θ is the angle of incidence.

3.5.2. Fourier Transform Infrared Spectrometry (FTIR)

FTIR stands for Fourier Transform Infrared Spectroscopy and it is a widely used technique for the characterization of materials based on their infrared absorption properties. FTIR spectroscopy provides information about the functional groups and chemical bonds present in a sample. FTIR analysis was used to determine the presence of different functional groups and organic impurities. FTIR (Model FTIR-6600 type A) was used in a transmission mode of the mid-infrared range with wave numbers from 500 to 4000 cm^{-1} using the KBr pellet technique. KBr pellet technique is widely used for FTIR spectroscopy with accuracy reading, because the KBr does not show any absorption spectrum in IR region and it has a 100 % transmission gap in the range of wave number (500 - 4000 cm^{-1}). 2 mg of synthesized material (corncob bio char and MgO modified corncob bio char adsorbent) powder compressed with 200 mg of KBr to form 12 mm diameter pellet and then placed on a specimen holder. Spectra were measured between in the range of 4000 cm^{-1} to 500 cm^{-1} at a resolution of 4 cm^{-1}, with number of scans 8 and scanning speed 2 mm/sec. Its pattern is plotted within the FTIR machine by generating the transmittance peaks (%) as the Y-axis versus wavenumber (cm^{-1}) as the X-axis.

3.5.3. Brunauer-Emmett-Teller (BET)

The Brunauer-Emmet-Teller (BET) is a widely used method for determining the specific surface area of porous materials, such as powders, catalysts and adsorbents. The BET theory is based on the adsorption of gas molecules onto the surface of a solid material. It assumes that the surface consists of a series of adsorption sites with varying energies. It assumes the formation of a mono-layer of gas molecules on the surface of the material and does not account for multi-layer adsorption and it provides valuable information for understanding the reactivity, adsorption capacity, and performance of materials in various applications, such as catalysis, gas adsorption, and surface modifications. BET commonly applied to calculate the specific surface area based on nitrogen adsorption isotherm measurements at 77 K. In this study the specific surface area of the corncob bio char and MgO modified corncob bio char adsorbent were carried out using Horiba Instruments, Inc SA-9600 Series surface area analyser at 200 ^{0}C degassing temperature for 2 hr. in the presence of nitrogen gas.

3.5.4. Thermal Gravimetric Analysis (TGA)

Thermal gravimetric analysis (TGA) analysis was performed using (Beijing, HCT-1, TGA) analyser. The Nitrogen gas used as carrier gas and the heating rate was set at 10^{o}C/min to determine the thermal stability of 5 mg of the corncob biomass for MgO modified loaded corncob bio char adsorbent. The temperature was adjusted between 20 ℃ to 700 ℃ and the decomposition of sample weight (%) against temperature (℃) was recorded. This analysis resulted the thermal gravimetric analysis (TGA) curve which used as the thermal stability of the corncob biomass sample.

3.6. Batch Adsorption Experiments

A suitable amount of KH_2PO_4 was dissolved in deionized water to prepare the phosphorus stock solution with a concentration of 1000 mg/L and the phosphorus working solution was prepared via the dilution method. All adsorption experiments were carried out in beakers at 25 ℃ on a magnetic stirrer at a shaking speed of 400 rpm and to identify the effect of the adsorbent dosage on the phosphorus removal, batch experiments were carried out by adding various dosages in the range of 20 to 100 mg of adsorbent into 100 mL of a 100 mg/L phosphorus solution and the initial PO_4^{3-} concentration in the range of 1 to 10 mg/L as well the determination of the phosphorus adsorption kinetics, 500 mg adsorbent was added into a 100 mL phosphorus solution with a concentration of 100 mg/L. The phosphorus adsorption isotherm experiments were conducted with the initial phosphorus concentrations in the range of 1 to 10 mg/L and 5 g/L of corncob adsorbent was used

to adsorb the phosphate solution for 24 hrs. In the pH effect experiments, phosphorus solutions 100 mg/L and in the pH range of 2-13 was treated with 5 g/L of corncob adsorbents for 6 hrs and the pH value of the phosphorus solution was regulated by 0.1 M HCl and 0.1 M NaOH. To study the influence of competitive ions on phosphorus adsorption, 10 mg/L Cl^-, CO_3^{2-}, SO_4^{2-} and NO_3^- interfering ions was added to a 100 mg/L phosphorus solution and these solutions was treated at the adsorbent dosage of 0.5 g/100 mL.

After each adsorption experiment, samples were filtered and absorbance of the residual PO_4^{3-} concentration could be determined by UV-Visible spectrophotometer at 520 nm wavelength. Adsorption studies consist of adsorption kinetics and adsorption isotherm model. Adsorption kinetics is used to understand adsorption rate and the effect of contact time on adsorption. Adsorption isotherm model used to understand adsorption mechanism and effect of concentration on adsorption. In this study, the effect of major parameters like pH, adsorbent dose, contact time and initial phosphate concentration were optimized to investigate the maximum phosphate removal efficiency by MgO modified corncob bio char adsorbent. The adsorption capacity and rate of PO_4^{3-} ion in a solution could be calculated by using the formula.

$$Q = \frac{(C_i - C_f) \times v}{M} \quad \text{.....3.3}$$

$$R = \frac{(C_i - C_f)}{C_i} \times 100\% \quad \text{.....3.4}$$

$$D = \frac{C_{des}}{C_{ads}} x\ 100\% \quad \text{.....3.5}$$

where, Q is PO_4^{3-} ion adsorption capacity (mg / g), C_i is Concentration of PO_4^{3-} ions (mg/L) in the solution before adsorption, C_f is PO_4^{3-} ion concentration (mg/L) in the solution after adsorption, V is the volume of the solution (L), M is the amount of adsorbent (g), and R is the removal rate of PO_4^{3-} ions, D is desorption of PO_4^{3-} ions, C_{des} concentration of phosphate desorbed (mg/L) and C_{ads} concentration of phosphate adsorbed (mg/L).

3.7. One Factor at a Time (OFAT)

One factor at a time (OFAT) is an experimental approach used in scientific research and engineering to investigate the effect of individual factors on a system or process by varying one factor while keeping all other factors constant. It involves changing one factor at a time and observing the resulting changes in the systems response or output. The OFAT approach is

commonly used when the system is complex and the relationship between the factors and the response is not well understood. It allows researchers to systematically evaluate the influence of each factor in isolation providing insights into their individual effects.

3.7.1. Effects of pH on Phosphate Removal Efficiency

To study the effect of pH on phosphate removal by modified corncob bio char adsorbent, 100 mL of 5 mg/L of phosphate solution was taken and pH values was adjusted to 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 and 13 by using 0.1 M HCl and 0.1 M NaOH and the adsorbent dose was remained constant acidic, neutral, and basic media. That is 0.5 g of synthesized MgO modified corncob bio char was added to each of the solution and tested separately and stirred for 30 min to reach equilibrium. Then, the solution was shaken by using mechanical shaker at a speed of 150 rpm for 6 hrs. After a given time was completed the solution was filtered by using vacuum pump and then, the phosphate (PO_4^{3-}) ion concentration of filtrate solution was determined by using UV-Visible spectrophotometer readings. Finally, the pH versus percentage removal graph was plotted to explain the effect of pH on adsorption performance of the MgO modified corncob bio char adsorbent.

3.7.2. Effects of Adsorbent Dosage on Phosphate Removal Efficiency

To study the effect of the synthesized MgO modified corncob bio char adsorbent dose on removal of phosphate, 100 mL of 5 mg/L of phosphate solution was adjusted to a pH of 9, which have high removal efficiency. Then various dosages of MgO modified corncob bio char adsorbent (0.25 g, 0.3 g, 0.4 g, 0.5 g, 0.7 g, and 0.8 g) were added into the solution and then, the solution was shaken by mechanical shaker at a speed of 150 rpm for 6 hrs. After 6 hrs was completed the solution was filtered and then, the phosphate ion concentration of filtrate solution was determined by using UV-Visible spectrophotometer. Finally, adsorbent dosage versus percentage removal graph was plotted to explain effect of adsorbent dose on the adsorption performance of the MgO modified corncob bio char adsorbent.

3.7.3. Effects of Contact Time on Phosphate Removal Efficiency

To study the effect of contact time on phosphate removal by using MgO modified corncob bio char adsorbent, 100 mL of 5 mg/L of phosphate solution was taken and then, the pH was adjusted at 9 which have high removal efficiency. Then 0.5 g of MgO modified corncob bio char adsorbent with high removal efficiency of phosphate was added into each solution. Then, the solution was shaken by mechanical shaker at a speed of 150 rpm for different contact time (15 min, 30 min, 45

min, 60 min ,75 min and 90 min). After these periods of intervals, the solution was filtered and then, the phosphate ion concentration of filtrate solution was determined by using UV-Visible spectrophotometer. Finally, time versus percentage removal graph was plotted to explain the effect of contact time on adsorption performance of the magnesium modified corncob bio char adsorbent.

3.7.4. Effects of Initial Concentration of Phosphate Ions on Phosphate Removal Efficiency

To study the effect of initial concentration of phosphate ions on phosphate removal by MgO modified corncob bio char, 100 mL of phosphate solutions with different concentration (1 mg/L, 3 mg/L, 4 mg/L, 5 mg/L, 7 mg/L and 8 mg/L) were taken and then, the pH was adjusted at 9 which have high removal efficiency of phosphate and then 0.5 g of magnesium modified corncob bio char with high removal efficiency of phosphate was added into each solution. Then, the solution was shaken by mechanical shaker at a speed of 150 rpm for 6 hrs, which have high removal efficiency of phosphate. After 6 hrs was completed the solution was filtered by using vacuum pump and then, the phosphate ion concentration of filtrate solution was determined by using UV-Visible spectrophotometer. Finally, initial concentration versus percentage removal graph was plotted to explain the effect of initial concentration of phosphate adsorption performance of the MgO modified corncob bio char adsorbent.

3.8. Effects of Co-existing (Common) Ions

The presence of co-existing ions in water can significantly impact the phosphate removal efficiency of adsorbents. Common ions, such as sulphate, carbonate, chloride, and nitrate often co-exist with phosphate in water and can compete for adsorption sites on the adsorbent surface. The effects of these co-existing ions on phosphate removal efficiency can vary depending on several factors, including their concentration, and affinity for the adsorbent. To study the co-existing of ions four different ions such as sulphate, nitrate, chloride and carbonate were selected, which are commonly present in water, and competes with phosphate during the adsorption process (Loganathan et al., 2013). For each ions, 10 mg/L of each initial concentration for optimum 5 mg/L of initial phosphate concentration conducted based on the work of (Waktole et al., 2019). The adsorption of co-existing ions was involved at optimum operating parameters.

3.9. Desorption Experiments

Desorption of the adsorbent refers to the process of releasing or removing the adsorbed substances from the surface of the adsorbent material. In this study, desorption of the adsorbent would involve

removing the adsorbed phosphate ions from the surface of the modified bio char. During the adsorption process, phosphate ions are attracted and held onto the surface of the modified corncob bio char through chemical or physical interactions. It helps to assess the extent to which the adsorbed phosphate can be released from the adsorbent surface and evaluate the adsorbent's potential for regeneration and reuse and also provides insight into the desorption capacity, reversibility, and potential reusability of the modified corncob bio char adsorbent. According to (Almanassra et al. 2021b), a suitable phosphate adsorbent should have a high adsorption capacity, be affordable, and be reusable over an extended period of time. Acids, bases, and salts can all be used to desorb phosphate. Acids and bases perform better in certain situations. The most typical base for phosphate desorption is sodium hydroxide. Sodium hydroxide can be used to regenerate the active sites on the adsorbent's surface after it has been filtered to separate the adsorbent from the mixed solution in a batch adsorption experiment, and the sample is then dried before being used in the following batch research (Trinh et al., 2020). The regeneration efficiency will rise when sodium hydroxide concentration does as well. The loss of functional groups on the adsorbent surface causes the desorption efficiency to diminish over the course of the regeneration cycle. This is brought on by the metal's leaching, which decreased the active sites on the adsorbent (Li et al. 2020 ; Akram et al.,2021). After adsorption, the supernatant was analysed for residual adsorbate after separating the adsorbate by vacuum pump separation. The MgO modified corncob bio char adsorbent was treated with 1M NaOH, and gently agitated followed by washing by distilled water. The treated and separated adsorbent was subjected to oven dry for six hours at 105 ^{o}C. Then the adsorbent was ready for further adsorption and the adsorption-desorption was repeated for five cycles.

3.10. The Performance Evaluation of the Adsorbent Using Real Wastewater

Performance evaluation refers to the systematic assessment and analysis of the effectiveness, efficiency, and quality of a product, system, process, or individual in achieving specific objectives or desired outcomes (Kulkarni & Kaware, 2014). It involves the measurement, comparison, and interpretation of performance indicators or metrics to provide insights into the performance level and identify areas for improvement. In the performance evaluation of the MgO modified corncob bio char adsorbent using real wastewater would involve the collection of real wastewater from Adama Science and Technology University water treatment plant and the adsorption experiment was conducted to analysis the performance of the adsorbent as compared to the synthesized water and assess the performance of the adsorbent by analysing the data obtained from the adsorption experiment.

CHAPTER FOUR

4. RESULTS AND DISCUSSIONS

4.1. Characterization Result Analysis of the Synthesized Corncob Bio char

4.1.1. Fourier Transform-Infrared Spectroscopy(FTIR)

The functional group and additional impurities were characterized by using Fourier Transform - Infrared Spectroscopy(FTIR). The functional groups of corncob bio char before modification and MgO modified corncob bio char adsorbent composition before and after adsorption were characterized by using FTIR spectra in the range from 4000-500 cm^{-1}. Figure 4.1 shown the FTIR spectra of corncob bio char material before modification (BM), after modification (MBA) and after adsorption (MAA) in which the wide peak between (3600-3000 cm^{-1}), which confirmed the presence of (-OH) stretching due to phenols, alcohols, carboxylic acids and typically from bio char components and moisture absorption (Balan et al., 2021). On (BM) the peak at a wave number of 1578 cm^{-1} indicated C−H bend according to the study (Budai et al., 2017). The peak at the wave number of 1170 cm^{-1} corresponded to C−O−C stretching vibrations in cellulose and hemicellulose, which was typically observed for corncob and other bio chars (Budai et al., 2017; Keiluweit et al., 2010). The peak at a wave number 1250-850 cm^{-1} indicated that the presence of C−H bend (methyl $-CH_3$) on the corncob bio char and the peak at 756 cm^{-1} representing aromatic C−H out of plane deformation (Vu et al., 2017; Xin et al., 2017). The FTIR graph of MgO modified corncob bio char shown a series of peaks at different wave numbers indicated the presence of various functional groups and chemical bonds in the material, following the modification shown new or altered peaks associated with the introduction of modifying agent. The peak at the wave number of 1700 cm^{-1} on (MBA) indicated that C = O stretching suggests the presence of carbonyl functional groups, such as ketones and aldehydes the same with the studied in research (Shen et al., 2018a; Shen et al., 2018b). The sharp peak at 1450 and 881 cm^{-1} indicated the presence of alkyl or methylene groups (C−H) commonly found in lingo-cellulosic materials (Hao et al., 2013; Keiluweit et al., 2010). The appearance of peaks in the region associated with MgO (Mg-O) stretching vibrations (around 500-1000 cm^{-1}) would indicated the successful incorporation of MgO onto the bio char surface. After adsorption (MAA) the peaks at the wave number of 1580 cm^{-1} indicated the presence of C = C stretching vibrations shown that lignin intensity and aromatic structure (Jung et al., 2015). The peak at the wave number of 1380 cm^{-1} OH bend, 1230 CH bend (Katal et al., 2018). Likewise, the peaks at 876, and 727 cm^{-1} showed the adherence of phosphate ion on the bio char surface (Budai et al., 2017; Xin et al., 2017). After

adsorption shown that the appearance of new peaks, which indicated the formation of new chemical species resulting from the interaction between the bio char surface and phosphate ions in adsorption process.

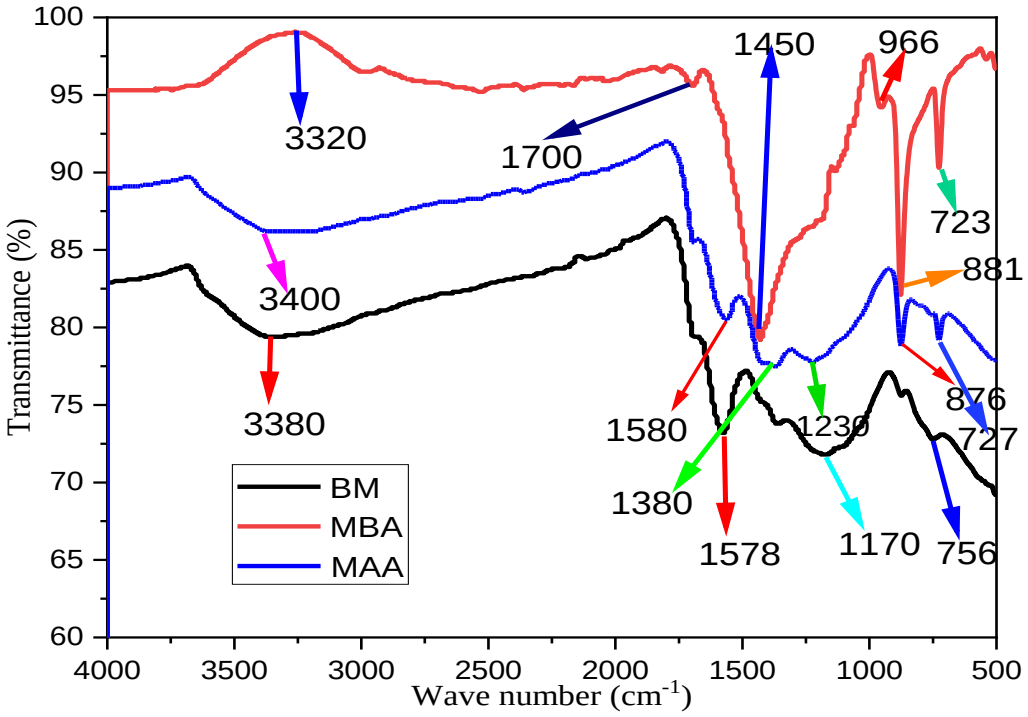

Figure 4. 1: FTIR spectra of corncob bio char adsorbent before modification, before and after adsorption.

4.1.2. TGA Analysis of Corncob Biomass

The TGA (mass loss) and DTA (rate of mass loss) results of corncob at a heating rate of 10 °C/min shown different pyrolysis characteristics since, it has different components of biomass, such as cellulose, hemi-cellulose and lignin, which had different chemical structure, thermal stability and thus, degrade at different temperatures (Gupta et al., 2017). For instance, lingo-cellulosic, hemi-cellulosic biomass decomposes in the temperature range of 220-310 °C, cellulose at 310-400 °C and lignin was most difficult to break and it covered a wide temperature range of up to 800-900 °C (Fang et al., 2022). The smashed or crushed corncob biomass was subjected to thermos-gravimetric analysis (TGA-DTA) to get the weight loss against temperature profile. Figure 4.2 depicted thermo-gravimetric analysis of corncob biomass weight loss over the temperature range. Based on the TGA and DTA curves of corncob, pyrolysis process was divided into three different stages namely, drying, decomposition and carbonization. In the first stage i.e. drying stage, between the temperature 50 -150 °C a slight mass loss of around 5 % took place that confirmed

the removal of moisture and volatile matter from the corncob sample. The second stage i.e. decomposition stage was the main mass loss stage and the mass loss started at around 240 °C and ended up at approximately 480 °C. Within this temperature range pyrolytic decomposition of hemi-cellulose, cellulose, part of lignin and decomposition of other organic substances that existed in corncob biomass took place inside the furnace. The two major peaks that appeared in the DTA curve in this temperature zone belongs to hemi-cellulose (first peak at around 310 °C) and cellulose (second peak at around 440 °C). The volatile produced after thermal breaking of chemical bonds comprised of non-condensate gases (e.g., CO_2, CO and CH_4) and condensate gases at ambient temperature (organic compounds and water) (A.Shahab et al., 2021). The final carbonization stage was the result of condensation reaction followed by slow thermal decomposition of corncob to solid residue like chars and organic residues. Although, there is no change in the nature of the curve but the pyrolysis temperature needed to get the same weight loss and conversion becomes higher however at lower heating rate, heating of biomass particles occurs more gradually and leads to better heat transfer to the interior of biomass as there was as larger temperature gradient (G. Wang et al., 2019). The peak on DTA curve gave the maximum mass loss rate during the pyrolysis process (DTAmax). For the corncob sample, the maximum mass loss rate was found to be in the temperature range of 370 - 420 °C. Moreover, a previous study by (Khesheti et al., 2019) indicated that the decomposition of organic substances occurred at the range of 200-600 °C.

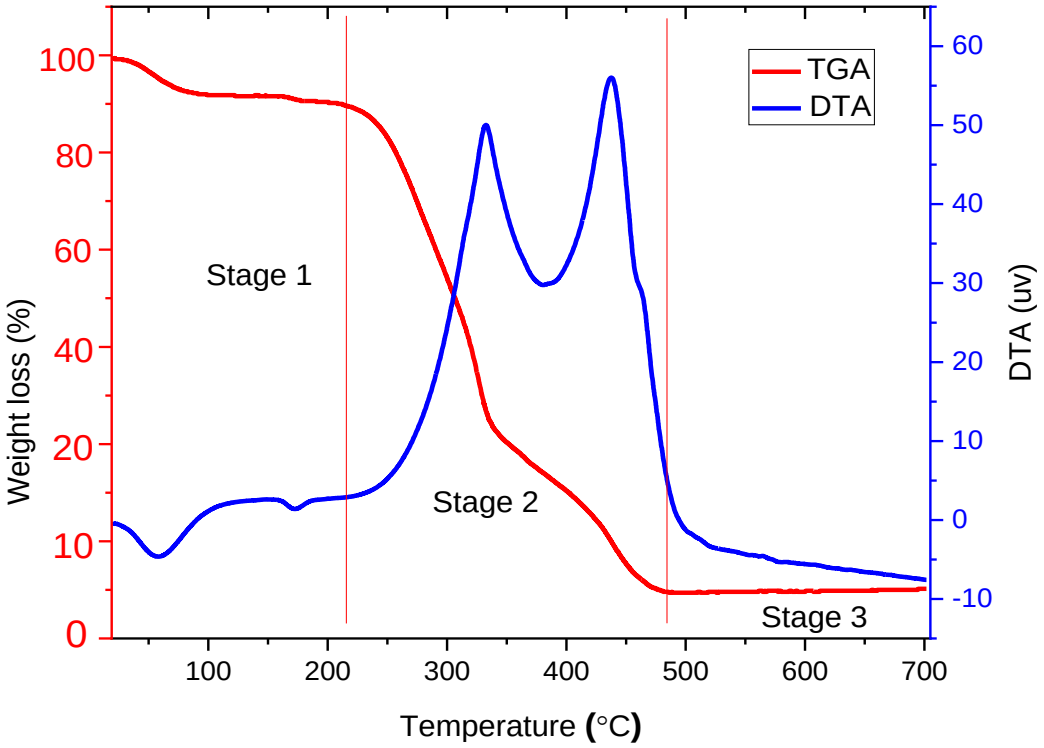

Figure 4. 2: Thermo-gravimetric Analysis of Corncob biomass.

4.1.3. XRD Result Analysis

The X-ray diffraction (XRD) patterns displayed well defined crystal phases and composition structures of MgO modified corncob bio char before modification, after modification and after adsorption as shown in Figure 4.3. The degree and positions of the peaks observed in the XRD pattern could provide information about the crystalline phases formed. On (BM) around 2θ values of 17.2° - 29.6° there was no well-defined diffraction peaks in the XRD pattern since, bio char was primarily composed of amorphous carbon but the peaks at 43.9°,64.8° and 78.7° from corncob (CB) were typically observed from bio char and carbon-based materials (Samaraweera et al., 2021). On (AM) after MgO coating, significant peaks of MgO at 32.7°,41.9°,51.2° and 53.6° were observed, which suggested that MgO was successfully coated on the corncob bio char surface and thus, the face centred cubic (FCC) crystal structure of MgO with lattice parameters and the main diffraction peak was commonly observed at 2θ angles around 31.7° (Hao et al., 2013; Keiluweit et al., 2010). On (AA) there was a sharp peak at 2θ values of 31.1° and there was peaks at 33.7°, 35.4°, 37.5°, 42.3°, 45.8°, 50.7°, 51.2°, 59.9° and 70.6°, which indicated after phosphate adsorption the diffraction peaks listed above were appeared and suggested that phosphate ion was adsorbed successfully on the positive MgO modified corncob bio char adsorbent in water, which confirmed the result that was done by (Tu et al., 2023). The XRD analysis was carried out to identify the crystal nature, phases and average particle size of the powders of MgO and the pattern of XRD shown a number of Bragg's reflection that may be indexed based on the face-centred cubic structure of MgO (Zhengato et al., 2019). The XRD spectrum exhibited peaks corresponding to their crystal plane in a crystal lattice of 111,120,200, 220, 311,222,422, 440, 620 and 622 respectively. The broad peaks indicated the ultra-fine as well as small crystalline size of the particle, therefore the observed peak positions and their relative intensities indicates the formation of high purity crystalline MgO products, which was the same with the result found by (Shi et al., 2021). Based on Scherer's equation the average crystalline size of 16.26 nm was obtained, thus the result was the same as with the study on the literature (Yousefi & Ghasemi, 2020).

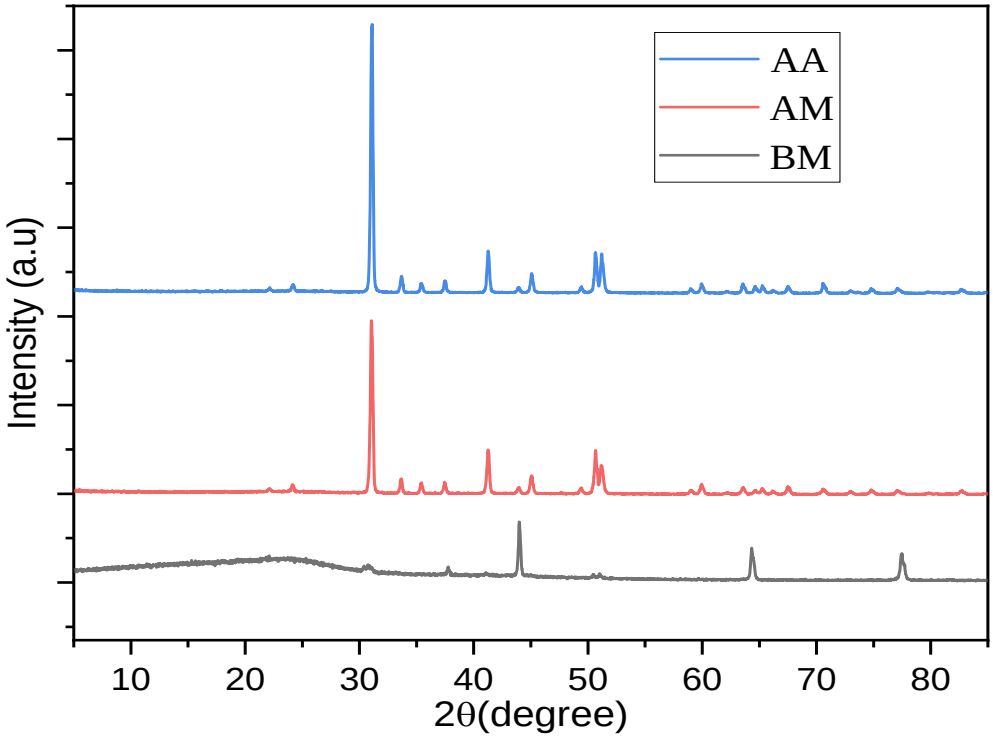

Figure 4. 3: X-ray diffraction pattern of corncob bio char before modification, before and after adsorption.

Table 4. 1: Crystalline size and d-spacing for MgO loaded corncob bio char adsorbent.

Peak positions (2 Theta)	Theta	FWHM	d-spacing	Crystalline size D (nm)	D, average (nm)
31.1019	15.55095	0.24187	0.287406	33.04919412	16.2606575705
33.79354	16.89677	0.23812	0.265785	33.34900976	
35.44089	17.72044	0.33818	0.25314	23.37127523	
37.53861	18.76930	0.45126	0.218377	17.20484617	
41.28422	20.64211	0.56464	0.190901	13.44525594	
45.16423	22.58212	0.614326	0.187652	14.62760415	
50.76211	25.38106	0.69731	0.178981	10.7404825	

51.24316	25.62158	0.92476	0.17226	8.025232934
59.98353	29.99177	0.83215	0.163421	8.793674901
70.64785	35.32392	0.71367	0.138669	9.667391687

4.1.4. BET Result Analysis

Brunauer-Emmett-Teller (BET) analysis is a commonly used method to determine the specific surface area of adsorbent materials, including corncob bio char, MgO modified corncob bio char before and after adsorption. The specific surface area provided valuable information about the adsorption capacity and effectiveness of the material (Shen et al., 2019). The specific surface area of corncob bio char before modification (BM) and MgO modified corncob bio char before and after adsorption were determined using Brunauer-Emmett-Teller (BET). The specific surface area of MgO modified corncob bio char adsorbent before adsorption was found to be 26.94 m^2/g, which was higher than the corncob bio char before modification of 2.166 m^2/g and after adsorption 19.32 m^2/g. The increase of the specific surface area of MgO loaded corncob bio char adsorbent could be due to the presence of MgO on the surface of corncob bio char. The increased specific surface area provided a large number of active sites for the adsorption of the phosphate ion (S. Wang et al., 2023). In addition, materials with a higher surface area excellent adsorption properties such as lack of internal diffusion, high surface binding energy, and adsorption activity (Tyagi et al., 2021). The specific surface area result found by (Zhang et al., 2015) for MgO modified corncob bio char was 26.94 m^2/g. The smaller amount of the surface of MgO loaded corncob bio char after adsorption could be because of the adsorbate molecules accumulate on the surface, they could block or partially fill the pore spaces, reducing the effective surface area accessible for further adsorption and pore blocking (Qian et al., 2023).

4.2. The pH at Point of Zero Charge (pH_{PZC})

The pH_{PZC} determination of MgO modified corncob bio char was carried out at pH starts from (3 – 12) by one-unit pH increment Table 4.3. Determination of the pH_{PZC} value helps to identify the working pH value for adsorption studies. Figure 4.5 shown the point of zero charge is 8.0 in agreement with (Qian et al., 2023, Mehta et al.,2016). Below the PZC the adsorbent has positive charge while above the point of zero charge it has negative charge. The higher phosphate adsorption was occurred at pH 8.0 due to highly electrostatic attraction between the positively charged adsorbent surface and highly electro-negative phosphate ions. The low removal efficiency

of phosphate was achieved above pH 8; this was due to weak electrostatic attraction between the negatively charged adsorbent surface and highly electro negative phosphate ions. MgO modified corncob bio char is typically considered to be a negatively charged adsorbent at pH values above 8. At higher pH levels, the surface of the adsorbent became more basic, leading to the deprotonation of functional groups on the surface. This deprotonation process results in the generation of negatively charged sites on the adsorbent's surface. The negative charge on the adsorbent surface could attract and interact with positively charged species or ions present in the solution. This interaction might involve electrostatic attraction or other adsorption mechanisms, depending on the specific properties of the adsorbent and the nature of the adsorbate.

Table 4. 2: Point zero charge (PZC) analysis of corncob bio char.

No of flasks	pH initial	pH final	ΔpH (pH final-pH initial)
1	3	6.07	3.07
2	4	7.94	3.94
3	5	8.08	2.08
4	6	7.78	1.78
5	7	8.03	1.03
6	8	7.89	-0.11
7	9	7.64	-1.36
8	10	7.98	-2.02
9	11	8.15	-2.85
10	12	10.05	-1.95

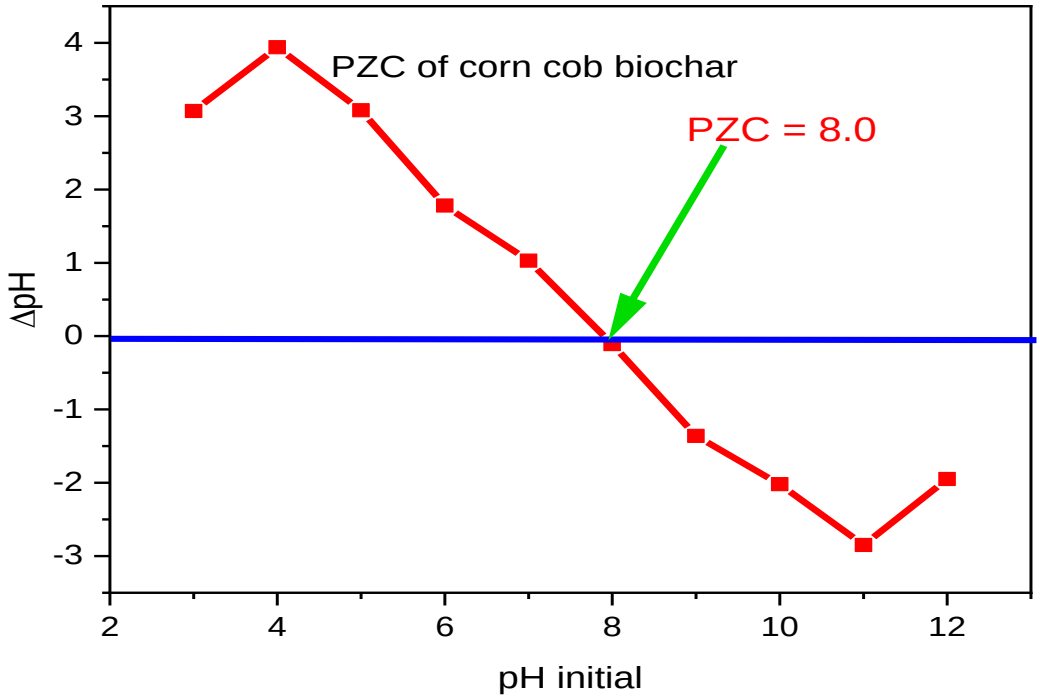

Figure 4. 4: Plot of initial pH vs. ΔpH of the adsorbent to determine the point of zero charge of the adsorbent surface.

It has been investigated in whether the pH of the solution affected the removal of phosphate utilizing MgO modified corncob bio char adsorbent. According to (Banerjee and Chattopadhyaya et al., 2017), the pH of the solution was crucial for regulating the surface charge of the adsorbent, the degree of ionization of the adsorbate in the solution, and the dissociation of various functional groups on the adsorbent's active sites. With starting pH values ranging from 3.0 to 12.0, Figure 4.4 shown the impact of the solution pH on the phosphate adsorption by MgO-modified corncob bio char. It was clear that the capacity of the adsorbent to bind phosphate reduced with increasing solution pH from 3.0 to 12.0, and that phosphate adsorption on the MgO modified corncob biochar adsorbent was strongly pH dependent. The pH of the solution influenced the degree to which the hydrogen ion and hydroxyl ions are adsorbed on the adsorbent, which in turn affects how well the phosphate anions were adsorbed. The repulsion between hydroxylic ions (OH^-) on the surface of MgO modified corncob bio chars and the presence of P in the form of phosphate anions ($H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}) could be, thus used to explain the decrease in adsorption at higher pH levels. Due to increased protonation and the corresponding electrostatic interaction between the phosphate anions and the adsorbent surface, adsorption increased at the adsorption sites at lower pH levels. At high pH levels, phosphate adsorption reduced because of the increased competition between the phosphate anions (PO_4^{3-}) and the hydroxyl ions (Antelo et al., 2015).

4.3. Effects of Adsorption Factors

The effect of different parameters was studied such as; pH, adsorbent dosage, contact time and initial concentration of phosphate ion (Adekanye et al., 2022). Adsorption was not a uniform process, and a number of variables influence how effective it was thus, in an adsorption system the performance of an adsorbent significantly affected by a number of solution parameters among them in this study the following were included.

4.3.1. Effects of pH on Phosphate Removal

The solution's pH needed to be determined because it was crucial to the adsorption process. In acidic, neutral, and basic medium, the solution's pH was measured. The pH effect investigation, however, only looked at the basic media because it had a PZC of 8.0 after the surface charge of the corncob bio char was analysed. Adsorbent was dissolved at very low pH levels due to the solution's increasing acidity. In accordance with Figure 4.5 a pH of 9 results in an 89 % removal effectiveness of phosphate ions. According to the pH optimization results, phosphate ion removal was shown to be low at high pH levels and high at low pH levels. The modified corncob bio char surface gains a positive charge in acidic media due to the high concentration of H^+ ions present. This attracts more phosphate ions, increasing the bio char's capacity to remove phosphate at lower pH levels. According to (Chowdhury et al., 2011), the high absorption at low pH was explained by the fact that low pH results in a high concentration of hydrogen ions, which raised the positive charge on the surface of the adsorbent and causes a greater removal of phosphate ions. Due to the negatively charged surface of the corncob bio char caused by the deprotonation of hydroxyl groups, phosphate ion adsorption was low at pH levels above the PZC (Mourabet et al., 2012). The negatively charged phosphate ion was attracted to the correspondingly charged adsorbent surface by a repulsive attraction. The removal of phosphate ions was decreased as a result of the repulsion force between the two negatively charged ions.

Table 4. 3: Investigation of the removal of phosphate ion above the PZC value of the adsorbent.

pH	8	9	10	11	12	13
Removal efficiency (%)	36	89	62	78	43	41

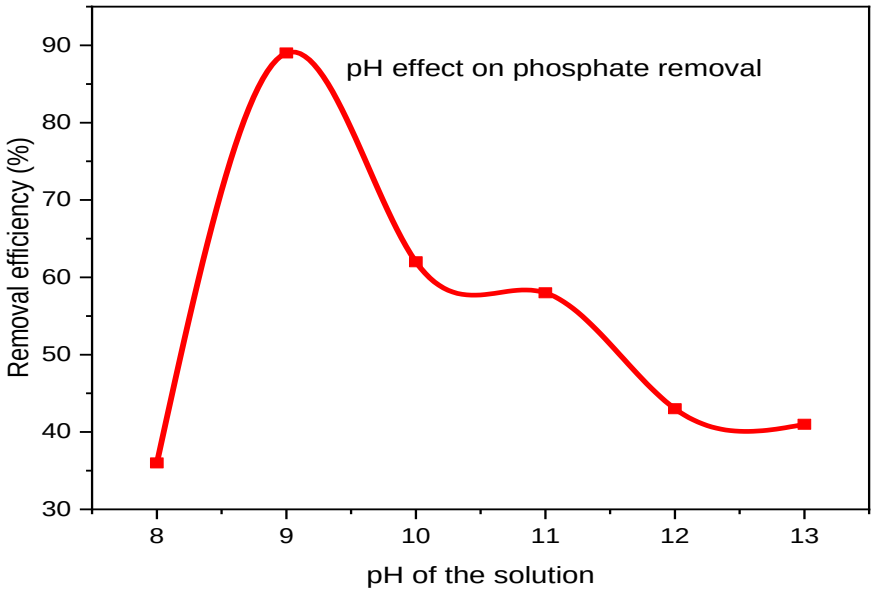

Figure 4. 5: Effect of pH on the removal of phosphate ion was carried out by keeping all parameters constant.

4.3.2. Effects of Adsorbent Dosage on Phosphate Removal

During the adsorption procedure, it was crucial to determine the appropriate amount of the produced MgO modified corncob bio char adsorbent material. By using varied masses while keeping all other parameters constant, the effect of the adsorbent dosage for the MgO modified corncob bio char adsorbent was becoming accustomed. As shown in Figure 4.6 a 0.5 g adsorbent dosage resulted in an 86 % removal efficiency of the phosphate ion and the result shown that in Figure 4.6 the dosage of MgO modified corncob bio char adsorbent increased up to 0.5 g at the optimal dose, up to this the removal efficiency of phosphate ion was increased. This is due to the active sites' high availability at high doses. The availability of more effective sites for interaction as well as the quantity of binding sites brought about by higher adsorbent dosage simultaneously played a role in the result that was observed (Qian et al., 2023). The overlap or blocking of the adsorbent's functional surface sites, however, resulted in a reduction in the removal efficiency of phosphate at 0.8 g dosage. Another reason was that the solution's phosphate concentration decreased when the amount of adsorbent is increased.

Table 4. 4: Effects of adsorbent dosage on removal efficiency of phosphate ion.

Dosage (g)	0.25	0.3	0.4	0.5	0.7	0.8
Removal efficiency (%)	65	68	73	86	63	54

Table 4.4 shown that the remaining concentration of phosphate ion in the solution for all six doses. The removal efficiency of phosphate ion for each adsorbent dose clearly shown in Figure 4.6.

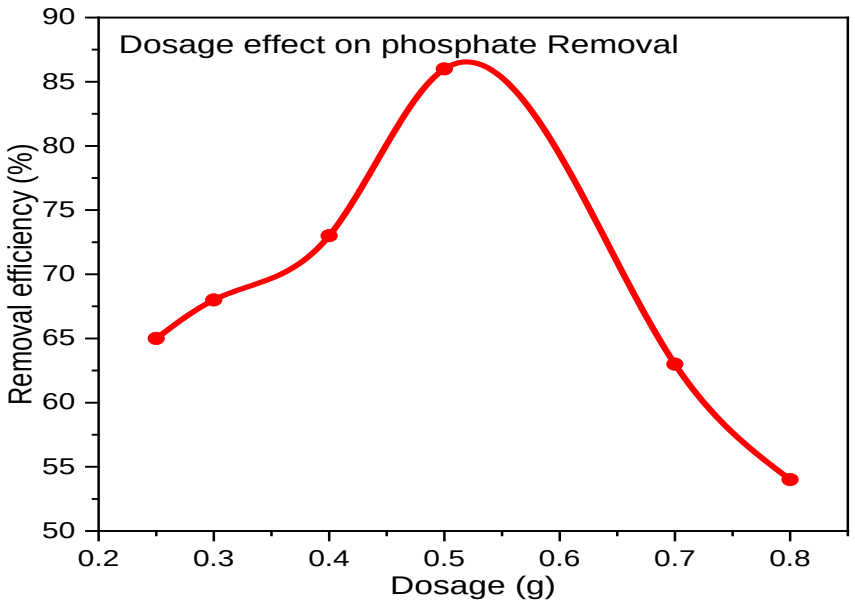

Figure 4. 6: Effect of adsorbent dosage on the removal of phosphate ion was carried out by varying dose and by keeping all parameters constant.

4.3.3. Effects of Contact Time on Phosphate Removal

Determining the effect of contact time during the adsorption process was fundamental. By changing the contact time while keeping the same values for all other factors, the effect of contact time was enhanced. Figure 4.7 demonstrated that a high removal efficiency and rapid phosphate removal was also observed from the time of initial contact to the time of equilibrium. The greatest phosphate ion removal efficiency, which is 87 %, was achieved at contact time an hour shown in Figure 4.7. The removal efficiency of phosphate ion was enhanced when the contact time increased from 15 minutes to an hour. This occurs as a result of an extensive initial number of active sites that cause a high rate of phosphate ion migration towards the adsorbent surface. But after the equilibrium time is reached the removal efficiency of phosphate was decreased. This was due to the saturation of the active sites and lack of enough additional active sites of adsorbent with increasing contact time.

Table 4. 5: Effects of contact time on removal efficiency of phosphate ion.

Contact time in (min).	Remaining concentration of phosphate ion in (mg/L)	Removal efficiency of phosphate ion in (%)

15	0.43	57
30	1.05	65
45	1.08	73
60	0.65	87
75	1.26	82
90	1.68	79

Table 4.5 shown that the remaining concentration of phosphate ion at each contact time. All concentrations were calculated from UV-visible spectrometer instrument readings. The removal efficiency of phosphate ion at each contact time clearly shown in Figure 4.7.

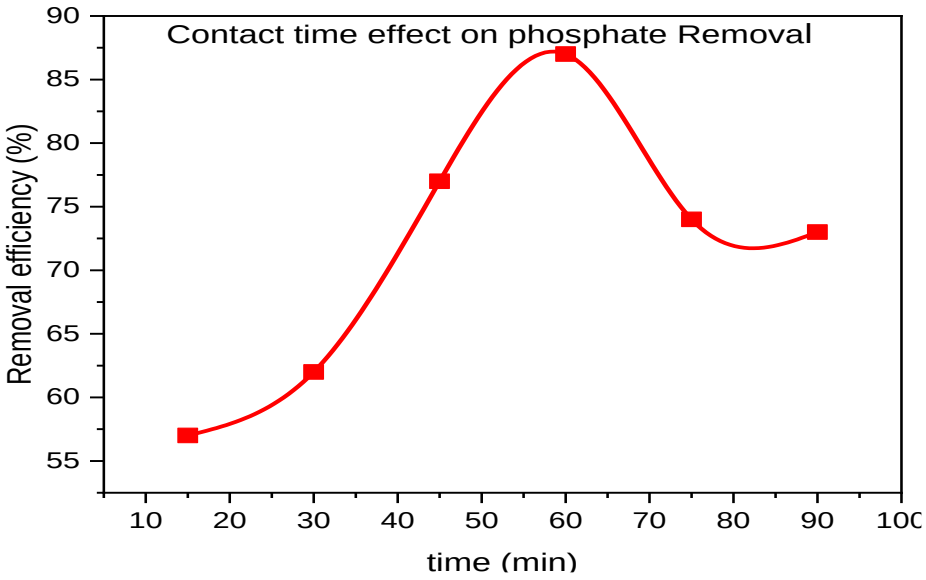

Figure 4. 7: Effect of contact time was carried out by varying the contact time and by keeping all parameters constant.

4.3.4. Effects of Initial Phosphate Concentrations on Phosphate Removal

By altering the initial concentration of phosphate ion while keeping the same values for all other parameters, the impact of initial phosphate concentration was examined. Figure 4.8 demonstrated that at an initial concentration of 5 mg/L, or 88 %, the maximum removal efficiency of phosphate ions was achieved. At lower initial phosphate concentrations, there was a slight increase in phosphate removal efficiency. This was due to the high active site of the adsorbent surface at low

concentration. According to the findings of this investigation, the effectiveness of phosphate removal reduced as the initial concentration of phosphate ion increased. This was because there wasn't enough surface area to hold all of the phosphate ions that were present in the solution. Because all of the active sites of the MgO modified corncob bio char adsorbent were already filled by phosphate at initial concentration, there was no further phosphate removal when the initial phosphate concentration increased for a fixed mass of adsorbent.

Table 4. 6: Effects of initial phosphate concentration on removal of phosphate ion.

Initial phosphate concentration (mg/L)	Final concentration of phosphate ion (mg/L)	Removal efficiency of phosphate ion (%)
1	0.34	66
3	0.81	73
4	0.84	79
5	0.60	88
7	3.08	56
8	3.68	54

Table 4.6 shown that the final concentration of phosphate ion from each initial concentration. All final concentrations of phosphate ion were calculated from UV-visible spectrometer instrument reading. The removal efficiency of phosphate ion for all initial concentration clearly shown in Figure 4.8.

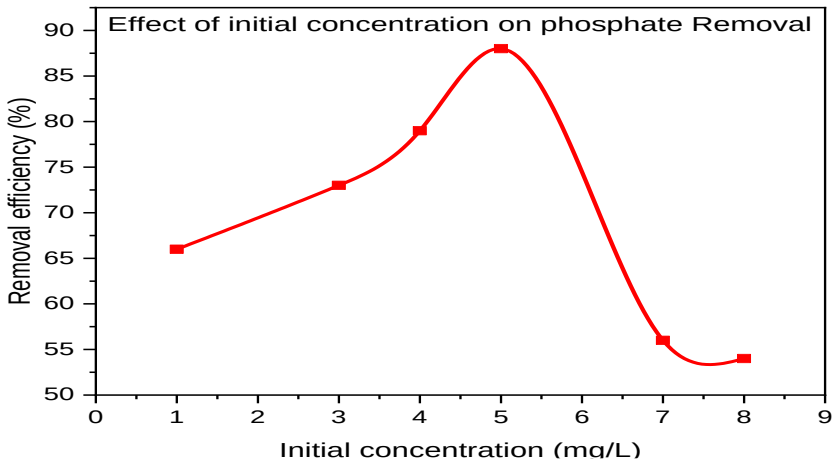

Figure 4. 8: Effect of initial phosphate concentration on the removal of phosphate ion was carried out by varying initial concentration and keeping all parameters constant.

4.4. Equilibrium Isotherm

Adsorption system could be designed with the aid of adsorption isotherms typically referred to as equilibrium isotherms, which constitute the amount of solute adsorbed per unit weight of adsorbent. These isotherms use equilibrium concentration of adsorbent at a fixed temperature. To remove the phosphates ions from the water, a particular design was optimized in order to generate proper correlations for experimental data, which was referred to as adsorption isotherm (Batool et al., 2018).

4.4.1. Adsorption Isotherm

Adsorption isotherm described about the adsorbate adsorbed on adsorbent surface at equilibrium at constant temperature. It gave general idea about the effectiveness of the MgO modified corncob bio char adsorbent in removing phosphate ions from wastewater. Analysis of the isotherm data was very important because the isotherm describe equilibrium relationship between adsorbate and adsorbent for the adsorption process. The interaction of adsorbate with adsorbent could be identified by studying isotherm, which was critical to optimizing and designing the desired adsorption system (H. Zhang et al., 2015). The equilibrium concentration of phosphate ion at constant optimized parameters of 60 min, 0.5g/100 mL of MgO modified corncob bio char adsorbent dose and, a pH of 9 at a room temperature were carried out. For this study, the Langmuir adsorption isotherm, Freundlich adsorption isotherm and Temkin isotherm model were used to evaluate adsorption process. The adsorption of isotherm data for phosphate (PO_4^{3-}) ion was analysed by applying the commonly used isotherms known as Langmuir, Freundlich and Temkin. Their correlation coefficients and constant parameters of the adsorption of PO_4^{3-} by MgO modified corncob bio char were obtained from the slope and intercept of the graph for each equations of the isotherms.

4.4.1.1. Langmuir Isotherm Models

The adsorption isotherm determined the difference between the amounts of adsorption and the solute concentration at equilibrium. The adsorption isotherm of phosphate ion using MgO loaded corncob bio char was investigated. The concentration of phosphate ions in their respective equilibrium phase at room temperature was studied to obtained maximum adsorption capacity of MgO modified corncob bio char for phosphate ion removal. The result obtained from Langmuir

model indicated that the value of separation factor ($R_{L)}$ for all initial phosphate concentrations were greater than 0 and less than 1, which implied that the Langmuir isotherm was favourable. The values of R_L for initial phosphate concentration of 1, 2, 3, 4, 5,7 and 8 mg/L were listed as 0.422, 0.267, 0.195, 0.154, 0.127, 0.094 and 0.084 respectively. The maximum adsorption capacity (q_{max}) could be determined from the intercepts of Langmuir plots of $\frac{1}{C_e}$ vs $\frac{1}{q_e}$. The maximum adsorption capacity (q_{max}) and energy of adsorption (K_L) from Langmuir isotherm model were to be determined 26.12 mg/g and 1.3722 L/mg respectively. The values of correlation factor (R^2) gained for Langmuir isotherm equals to 0.9857.

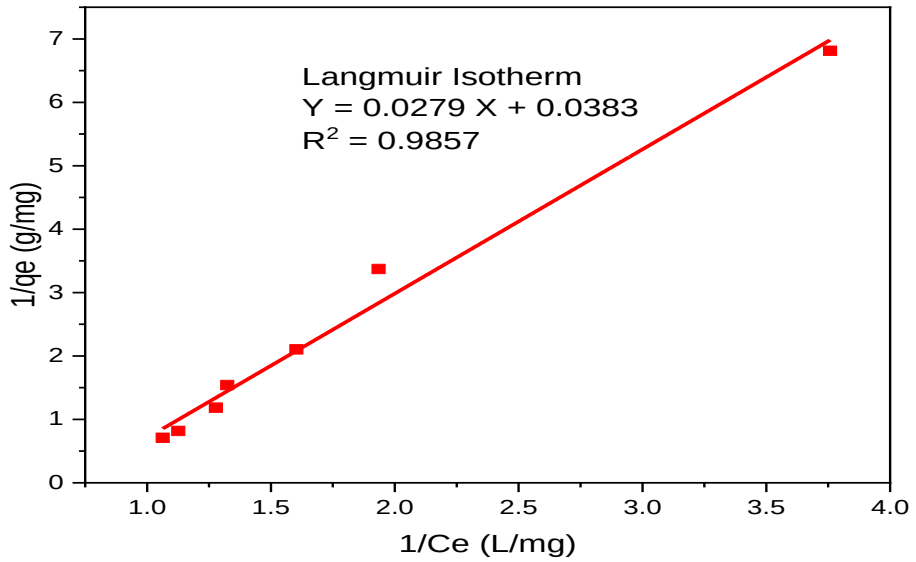

Figure 4. 9: Langmuir isotherm for phosphate adsorption by MgO modified corncob bio char.

Table 4. 7: Isotherm data for the removal of phosphate by MgO loaded corncob bio char adsorbent.

C_o (mg/L)	C_e (mg/L)	$1/C_e$ (L/mg)	lnC_e	v(L)	m(g)	q_e = ((Co-Ce)/Co)*v/m (mg/g)	$1/q_e$ (g/mg)	lnq_e	C_e/q_e (g/L)
1	0.2661	3.7580	-1.324	0.1	0.5	0.1468	6.8129	1.918	1.812
2	0.5168	1.9350	-0.660	0.1	0.5	0.0483	20.695	3.029	10.69
3	0.6237	1.6033	-0.472	0.1	0.5	0.0251	39.862	3.685	24.86
4	0.7552	1.3241	-0.281	0.1	0.5	0.0122	81.699	4.403	61.69
5	0.7826	1.2778	-0.245	0.1	0.5	0.0087	114.99	4.745	89.99
7	0.8881	1.126	-0.119	0.1	0.5	0.0032	312.78	5.745	277.7
8	0.9407	1.0630	-0.06	0.1	0.5	0.0015	674.54	6.514	634.5

Table 4. 8: Isotherm parameters for the removal of phosphate MgO loaded corncob bio char adsorbent.

Isotherms	Parameters	Values
Langmuir	q_{max}(mg/g)	26.12
	K_L (L/mg)	1.3722
	R^2	0.9857
Freundlich	n	0.2992
	1/n	3.3422
	K_f(mg/g)(L/mg)$^{1/n}$	330.696
	R^2	0.8568
Temkin	B	-0.1167
	b(J/mole)	-71.243
	K_T(L/mg)	1.163
	R^2	0.964

4.4.1.2. Freundlich Isotherm Models

Freundlich isotherm is an empirical equation that can be employed to describe the heterogeneous systems. The linear form of the Freundlich isotherm model from equation 2.7 was used to investigate the multi-layer adsorption of phosphate on the surface of the adsorbents. The magnitude of the exponent $\frac{1}{n}$ indicated the favourability of the adsorption. $\frac{1}{n}$ was a heterogeneous factor, which was related to adsorption intensity or surface heterogeneity? The value of $\frac{1}{n}$ >1, which equals to 3.34 indicated normal adsorption (Keshav et al., 2019). In order to reach a favourable adsorption process, the value of n should be in the range of 1 to 10. But, as Table 4.9 depicted the value of n that I found was 0.299, which confirmed unfavourable adsorption. Since, the value of "n" is not between 1 to 10. From the Freundlich isotherm model the values of constant parameters such as K_f and n were determined by linear regression plot of ln (q_e) vs ln (C_e) and thus, the Freundlich isotherm model analysed showed the equilibrium isotherm data did not fit to the experimental data which implies that adsorbed phosphate forms a multilayer surface coverage on the MgO loaded corncob bio char adsorbent and the collaborative adsorption mechanism takes place. The values of correlation factor (R^2) gained for Freundlich isotherm equals to 0.86 which is the smallest correlation factor than the other.

As (Pan et al., 2017) studied in his research, the Langmuir and Freundlich adsorption isotherms relative parameters were calculated from their respective slope and intercept of the linear plots. The result obtained from adsorption equilibrium isotherm confirmed that the fitting in equilibrium data the Langmuir isotherm models suggested that the presence of homogenous adsorption surfaces on the adsorbent involved during the adsorption of phosphate ions. By comparing the values of correlation factor (R^2), the Langmuir models better suitable fits to with the equilibrium adsorption which gave a larger R^2 equals to 0.98 and maximum adsorption capacity of 26.12 mg/g for phosphate ion adsorption.

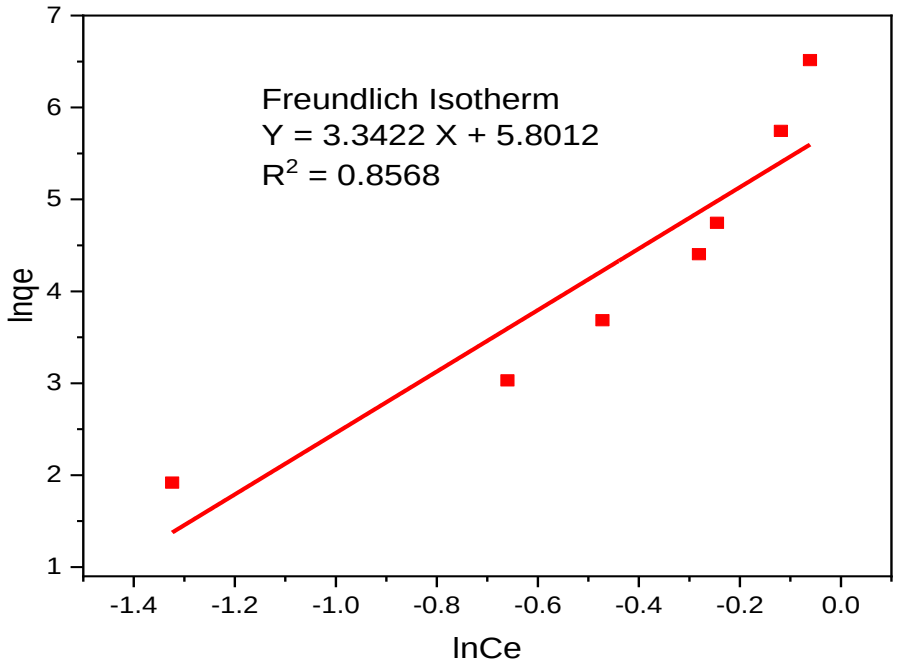

Figure 4. 10: Freundlich Isotherm for phosphate adsorption by MgO loaded corncob bio char.

4.4.1.3. Temkin Isotherm Model

Equilibrium constant of binding K_T provided information about binding energy, and B expresses heat of adsorption for a particular adsorption experiment. The correlation coefficient (R^2) obtained from this model was 0.964. The result shown that the experimental data fitted to the model. However, when comparing with Langmuir the result found by Temkin model was slightly smaller correlation coefficient. The negative value of B (-0.1167) indicated the adsorption process was endothermic.

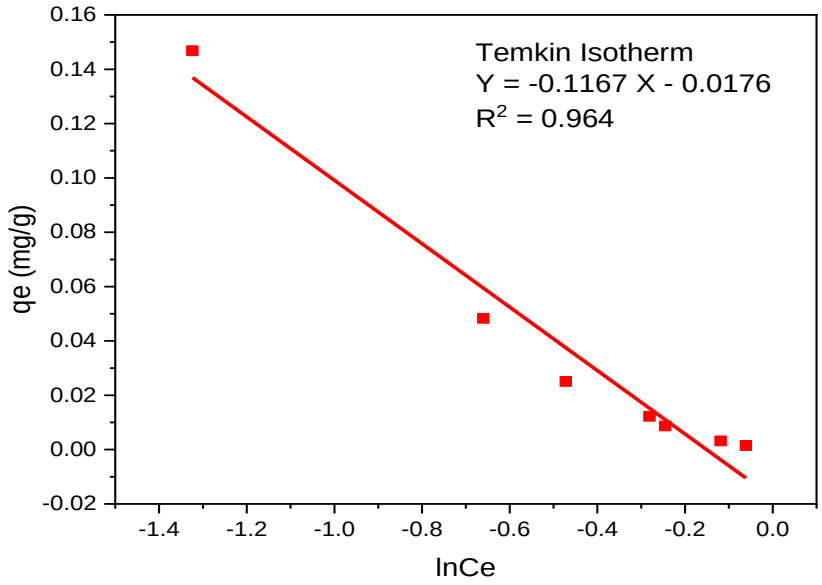

Figure 4. 11: Temkin Isotherm model for the removal of phosphate ion from wastewater.

4.5. Adsorption Kinetics

Kinetics experiment was investigated to examine the rate of phosphate adsorption by MgO modified corncob bio char adsorbent and the time required to reach equilibrium. The purpose of studying equilibrium kinetics is to identify the adsorbent retention time and provide information about the specified time to reach the maximum capacity of adsorption and the controlling mechanism in the process that includes mass transfer or chemical reactions (Tohfegar et al., 2019). In this study Pseudo-first-order, Pseudo-second-order and Intra-particle diffusion kinetic models were analysed to obtain the best kinetic models for phosphate removal. The kinetics study time dependence of phosphate was investigated from 0 to 90 min at constant room temperature, 5mg/L initial phosphate concentration, pH = 9, adsorbent dose = 0.5 g/100 mL. Comparing the correlation coefficients of the three kinetic models, it definitely revealed that the pseudo-second-order model best fit the adsorption kinetic of phosphate by MgO modified corncob bio char and the adsorption processes were chemisorption. As shown in the Figure 4.13 the Pseudo-second-order rate model show the best agreement with the experimental results, which implies that the whole process was controlled by chemical adsorption is the rate limiting steps of the process. Pseudo-second-order kinetic model predicts that adsorption behaviour involves valance forces through sharing of electrons among phosphate ions and the MgO loaded corncob bio char adsorbents. In addition, the experimental adsorption capacity was in agreement with that of calculated adsorption capacity, which proved the model adopted was reasonable. The value of kinetic parameters was summarized in Table 4.9.

Table 4. 9: Kinetics model parameters for Pseudo-first-order and Pseudo-second-order.

Kinetics	Parameters	Value
	q_e (mg/g)	0.543
Pseudo-First Order	K_1	-0.022
	R^2	0.929
	q_e (mg/g)	1.174
Pseudo-Second Order	q_e^2	1.379
	K_2	0.017
	R^2	0.974
Intra-particle Diffusion	K_p	0.0915
	R^2	0.973

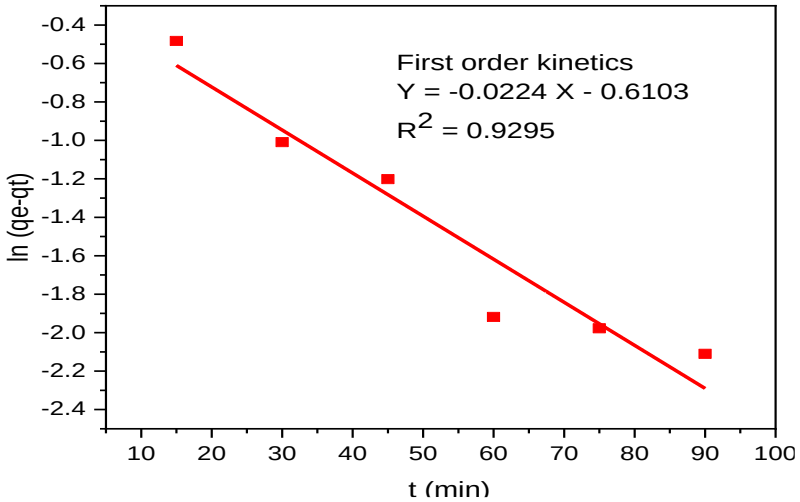

Figure 4. 12: Pseudo first order for adsorption of phosphate ions.

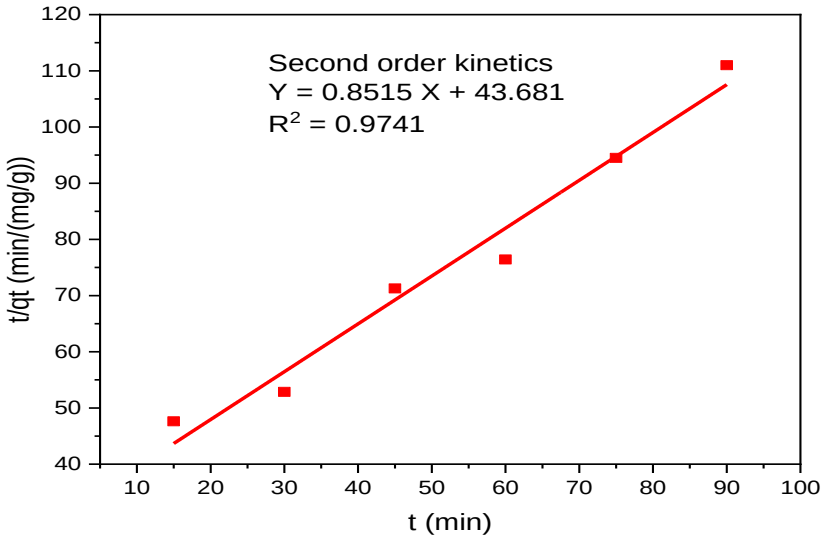

Figure 4. 13: Pseudo second order for adsorption of phosphate ions.

The intra-particle diffusion model could be describing the rate of adsorption process depends on the speed at which adsorbate diffuses towards adsorbent. The result analysed from the adsorption equilibrium data of intra-particle diffusion model the graph $t^{0.5}$ versus q_t was linear, which demonstrated that the intra-particle diffusion was involved inside the adsorption process as shown in the Figure 4.14. This shown that intra-particle diffusion became not the only rate-limiting step within the adsorption of phosphate. Consequently, other mass transfer processes like film diffusion and bulk diffusion could be there in determining the mass transfer mechanism of phosphate ions from the bulk solution to the MgO modified corncob adsorbent surface. The diffusion process might affect the phosphate ion adsorption process on MgO loaded adsorbent as result of the porous structure of the adsorbent and the attractive effect of phosphate ions.

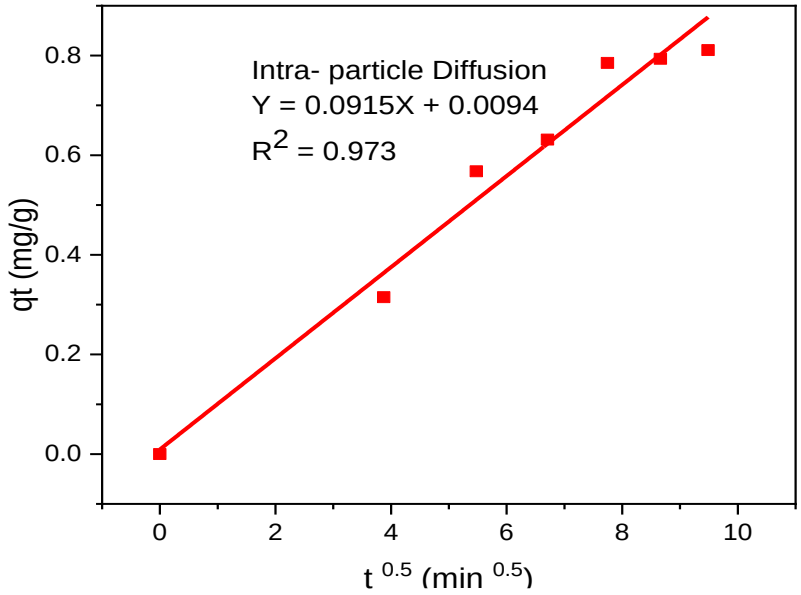

Figure 4. 14: Intra-particle diffusion model for phosphate removal by MgO modified corncob bio char adsorbent.

4.7. The Effect of Co-Existing (Common) Ions

Normally, the common inorganic anions, which include NO_3^-, Cl^-, SO_4^{2-}, and CO_3^{2-} frequently coexist with PO_4^{3-} in natural water sources, that could act as a competing ions and strongly interfere with the adsorption process of phosphate removal, resulting in inefficiency. Due to this reason, it was necessary to evaluate the effect of the competing anions. Increasing the coexisting anion would cause an obvious decrease in phosphate adsorption capacity, which would result from the competitive effect of anions for available adsorption sites of adsorbent. Therefore, in this study the effects of these competitive anions were investigated. Figure 4.15 the effect of four co-existing

ions such as nitrate, chloride, sulphate and carbonates of 10 mg/L of each on phosphate removal at optimum parameters were investigated. The results indicated that the anions have substantial effect on phosphate removal. The effect of carbonate was not prominent as compared to sulphates, nitrates and chlorides. The presence of sulphate ion within phosphate reduced the percentages of phosphate removal from 88 % to 57.84 %. In addition, nitrate was another influential ion, which reduced the phosphate removal efficiency to 63.15 % and also the presence of chloride reduced to 72.34 %. Therefore, sulphate was the greatest competitor for phosphate followed by nitrates, chlorides and carbonates. (Alighardashi, 2018) confirmed that sulphate ions were the most influential ions, which compete with phosphate. These was the result of high concentration of sulphate leads to lack of available surface area on MgO modified corncob bio char adsorbent sites. The basic characteristics of anions to be considered for the selective adsorptions includes the solubility, ionic radius, hydration energy and bulk coefficient (Rafiee, 2014). The competing anions reduced the removal efficiency of phosphate in the order of carbonate > chloride > nitrate > sulphate. The effect of nitrate ion could be obtained from greater tendency of nitrate to undergo ion exchange reaction.

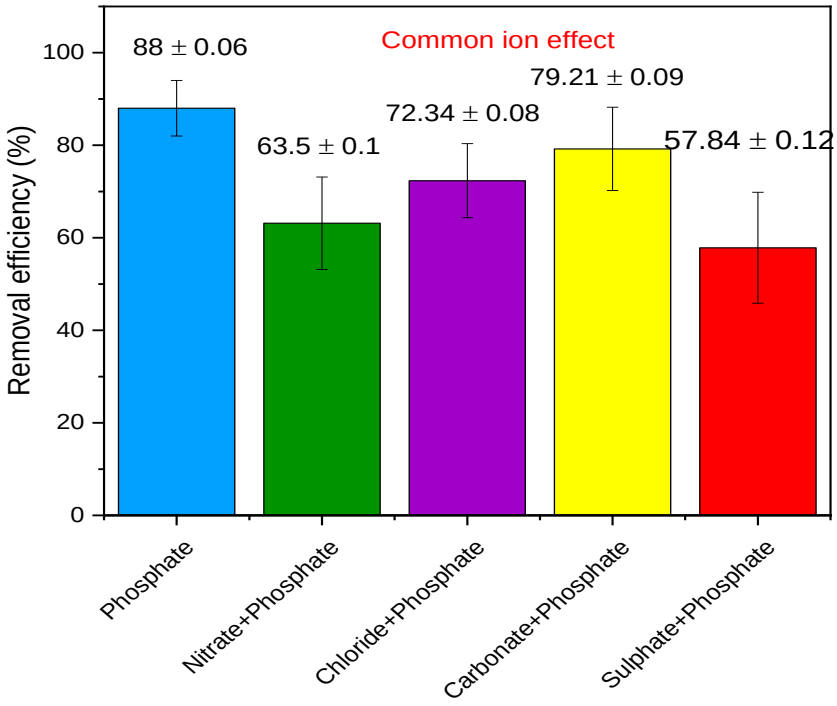

Figure 4. 15: Effects of common ions on phosphate removal by MgO modified corncob bio char adsorbent.

4.8. Desorption and Regeneration of Adsorbent

Regeneration is used to reuse the adsorbent after desorption process was occurred. Regeneration techniques are very important to evaluate the application of adsorbent, its duration time, reduce

the cost of the process and decrease the amount of undesired wastes. To evaluate the application value of the prepared bio chars, it was investigated their regeneration abilities when they were saturated with the pollutant. The adsorption of phosphate could be attributed to electrostatic interactions between the surface charge of adsorbent and phosphate ions in the aqueous solution (Medellin-castillo., 2014). The mechanism of adsorption, the interaction between the surface of adsorbent and the phosphate do not lead to a chemical reaction because it has been demonstrated that the adsorption of phosphate on MgO modified corncob bio char adsorbent was reversible. Desorption was the reverse process, that was release of the adsorbed adsorbate from the surface of adsorbent. Phosphate ion adsorbed on surface of MgO modified corncob bio char was desorbed and released into solution by NaOH solution. In the determination of regeneration and desorption, the residual of adsorbent was washed and dispersed by using 1 M NaOH solution having the pH of 13. This was because, with increasing pH, the phosphate ion captured in the MgO corncob bio char adsorbent structure was released into solution, exchanged by the hydroxide ion, an ionic substitution mechanism already described in other studies (Medellin- castillo et al., 2014; Sundram et al., 2018). To assessed the durability of this adsorbent, regeneration, and reuse studies were carried out for the adsorption of phosphate over five consecutive adsorption-desorption cycles. A solution of 1M of NaOH was chosen as the eluent in the desorption process. High reusability of adsorbent was very indispensable for any adsorbent, which significantly increased the economic value of the adsorption process. To study regeneration study 0.5 g of adsorbent dose, 9 of pH, 5 mg/L of initial phosphate concentration at an hour, with removal efficiency of 88 % were used to regenerate MgO modified corncob bio char adsorbent. As shown in the bar graph Figure 4.16 the removal efficiency of the first cycle was 84.23 % the second cycle resulted 82.09 %, while the third cycle was 78.89 %. At the fourth and the fifth cycle, the removal efficiency of phosphate ion was 76.20 and 69.29 %, respectively. This value ensured that the prepared adsorbent could be reused different times without any loss of adsorption ability. Therefore, MgO loaded corncob bio char adsorbent was a promising adsorbent for the removal of phosphate ion from contaminant water.

After the adsorption-desorption process, the adsorbed phosphate ion was concentrated in a caustic solution. The use of NaOH solutions was better used for regeneration and desorption of MgO modified corncob biochr when compared to other compounds. The OH^- remove the proton from adsorbent surface site and form water, the Na^+ remove PO_4^{3-} from adsorbent surface site. The results indicated that the desorption properties of the adsorbents were significantly different. Figure 4.16 after five cycles of adsorption–desorption, the PO_4^{3-} removal efficiencies deceased

from 84.23 %, to 82.09 %, 78.89 %, 76.20 % and 69.29 %, respectively. After the first two cycles, the acidic medium considerably enhanced the desorption efficiency, which could be attributed to the widespread distribution of negative charges on the material surface. Thus, the phosphate became attached to some positively charged functional groups and could be easily removed by the H^+ ions, which exerted a strong attractive force. After the third cycle, the phosphate adsorption capacity decreased significantly and remained at approximately 75 % thereafter and this could be attributed to the inevitable phosphate ion leaching or the permanent occupation of active sites after the first adsorption cycle. With the increase of cycles, the decline of adsorbent performance was possibly due to incomplete desorption, changes in adsorbent characteristics (e.g., porosity, crystallinity, and surface area) during desorption and regeneration, and loss of active sites due to material wear.

Table 4. 10: Removal efficiency of phosphate ion regeneration and desorption.

Initial concentration (mg/L)	Adsorption concentration (mg/L)	Desorption concentration (mg/L)	Removal efficiency of adsorption for regeneration (%)	Desorption efficiency (%)
5	4.35	3.705	87	85.17
5	4.28	3.608	85.6	84.23
5	4.22	3.461	84.5	82.09
5	4.17	3.290	83.4	78.89
5	4.13	3.147	82.7	76.20
5	4.09	2.834	81.8	69.29

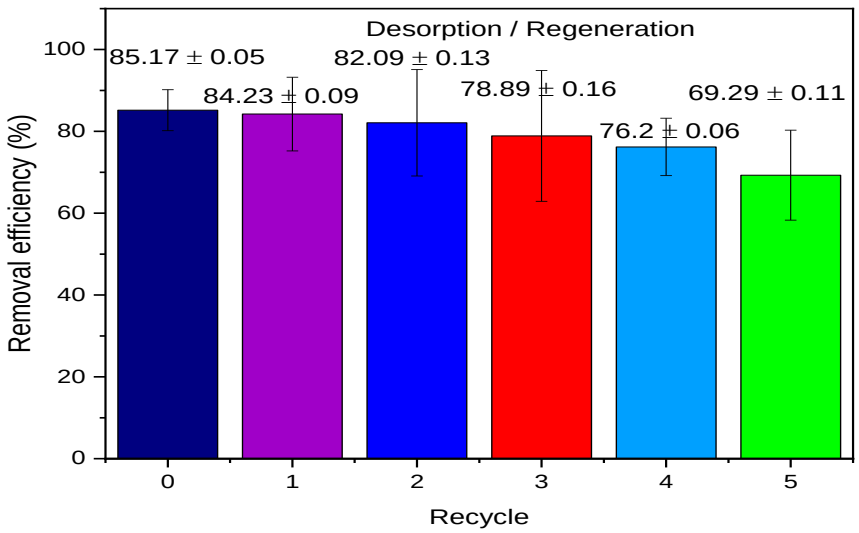

Figure 4. 16: Reusability performance of MgO modified corncob bio char adsorbent.

From Table 4.12 the regeneration removal efficiency of phosphate, the phosphate removal was decreased. This was because the mass of residual adsorbent was decreased, while the volume of solution and concentration of phosphate in solution were constant in all five cycles. Another reason was the phosphate adsorbed on adsorbent was not total desorbed. For every cycle, desorption of phosphate from residual adsorbent and regeneration of the residual adsorbent were measured Table 4.12. After every cycle, regeneration and desorption the mass of the residual adsorbent was measured. The phosphate removal was changed by small amount. Therefore, the synthesized adsorbent was suitable for regeneration and reusing.

4.9. The Performance Evaluation of the Adsorbent Using Real Wastewater

In order to apply the laboratory experimental result into the practical real world application, the investigation carried out by taking the real wastewater, which have highest amount of total phosphorus from Adama Science and Technology University water treatment plant. There was huge amount of total phosphorus contains water from different sources flow in to the treatment plant. For experimental work, the water at inlet of ASTU treatment plant selected for adsorption process. Average lab results from ASTU treatment plant indicates the influent contains total nitrogen of 125 mg/L and 75 mg/L of total phosphorus. For the adsorption of water contains PO_4^{3-}-P the optimum parameter from batch adsorption of synthetic water were used. The optimum parameter includes, pH = 9, contact time = 60 min, MgO loaded corncob bio char adsorbent dose = 0.5 g/100 mL. The initial PO_4^{3-} - P obtained from ASTU treatment plant from total phosphorus result, which was 47.83 mg/L.

Table 4. 11: Adsorption results of real wastewater of ASTU water treatment.

Initial Phosphate-phosphorus (PO_4^{3-}-P) (mg/L)	Final Phosphate - Phosphorus Concentration (PO_4^{3-} -P) (mg/L)	Average	Removal Efficiency R (%)	Adsorption Capacity (mg/g)
47.83	14.38 15.71 15.06	15.05	68.53	6.56

The removal efficiency of phosphate-phosphorus on the MgO loaded corncob bio char adsorbent was found 68.53 %. This result was much lower than that of removal efficiency of synthetic water

containing phosphate-phosphorus. The reason behind this result could be the presence of a large amount of total phosphates, phosphate-phosphorus. Those ions compete in the adsorption process, which lead decrement in the removal efficiency of phosphate-phosphorus. These huge decreased in phosphate-phosphorus removal may be due to the organic content and high electrical conductivity that might have halted the adsorption process through blocking and competition for the adsorbent sites, respectively. The maximum adsorption capacity and higher phosphate removal efficiency would be obtained by separating those ions at the influent of the plant.

4.10. Comparison Study of Phosphate Removal by Different Adsorbent

The synthesized MgO modified corncob bio char adsorbent compared with other different sources studied previously. As shown the Table below the optimum pH, isotherm model, kinetics model, and the adsorption capacity could be compared for phosphate removal.

Table 4. 12: Adsorption capacities and other parameters for removal of phosphate by different adsorbent.

Adsorbent	Optimum pH	Isotherm	kinetics	q_{max} (mg/g) K_f(mg/g).(L/mg)$^{1/n}$	Reference
Modified pumice	3	Freundlich	Pseudo-first order	141.939	(O.Orbulet et al., 2018)
Bio char from agricultural residue	7	Langmuir	Pseudo-second order	15.92	(Ma et al., 2020)
Water glass-based silica Aerogel	7	Langmuir	Pseudo-second order	9.08	(T.T.Nguyen, 2022)
Magnetic Mg/Fe hydrotalcite	3	Langmuir	Pseudo-first order	109.9	(Alagha et al., 2020)
ZnCl-modified Coconut	4.3	Langmuir	Pseudo-second order	14.01	(L. Liu et al., 2018)

granular Activated Carbon					(Khan et al., 2011)
Solid waste from Factory	5	Freundlich	Pseudo-second order	o. o65	(Berkessa et al., 2021)
Modified rice husk	6.4	Freundlich	Pseudo-second order	55.55	(Katal et al., 2022)
MgO modified corncob bio char	9	Langmuir	Pseudo-second order	**26.12**	**This study**

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

This research work focused on the synthesized corncob bio char and the characterization of MgO modified corncob bio char adsorbent. The modification of bio char with MgO enhances its adsorption capacity and provided an effective sustainable solution for phosphate removal and the unique properties of MgO modified bio char were increased surface area, porosity, and functional groups to contribute its excellence adsorption performance for phosphate ions and the presence of MgO on the bio char surface enhanced the adsorption affinity and facilitated the capture of phosphate ions from wastewater. The adsorption process was influenced by various factors, including contact time, adsorbent dosage, pH, initial phosphate concentration enhanced the removal efficiency of phosphate. The negatively charged nature of the modified bio char at elevated pH levels (above 8) promoted electrostatic attraction between the negatively charged phosphate and the positively charged surface sites of the adsorbent. This electrostatic interaction, combined with other adsorption mechanisms, contributes to the overall effectiveness of phosphate removal. The XRD, FTIR, and BET result analysis confirmed that phosphate ion was successfully adsorbed by MgO modified corncob bio char adsorbent. The adsorption peaks from 500-1000 cm^{-1} indicates the stretching vibration of MgO, which well confirmed successful attachment of MgO to the corncob bio char adsorbent. In addition, the peak at 1348 cm^{-1} after adsorption was responsible for phosphate ion, which shows phosphate adsorption by MgO loaded corncob bio char. Moreover, the diffraction peak at 2θ of 20.5° and 35.8° illustrated the adsorption of phosphate on the surface of corncob bio char adsorbent. The specific surface area of MgO loaded corncob bio char before adsorption obtained from BET analysis was 26.94 m^2/g.

One factor at a time (OFAT) involved changing one factor at a time and observing the result changes in the system response or output. The optimum removal efficiency of 89 % was obtained at a pH = 9, Co = 5 mg/L, t = 60 min, and dosage = 0.5 g. The Langmuir isotherm model was a better agreement with the experimental data with maximum adsorption capacity and correlation coefficient (R^2) of 26.12 mg/g, and 0.9857 respectively. This suggests that the adsorption process followed monolayer adsorption onto the surface of a finite number of adsorption sites. Phosphate adsorption kinetics was explained properly through the pseudo-second-order kinetics model (R^2 = 0.9741), which indicated that the chemical adsorption became the controlling mechanism of the adsorption process. The effects of competing ions on phosphate adsorption by MgO modified

corncob bio char adsorbent was found to follow by this order CO_3^{2-} < Cl^- < NO_3^- < SO_4^{2-}. Adsorption regeneration study of MgO modified corncob bio char adsorbent was investigated using 1M of NaOH as an eluent, which was the most prominent desorption agent. The adsorption – desorption of phosphate was successfully carried out in five cycles. According to this study, the result found indicated that the adsorbent is determined to be the best promising and effective for removal of phosphate ion from aqueous solution and water. However, further research is needed to optimize the operational parameters and understand the long term performance and stability of MgO modified bio char adsorbent. Additionally, the regeneration and reusability of the adsorbent should be explored to ensure its practical application in continuous phosphate removal process.

5.2. Recommendations

This paper work on the study of the removal efficiency of MgO modified corncob bio char adsorbent for the removal of phosphate ion from wastewater. MgO modified corncob bio char adsorbent has a promising potential for the removal of aqueous solution. But as most wastewater contain a lot of different species than just water, there is a need to undertake further research on the material. For future work, the following recommendations are suggested based on the result obtained from this study. The most important further research works were identified.

- ✓ The efficiency of this material should also be investigated for the removal of turbidity, BOD, TDS, and COD from aqueous solution and also the application of the material.
- ✓ The effects of other metal oxides like calcium, aluminum, and the like on modified corncob bio char for phosphate ion removal should further studied to obtain the best adsorbents with high efficiency and capacity.
- ✓ The regeneration of the adsorbent was investigated by using NaOH as eluent agent with 1M. The determination of the most preferable regenerating solution is a very essential. Therefore, further studies on effectiveness of other regenerating solution such as H_2SO_4, HCl, $NaNO_3$, NH_4Cl, HNO_3 and $CaCl_2$ could be investigated and also by varying the concentration of NaOH.
- ✓ It is recommended that study the effects of adsorption parameters such as agitation speed, mixing ratio, and temperature.
- ✓ In this work post pyrolysis, batch experiment, equilibrium isotherm, adsorption kinetics was conducted. However, thermodynamic properties, pre pyrolysis, and studies should be considered for future work with continuous column adsorption study.
- ✓ This study employed only a constant concentration of common ions effect for the removal of phosphate but it recommends that the study should be considered by varying the concentration of the common ions.

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APPENDICES

Appendix A: Preparation of stock solutions whether it is primary or secondary

Sample Calculations

Molecular Weight (MW)

MW of KH_2PO_4 = 136.09 g/mole

MW of PO_4^{3-} = 94.93 g/mole

To make 1000 ppm or (1000mg/L) of PO_4^{3-} stock solution dissolve 1.433 g in 1000 mL distilled water, since

Stock (1000ppm) = $\frac{\text{Molecular weight}}{\text{Atomic weight}} = \frac{136.09}{94.93} =$ 1.433

Then prepare different concentration from the stock = $\frac{\text{Required concentration} \times \text{Required volume}}{\text{stock}}$

And applying **Dilution law**, $\mathbf{c_1v_1 = c_2v_2}$**,** but

If it is primary the concentration is greater than 10 mg/L (i.e, c_1 is 1000 mg/L or 1000ppm) and if it is secondary the concentration is less than 10 mg/L (i.e, c_1 is 100 mg/L or 100ppm). So, secondary stock solution prepared by using 10 mL from stock and 90 mL of distilled water.

Moisture Content Determinations

Initial mass (W_1) = 5 g

Dry mass (W_2) = 0.172 g

% m = $\frac{(w_1 - w_2)}{w_1} \times 100 = 3.44\%$w/w

Ash Content Determinations

Sample mass (W_1) = 2 g

Mass of ash (W_2) = 0.063 g

%ash = $\frac{w_2}{w_1} \times 100 =$ 3.15 %w/w

Reagent Preparation

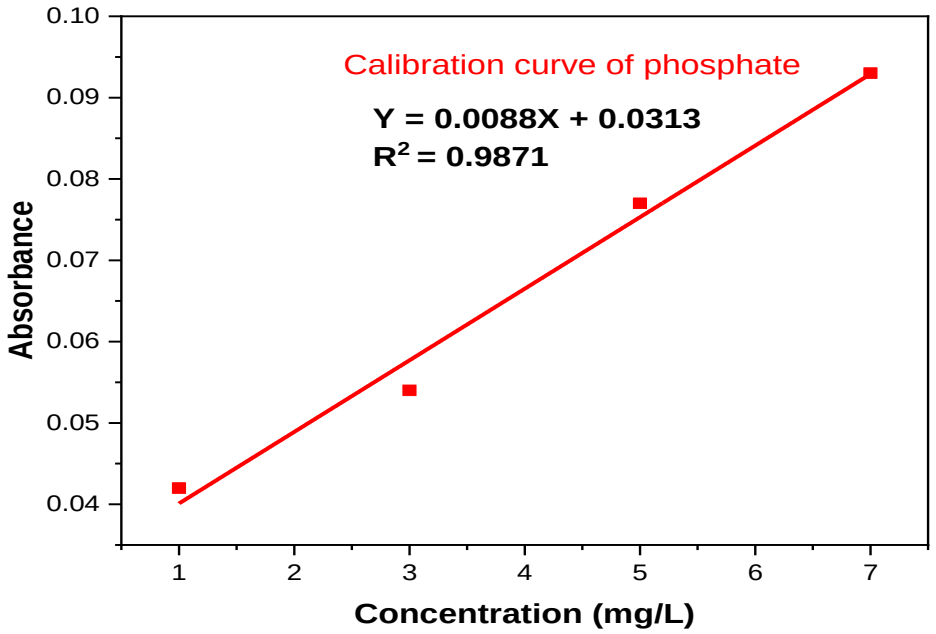
1. Weight 1.25 g of ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}.4H_2O$)
2. Transfer the weighted ammonium molybdate tetrahydrate into a 100 mL volumetric flask
3. Add 75 mL of distilled water to the volumetric flask
4. Add 2.5 mL of concentrated H_2SO_4 to the volumetric flask
5. Swirl the flask gently to dissolve the ammonium molybdate tetrahydrate and mix the solution
6. Allow the solution to cool room temperature

Reducing Agent Preparation

1. Weight 1 g of ascorbic acid ($C_6H_8O_6$)
2. Transfer the weighted ascorbic acid into 100 mL volumetric flask
3. Add 100 mL of distilled water into the volumetric flask
4. Gently shake the mixture

Finally, mix by 1:10 of the ammonium molybdate tetrahydrate with ascorbic acid, so ammonium molybdate blue reagent is formed.

Appendix B: Calibration curve of phosphate ion



Appendix C: Photographic representation of laboratory work

Raw material collection

Washing the raw material

Sun drying of the raw material

Size reduction of the raw material

Sieve analysis

Pyrolysis was takes place

Bio char is formed

Stirr the bio char at 25 °C

MgO modified bio char is synthesized

Digital pH meter

Electronic balance

Appendix D: FTIR graph band description

Functional groups of feedstock and char derived from hydrothermal and pyrolysis (Srilek & Aggarangsi, 2019).

Frequency(cm^{-1})	Functional groups	Description
3100-37000	O-H stretching	Hydroxyl or Carbonyl groups (acid), alcohols from cellulose or phenols from lignin (strong and broad, intense smooth)
1640 - 1550	O-H bend	Hydroxyl or phenols in lignin

2928,2870	C-H stretching	Aliphatic (Small double peak)
1725	C=O stretching	Vibration in hemicellulose
1700	C=O stretching	Carbonyl, ester or carboxyl from cellulose and lignin
1600, 1580, 1515, 1500,1450	C=C stretching	Aromatic skeletal in lignin
1240	C-O stretching	Hemicellulose esters
1205	C-O stretching	Vibrations in lignin
1149,1131	C-C stretching	Aromatic skeletal and stretching vibration in cellulose
1160	C-O-C stretching	Vibrations in cellulose and hemicellulose
1103	C-O stretching	Vibrations in cellulose, lignin
1060,1020,1031	C-O stretching	Vibrations in cellulose, hemicellulose
875 – 850	C-H bend	Aromatic