

Synthesis and Characterization of Calcium Decorated Bone-derived Biochar
Composite for Phosphate Removal from Wastewater Effluent



Wogayehu Mulugeta Woldemeskel

A Thesis Submitted to

Department of Chemical Engineering

School of Mechanical, Chemical and Material Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master's
in Chemical Engineering (Specialization in Process Engineering)

Office of Graduate Studies

Adama Science and Technology University

September, 2023

Adama, Ethiopia

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DECLARATION

I hereby declare that this Master Thesis entitled “**Synthesis and Characterization of Calcium Decorated Bone-derived Biochar Composite for Phosphate Removal from Wastewater Effluent**” is my original 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.

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RECOMMENDATION

We, the advisors of this thesis, hereby certify that we have read the revised version of the thesis entitled “**Synthesis and Characterization of Calcium Decorated Bone-derived Biochar Composite for Phosphate Removal from Wastewater Effluent**” prepared under our guidance by Wogayehu Mulugeta Woldemeskel 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.

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We, the advisors of the thesis entitled “**Synthesis and Characterization of Calcium Decorated Bone-derived Biochar Composite for Phosphate Removal from Wastewater Effluent**” and developed by Wogayehu Mulugeta Woldemeskel, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

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LIST OF ABBREVIATIONS

AC	Activated carbon
ACF-ZrFe	Iron-zirconium modified activated carbon nanofiber
AgNps-TAC	Silver nanoparticles
AlOOH	Aluminium oxyhydroxide
ANOVA	Analysis of variance
APHA	American Public Health Association
ASTU	Adama Science and Technology University
BBC	Bone-derived biochar
BC	Bio-char
BET	Brunauer–Emmett–Teller
BRM	Rosmarinus officiali biochar
Ca-BBC	Calcium-decorated bone-derived biochar
Ca-BC	Calcium-decorated biochar
CCD	Central composite design
CSH	Calcium silicate hydrate
DTG	Derivative of the Thermogravimetric
EBPR	Enhanced biological phosphorus removal
EPA	Environmental Protection Agency
FTIR	Fourier transform infrared spectroscopy
GAA	Global Aquaculture Alliance
GAC-Fe	Iron coated granular activated carbon
HAP	Hydroxyapatite

LDHs	Layered double hydroxides
MBMA	Meat and bone meal incineration ash
MCs	Microcystins
PBC	Plant-derived biochar
PZC	Point zero charge analysis
RSM	Response surface methodology
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
UV	Ultraviolet–visible
VM	Volatile matter
XRD	X-ray diffraction

ABSTRACTS

Phosphate-rich wastewater discharge from industry, agriculture, and urban areas has been led to serious eutrophication of water ecosystems, which poses various risks to aquatic lives and human health. Therefore, developing readily available, sustainable, effective, and low-cost adsorbent for phosphate removal was important to combat the problem. In this study, calcium-decorated bone-derived biochar (Ca-BBC) was prepared in different pyrolysis temperatures (400-800 °C), residence times (1-4 hr), and mass ratios (1:2 - 4:1) of Calcium to bone-derived bio char to effectively adsorb phosphate from aqueous solution. Results have shown that the best condition for Ca-BBC adsorbent preparation occurred at the pyrolysis temperature of 600 °C, the residence time of 2 hr, and a mixing ratio of 2:1. The synthesized Ca-BBC was characterized using XRD, FTIR, SEM, BET, and TGA to determine the crystalline structure, specific functional groups, morphological properties, specific surface area, and thermal stability, respectively. Response surface methodology (RSM) was carried out to assess a model equation that correlates the phosphate removal efficiency (R %) with the factors affecting adsorption namely adsorbent dosage, pH, and contact time (t). The optimum removal efficiency of 89.5 % was achieved at adsorbent dosage = 3 g/L, pH = 7.5, t = 12 hr, and at constant initial phosphate concentration ($C_o = 5$ mg/L). The adsorption isotherm data were best fitted to the Langmuir ($R^2 = 0.993$) with a maximum adsorption capacity of 63.65 mg/g. Moreover, the adsorption kinetics experimental data well fitted to the pseudo-second-order model ($R^2 = 0.999$), implying that chemisorption was the dominant adsorption mechanism for phosphate adsorption on Ca-BBC. XRD and FTIR analysis indicated that the preferable phosphate adsorption was due to the reaction of $\text{Ca}(\text{OH})_2$ and PO_4^{3-} , forming the hydroxylapatite crystal. Fluoride and carbonate were observed highly compete for active sites on the adsorbent during phosphate removal. The synthesized Ca-BBC was tested for its phosphate removal (R = 61.7%) using real wastewater. The adsorption-desorption test revealed that the adsorbent could be used repetitively without the adsorbent losing its active sites. Thus, the synthesized Ca-BBC could be considered as a competitive low-cost adsorbent for phosphate removal.

Keywords: Adsorption; Calcium decorated bone-derived biochar; Isotherm; Kinetics; Phosphate

CHAPTER ONE

1. INTRODUCTION

1.1. Background

Eutrophication has emerged as a serious threat to aquatic ecosystems in recent decades due to the rapid expansion of industry, intensification of agriculture, and increased wastewater generation. The continuous discharge of pollutants into aquatic environments is leading to the deterioration in the quality of water resources (Nsenga Kumwimba et al., 2020). There has been a growing presence of phosphates in water resources over the years from various sources. Phosphate is the main cause of eutrophication, which poses various risks to humans, animals, and plants (L. Fang et al., 2020). Municipal wastewater that is insufficiently treated plays a key role in accelerating eutrophication (Preisner et al., 2020). Extreme algal growth and the generation of microcystins (MCs) on the surface of water have been related to the problem of phosphate from fertilizer runoff and other potential sources (Akram et al., 2021; Pimentel & Giani, 2014). Algae transport into water tanks causes additional issues, including blockages in turbines and water pipes in reservoir pumping and power generation facilities (Almanassra et al., 2020). The prevalence of toxic red algae and dinoflagellates in seashore areas has resulted in the loss of millions of dollars in fish farming stocks, resulting in further economic disturbances. A family of toxins known as MCs can build up in aquatic environments, which reduces aquatic diversity and problems in fish farming (Pimentel & Giani, 2014). Moreover, MCs can infiltrate the food chain through irrigation and travel to drinking water, which may have an impact on human health (Kudela et al., 2015; Naushad et al., 2018). The initial Global Aquaculture Alliance (GAA) total phosphate standard was set at 0.5 mg/L. In most coastal rivers and lakes, these concentrations were regarded to be low enough to prevent eutrophication, and generation of microcystins (Mittelstet et al., 2016).

Various phosphate-polluted wastewater removal technologies, including chemical precipitation (B. Wang et al., 2020), enhanced biological phosphorus removal (EBPR) (Xu et al., 2018), and adsorption processes, have been proposed and evaluated to date (Shaheen et al., 2022). Technologies namely chemical precipitation and enhanced biological phosphorus removal were

reported as not suitable for phosphate removal due to chemical consumption and toxic environment to grow microorganisms, respectively. Adsorption technology is effective in removing phosphates from wastewater, even at low concentrations, compared to the chemical, physical, and biological methods (Almanassra et al., 2021). In addition to its adaptability, ease of design, potential for adsorbent reuse, low cost, and environmental friendliness, adsorption is regarded as one of the most effective methods for the removal of phosphate from wastewater and has received extensive research and widespread use (Aibinu et al., 2022). The most difficult part of the adsorption process is choosing the right adsorbent material, so scholars are working extremely hard to create sustainable, affordable, and non-toxic adsorbents for better remediation performance of phosphate from wastewater (Almanassra et al., 2020). Several adsorbents have been employed for phosphate elimination from aqueous solutions such as biochar (Usman et al., 2022), calcium silicate hydrate (CSH) (Taweekarn et al., 2022), zeolites (Deng et al., 2022), activated carbon (Bacelo et al., 2020) and clay minerals (Loganathan et al., 2014). Amongst these adsorbents, biochar is a vital and powerful adsorbent used to remove phosphate from an aqueous solution (Qiu & Duan, 2019; Xiao et al., 2020).

According to several studies, biochar is a solid substance created when biomass is carbonized. Agricultural waste, food processing waste, animal waste, and municipal sludge are examples of biomass resources that thermally decompose under oxygen-limited circumstances to synthesize biochar (Lee et al., 2019). Biochar has been widely used for phosphate removal due to its porous structure, stability, and high surface area. However, many of the biochars often possess very weak charged groups on their surface, and hence they demonstrated a poor phosphate adsorption capacity (Mezenner & Bensmaili, 2009). In this regard, biochar was impregnated or modified with metal ions to improve its phosphate adsorption capacity (Bacelo et al., 2020). Accordingly, the application of biochar is a potential technical approach to removing phosphate from wastewater, and it is worthy of further study. Despite this, the search for cheaper adsorbents with higher phosphate capacity is still an ongoing research endeavor.

There were no sufficient biochar adsorbents reported in the literature for phosphate removal at low concentrations, hence inspired to creation of a cost-effective adsorbent with a low adverse impact on the environment and human health, namely bone-derived biochar (BBC). BBC is among the most promising low-cost adsorbents mainly for fluoride and heavy metals removal

(Alkurdi et al., 2019; Flores-Cano et al., 2016; Yami et al., 2015). Because of its advantages over other biochar's, BBC has recently received a lot of interest in the wastewater treatment industry. The rapidly expanding meat consumption in Ethiopia generates massive amounts of solid waste in the form of unused bones and most of them end up in the landfill. Few studies on the adsorption of phosphate onto BBC reported the material as a promising adsorbent for phosphate removal from wastewater (Kasim et al., 2020; Leng et al., 2019). However, the experiments were performed in synthetic water that contains only a solution of salts of phosphate. As a result, the initial phosphate concentrations were larger for practical application in tertiary wastewater treatment, and its performance was not evaluated in real wastewater samples. Furthermore, the studies did not assess the effect of pyrolyzing conditions (i.e. temperature, time, and mixing ratio) and major coexisting ions such as Cl^- , F^- , HCO_3^- , SO_4^{2-} , and NO_3^- .

Moreover, the adsorption capacity of BBC can be improved by modifying the crystallinity and surface chemistry. Choi et al., (2019) found that calcium-modified biochars have shown high phosphate removal capacity from wastewaters and natural waterbodies. The chemisorption of calcium and phosphate is one of the major mechanisms that contribute to the adsorption process. Furthermore, due to its nontoxicity and widespread availability, calcium (Ca) is regarded as another promising element for modification to improve phosphate adsorption (S. Wang et al., 2018). The decoration of Ca could offer several active spots for binding phosphates. As a result, adding calcium to functionalize bone-derived biochar could be a way to improve its adsorption capacity to remove phosphate.

Therefore, this batch adsorption study was conducted using synthetic phosphate solutions as well as effluents from the Adama Science and Technology University wastewater treatment plant. The study aimed to determine the adsorption efficiency of phosphate onto BBC and Ca-BBC; identifying optimum design parameters, such as contact time (3-11hr), pH (3-12), adsorbent dose (1-5g), initial phosphate concentration (5.1mg/L), competing anions (10 and 25 mg/L), pyrolyzing temperature (400-800 °C), pyrolyzing time (1-4 hr) and mixing ratio for modification purpose (1:2-4:1); effect of coexisting ions (i.e. Cl^- , F^- , CO_3^{2-} , SO_4^{2-} , and NO_3^-), and evaluating the regeneration and reusability potential of Ca-BBC for practical application.

1.2. Statement of the Problem

The growth of invasive aquatic weeds, such as blue-green algae, and water hyacinth, is dependent on the phosphate concentration in water bodies (Y. Zhang et al., 2019). Concentrations for its development in water bodies have been supported by various experimental data. According to Gaikwad and Gavande (2017), the minimal requirement for water hyacinth survival is 1.66 mg/L phosphate. In Ethiopia, the great contributor of water in the Abay River (Gilgel Abay) contains about 20 mg/L phosphate (Taffese et al., 2014). Another study shows that the average phosphate concentration in Lake Hawassa was found to be 6.56 mg/L (Lencha et al., 2021). In the Adama Science and Technology University wastewater treatment plant, the treated wastewater contained 5.1 mg/L phosphate in its effluent. During this study measurement that is beyond the standard value and creates suitable conditions for the growth of aquatic weeds was observed. This can block sunlight from reaching native water plants and deplete the oxygen in water – often choking aquatic animals like fish. It also affects transportation, agriculture, industry, recreation, tourism, and temperature regulation. Unfortunately, in Ethiopia, it has been monitoring the water bodies' nutrients (specifically phosphorus) as part of our water management policy program.

The Environmental Protection Agency (EPA) has recommended that the phosphate discharge limit should not exceed 5 mg/L. Nevertheless, it becomes a pollutant if its concentration is more than the threshold recommended limit (Ghorai & Ghosh, 2022). Ethiopia tried to adopt its phosphate discharge standard from these established standards, as did the majority of African nations. The removal of phosphate using various conventional and cutting-edge technologies is strongly advised due to the established discharge limit, environmental effects, and other driving forces. However, there were no sufficient adsorbents reported in the literature for phosphate removal at low concentrations, hence inspired to develop readily available, simple to use, effective, cheap, and adaptable phosphate adsorbent for practical application. To the best of my knowledge, there is no previous work on the calcium-decorated bone-derived biochar (Ca-BBC) composite as an adsorbent to remove phosphate from wastewater effluent.

1.3. Basic Research Questions

1. Is it possible to decorate calcium ions (Ca^{2+}) on the surface of BBC to synthesize effective adsorbents for phosphate removal?
2. What is the best CaCl_2 to BBC composite ratio to develop an effective adsorbent that gives maximum phosphate removal from wastewater?
3. What is the role of calcium ions in the development of an adsorbent to remove phosphate from wastewater effluent?
4. What would be the effect of synthesizing factors (i.e. pyrolysis temperature, time, and mixing ratio) and optimum parameters (i.e. pH, adsorbent dose, and contact time) for phosphate removal?

1.4. Objective of the Study

1.4.1. General Objective

The major objective of this research work was to synthesize and characterize calcium-decorated bone-derived biochar (Ca-BBC) composites for the efficient removal of phosphate from wastewater effluent.

1.4.2. Specific Objectives

To achieve the above-mentioned general objective, the following specific objectives were articulated as follows:

- i. To synthesize and characterize BBC and Ca-BBC and study the effect of its synthesizing factors (i.e. pyrolysis temperature, time, and mixing ratio) on the removal efficiency of phosphate.
- ii. To evaluate the effect of pH, adsorbent dosage, and contact time on the removal efficiency and adsorption capacity of phosphate from wastewater.
- iii. To examine the effect of competitive ions on the removal efficiency of phosphate.
- iv. To evaluate the desorption and regeneration properties of Ca-BBC adsorbents.
- v. To establish adsorption isotherms and kinetics model for phosphate removal by Ca-BBC adsorbents.

1.5. Scope of the Study

This research is mainly focused on the investigation of the performance of Ca-BBC for the removal of phosphate from wastewater. It covers the laboratory bench scale preparation and characterization of BBC and Ca-BBC. The effect of pyrolysis temperature, time, and CaCl_2 to BBC mixing ratio on the adsorption efficiency of phosphate removal from wastewater was evaluated. The XRD, SEM, TGA, BET, and FTIR were used to characterize BBC, and Ca-BBC before and after adsorption. Furthermore, adsorption studies of various effects such as adsorbent dosage, pH, and contact time on phosphate removal by Ca-BBC were investigated. Moreover, adsorption kinetics, adsorption isotherm model, and regeneration study were conducted. Not only the effect of co-existing ions within phosphate ions but also the performance of Ca-BBC composite for real wastewater was evaluated in this work.

1.6. Significance of the Study

Ethiopia has one of the most rapidly growing economies in the world and a lot of interest in the expansion of industry and agriculture. Nevertheless, a weak nutrient removal and recovery system was observed. Phosphate discharge from industries, Sewage systems, and animal manure can cause several environmental problems that affect aquatic mediums and human health. Thus, in this study, a calcium-decorated bone-derived biochar (Ca-BBC) composite was developed for the removal of phosphate ions from wastewater. This research has great significance in terms of assuring the development of cheap, simple to use, readily available, efficient, and adaptable adsorbent to remove phosphate from wastewater at low concentrations. It has a great role in following the government policy on phosphate removal from wastewater to improve the quality of water resources. The removal of phosphate ions by using low-cost adsorbents from unused bone is found to be promising in the long term due to the adsorbent product obtained from material locally and readily available in Ethiopia. Moreover, achieving effective removal of phosphate to prevent eutrophication is one of the important goals of this study.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Introduction

Globally, phosphate contamination in water sources has been recognized as a serious issue. Phosphorus is the main contributor to eutrophication, which poses several risks to people, animals, and plants (L. Fang et al., 2020). Figure 2.1 indicates different phosphate sources to water resources and their consequences on water quality at high phosphate concentrations. Inadequate treatment of municipal wastewater is a major factor in the acceleration of eutrophication (Preisner et al., 2020).

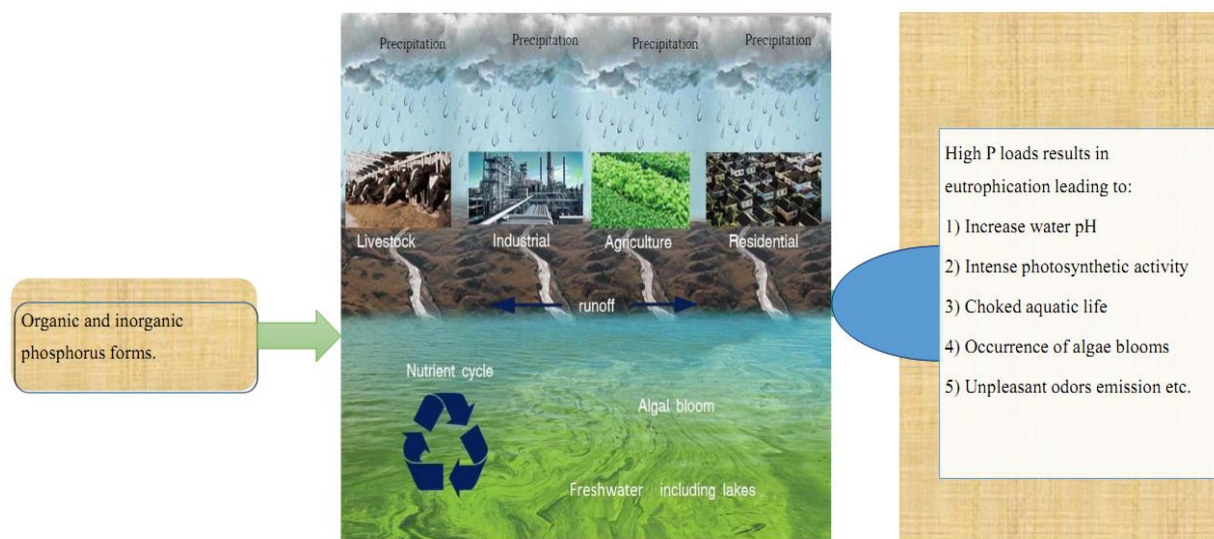


Figure 2.1: Source of phosphate and its consequences (Y. Zhang et al., 2019)

Essentially, biological, physical, and chemical techniques are often used to remove phosphates from wastewater. The benefits and drawbacks of the primary conventional methods for phosphate removal from water and wastewater effluents are listed in Table 2.1. Amongst these methods, adsorption technology is effective in removing phosphates from wastewater, even at low concentrations (Awual, 2019; Bacelo et al., 2020; Vikrant et al., 2018). Adsorption is one of the most efficient techniques for removing phosphate from wastewater and has received

substantial research and broad application because of its versatility, simplicity in design, the potential for reusing adsorbent, low cost, and environmental friendliness (Aibinu et al., 2022).

Table 2.1: Benefits and drawbacks of the main methods used for phosphate removal from wastewater.

Method	Benefits	Drawbacks	References
Adsorption	➤ Easy process operation. ➤ Effective at low phosphate concentration. ➤ Low initial cost. ➤ Low amount of by-products. ➤ Fast process.	➤ Adsorbent may reach saturation point. ➤ Effect of co-existing ions.	Usman et al., (2022)
Biological	➤ Can achieve complete removal of phosphate. ➤ Cost-effective and environmentally sustainable.	➤ Strict control of operational parameters is required. ➤ Requires skilled operators. ➤ Fluctuating performance of microorganisms	Lognathan et al., (2014)
Chemical	➤ Well-established process. ➤ Reliable process. ➤ Can achieve high phosphate removal capacity	➤ Requires continuous effluent neutralization. ➤ High chemical consumption. ➤ Sludge disposal. ➤ Not effective at low phosphate concentrations.	Almanassra et al., (2021)

2.2. Phosphate Adsorbents

The most effective method for removing pollutants from wastewater is adsorption, which makes use of a variety of adsorbents. Adsorbents with characteristics such as high selectivity, high adsorption capacity, low cost, high stability, and long life are more suitable for removing pollutants (Aibinu et al., 2022). Different adsorbents have their unique properties which are a function of their active surface, pore diameter, pore distribution, and surface functional groups (Almanassra et al., 2021). Most adsorbents, particularly nano-modified adsorbents, are recyclable, making adsorbed pollutants easily removed from the nano-adsorbents' surfaces (Jung et al., 2015). Nano-adsorbents are a class of nano-sized particles with a strong affinity for contaminants and are synthesized from organic or inorganic materials. Their strong affinity for pollutants stems from their distinct characteristics, which include their small size, catalytic potential, high reactivity, and high surface energy (Razanajatovo et al., 2021). The use of nano-adsorbents for phosphate removal in water has also received a lot of attention because of their smaller particle sizes, which increase the adsorption capacity of the adsorbents.

Several adsorbents have been employed for phosphate elimination from aqueous solutions such as biochar (Almanassra et al., 2020), calcium silicate hydrate (CSH) (Taweeakarn et al., 2022), zeolites (Deng et al., 2022), activated carbon (Bacelo et al., 2020) and clay minerals (Loganathan et al., 2014). Extensive research is being conducted on the synthesis and modification of such materials to identify adsorbents with the best physical and chemical properties for removing phosphate from wastewater. Researchers used this information to learn about the adsorption capacity, removal efficiency, and mechanism of phosphate removal by such adsorbents. The techniques used to synthesize and modify some of the adsorbents used in the removal of phosphate from wastewater are highlighted in Figure 2.2.

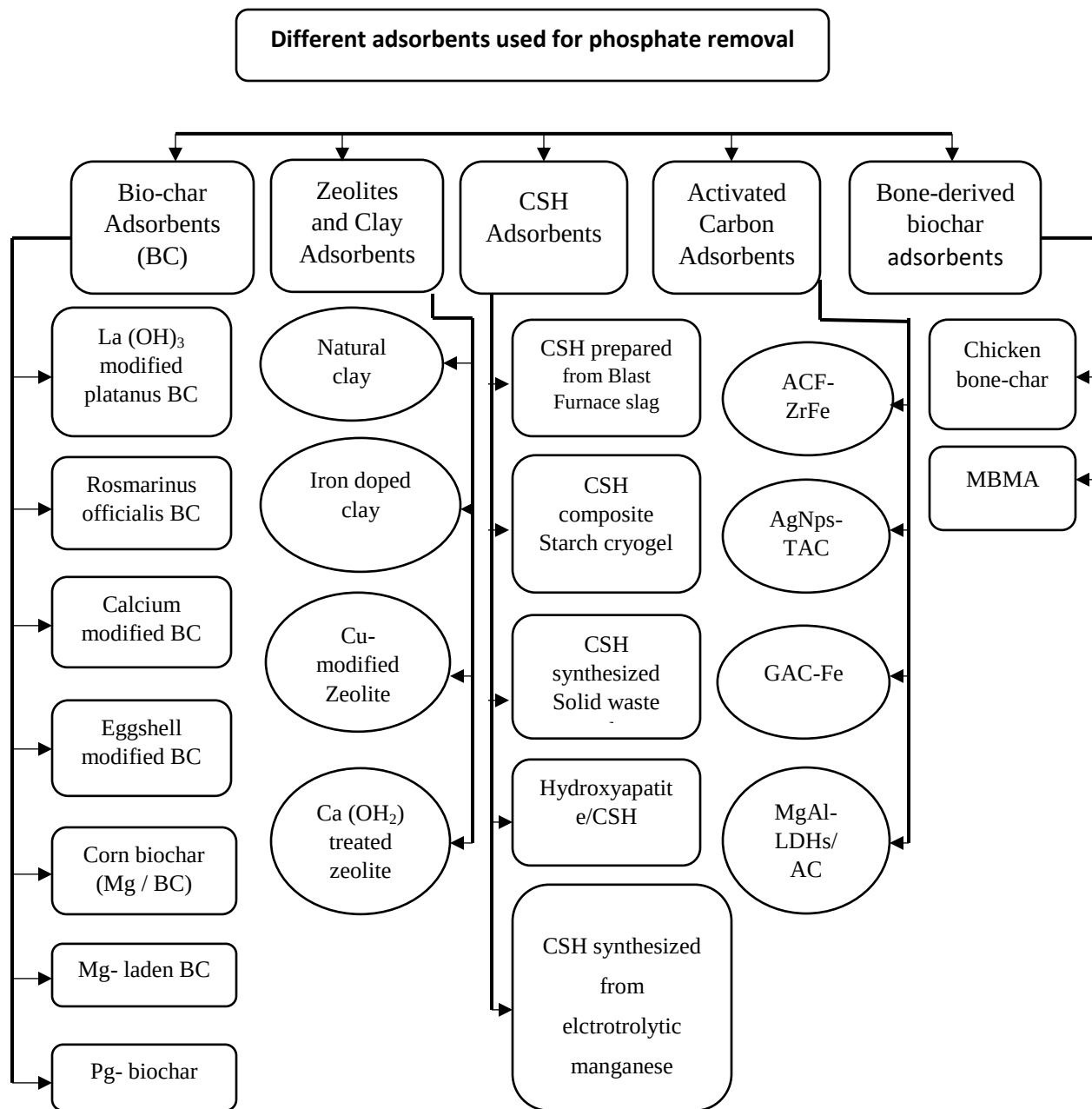


Figure 2.2: List of different adsorbents used for the removal of phosphate from wastewater

Figure 2.2 summarizes several adsorbents, which have been used for phosphate removal. In addition, adsorption capacity, isotherm, kinetics, pH, adsorbent dose, contact time, and initial phosphate concentration of different adsorbents for phosphate removal from wastewater have been presented in Table 2.2.

2.2.1. Bio-char Adsorbents (BC)

A solid material known as biochar is created by biomass carbonization (Almanassra et al., 2020). Pyrolysis is a thermal decomposition process that uses oxygen-limited conditions to break down biomass resources like agricultural residue, waste from food processing, animal waste, and municipal sludge (Y. Lee et al., 2019). Since Chen et al. (2019) started removing phosphate using BC in 2011; there has been an annual increased in scientific research on removing phosphate using BC and its composites. This is primarily due to its low cost, broad range of feedstock, and simplicity of modification. From the standpoint of the environment, on the one hand, BC made from a variety of wastes lessens the environmental burdens; on the other hand, the exhausted BCs after phosphate removal have been effectively used for soil remediation and as a slow-release fertilizer, which is advantageous for BCs among other available adsorbents (Almanassra et al., 2020).

Engineered biochar, also known as biochar composites, is pristine biochar that has been added to with hydroxides, microorganisms, metals, and nanomaterials (B. Wang et al., 2021). Recently, there has been a lot of interest in the development of Engineered BCs, and numerous reports have demonstrated the effective removal of heavy metals, toxic dyes, and contaminants from industrial effluent and municipal wastewater (Yaashikaa et al., 2020). According to Wang et al. (2021), biochar produced from oilseed rape straw (700 °C) were modified with coal gangue. Owing to this modification, adsorption of 7.9 mg /g phosphate was achieved. The authors explained the process of adsorption on this composite based on the mechanisms of ion exchange, surface precipitation, and electrostatic attraction.

The addition of additional metallic materials, such as Mg or Fe, may also be part of the modifications. This increases the content of the mineral fraction and contributes significantly to the binding of phosphate. Zhang et al. (2021) modified sludge biochar with Mg and Mg-Fe. Lower values were found for the Mg-Fe biochar (35.4 mg/g) and the phosphate adsorption on the Mg-biochar composite was 142.3 mg/g. The impregnation of Mg-biochar seems to be an effective method to increase phosphate adsorption, which was also confirmed in a study by Shin et al. (2020). The modification of biochar from ground coffee bean waste with Mg resulted in an adsorption of 56 mg/g. Xiao et al. (2020) also indicated that Mg-coated biochar composites were efficient for phosphate removal.

Modification suggested by Peng et al. (2021) involved the formation of Mg/Al layered double hydroxides (LDHs), composed of both positively and negatively charged layers, and water filling the interlayer spacing on the surface of the biochar (corn straw, 950 °C). The adsorption of phosphate on the obtained composite was found to be 286.2 mg/g. Yang et al. (2019) also confirmed the high efficiency of Mg/Al LDH biochar composites for phosphate adsorption. The adsorption of phosphate using the produced biochar composite (corn stalk, 600 °C) was 152 mg/g. The high results for phosphate adsorption on the BC-LDHs composites could be explained by the good dispersion of colloidal LDH flakes in the aqueous solution, which increased the number of active sites and enabled efficient adsorption on the composites.

Calcium-decorated biochar (Ca-BC) was designed in different Ca to BC mass ratios by Wang et al., (2017). It was discovered that the decorated Ca on the BC surface has preferential phosphate adsorption capacity. It was discovered that a design containing calcium hydroxide ($\text{Ca}(\text{OH})_2$) and flour in a mass ratio of 2:1 has a maximum phosphate adsorption capacity of 314.22 mg/g. The adsorption process is well-fitted by the Langmuir and pseudo-second-order models. According to XRD analysis, the reaction between $\text{Ca}(\text{OH})_2$ and PO_4^{3-} , which produced the hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$) crystal, was reported phosphate preferable adsorption ability. The phosphate in the solution was transformed into the crystal.

Aluminum has also been applied to BC modification in phosphate removal. By submerging the feedstock in Al-containing solutions (Novais et al., 2018), or by a novel electrochemical modification method using Al electrodes (Jung et al., 2015), BCs were doped with Al nanoparticles. Al was shown to be doped in both methods as AlOOH on BC. Additionally, several studies have noted an increase in surface area with Al doping, which provides more adsorption sites (Q. Yin et al., 2018). The highest reported phosphate adsorption capacity onto BCs was found in poultry manure and sugarcane straw BC modified with Al (Novais et al., 2018). These values were 701.65 mg /g and 758.96 mg /g phosphate removal, respectively.

Investigations have been done on the simultaneous modification of Al with other elements like Mg (Zheng et al., 2020), Fe (Y. Peng et al., 2021), and Mn (G. Peng et al., 2020). Using BC that had been electrochemically modified with Mg/Al, the Mg/Al modified BC had the highest adsorption capacity of 887 mg/g phosphate among these combinations. For the treatment of eutrophic water, Yin et al. (2018) suggested the bicomponent Mg/Al modified BC; the presence

of Mg offers new adsorption sites that lead to higher adsorption capacity. The Mg/Al-modified BC has the highest capacity for phosphate adsorption when compared to single-modified BC. Liao et al. (2018) created $\text{La}(\text{OH})_3$ modified magnetic pineapple biochar (Lax-MC) with a maximum adsorption capacity of 101.16 mg/g phosphate. This was attributed to the abundance of functional groups and the higher AlOOH content on the BC surface. Additionally, the Mg/Al-modified BC experiences both chemical and physical adsorption.

2.2.2. Zeolites and Clay Adsorbents

Natural clay minerals, kaolin clay, and zeolites, which consist of metal oxides such as Al_2O_3 , SiO_2 , MgO , and CaO , were among the diverse adsorbents that have been tested for phosphate removal and recovery. Kaolin clay, in particular, is well known for its excellent bonding properties, high whiteness, superior electrical insulating properties, and thermal stability.

The zeolite adsorbents were subjected to a series of adsorption experiments to remove phosphate ions from aqueous solutions. According to Mokrzycki et al. (2022), the highest adsorption capacity was obtained for zeolite X modified with 0.05 M $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{H}_2\text{O}$ solution, and they obtained adsorption capacity was 87.7 mg/g phosphate. The interaction between phosphate ions and Cu species on the zeolite surface was found to be the guiding mechanism of adsorption. Additional mechanisms, including precipitation as calcium phosphate and electrostatic attraction, should also be taken into account. A single-point adsorption of phosphate ions was also studied to evaluate the effects of adsorbent dose (1, 2, and 3 g/L) and adsorption temperature (18, 25, and 40 °C). Increased adsorbent dose resulted in significantly greater removal of phosphate ions for zeolite Cu 0.05X (up to 65.4 %). The temperature of 25 °C was found to be the most suitable for conducting adsorption of phosphate ions (Schaefer & Cheung, 2018).

2.2.3. Calcium Silicate Hydrate (CSH) Adsorbents.

CSH was a promising adsorbent for removing and recovering phosphate from wastewater, sludge, and solid waste ashes. It served as the seed crystal and calcium ion donor in the phosphate adsorption process and it aided pH adjustment. As a result, phosphate could be easily removed without the need for additional chemicals for pH adjustment (Kuwahara & Yamashita, 2017). In the phosphate recovery process, C-S-H acts as the seed crystal, the calcium ion donor, and the pH adjuster at the same time, and therefore it could recover phosphate in a one-step

crystallization process without adding other chemicals (Okano et al., 2015). This process was less affected by carbonate, and the recovered product can be easily separated from wastewater (C. G. Lee et al., 2018). However, the artificial synthesis of C-S-H was tricky. In general, C-S-H was synthesized in an alkaline and hydrothermal environment at 170 – 220 °C (Okano et al., 2013). This synthesis method was reported as sufficient to obtain a valuable product, but the cost was high. Some further studies suggested that C-S-H should be synthesized by a precipitation process at low temperatures to save energy and simplify operation. However, the C-S-H synthesized by the low-temperature reaction often has a heterogeneous structure and a low specific surface area, thus impairing its usefulness (Okano et al., 2013). Furthermore, this material could not even be considered as single-phase C-S-H, because there were significant structural differences between the fractions containing various Ca/Si ratios.

Taweekarn et al. (2021), have reported a novel calcium silicate hydrate composite cryogel (Cry-CSH) was thus successfully prepared for phosphate removal and recovery. Calcium silicate hydrate (C-S-H) was mixed with the gel precursor (7.5% w/w) prepared from native starch and limewater (saturated calcium hydroxide solution as the cross-linker). The mixture was frozen and thawed for 3 cycles giving an interconnected macroporous composite. This had C-S-H nanoparticles (75 mg) immobilized on a monolithic floatable cryogel network (2.5 cm diameter × 1.0 cm height) enabling an easier recovery without the losses that occur when using C-S-H nanoparticles. The phosphate adsorption reached equilibrium at 120 min with an adsorption capacity of 2.50 mg/g Cry-CSH (65.42 mg/g phosphate C-S-H) under optimum conditions (Taweekarn et al., 2022). Similarly, Fang et al. (2018) investigated porous calcium silicate hydrate (CS-CSH) derived from carbide slag for phosphate removal, with a surface area of 8.802 m²/g and pore volume of 0.024 cm³/g. In their experiment, the CS-CSH was autoclaved for 6 hours at 150 °C. According to this study, the CS-CSH had a phosphate removal capacity of 14.79 mg/g after nine reusing cycles. Calcination of CS-CSH at 700 °C resulted in a 3.23 mg/g increased in phosphate removal capacity. This study also found that controlling the equilibrium pH between 5.3 and 10.2 can reduce the negative effect of SO₄⁻² and HCO₃ on phosphate adsorption (D. Fang et al., 2018).

2.2.4. Activated Carbon-based Adsorbents

Activated carbon (AC) has been widely used for the removal of organic and inorganic pollutants due to its high surface area, low cost, availability, and surface porosity (Yagub et al., 2014; Zare et al., 2015). According to the application of the AC, it is produced in different forms, powdered activated carbon, granulated activated carbon, and activated carbon fibers. The properties of the AC depend on the raw material source and the preparation/activation method.

The AC can be produced from different carbon-rich materials including nutshell, lignin, pine cone mass, coir pith, and so on. However, most ACs possess negatively charged functional groups on their surfaces, and hence, the AC demonstrates low adsorption removal of anionic pollutants such as phosphate (Bacelo et al., 2020). Phosphate removal by activated carbon began 30 years ago in 1990 by using AC produced from almond shells and olive stone produced by CO₂ activation (Ferro-García et al., 1990). The produced ACs were of high surface area, however, with a limited phosphate adsorption capacity. As such, in the following decades, the ACs were either activated by other methods or impregnated by some materials, which demonstrate an affinity toward phosphate ions to improve the adsorption capacity of phosphates onto ACs. This section has been divided according to the origin of the AC, modified and unmodified commercial AC, the effect of the AC activation method produced from the different sources of biomass, phosphate removal by modified biomass-derived AC, activated carbon fiber composites, and granulated activated carbon composites. In general, as shown in Table 2.2, the adsorption data most of the phosphate adsorbents best fitted to the pseudo-second-order kinetic model and Langmuir and Freundlich adsorption isotherm model.

Table 2.2: Adsorption capacity, models (kinetic and isotherm), and adsorption optimum conditions of selective phosphate adsorbents

Adsorbents	Adsorption Capacity	Kinetic Model	Isotherm Model	pH	T (°C)	Initial con. (mg/l)	t (min)	Reference
Biochar adsorbent								
.Rosmarinus officialis BC	65.41	2 nd	Langmuir	6	45	160	60	(Mohammadi et al., 2021)

La (OH) ₃ modified platanus Biochar	148.11	PSO	Langmuir	6	35	-	20	(Jia et al., 2020)
Calcium-based BC (Ca- 900)	83.95	PSO	Langmuir	-	-	10.3	-	(Qin et al., 2022)
Rice straw-derived BC	50	PSO	Langmuir	-	25	50	10	(Huang et al., 2022)
Eggshell modified BC	460	PSO	Langmuir	5-13	-	-	25	(Sun et al., 2022)
Corn BC (Mg/BC)	239	PSO	Langmuir	9	25	50	30	(C. Fang et al., 2014)
Mg-laden BC	344	PSO	Langmuir	8	25	20–498	90	(Jiang et al., 2018)
Pg- BC	102.4	PSO	Freundlich	6	25	100	40	(B. Wang et al., 2020)
CSH adsorbent								
CSH prepared from Blast Furnace slag	53.1	PSO	Langmuir	7	25	-	1440	(Yamashita, 2017)
CSH synthesized from elctrotrolytic manganese	85.47	PSO	Langmuir	11	35	120	100	(Li et al., 2019)
CSH composite Starch cryogel	65.42	PSO	Langmuir	-	-	2.8	120	(Taweekarn et al., 2022)
CSH synthesized Solid waste residue	82.58	PSO	Langmuir	5	45	5.5	90	(Gizaw et al., 2022a)
Zeolites and clay Adsorbent								
Natural clay	21.4	PSO	Langmuir	3-10	22	100	60	(Guaya et al., 2021)
Cu- modified Zeolite	87.7	PSO	Langmuir	-	25	50	1440	(Mokrzycki et al., 2022)
Ca (OH ₂) treated zeolite	15.54	-	Langmuir	5.8	25	189.5	96	(Mitrogiannis et al., 2018)

Activated carbon adsorbents

AgNps-TAC	13.62	SFO	Langmuir	3	-	150	30	(Trinh et al., 2020)
GAC-Fe	2.874	-	Langmuir	3	25-45	-	-	(Braun et al., 2019)
MgAl-LDHs/AC	67.92	PSO	Freundlich	-	30	250	-	(P. Zhang et al., 2022)

BBC Adsorbent

MBMA	111	PSO	Langmuir	6.9	25	1-525	60	(Leng et al., 2019)
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Due to the variations in their operational conditions as shown in Table 2.2, it is challenging to compare all of the described adsorbents for practical usage selection. The characteristics relating to the cost of the adsorption process are more suitable for practical application. Adsorption affinity, adsorption kinetics, selectivity (impact of competing ions), temperature, contact time, adsorbent dosage, initial phosphate concentration, and pH effects were all factors in practical application. Moreover, the reported strengths and limitations of some of the phosphate adsorbents are highlighted in Table 2.3.

Table 2.3: Strength and limitation of different phosphate adsorbents reported in the literature

Adsorbents	Strength	Limitation	Reference
Meat and bone meal incineration ash (MBMA)	✓ Removed phosphate due to HAP formation ✓ High removal capacity (115mg/g) ✓ Low-cost, available, and non-toxic ✓ It contributed greatly to the feasibility of phosphate recovery	✓ Removal of phosphate from synthetic phosphate wastewater only ✓ Its performance is not applied to real wastewater treatment ✓ Use another chemical for pH adjustment	(Leng et al., 2019)

Dolomite-modified biochar	✓ High phosphate removal efficiency of 96.8% ✓ Investigated the effect of competitive ion ✓ The cost-effective method and its cost were evaluated to be 1.76 \$/kg P.	✓ Low mechanical strength and thermal stability ✓ Use another chemical for pH adjustment	(J. Li et al., 2019)
Calcium-decorated biochar (Ca-BC)	✓ Removed phosphate due to HAP formation ✓ High removal capacity (314.22mg/g) ✓ Environmentally friendly and low-cost sorbent for phosphate removal	✓ Use another chemical for pH adjustment ✓ It is not applied to real wastewater ✓ Adsorbed phosphate slowly	(Wang et al., 2017; Wang et al., 2018)
Lanthanum based adsorbent	✓ High removal capacity ✓ Higher affinity for phosphate than other metal elements. ✓ Relatively low cost ✓ Most of them are effective in real wastewater phosphate removal. ✓ Fastest adsorbent than others.	✓ Use another chemical for pH adjustment ✓ Unstable adsorption performance ✓ Complicated preparation process	(Almanassra et al., 2021; Chen et al., 2019; Dong et al., 2017)
CSH	✓ Not require any chemicals for pH adjustment ✓ Low -cost ✓ It is biocompatible ✓ Insignificant toxic materials	✓ High manufacturing costs ✓ Poor stability ✓ Excess sludge production ✓ Variable stoichiometry	(Kuwahara & Yamashita 2017; Zhang et al. 2019; Peng et al., 2018)

Zeolites and clay adsorbents	✓	High thermal stability	✓	Low removal capacity	(Deng et al., 2022; Mitrogiannis et al., 2018)
	✓	Excellent bonding ability	✓	Sensitive operating conditions	
	✓	Easily regenerated			
Iron oxide adsorbents	✓	Some co-existing anions had no negative effect on phosphate adsorption	✓	Particles aggregate	(Cao et al., 2016; Nakarmi et al., 2019)
			✓	Medium adsorption capacity	
	✓	Magnetically recoverable phosphate adsorbents.	✓	Require high cost for large-scale application	

2.2.5. Bone-derived Biochar (BBC) Adsorbent

The rapidly expanding global meat industry generated massive amounts of waste in the form of unused bones; predictions have been made that global annual bone waste from the meat industry [including poultry (13%), pig (10%), and sheep (>21%)] will reach 40 million tones within the next 10 years (Alkurdi et al., 2019). Bone-derived biochar (BBC) was created by pyrolyzing animal bones in the same manner as plant-derived biochar (PBC), i.e., under low oxygen circumstances as shown in Figure 2.2. The BBC maintains more C, has a greater surface area, and contains less ash during this process (Azeem et al., 2021). BBC comprises macrospores containing 10-24% carbon, 75-90% inorganics (e.g., Ca and Mg), and 10-30% P₂O₅ fertilizer. These properties made BBC have excellent adsorption of pollutants from waste streams (Leng et al., 2019).

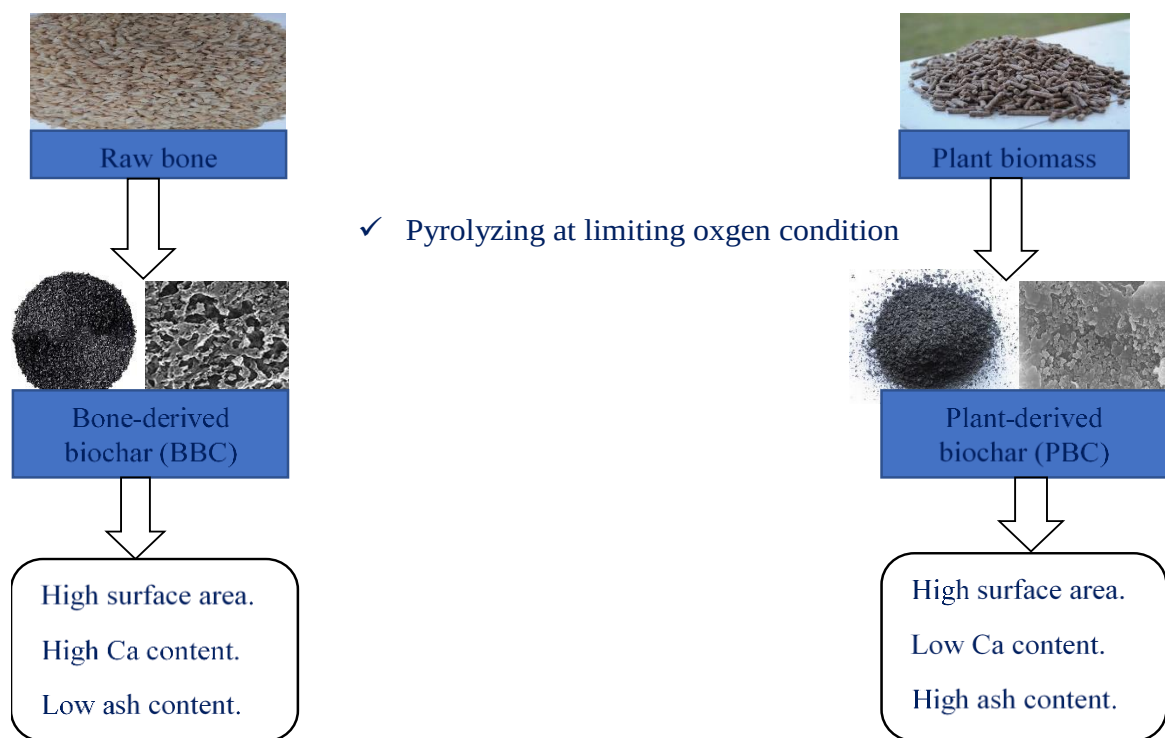


Figure 2.3: Characteristics of bone-derived biochar and plant-derived biochar

Carbonization of crushed animal bones entails heat treating a carbonaceous precursor in a confined oxygen environment at temperatures primarily greater than 500 °C and less than 700 °C to pyrolyze the raw material into a porous substance (Cheung et al., 2001). Partially evolving volatile matter from the carbonaceous precursor occurred in such a scenario. Any increase in pyrolysis temperature above 700 °C has changed the physical properties of the bone char. According to Rojas-Mayorga et al. (2015), after increasing the temperature from 650 °C to 1000 °C, a gradual color change of the bone to white was observed, indicating the complete elimination of the organic matter in the bone char structure. Alkurdi et al. (2019) reported that high pyrolysis temperature resulted in the degradation of the functional groups and lowered the efficiency of pollutant removal.

The surface area and pore volume of bone char were significantly influenced by the calcination temperature. For example, increasing the calcination temperature from 650 °C to 700 °C while using a CO₂ atmosphere increased the specific surface area of cow bone char from 62 to 69 m²/g and the total pore volume from 0.2 to 0.23 cm³/g, respectively (Rojas-Mayorga, Bonilla-Petriciolet, et al., 2015). However, a further raised in temperature to 1000 °C decreased the

material's surface area and pore volume to 2 m²/g and 0.02 cm³/g, respectively, and changed the color of the bone char to white. On the other hand, raising the charring temperature resulted in the dihydroxylation of the HAP. Table 2.4 presents a summary of the outcome of previous studies on the effect of temperature and heating rate on bone char properties.

Table 2.4: Effect of charring temperature and heating rate on the bone char surface properties (residence time = 2 hr) (Alkurdi et al., 2019).

Factors		Effect		Purging Gas Reference	
Temperature (°C)	Heating rate (°C/min)	BET surface area (m ² /g)	Total pore volume (cm ³ /g)		
650	5	-	-	N ₂ gas	Rojas-Mayorga et al. (2013)
	10	118	0.24		
700	5	-	-		
	10	110	0.233		
800	5	-	-		
	10	-	0.224		
900	5	-	-		
	10	-	-		
1000	5	-	-		
	10	-	-		
650	5	-	-	CO ₂ gas	Rojas-Mayorga et al. (2015)
	10	62	0.2		
700	5	-	-		
	10	69	0.3		
800	5	-	-		
	10	9	0.16		
900	5	-	-		
	10	4	0.04		

When evaluating the quality of bone char for used in various environmental applications, the purging gas utilized during pyrolysis is a crucial consideration. Bone char samples pyrolyzed in N₂ atmosphere showed larger specific surface area and total pore volume of 85m²/g, 0.24 cm³/g than those pyrolyzed at the same temperature, residence time, and heating rate using CO₂ purging gas, despite both samples having a mesoporous structure (Tables 2.4 and 2.5).

Table 2.5: Effect of charring temperature and residence time on the bone char surface properties (heating rate=10 °C/hr) (Alkurdi et al., 2019)

Factors		Effect		Purging Gas Reference	
Temperature (°C)	Residence time (hr)	BET Surface area (m ² /g)	Total pore volume (cm ³ /g)		
650	2	118	0.24	N ₂ gas	Rojas-Mayorga et al., (2013)
	4	-	-		
700	2	110	0.233		
	4	-	-		
800	2	96	0.224		
	4	-	-		
400	1	98.626	0.291	Limited O ₂	Patel et al., (2015)
	2	114.149	0.294		
	3	92.402	0.315		
450	1	98.138	0.305		
	2	83.948	0.302		
500	1	78.172	0.294		
	2	69.788	0.321		
600	1	57.939	0.293		
	2	50.37	0.305		

As shown in Tables 2.4 and 2.5, pyrolyzing circumstances had a significant impact on the chemical and textural makeup of bone char. The quality of the bone char produced at various

temperatures can be controlled by residence time and heating rate. A crucial pyrolysis temperature for bone char appears to be between 500 and 700 °C, depending on the source of the bone. Lowering the temperature below 500 °C caused more organic matter to be added to the treated water due to inadequate removal of organic matter in the bone structure. Increased charring temperature, on the other hand, resulted in the degradation of the functional group and altered the physical property of bone char. The substance could adsorb many organo-chlorine pesticides and herbicides, as well as chlorine, phosphate, and fluoride. Compared to other waste-based adsorbents like, wood char and activated alumina, bone char was one of the adsorbents with a low adverse impact on the environment and human health (Yami et al., 2015). Therefore, it had high pollutant removal efficiency attributed to its principal characteristics represented by the textural properties of bone char and the hydroxyapatite content.

2.2.5.1. Bone-derived Biochar (BBC) Modification

Suitable activation methods could improve the adsorption capacity of carbonaceous materials by increasing the surface area, and pore volume, providing the adsorbent with a variety of pore sizes; or altering surface functional groups in a way that increased the adsorbent's selectivity toward specific contaminants. However, bone char examinations followed by various modification methods showed an insignificant increase in surface area (Delgadillo-Velasco et al., 2017). Thus, considerations for improved bone char adsorption capacity were mostly related to changes in the functional groups on the surface. In general, biochar including bone char had a potential technical approach to remove phosphorus from wastewater, and it was worthy of further study. In aqueous solutions, phosphorus typically existed in the forms of orthophosphate, polyphosphate, and organic phosphate, and anion always possessed negative charges due to its anion state (Mezenner & Bensmaili, 2009). However, the biochar surface was also dominated by negative charges owing to the existence of oxygenated functional groups (J. Liu et al., 2019), which led to the limited biochar adsorption capacity for phosphate in wastewater (H. Li et al., 2016). Therefore, it was necessary to form some modifications to the physicochemical properties of biochar to deal with the above problem (Li et al., 2016; Vikrant et al., 2018). Recent studies suggested modifying biochar with calcium and then using the Ca-decorated biochar to filter out different contaminants from aqueous solutions. As a result, adding calcium to functionalize biochar could be a way to improve its capacity to remove phosphate.

2.3. Adsorption Kinetics and Isotherm Measurement for the Removal of Phosphate Ions

Kinetics are measured in an adsorption experiment to determine the rate of adsorption and the proper contact time between the aqueous solution and adsorbents (Akram et al., 2021). Kinetics describes the rate and mechanism of adsorption caused by physical or chemical phenomena (Sabzehmeidani et al., 2021). There are two standard kinetics models: pseudo-first-order (Equation (2.1)) and pseudo-second-order (Equation (2.2)).

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad \dots\dots\dots (2.1)$$

where q_e is the adsorption capacity at equilibrium (mg/g), q_t is the adsorption capacity at time t (mg/g), and k_1 is the first-order rate constant min^{-1} . The plot of $\log (q_e - q_t)$ versus t gives a relationship that is linear from which k_t and q_e can be determined from the slope and intercept of the plot.

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e^2 k_2 t} \quad \dots\dots\dots (2.2)$$

where q_e is the adsorption capacity at equilibrium (mg/g), q_t is the adsorption capacity at time t (mg/g), k_2 is the second-order rate constant, g/mg.min .

There are five basic assumptions of adsorption based on a pseudo-first-order equation and these are: (1) adsorption occurs only on localized sites with no consideration for the interaction surface adsorbates. (2) the energy of adsorption does not depend on surface coverage. (3) maximum adsorption corresponds to a saturated monolayer of adsorbates on the adsorbent surface. (4) the concentration of adsorbates is considered to be constant. (5) the uptake of adsorbate obeys pseudo-first-order (Sabzehmeidani et al., 2021).

Some assumptions of the pseudo-second-order include; (1) a linear relationship between energy and surface coverage; (2) keeping the concentration of adsorbate constant, and (3) negligible ion uptake on activated carbons before the exponential for an energetically heterogeneous surface as described by the Elovich model to support the pseudo-second-order kinetic theory

(Sabzehmeidani et al., 2021). These assumptions give information about the rate of removal of the adsorbate and ideas about the rate of particle diffusion.

The most common isotherm models used in adsorption studies are Langmuir, Freundlich, and Temkin, isotherm models. The Langmuir model (Equation (2.3)) allows accumulation only up to a monolayer. This model assumes that monolayer adsorption occurs on a homogenous or heterogeneous surface and energy of adsorption of all the available active sites is at all times comparable (Vadi et al., 2013).

$$\frac{C_e}{q_e} = \frac{1}{k_1 q_{max}} + \frac{1}{q_{max}} C_e \dots\dots\dots (2.3)$$

where q_e (mg/g) and q_m (mg/g) are the adsorption capacity at equilibrium and the maximum saturated adsorption capacity, C_e (mg/L) is the adsorbate concentration at equilibrium, K_1 (L/mg) is the Langmuir constant. The plot of C_e/q_e versus C_e gives a straight line of slope $1/q_m$ and intercept $1/K_1 q_m$.

The Freundlich model (Equation (2.4)) on the other hand presumes the occurrence of multilayer adsorption on a heterogeneous surface, thus describing that all the adsorption locations possess different affinities (Al-Ghouti & Da'ana, 2020).

$$\log q_t = \log k_F + \frac{1}{n} C_e \dots\dots\dots (2.4)$$

where K_F (mg/g) is the Freundlich constant, and $1/n$ is the sorption intensity which indicates the favorability and capacity of the adsorbent/adsorbate system. The plot of $\ln q_e$ versus $\ln C_e$ gives a straight line of slope $1/n$ and intercept $\ln K_F$.

The Temkin isotherm model (Equation (2.5)) is based on the assumption that the heat of adsorption (ΔH_{ads}) of all molecules in the layer decreases linearly with the increase in surface coverage of the adsorbent and thus, the adsorption has a uniform distribution of binding energies, up to maximum binding energy (Ayawei et al., 2017).

$$q_e = \frac{RT}{b} \ln k_T + \frac{RT}{b} \ln C_e \dots\dots\dots (2.5)$$

where K_T is the equilibrium binding constant (L mol^{-1}) corresponding to the maximum binding energy, b is related to the adsorption heat, R is the universal gas constant ($8.314 \text{ K}^{-1}\text{mol}^{-1}$), and T is the temperature (K). The plot of q_e versus $\ln(C_e)$ gives a straight line of slope RT/b and intercept $(RT \ln K_T)/b$.

It has been demonstrated that both Langmuir and Freundlich isotherms can adequately represent the experimental data in studies involving the adsorption of phosphate from wastewater with corresponding correlation coefficients (R^2) (Cao et al., 2016). However, in the majority of adsorption studies, the Langmuir model produces a better fit than the Freundlich model (Cao et al., 2016; Chen et al., 2019; Jia et al., 2020). This explains why the majority of phosphate adsorption is monolayer adsorption, each molecule's adsorption has an equal activation energy, and the adsorbate-adsorbate interaction can be limited (Sabzehmeidani et al., 2021). The phosphate adsorption mechanism is described by the results of isotherm and kinetics models.

2.4. Phosphate Removal Mechanism

The adsorption mechanism is of significant importance to understand the interaction between phosphate ions and the adsorbent molecules. The mechanism of adsorption is also the core element of controlling the adsorption kinetics, energy, capacity, and thermodynamics. According to reports, the adsorption mechanism was highly dependent on the nature, charge, and molecular content of the adsorbent. The adsorption mechanism also varied with pH and different adsorption mechanisms can be found in the same adsorption system. Adsorbents have been explained by different mechanisms, such as ion exchange electrostatic interactions, ligand exchange, precipitation, Lewis acid–base interaction, inner sphere complexation, and outer sphere complexation as shown in Figure 2.4.

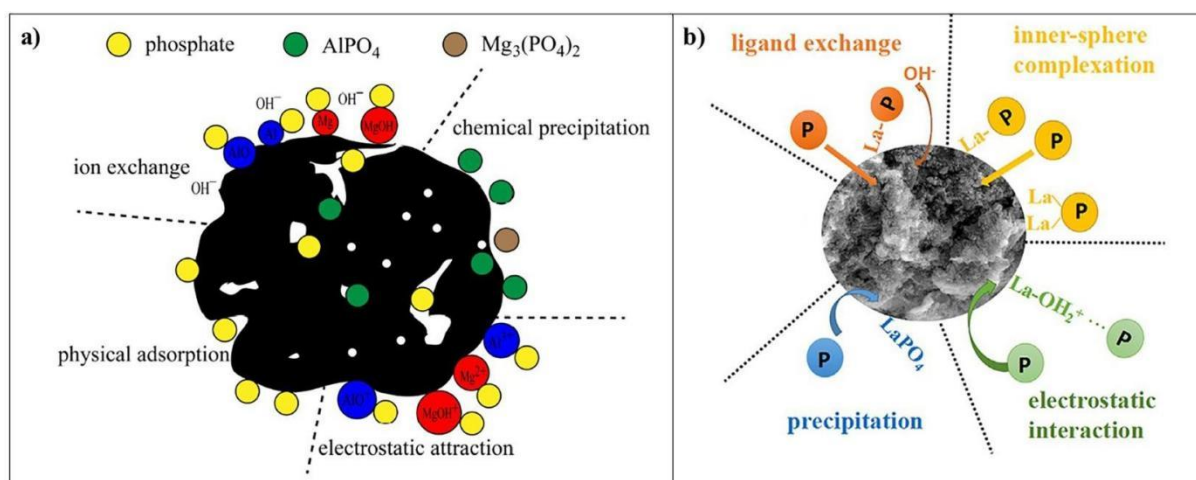


Figure 2.4: Adsorption mechanisms of phosphate onto a) Mg/Al modified BC and b) La modified magnetic BC (Liao et al., 2018; Zheng et al., 2020).

2.4.1. Ion Exchange

In water treatment applications, ion exchange involves the replacement of an ion in the aqueous phase with an ion from the resin phase. The ion exchanger is insoluble in water and can be a substance of natural origin such as zeolite or kaolinite, or a synthetic substance such as a polymer. These materials have fixed-charged functional groups on their internal and/or external surfaces, and the opposite charged (counter-) ions attached to these groups are found. If the functional group is negative, the counter-ion attached is a cation. If it is positive, the counter-ion is an anion and can be exchanged with another counter-ion in the aqueous phase. According to Almanassia et al., (2021), ion exchange is related to ion replacement in which a phosphate ion replaces an ion from the structure of the BC. Often ion exchange is related to the outer sphere complexation. This kind of adsorption is considered to be reversible where the phosphate ions can be recovered from the BC surface. Iron oxide-modified BCs are an example of phosphate removal by an ion exchange mechanism (Bektaş et al., 2021; Ren et al., 2015; Yang et al., 2019)

2.4.2. Electrostatic Attraction

The electrostatic force of long-range interaction that occurs between electrostatic adsorption in aqueous solution with differently charged particles or uncharged particles is referred to as electrostatic attraction (B. Wang et al., 2021). Understanding the adsorption mechanism is critical because it is linked to adsorption isotherms, kinetics, capacity, and adsorption

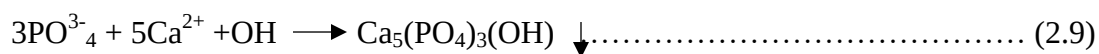
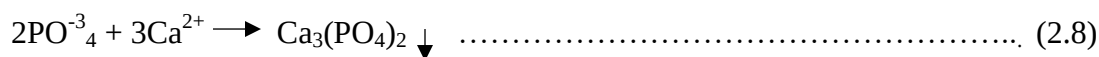
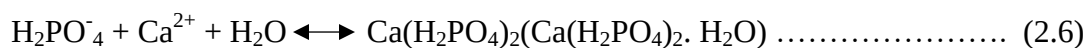
thermodynamics. Most studies suggest the adsorption of phosphate onto BCs is governed by electrostatic interactions. BC as a carbon-based adsorbent possesses a negative surface charge in aqueous solutions and phosphate ions dissociate with pH (Almanassra et al., 2020). The electrostatic mechanism is present in both chemical and physical adsorption processes. Electrostatic interactions are thought to be simple and reversible adsorption steps when compared to other mechanisms (Loganathan et al., 2014).

2.4.3. Ligand Exchange

Ligands are ions or neutral molecules with electron pairs that they can donate to the metal atom to form a coordinated covalent bond. Reports indicated that the adsorption mechanism via ligand exchange is also related to ion replacement, for instance, the phosphate groups replace the hydroxide groups (Yang et al., 2019). Phosphate adsorption via ligand exchange is associated with the formation of inner-sphere complexes, which results in stronger binding of phosphate ions with BC than ion exchange (Loganathan et al., 2014).

2.4.4. Precipitation

In an aqueous solution, precipitation is the process of transforming a dissolved substance into an insoluble solid from a super-saturated solution. The solid formed is called the precipitate. Precipitation of low soluble phosphate salts occurs when the concentration of the phosphate exceeds its solubility. It can also occur at lower concentrations when the finite volume beside the adsorbent mineral surface is oversaturated with phosphate according to the principle of thermodynamic solubility (H. Li et al., 2016). According to Leng et al. (2019), the Ca^{2+} ion was gradually released from the meat and bone meal ash into the solution, resulting in the precipitation of the calcium phosphate complex. The proposed precipitation reaction mechanism is as follows (Leng et al., 2019):



2.4.5. Lewis Acid-base Interaction

The Lewis acid-base interaction was also a controlling mechanism for phosphate adsorption onto carbon-based adsorbents. Under acidic conditions, the concentration of H^+ ions is high, which protonates the modified element on the adsorbent, thus, becoming a weak acid and working as an electron acceptor. The phosphate ions in acidic media are considered weak bases and function as electron donors. This phenomenon is reversed in the alkaline conditions. Accordingly, the electron donor-acceptor interaction occurs between phosphate ions and the elements attached to the carbon adsorbents. Examples of phosphate sorption by Lewis acid-base interactions are La-modified ACF (Z. Wang et al., 2016; L. Zhang et al., 2016).

2.5. Desorption and Regeneration of Adsorbents

The idea of sustainable development is currently being adopted by people all over the world, who use recycled materials, renewable resources, biodegradable items, energy-saving utilities, pollution-free or low-impact materials, and practical and affordable objects. Recycling used materials is one of the main principles of sustainable development (He et al., 2020). Desorption experiments can be used to examine adsorbent performance. According to Almanassra et al., (2021), a suitable phosphate adsorbent should have a high adsorption capacity, be reasonably priced, and be reusable over an extended period. Desorption, or reserving of adsorption, is a simple yet efficient regeneration method. Desorption investigations give us a complementary understanding of the type of adsorption, such as chemical or physical adsorption. It also concentrated on the adsorbent's effectiveness for subsequent usage, which reduced the cost of the adsorption process. There are three types of desorption:

- ✚ Thermal desorption, in which heat drives desorption. Although this method is quick and effective, it is also very expensive due to the need for pre-treatment, the release of hazardous contaminants, unsafe process conditions, difficulties with regulations and public perception, etc.
- ✚ Solvent desorption: This kind of desorption is economical, quick, highly effective, and environmentally feasible.
- ✚ Acid and base desorption: Acids and bases are highly effective when strong interaction between phosphate and the adsorbent is involved.

The most typical base for phosphate desorption is sodium hydroxide. The active sites on the surface of the adsorbent can be restored using sodium hydroxide after separation of the adsorbent from the mixed solution by filtration in a batch adsorption experiment, and the sample is dried before reuse in the following batch study (Trinh et al., 2020). According to Jia et al. (2020) study, employing lanthanum-modified platanus biochar as an adsorbent, the desorption efficiency of the base at 0.1 mol/L was reduced to 29% while that at 1 mol/L was maintained at 100% in three desorption cycles. Therefore, Increasing the concentration of sodium hydroxide will increase the regeneration efficiencies.

2.6. Effect of Physiochemical Properties of Phosphate Adsorptions

2.6.1. Effect of pH

It was widely acknowledged that an adsorbent's ability to capture a substance depends significantly on the adsorption factors (such as pH), which also influence the adsorption mechanism. Phosphate could occur in a variety of molecular and anionic forms at different pH levels, including H_3PO_4 , H_2PO_4 , HPO_4^{2-} , and PO_4^{3-} (Z. Zhang et al., 2018). In an acidic solution, the predominant phosphate ions are H_2PO_4 and HPO_4^{2-} , but in an alkaline solution, they are PO_4^{3-} (Trinh and Pham et al., 2020). Because the surface charge of the adsorbent is altered by the adsorption of charged phosphate ions, the pH of the solution could have a significant impact on the rate of adsorption (Akram et al., 2021).

The species of phosphate that are present in the solution were also influenced by pH (Qiu & Duan, 2019). The amount of phosphate removed reduces as the pH of the solution rises. The reason behind that at higher pH levels, the solution contained more OH^- , which is likely to compete with phosphates for the adsorption site and resulted in an evident drop. Additionally, at higher pH levels, the adsorbent surface became more repellent, increased repulsion, and lowered phosphate removal. Perassi et al. (2014) state that a variety of batch tests were conducted with phosphate concentrations ranging from 5 to 160 μM to study the adsorption of phosphate onto CaCO_3 montmorillonite (calcite-M). The results demonstrated that phosphate adsorption is pH-dependent, and increased as pH decreased (perassi et al., 2014).

2.6.2. Effect of Contact Time

The duration of contact time had a significant impact on the phosphate adsorption. For a specific dosage or initial concentration of the adsorbent, the contact time offered information on the adsorption kinetics of the adsorbate. The main goal of determining contact time is to figure out the minimal amount of time needed for adsorbents to optimally adsorb phosphate ions up until an equilibrium state between adsorbed and desorbed phosphates is reached. This clarifies the current rate of phosphate adsorption onto the adsorbents' surfaces as well as the adsorbent's effectiveness (Iftekhar et al., 2018).

Ramola et al. (2021) observed an increase in the phosphate adsorption efficiency of rice husk biochar-calcite composite from 10.5% to 50% at a time of 3–13 hours. This indicated that the increased contact time enhanced the phosphate removal efficiency. This was because the BRH-C surface had accessible active sites, which caused the adsorption process to proceed more quickly.

2.6.3. Effect of Adsorbent Dosage

The amount of adsorbent used was crucial to the phosphate adsorption process. According to studies, using small amounts of adsorbents caused the phosphate and adsorbent to interact, resulting in the anion's total attachment to the adsorbent (Nguyen, et al., 2020). According to the research Zhang et al., (2020), the adsorbent dosage was directly proportional to the removal effectiveness of phosphates. The rate of phosphate adsorption increased with increased amounts of adsorbent. However, aggregation of particles could decrease the active surface area and active site for the adsorption of phosphate from the solution in the presence of an excessive amount of adsorbent, which may decrease the adsorption (Trinh et al., 2020).

2.6.4. Effect of Competitive Ion in Phosphate Removal

Phosphate ions coexist with other ions in actual wastewater, municipal, and industrial water, where they may compete for active adsorption sites. As a result, it is critical to investigate the effect of coexisting ions on phosphate adsorption. Investigating such factors can obtain useful information about the practical applications of adsorbents. Phosphate coexists with several inorganic anions, including SO_4^{-2} , CO_3^{-2} , HCO_3^- , NO_3^- , Cl^- , and F^- . Other pollutants, such as humic acids, organic ions, and pharmaceutical chemical species, may be found in water effluents.

It is vital to investigate the effect of co-existing ions on the performance of the adsorbent in any adsorption experiment to provide important information about the application and selectivity of the adsorbent towards phosphate ions. The presence of divalent anions such as SO_4^{-2} , and CO_3^{-2} , poses a higher effect on the adsorption capacity of adsorbents than monovalent anions such as Cl^{-1} , NO_3^{-1} . In many studies, the presence of CO_3^{-2} was found to decrease the adsorption capacity of phosphates. The Cl^{-1} , SO_4^{-1} , and NO_3^{-1} showed no obvious decrease in the removal rate of phosphate. In another study, Rashid et al. (2017) reported that the presence of CO_3^{-2} changed the overall phosphate solution to alkaline. The increase in pH might be the reason for the decreased phosphate adsorption by the humic acid-coated magnetic nanoparticles. This was because; CO_3^{-2} possessed a strong affinity towards active adsorption sites. The presence of HCO_3^{-1} and CO_3^{-1} was also found to increase the pH of the solution and inhibit phosphate removal (Almanassra et al., 2021; Rashid et al., 2017). Zhou et al. (2012) observed that the effect of coexisting anions on phosphate adsorption by hydrated ferric oxide doped activated carbon fibre decreased in the order $\text{F}^{-} > \text{NO}_3^{-} > \text{Cl}^{-} > \text{SO}_4^{-2}$. It was observed that F^{-} had the highest effect on the adsorption of phosphate and the decrease in the adsorption ranged from 12.86 to 5.51 mg/g. This is attributed to the ion exchange reaction between phosphate ions and the hydroxide of Fe (III). The decrease in the adsorption capacity of the adsorbent is ascribed to an ion-exchange mechanism in which the co-existing ions possessed the highest affinity for the adsorbent material and compete with phosphate for the adsorption site (Zhou et al., 2012).

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Materials and Chemicals

3.1.1. Materials/ Equipment's

For the synthesis and characterization of BBC and Ca-BBC, and to analyze their physiochemical properties, different materials/equipment namely, analytical balance, water bath, pH meter, spatula, ball mill, hot plate, sieve, measuring cylinder, beaker, grinder, jaw crusher, temperature controlled reactor/oven, magnetic stirrer, centrifuge, furnace, flask, vacuum pump, and mixer were used. Instruments such as fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), surface area and pore size analyzer (BET), powder X-ray diffraction (XRD) and ultraviolet–visible (UV–visible) spectrophotometer were also used for analysis purposes.

3.1.2. Chemicals

The raw bone for this study was collected from a local butcher shop located in Adama, Ethiopia. All chemicals used in this study were of analytical grade. Potassium dihydrogen phosphate (KH_2PO_4 , 99.0%), potassium nitrate (KNO_3 , 99.0%), sodium chloride (NaCl , 99.0%), sodium carbonate (NaCO_3 , 99.5%), potassium sulfate (KSO_3 , 99.0%) and sodium fluoride (NaF , 99.0%), were dissolved in deionized water to prepare phosphate, nitrate, chloride, carbonate, sulfate, and fluoride stock solutions (1000 mg/L each), respectively. During the experimental work, the pH was adjusted using diluted (0.1 M) hydrochloric acid (HCl , 37.0%) and sodium hydroxide (NaOH , 99.0%). Calcium chloride (CaCl_2 , 99.0%) was used to modify bone-derived biochar for the synthesis of calcium-decorated adsorbents. All the above chemicals, ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$, 96.0%), acetone ($\text{C}_3\text{H}_6\text{O}$, 99.5%), deionized water, and other analytical chemical reagents were used from Adama Science and Technology University (ASTU) Chemical Engineering Department Laboratory. The reagents that were used to determine the initial and final concentration of phosphate from water (i.e. PhosVer ® 3 phosphate reagent powder pillows) for a 10 mL sample were purchased from Astra Lab Trading PLC Addis Ababa, Ethiopia.

3.1.3. Wastewater Sample

The wastewater effluent used in this study was collected from the ASTU wastewater treatment plant, which is located in Adama, Ethiopia, in June 2023, the rainy season in the Ethiopian weather. Composite effluent samples were collected four times per day from 9:00 a.m. to 6:00 p.m. at 3-hour intervals. The effluent samples were collected using sterilized polyethylene bottles. After collecting the samples, the bottles were stoppered and immediately transported to the Laboratory of the Department of Chemical Engineering, Adama Science and Technology University (Ethiopia). Suspended solids in the collected wastewater were removed by filtrating with the membrane filter and stored at 4°C for systematic analysis. The physicochemical characteristics and the number of ions present in the samples were analyzed using wastewater examination standard methods (APHA, 2005).

3.2. Methods

3.2.1. Pretreatment and Synthesis of Bone-derived Biochar (BBC)

3.2.1.1. Pretreatment of Raw Bone

The used bones carry different impurities including lipids or oil contents and traces of other food materials. Hence, pre-treatment was conducted to remove the attached impurities (Rojas-Mayorga et al., 2015). The bones were cut into uniform segments and cleaned thoroughly with fresh water several times and then, boiled in fresh water at 90 °C for 24 hr using a thermostat water bath (model HH-6) to remove the traces of protein and fats. The cleaned bones were then oven-dried at 105 °C overnight. The dried bone was first ground using a jaw crusher (SPEM 01, India) to decrease the size, then further ground with a grinder to obtain the required size for 2 minutes. The preparation of the ball meal sieved (mechanical sieve, CEN-MKII-00-A, Germany) with a size of (1.0 to 2.0 mm), followed by soaking in 0.1 M HCl solution for 1 hr as shown in Figure 3.1. This procedure resulted in a bone meal with high purity on the surface and enhanced the quality of the bone char, without changing the mass and chemical composition of the material (Nigri et al., 2017). Then, the bone meal was washed with deionized water and ethanol three times, to remove the excess acid present on the surface, and oven-dried at 80 °C for 24 hr, stored in air-tight low-density polyethylene (LDPE) zipper bags for use.

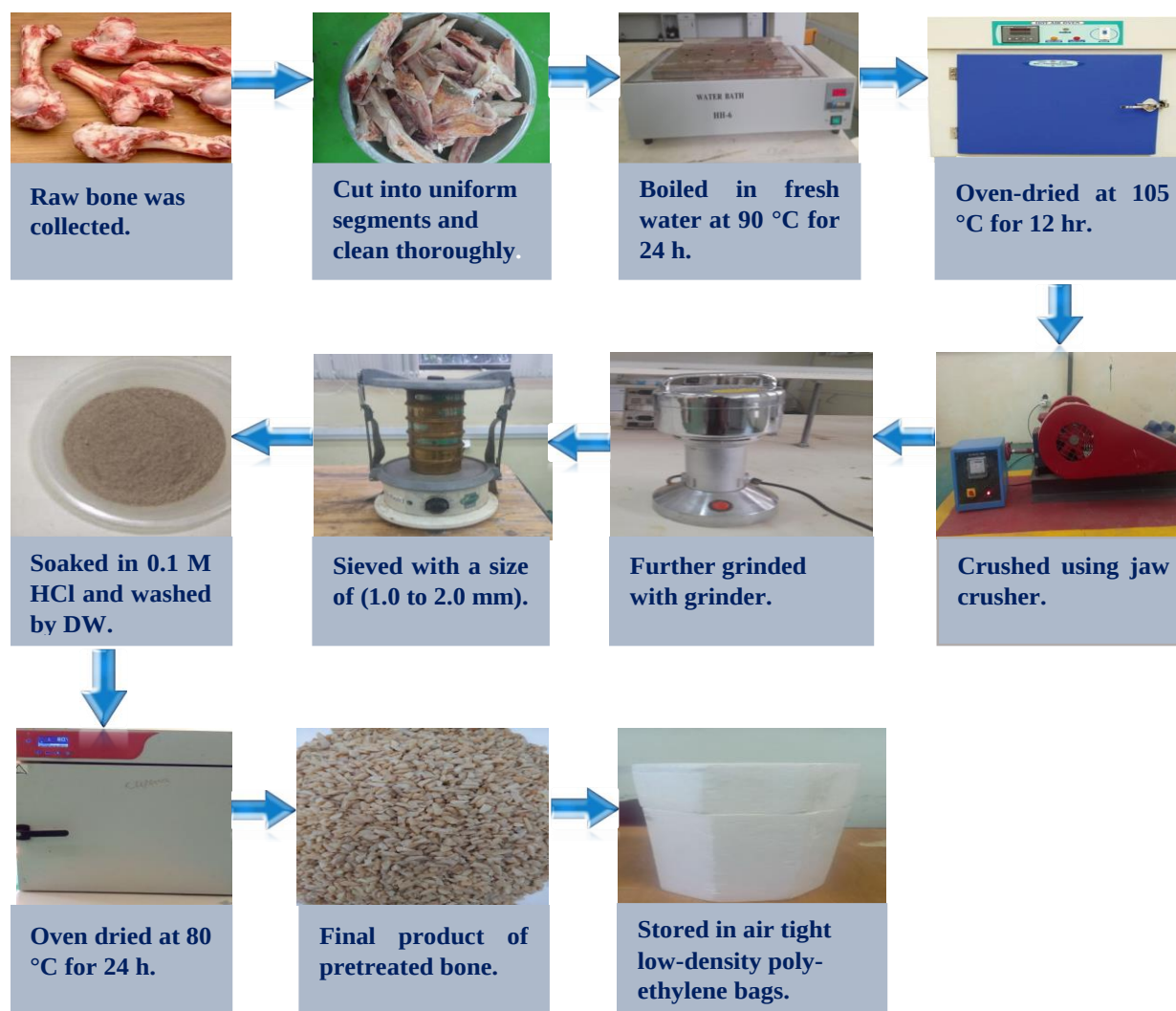


Figure 3.1: Thermal and acidic pretreatment bone for the synthesis of BBC

3.2.1.2. Synthesis of Bone-derived Biochar (BBC)

The pyrolysis process of the pre-treated bone was conducted by adding 30 grams of bone meal into a porcelain capsule and then placing the capsule in an electric muffle furnace model SX-2.5-12. The effect of its synthesizing factors on the efficiency of phosphate removal was varied using the one-factor-at-a-time (OFAT) method. Pretreated raw bone was pyrolyzed at temperatures (400-800 °C) and pyrolysis times (1-4 hr) with a heating rate of 10 °C/min. Bone-derived biochar (BBC) was left to cool down at room temperature and conserved in a desiccator. Then, the BBC was ground in a ball mill (Idar- Oberstein, Germany) with a speed of 200 rpm for 1hr and sieved to different particle size fractions (250–355 µm) as shown in Figure 3.2. Finally, the samples

were stored in a sealed plastic container. The BBC samples obtained at pyrolysis temperatures of 400, 500, 600, 700, and 800 °C were labeled as BBC400, BBC500, BBC600, BBC700, and BBC800 respectively. Preliminary duplicate adsorption tests were conducted using these all adsorbents to select BBC with the highest adsorption efficiency for further calcium modification.

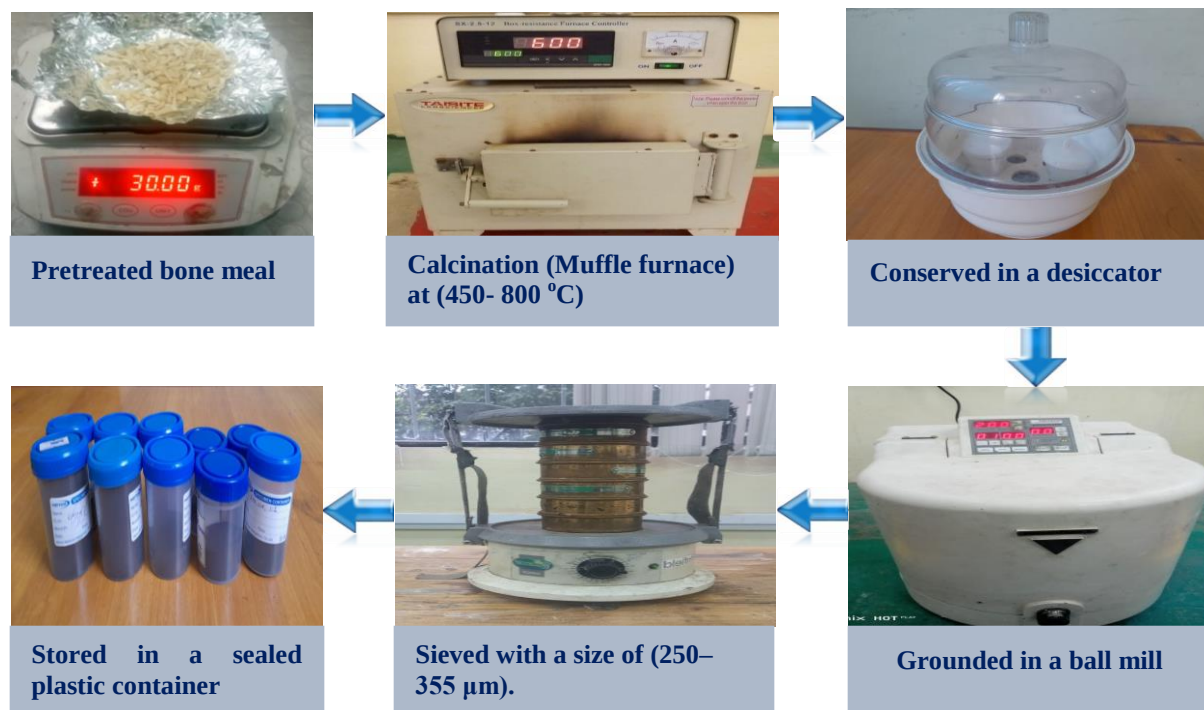


Figure 3.2: Synthesis of bone-derived biochar (BBC) from pretreated bone meal

3.2.2. Modification of Bone-derived Biochar (BBC)

The Ca-BBC was prepared by using a method modified from those for coating calcium onto biochar at room temperature as reported by Choi et al., (2019). For decoration of calcium ions onto pyrolyzed BBC under ambient conditions, first, the predetermined weight of CaCl_2 and BBC were mixed in varied mass ratios of 1:2, 1:1, 2:1, and 4:1. Subsequently, deionized water was added to form dilute gels and stirred by mixer (SciQuip pro- 40, Germany) with speed 200 rpm for 24 hr at 25 °C as shown in Figure 3.3. While the calcium ions from the CaCl_2 solution were fully mixed with the pyrolyzed BBC, they were reacted with the hydroxyl groups of BBCs to make calcium hydroxide on the surface as shown in Equation 3.1:



After that, the pyrolyzed BBC coated with calcium hydroxide was separated by centrifugation (x 4,000 g, 30 min) and placed in an oven for drying at 80°C for 24 hr and conserved in a desiccator and named Ca-BBC (1:2), Ca-BBC (1:1), Ca-BBC (2:1) and Ca-BBC (4:1) according to the mixed ratio of CaCl_2 to BBC, where the values in the parentheses represented the ratios. The bone char in the absence of Ca was named BBC and used as blank or control. The treated adsorbent showed the best phosphate removal efficiency in preliminary duplicate adsorption tests that were used to select suitable adsorbents for subsequent adsorption tests.

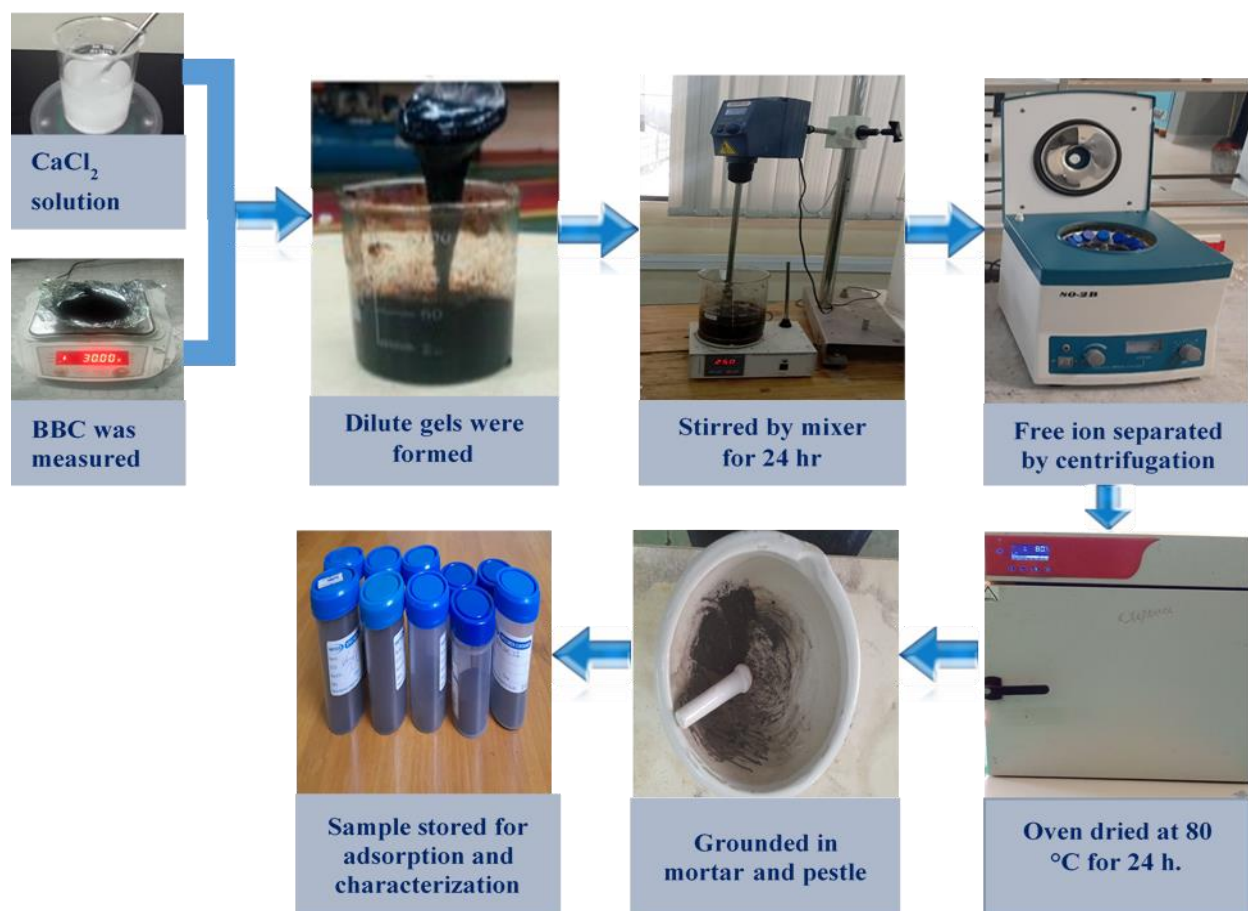


Figure 3.3: Modification of bone-derived biochar (BBC) by decorating with calcium ion to form Ca-BBC.

3.2.3. Characterizations and Analytical Methods

3.2.3.1. Characterizations

Different characterization methods were used to examine the properties of the BBC, Ca-BBC before and after adsorption. All the measurements in this study were performed in duplicate to ensure the quality and repeatability of the work.

FTIR analysis: The surface functional groups of modified bone-derived biochar samples before and after adsorption were examined with a Fourier-transform infrared spectroscopy (FT-IR). The attenuated total reflectance FTIR with model name FTIR-6600 type A and serial number A013861790 in the range of 4000 to 500 cm^{-1} was used. The sample for the FTIR analysis was prepared by weighting the amounts of sample, 1 gm, and Potassium Bromide (KBr) powder, 100 gm into an agate mortar. The FTIR pattern is plotted within the FTIR machine by generating the transmittance peaks (%) as the Y-axis versus wavenumber (cm^{-1}) as the X-axis.

XRD analysis: The crystallographic structure in raw bone and modified bone-derived biochar before and after adsorption were identified by X-ray diffraction (XRD) analysis model Shimadzu XRD-7000 x-ray diffractometer using $\text{Cu-K}\alpha$ radiation. The measurement condition for each test includes voltage = 40.0 (kV), current = 30.0 (mA), and scan range from 10.00 to 70.00 with 0.02 step size.

TGA analysis: The thermogravimetric analysis and the thermal stability of raw bone samples were carried out using a thermogravimetric analyzer (Beijing, HCT-1, TGA). The Nitrogen gas was used as carrier gas and the heating rate was set at 20°C/min to determine the thermal stability of 10 mg of raw bone. The temperature was adjusted between 100 °C to 1100 °C and the decomposition of sample weight (%) against temperature (°C) was recorded. This analysis resulted in two types of curves, the TGA curve and the derivative of the Thermogravimetric (DTG) curve.

SEM analysis: A scanning electron microscope (JCM-6000PLUS Bench Top SEM, JEOL, Japan) was employed to visualize the surface morphology and structure of the Ca-BBC before and after adsorption. The procedure of analysis includes a 30 mg specimen mounted on a metal stub using a sticky carbon tape, which increases conductivity. The clip holds the sample securely

and the clip does not obscure any area that you intend to image. The specimen must be electrically grounded to the sample holder to minimize specimen charging. Specimen exchange, evacuation, and automatic adjustment of the image were carried out for photographing and finally, the image was saved.

BET analysis: The textural properties of BBC and Ca-BBC (surface area, pore volume, and average pore diameter) were determined by the N₂-BET method using a surface area and porosimetry analyzer (SA-9600 Series, Horiba Instruments, Inc.) at 200 °C degassing temperature for 2 hr in the presence of nitrogen gas.

UV/vis spectrophotometer analysis: The phosphate concentration (initial and final), and nitrate concentration were determined using the UV–Vis spectrophotometer (Hach DR6000TM, LPV441.99.00002, USA). Wastewater alkalinity was analyzed using a digital burette (model AL-DT). In addition, fluoride concentration in the real wastewater was analyzed using an ion-selective electrode.

3.2.3.2. Analytical Methods

Proximate analysis: Proximate analysis of the bone samples, and Ca-BBC including moisture content, volatile matter, ash content, and fixed carbon was conducted following ASTM standards (ASTM D1762-84). One gram of sample was placed in the oven at 105 °C and allowed overnight to determine the moisture content. The crucible and its content were retrieved and cooled in a desiccator. The difference in mass was recorded and the moisture content (MC) was calculated from Equation 3.2 as loss in mass on drying divided by the initial weight of the sample multiplied by 100.

$$MC = \frac{W_w - W_d}{W_w} * 100 \dots\dots\dots (3.2)$$

where W_w is the weight of the bone sample before drying in grams, w_d is the weight of dried bone in grams, MC is moisture content.

The dried samples were utilized to determine the volatile matter by calculating weight differences before and after heating samples in covered crucibles, using a programmable muffle

furnace at 950 °C for 11 minutes. The volatile matter content was determined using Equation 3.3:

$$\%VM = \frac{W_1 - W_2}{W_1 - W_3} * 100 \dots\dots\dots(3.3)$$

where, %VM = percentage of volatile matter content, W_1 = weight of sample and crucible before heating, W_2 = weight of sample and crucible after heating, W_3 = weight of empty crucible.

The same procedure was applied to determine the ash content; however, the furnace temperature was set at a temperature of 700 °C and the sample crucibles were not covered (Alkurdi et al., 2020). After heating, the sample was removed, cooled in a desiccator, and then weighed to obtain a new weight (w_2). The ash content was then determined by applying Equation 3.4:

$$\%ash = \frac{W_2 - W_3}{W_1 - W_3} * 100 \dots\dots\dots (3.4)$$

where, W_1 = Mass of crucible + sample before heating

W_2 = Mass of crucible + ash sample after heating, W_3 =Mass of empty crucible

Fixed carbon is a calculated value and it is obtained by subtracting the summation of percentage of moisture content, ash content, and volatile matter content from 100 (Equation 3.5).

$$\% \text{ fixed carbon} = 100 - (\% \text{ moisture} + \% \text{ ash} + \% \text{ volatile matter}) \dots\dots\dots(3.5)$$

Point zero charge (PZC) analysis: The values of pH at the point of zero charge (pH_{pzc}) for the Ca-BBC were determined using a salt addition method previously described by Choi et al., (2019). 0.1 g of dry Ca-BBC sample and 50 mL of 0.1 M KCl solution were mixed in different 100 mL of Erlenmeyer flasks. The initial pH of the mixture solution was adjusted to the range of 3-11 using either 1 M HCl or 1 M NaOH solutions. Each flask was vigorously agitated in a water bath shaker for 24 h at 30 °C. After that, the suspensions were settled down and the final pH was measured immediately as shown in Figure 3.4. The differences between final and initial pH values (ΔpH) were calculated and plotted against the initial pH values. Therefore, the initial pH at which ΔpH is zero is the pH_{pzc} value. The pH of the solutions was monitored on a pH meter (Spectronics, India).

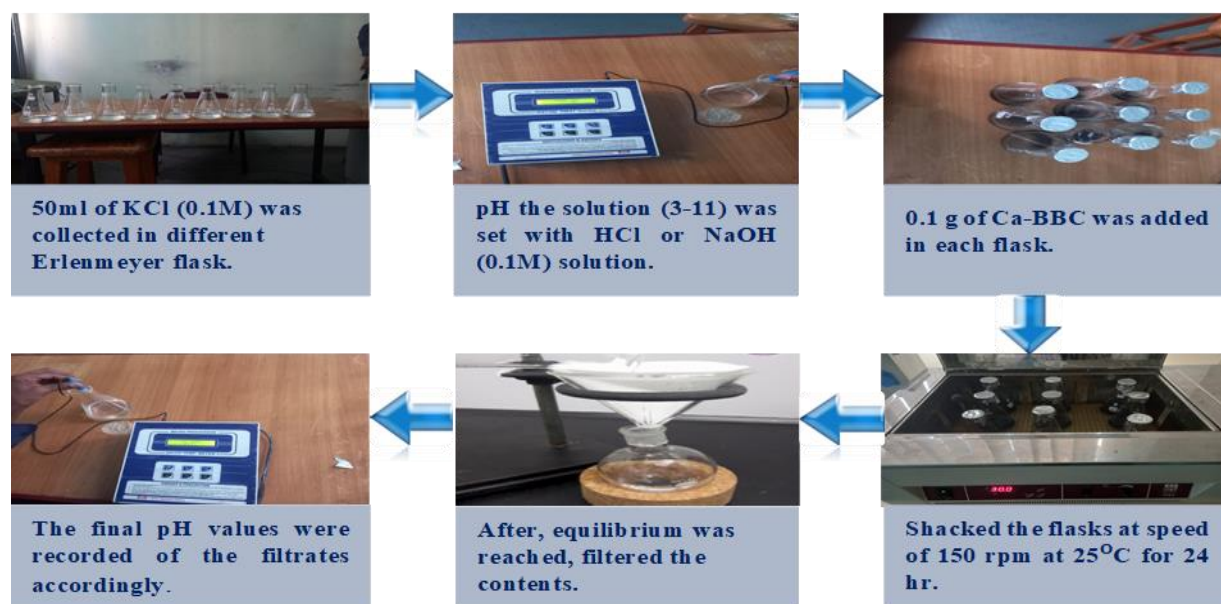


Figure 3.4: Point zero charge analysis of Ca-BBC using the salt addition method

3.2.4. Experimental Design for Phosphate Removal

Design Expert® version 13 software was used to randomize the design of the experiment and analysis of variance (ANOVA) was used to study the statistical significance of the experimental data. In this experimental design, 3 factors (i.e. pH, contact time and adsorbent dosage) with 2 levels selected among the parameters that affect the adsorption of phosphate. Considering these parameters, the design was composed of 2^k factorial points augmented by 2^k axial points and a center point where k is the number of variables. Thus, 20 experiments ($2^k + 2k + 6 = 20$) were performed. The central composite design (CCD) approach, which can provide useful information regarding the interplay between 3 important factors was selected and used (Fang et al., 2018). The biggest merit of this type of optimization model is its accuracy and no need for 3 levels factorial experiment to develop a quadratic model (Bhattacharya, 2021). Moreover, it turns out to be the extension of the 2-level factorial or fractional factorial design and estimates the nonlinearity of responses in the given data set. CCD is not only used to estimate curvature in obtained continuous response but also gives maximum information in a minimum experimental trial. Reduction in the number of trials required to estimate the squared terms in the second-order model. The levels of each factor are tabulated in

the following Table 3.1, below, and the levels of factors were valued based on the preliminary experimental results, illustrated in Appendix A.

Table 3.1: Experimental levels of the independent variables

S. No	Factor	Unit	Level	
			Low	High
1	Adsorbent Dosage	g/L	1	5
2	pH	-	3	12
3	Contact time	hr	3	11

Response surface methodology (RSM) based on CCD was adopted to study the interaction effect between three independent variables to optimize the removal efficiency of phosphate. To perform optimization in the process the fundamental tasks are screening, and identifying the significant factors.

The second-order quadratic polynomial equation was used to determine the interactions of the aforementioned experimental factors, with the phosphate removal efficiency (R%) as the experimental response. The presented response could be defined qualitatively as shown in Equation 3.6:

$$R(\%) = \beta_0 + \sum \beta_i x_i + \sum \beta_{ij} x_i x_j + \sum \beta_{ii} x_i^2 \dots\dots\dots (3.6)$$

where X_i , β_0 , β_i , β_{ii} , and β_{ij} are the input experimental parameters, the constant co-efficient, the linear co-efficient, the quadratic co-efficient, and the interactive co-efficient, respectively. More specifically, polynomial quadratic Equation 3.6 was rewritten as shown in Equation 3.7 by including experimental factors.

$$y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC \dots\dots\dots (3.7)$$

where A, B, and C, are linear effects, A_2 , B_2 , and C_2 are squared effects, AB, AC, BC are interaction effects and Y is the predicted response. β_0 is constant coefficient, β_1 , β_2 , β_3 , are linear coefficients, β_{11} , β_{22} , β_{33} are squared coefficients, and β_{12} , β_{13} , β_{23} are interactive coefficients, respectively. The overall process of designing an expert analysis flow chart for the optimization process is articulated in Figure 3.5.

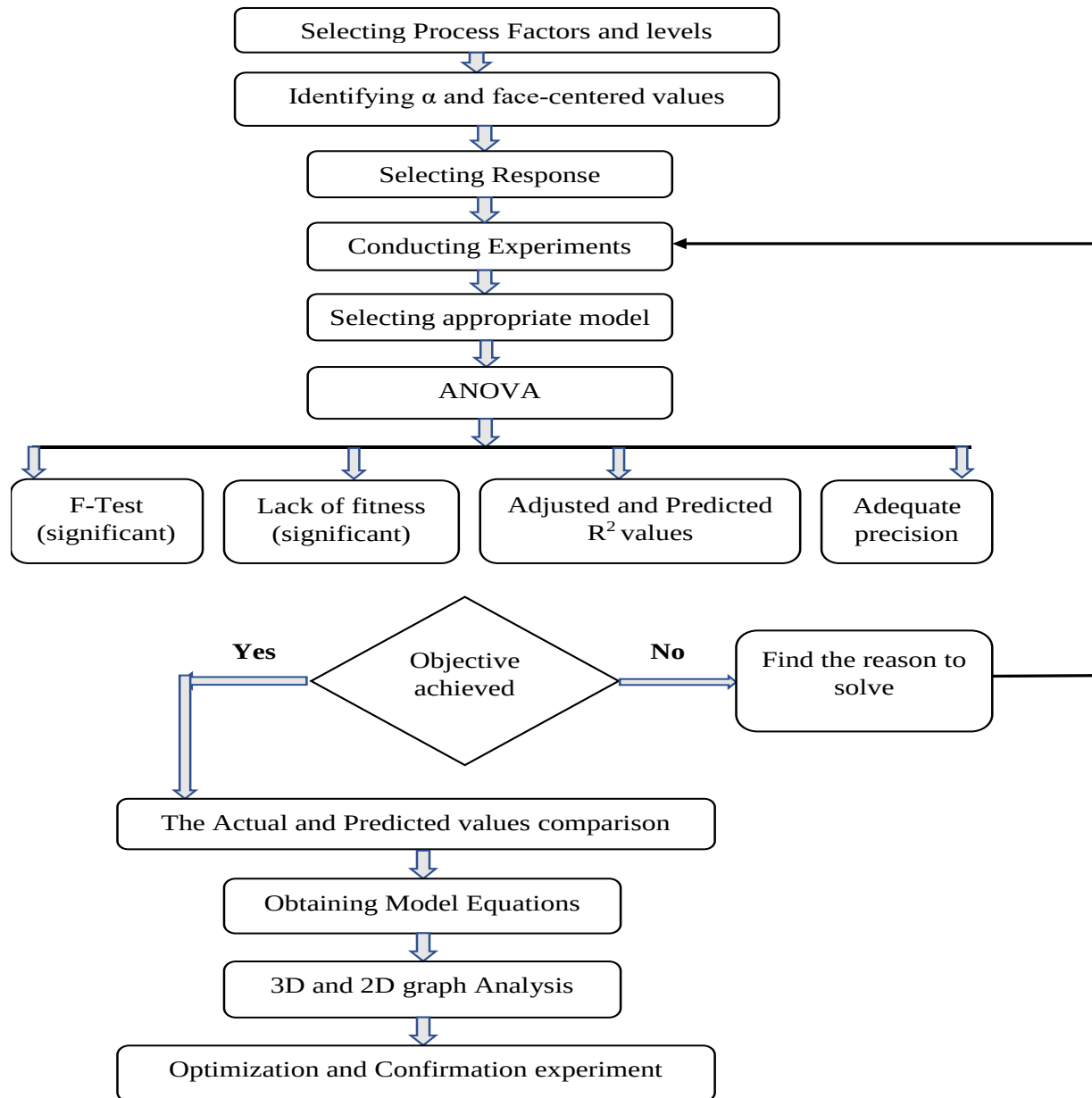


Figure 3.5: Design expert analysis flow chart for the optimization process

3.2.5. Batch Adsorption Experiments

Phosphate adsorption experiments were carried out using BBCs and Ca-BBCs synthesized under different conditions. An optimal synthesizing factor was selected based on findings involving synthetic water and further was used to optimize the adsorption factor and examine its performance on the waste water sample. A stock solution containing $1000 \text{ mg L}^{-1} \text{ P}$ was prepared by dissolving KH_2PO_4 in deionized water, and the desired solutions were prepared by diluting the stock solution (Gizaw et al., 2022b). The adsorption performance of the Ca-BBC towards phosphate was evaluated in the scenarios of experimental levels of the independent variables. The ranges for the experimental factors were fixed using reported experimental data. All batch adsorption experiments were performed in 500 ml Erlenmeyer flasks with a horizontal shaker (KS Oscillator, China) equipped with a thermostat at 150 rpm and at room temperature as shown in Figure 3.6.

In adsorption kinetic experiments, 3 g of the sample was added into 250 mL phosphate solution (5.0 mg/L phosphate) at room temperature. Then the mixture was agitated at different times (3, 5, 7, 9, 12, 15 hr), and analysis results were recorded. The experiment was performed at the initial pH of 7.5 in deionized water. Eventually, the phosphate removal efficiency ($R, \%$), was calculated by using Equation 3.8 (Kong et al., 2018):

$$R (\%) = \frac{C_0 - C_e}{C_0} * 100 \dots\dots\dots (3.8)$$

where R is the removal efficiency of phosphate Ca-BBC (%); C_0 and C_e are the initial and the equilibrium concentrations (mg/L) of phosphate. The phosphate concentration at 3, 5, 7, 9, 12, and 15 hours, was recorded and the phosphate adsorption amount (mg) per gram of the adsorbent at a different time ($q_t, \text{mg/g}$), was calculated by using Equation 3.9 (Mor et al., 2016):

$$q_t = (C_0 - C_t) * \frac{V}{M} \dots\dots\dots (3.9)$$

where C_0 and C_t (mg/L) are the phosphate concentrations at the initial and time t , respectively. V is the solution volume and M is the mass of Ca-BBC.

The adsorption isotherm experiments were carried out by adding 3g of adsorbent into 250 mL phosphate solutions with various concentrations (1, 15, 30, 45, 60, and 75 mg /L phosphate), then shacked the mixture in a horizontal shaker for 12 hr, while the remaining conditions were consistent with the above experiment. Afterward, each sample was separated using Whatman No.1 filter paper.

The phosphate concentrations before and after adsorption were detected by using the UV–Vis spectrophotometer (Hach DR6000TM, LPV441.99.00002, USA). The phosphate adsorption amount (mg) per gram of adsorbent (q_e , mg/g) at equilibrium was determined by using Equation. 3.10 (H. Yin et al., 2011):

$$q_e = (C_o - C_e) * \frac{V}{M} \dots\dots\dots (3.10)$$

where C_e (mg/L) is the phosphate concentration at equilibrium.

The effect of competitive anions Cl^- , F^- , SO_4^{2-} , and HCO_3^- , on phosphate adsorption was evaluated separately with various concentrations of ions (5.0 and 25.0 mg/L). All experiments were carried out at pH 7.5 with a 3 g absorbent dosage while keeping the initial phosphate concentration fixed at 5 mg/L. Moreover, at the end of each experiment, the sample filtration was followed by the determination of the phosphate removal efficiency.

3.2.6. Kinetic and Isotherm Mathematical Models

The adsorption kinetics data were simulated using pseudo-first-order, pseudo-second-order, and intra-particle diffusion models. Governing equations for these models are given as shown in Equation 3.11-3.13 (Sabzehmeidani et al., 2021):

$$\text{Pseudo-first-order: } \log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \dots\dots\dots (3.11)$$

$$\text{Pseudo-second-order: } q_t = \frac{q_e^2 k_2 t}{1 + q_e^2 k_2 t} \dots\dots\dots (3.12)$$

$$\text{Intra-particle diffusion: } q_t = k_p t^{0.5} + C \dots\dots\dots (3.13)$$

where q_t and q_e are the amount of sorbate removed at time t and equilibrium (mg/g), respectively. k_1 and k_2 are the first-order and second-order sorption rate constants (hr^{-1}), respectively. α is the initial sorption rate (mg/g) and K_p is the intra-particle diffusion constant ($\text{mg/g.hr}^{0.5}$).

The adsorption isotherms were simulated using the Langmuir, Freundlich, and Temkin models. Governing equations for these models are given as shown in Equations 3.14 and 3.15 (Sabzehmeidani et al., 2021):

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{1}{k_1 q_{\max}} + \frac{1}{q_{\max}} C_e \dots\dots\dots (3.14)$$

$$\text{Freundlich: } \log q_t = \log k_F + \frac{1}{n} C_e \dots\dots\dots (3.15)$$

where K and K_F are the Langmuir binding term related to interaction energies (L/mg) and the Freundlich affinity coefficient ($((\text{mg/g})(1/\text{mg})^{1/n})$), respectively. $q_{\max}$ is the Langmuir maximum capacity (mg/g), C_e is the equilibrium solution concentration (mg/L) of the sorbate, and n is the Freundlich linearity constant.

Temkin isotherm model can relate the effects of indirect adsorbate/adsorbate interactions on the adsorption process; it is also assumed that the heat of adsorption of all molecules in the layer decreases linearly as a result of increased surface coverage (Ayawei et al., 2017). This isotherm consists of an aspect that explicitly takes into consideration of adsorbent – adsorbate interactions by ignoring the extremely low and huge value of concentrations, the model assumes that heat of adsorption (function of temperature) of all molecules within the layer would decrease linearly instead of logarithmic with coverage (Dada et al., 2021). The linear form of the Temkin isotherm model is given by the following equations. The adsorption parameters (A_T and β) were determined from the slope and intercept of the q_e versus $\ln C_e$ plot based on the linearized are given as shown in Equation 3.16 and 3.17 (Ayawei et al., 2017):

$$\text{Temkin: } q_e = \frac{RT}{bT} \ln A_T + \frac{RT}{bT} \ln C_e \dots\dots\dots (3.16)$$

$$q_e = \beta \ln A_T + \beta \ln C_e \dots\dots\dots (3.17)$$

where A_T is Temkin isotherm equilibrium binding constant (L/g), bT is Temkin isotherm constant, R is the universal gas constant (8.314J/mol.k), T is the temperature (298 k) and, β is constantly related to the heat of adsorption (J/mol).



Figure 3.6: Adsorption of phosphate by using Ca-BBC as an adsorbent

3.2.7. Adsorption of Phosphate onto Ca-BBC in Real Wastewater

The phosphate adsorption capacities of the Ca-BBC were evaluated by vigorously stirring 3g of adsorbent with 250 mL real wastewater without any pH adjustment (initial pH of wastewater) for 12 hr at room temperature. After 12 hr of adsorption, the samples were filtrated through a Whatman No.1 filter paper to determine the final concentration of phosphate. preliminary tests indicated that this type of filter paper could completely separate the Ca-BBC particles from

water. The adsorption experiments were conducted at least in duplicate to ensure the performance of Ca-BBC on the efficiency of phosphate removal from a real wastewater sample.

3.2.8. Desorption and Regeneration Experiments

To study phosphate adsorption desorption, phosphate-saturated Ca-BBC was separated from the saturated solution, and dried in an oven at 60 °C for 24 hr. Afterward, the saturated Ca-BBC was abundantly added into 1 M NaOH (Jia et al., 2020), at constant stirring and temperature (200 rpm and 25 °C) over 24 hr to remove the excess phosphate on the adsorbent surface, then filtered and washed using deionized water until the stabilization of the pH (around 7). The saturated sorbent was dried in an oven at 60 °C for 24 hr and stored for subsequent use as shown in Figure 3.7 below. Regeneration studies were then conducted using the saturated Ca-BBC. A new sorption cycle using 5 mg/L phosphate solution and an adsorbent dosage of 3g, under constant stirring and temperature (200 rpm and 25 °C) for 12 hr was also performed with the regenerated Ca-BBC. A similar step was repeated for the subsequent cycles of this study.

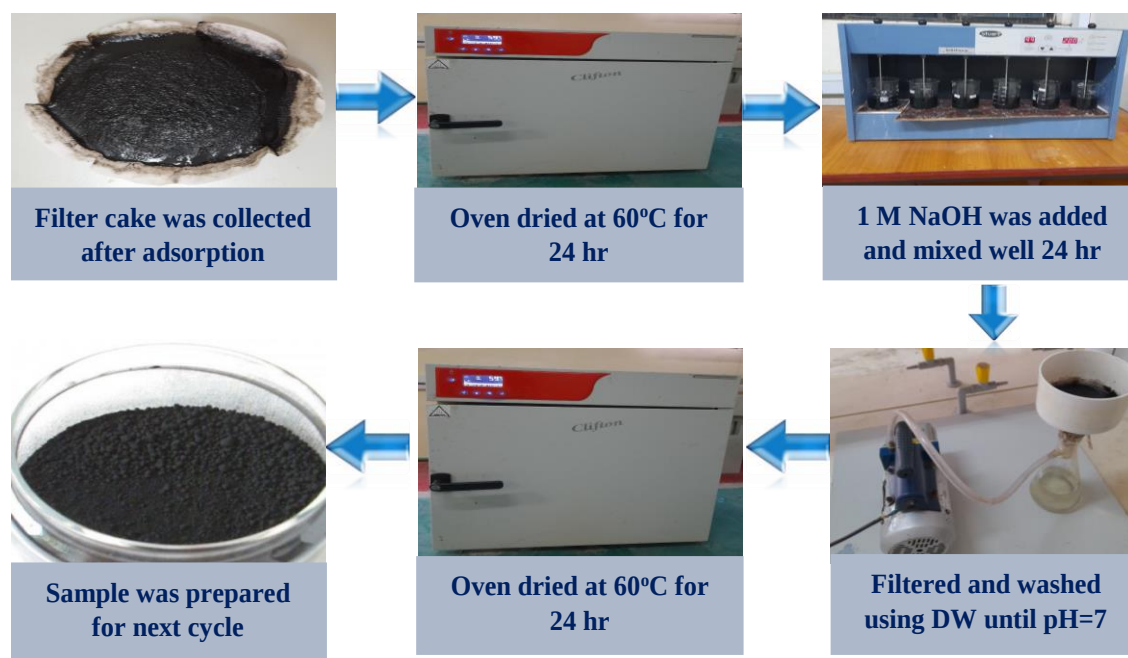


Figure 3.7: Desorption and regeneration experiments of Ca-BBC for one cycle

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1. Optimum Conditions for Synthesis of Adsorbents

4.1.1. Effect of the Pyrolysis Temperature

The effect of the pyrolysis temperature on the phosphate removal efficiency was investigated at different pyrolysis temperatures of 400, 500, 600, 700, and 800 °C. The greatest error measured across duplicate trials was 0.029 (2.9%), which is less than 0.05 (5%). During this experiment, the pyrolysis time, mixing ratio, initial phosphate concentration, contact time, adsorbent dosage, and solution pH were kept constant at 2 hr, 1:1, 5 mg/L, 6 hr, 2 g/L, and 7 respectively. As shown in Figure 4.1, the phosphate removal efficiency increased from 57.4 to 76.2 % as the pyrolysis temperature raised from 400 to 600 °C. This was due to low temperatures, below 500 °C caused more organic matter originally in the bone matrix to be added to the treated water due to inadequate removal of organic matter in the bone structure (Alkurdi et al., 2019). However, with further increased temperatures from 600-800 °C, the phosphate removal efficiency decreased from 76.2 to 53.2 %. According to Rojas-Mayorga et al., (2015), increasing the temperature from 650 °C to 1000 °C caused a gradual color change of the bone to white was observed, indicating the total elimination of organic content in the bone char structure, lowering removal efficiency. At lower pyrolysis temperatures an increase in temperature might help to increase pore volume and surface area on the adsorbent and the reverse is expected beyond the optimum pyrolysis temperature. Thus, to get the best removal efficiency of phosphate, a pyrolysis temperature of 600 °C was selected and used in the consequent experiments.

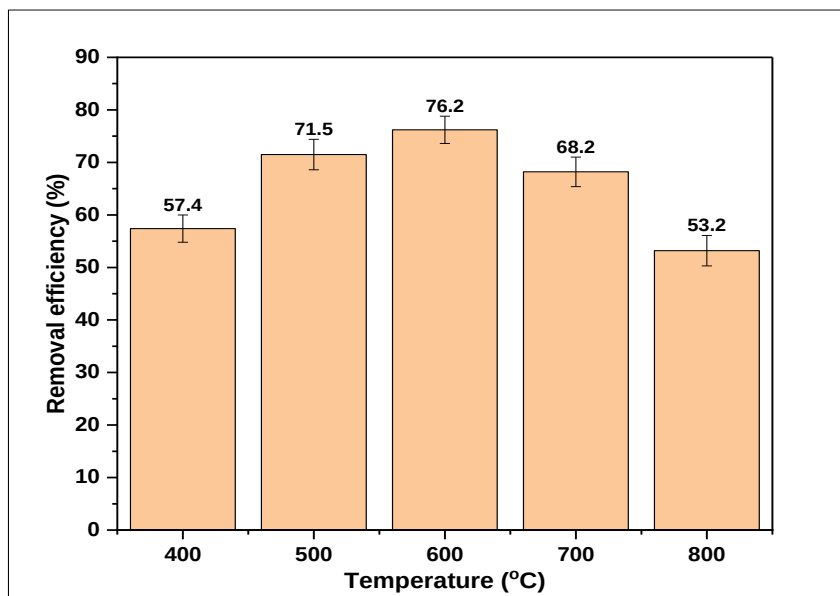


Figure 4.1: Effect of pyrolysis temperature on phosphate removal efficiency

4.1.2. Effect of Pyrolysis Time

To investigate the effect of pyrolysis time on the phosphate removal efficiency during the adsorption process, duplicate experiments were carried out (the maximum error observed was 0.042 or 4.2%). This experiment was employed at an initial phosphate concentration of 5 mg/L, a pyrolysis temperature of 600 °C, a mixing ratio of 1:1, a contact time of 6 hr, an adsorbent dosage of 2 g/L, and a pH of 7. While keeping these constant conditions, different pyrolysis times of 1, 2, 3, and 4 hr were varied and tested. As depicted in Figure 4.2, it was observed that phosphate removal efficiency increased at a time raised from 1 to 2hr, whereas an increase in the pyrolysis time beyond 2 hr, shown gradually decreased the phosphate removal efficiency. According to Alkurdi et al., (2019), lowering the pyrolysis time for BBC adsorbent synthesis resulted from incomplete conversion of raw bone to porous material, whereas further increased pyrolysis time beyond 2 hr caused the elimination of key organic matter for adsorption. Thus, a pyrolysis time of 2 hr was selected and used for the subsequent experiments.

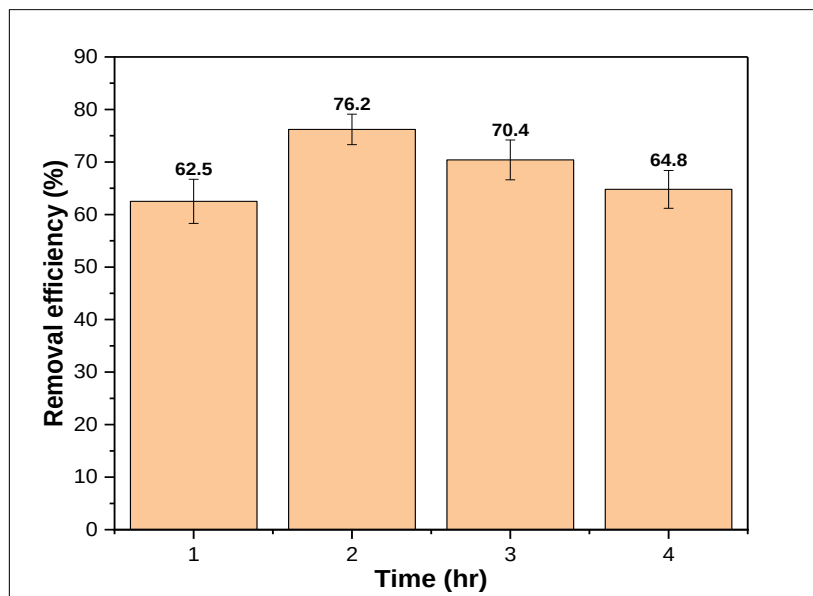


Figure 4.2: Effect of pyrolysis time on the removal efficiency of phosphate

4.1.3. Effect of Mixing Ratio

The effect of the mixing ratio on the phosphate removal efficiency was investigated at different calcium chloride to BBC mixing ratios of 2:1, 1:1, 1:2, and 1:4. The greatest error measured across duplicate trials was 0.027 (2.7%), which is less than 0.05 (5%). During this experiment, the pyrolysis temperature, pyrolysis time, initial phosphate concentration, contact time, adsorbent dosage, and solution pH were kept constant at 600 °C, 2 hr, 5 mg/L, 6 hr, 2 g/L, and 7 respectively. The Ca-BBC showed high phosphate removal efficiency than BBC as illustrated in Figure 4.3. Whereas, at all mixing ratios, it was observed that there a little change in the phosphate removal efficiency. Therefore, the results indicated that the calcium decorated on the surface of BBC made a significant contribution to the effective adsorption of phosphate in all mixing ratios. However, the mixing ratio at 2:1 was relatively better than others. Similar to this result, Wang et al., (2018) showed that a mixing ratio of 2:1 resulted in higher adsorption of phosphate on the Ca-impregnated biochar. Thus, a pyrolysis temperature of 600 °C, pyrolysis time of 2 hr, and mixing ratio of 2:1 were the optimum conditions for the synthesis of Ca-BBC adsorbent.

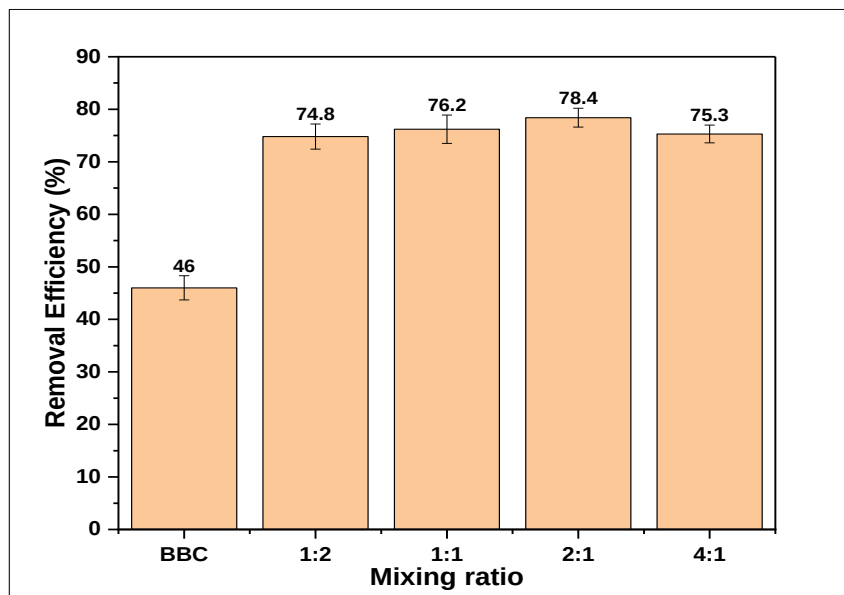


Figure 4.3: Effect of mixing ratio on the removal efficiency of phosphate

4.2. Characterization of Adsorbents

4.2.1. XRD Result Analysis

Figure 4.4 demonstrates the X-ray diffraction spectra of bone-derived biochar (BBC), Ca-BBC, and calcium hydroxide ($\text{Ca}(\text{OH})_2$). The results of phase analysis for calcium hydroxide (portlandite) particles have a consistent result within peaks that appear in the sample with the literature Joint Committee on Powder Diffraction Standards (JCPDS file, No. 00-004-0733) (Samanta et al., 2016). The XRD patterns of BBC showed that the diffraction peaks at $2\theta = 13.06^\circ$, 26.54° , 32° , 40° , and 53° corresponded to their crystal phase of hydroxyapatite, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (Leng et al., 2019). The angles that corresponded to the peaks at 2θ of 29.2° , represented the calcium carbonate crystal phase (Flores-Cano et al., 2016). The crystal phase of Ca-BBC was investigated after reacting with the hydroxyl groups of BBC to make calcium hydroxide during sample preparation. The peaks corresponded to the 2θ values of 17.5° , 33° , and 46° were typical characteristics of calcium hydroxide (Y. Choi et al., 2019). Additionally, the Ca-BBC XRD pattern at $2\theta = 26.5^\circ$ was attributed to apatite with higher crystallinity. This fact

revealed that the calcium metal successfully decorated onto BBC surface in the form of calcium hydroxide.

The XRD study was done to determine the portlandite (Ca(OH)_2) dried powder's crystal nature and phases to know whether the Ca^{2+} ion successfully binds with the hydroxyl group to form Ca(OH)_2 on the surface of BBC. The XRD pattern revealed several Bragg's reflections that could be labeled according to the portlandites' hexagonal structure. The crystalline phase of portlandite, represented by the angles of the peaks at 2θ of 17.5, 29.5, 33, 46, 54, and 64.36, was displayed in Figure 4.4. The XRD spectrum exhibited peaks corresponding to their crystal plane in a crystal lattice of 021, 104, 101, 221, 111, and 300 respectively. The result obtained was the same as the portlandite found by (Samanta et al., 2016).

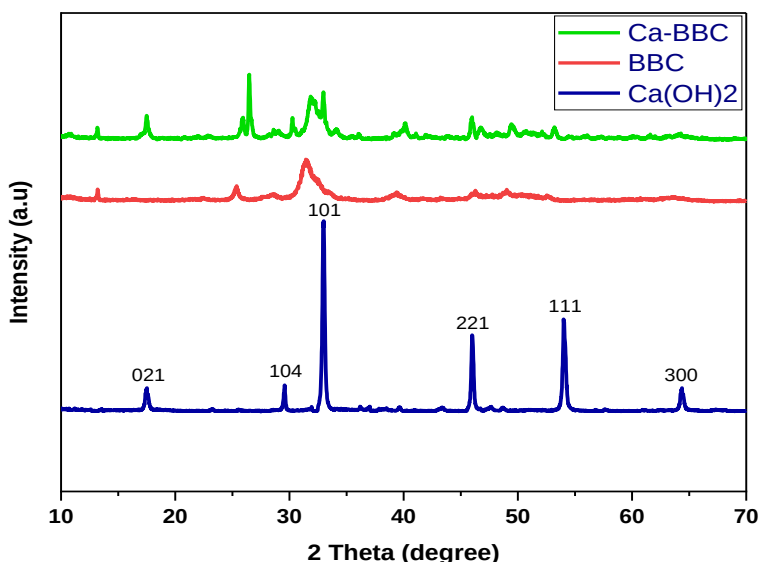


Figure 4.4: X-ray diffraction patterns of Ca(OH)_2 , BBC, and Ca-BBC

The crystalline phase of the Ca-BBC composite before and after adsorption was investigated using X-ray diffraction. Figure 4.5 illustrated that peaks corresponding to the 2θ values of 17.5° , 33° , and 46° represented Ca(OH)_2 in Ca-BBC before adsorption were close to disappearing after adsorption. This was due to the formation of HAP, showing that phosphate was removed from wastewater in the form of HAP precipitation. Similar results were reported by (Leng et al., 2019). The smallest peaks around 22.8° , 48.2° , and 64° corresponded to CaCO_3 in the Ca-BBC before adsorption and its peak intensity almost gone after adsorption was due to its consumption

during phosphate adsorption. This suggests that Ca^{2+} ions are involved in the precipitation of phosphate (Karthikeyan & Meenakshi, 2019).

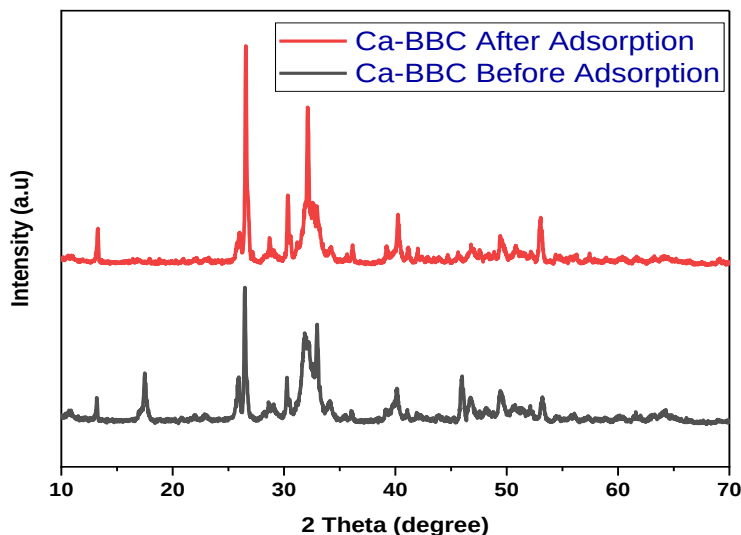


Figure 4.5: X-ray diffraction patterns of Ca-BBC Before and after adsorption

4.2.2. FTIR Analysis

The structural changes of the bone-derived biochar (BBC) sample, Ca-BBC before and after adsorption are depicted in Figure 4.6. The main FTIR absorption band of BBC and Ca-BBC at 3300 cm^{-1} represented hydroxyl stretching vibration (OH^-) (Medellin-Castillo et al., 2016). Additionally, the spectrum shows the bands related to hydroxyl bending vibration at 1635 cm^{-1} . Identification of these bands confirmed the existence of hydroxyapatite (Chagtmi et al., 2022), and more O-H of $\text{Ca}(\text{OH})_2$ formed during sample preparation (Y. Choi et al., 2019). According to Balan et al. (2021), the stretching frequencies of OH^- groups were mostly determined by the strength of hydrogen bonding and the nature of the adjacent cations. The smaller peaks around 1450 and 1411 cm^{-1} corresponded to CO_3^{2-} stretching vibration that demonstrated the sample contains calcium carbonate. Moreover, the peak around 872 cm^{-1} corresponded to CO_3^{2-} bending vibration, which was the same result found by Alkurdi et al., (2020). On the other side, the peak located at 1035 cm^{-1} was identified as the asymmetric stretching vibration of the HPO_4^{2-} groups, confirmed the presence of the some phosphate in the BBC and Ca-BBC samples. These results agreed with the research reported by Patel et al., (2015) and Medillin-castillo et al., (2016).

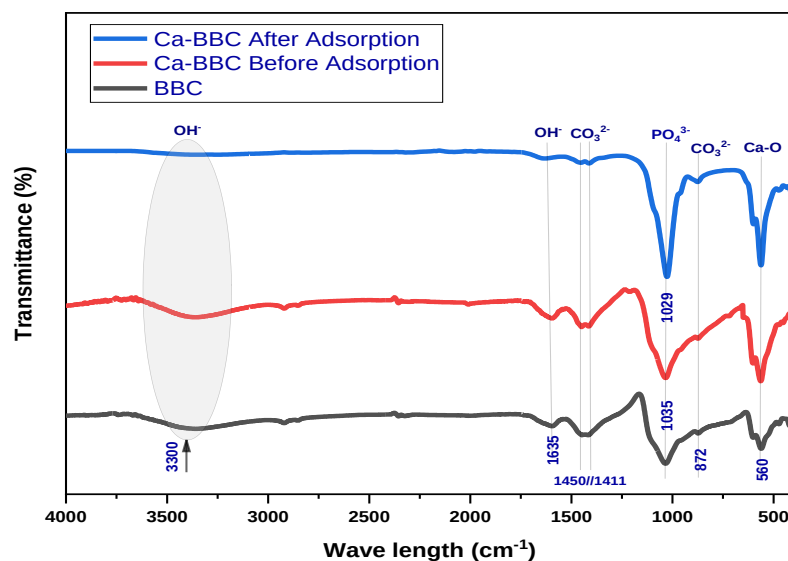


Figure 4.6: FTIR spectra of BBC, Ca-BBC before and after adsorption

The FTIR spectra of raw bone, synthesized BBC, and Ca-BBC samples are shown in Figure 4.7. Spectra of the raw bone samples had additional peaks, as aliphatic symmetric and asymmetric C–H stretching bands at around $2924//2864\text{ cm}^{-1}$ and composed of carboxylic acid C=O stretches at around 1747 cm^{-1} (Alkurdi et al., 2020; Chagtmi et al., 2022). However, Both peaks' intensities were decreased after synthesizing BBC and Ca-BBC. This was due to, the degradation of the organic functional group available in the bone structure during sample preparation at a pyrolysis temperature of $600\text{ }^{\circ}\text{C}$ (Rojas-Mayorga, Bonilla-Petriciolet, et al., 2015). The peak at the wavenumber around 560 cm^{-1} indicated the presence of Ca-O vibration groups in the bone structure. The formation of a sharp peak at the surface of Ca-BBC was observed around 560 cm^{-1} due to decorated calcium groups that could be found within the synthesized adsorbent in the form of $\text{Ca}(\text{OH})_2$. This result was confirmed by the XRD analysis results.

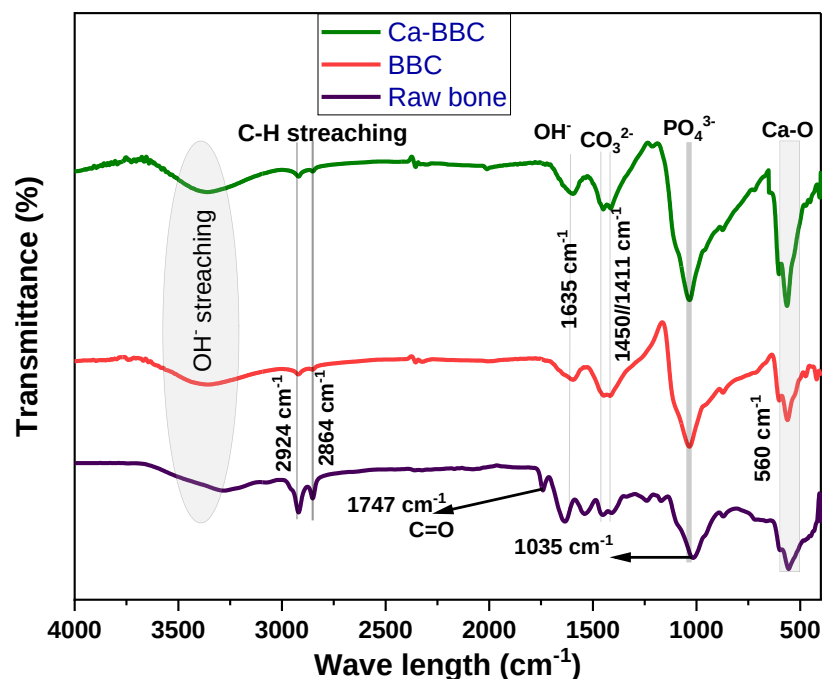


Figure 4.7: FTIR spectra of raw bone, BBC, and Ca-BBC

FTIR spectroscopy was conducted to identify the surface functional groups of Ca-BBC before and after the adsorption of phosphate ions from wastewater. As illustrated in Figure 4.8, the Ca-BBC before adsorption had more intensive peaks for symmetric stretching of O-H ($3420\text{--}3250\text{ cm}^{-1}$) and O-H bending (1599 cm^{-1}), which demonstrated that more O-H was observed during Ca-BBC preparation. However, The Ca-BBC after adsorption had little O-H and lowered C-O stretching vibration due to the formation of $\text{Ca}(\text{OH})_2$ -phosphate and C-O-phosphate complexation (Y.Choi et al., 2019). Thus, a large number of O-H groups on the Ca-BBC surface could contribute to the adsorption of phosphate.

A sharp band at 1016 cm^{-1} , attributed to the bending vibration of phosphates, appeared in the Ca-BBC after phosphate adsorption, as compared with Ca-BBC before adsorption. According to Daudzai et al., (2021), the peaks had appeared to confirm the formation of calcium phosphate complex, which indicated the true adsorption of phosphate onto Ca-BBC adsorbent. In addition, based on the spectra displayed in Figure 4.8, the O-H stretching vibration-related absorption broad peak at $3420\text{--}3250\text{ cm}^{-1}$ disappeared following the adsorption of phosphates. The disappearance of the O-H group suggested that the interaction of the O-H group with phosphates

could also be responsible for the favorable phosphate adsorption. Similar results were reported by (S. Wang et al., 2018). Thus, favorable phosphate adsorption could be achieved due to the bonding of $\text{Ca}(\text{OH})_2$ with PO_4^{3-} during phosphate adsorption at basic pH. This implied additional hydroxyapatite was formed on the surface adsorbent after adsorption. The results obtained in this experiment confirmed that the binding of phosphate with $\text{Ca}(\text{OH})_2$ to form HAP was the main determinant in the removal of phosphate from the wastewater. The outcome of this experiment was verified by the FTIR and XRD analysis results.

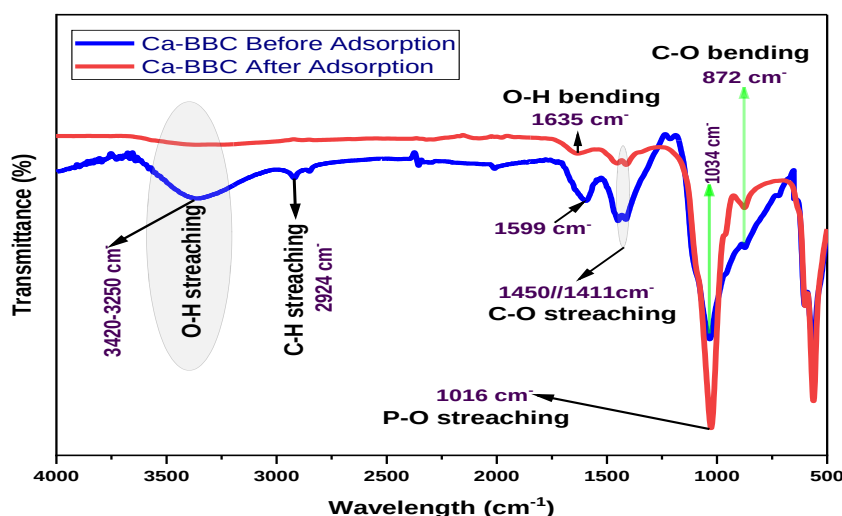


Figure 4.8: FTIR spectra of Ca-BBC before and after adsorption

4.2.3. BET Result Analysis

The specific surface area of BBC and Ca-BBC were determined using the Brunauer–Emmett–Teller (BET). The specific surface area of the Ca-BBC composite was found to be $331.478 \text{ m}^2/\text{g}$, which was relatively higher than the BBC of $327.675 \text{ m}^2/\text{g}$ as observed in Table 4.1. According to Delgadillo-Velasco et al., (2017) examinations of BBC following various modification techniques, showed that there were insignificant increases in the surface area. Thus, calcium ion was used to alter the functional groups of BBC to improve the adsorption capacity. This result was confirmed by FT-IR analyses. Chatterjee et al. (2018) reported that thermally treated bone meal with calcium oxide improved the adsorption capacity via altering surface functional groups in a way that enhanced the selectivity of the adsorbent towards specific contaminants rather than

significant change in the surface area, and pore volume. This was due to calcium aggregates deposited on the surface of BBC.

Table 4.1: BET surface property result for BBC and Ca-BBC composite

Sample	Surface area(m ² /g)	Pore volume (cm ³ /g)	Pore radius (Å ^o)
BBC	327.675	0.131	14.48
Ca-BBC	331.478	0.138	13.82

4.2.4. Scanning Electron Microscope (SEM) Analysis

Scanning Electron Microscope (SEM) investigated the morphological structures of Ca-BBC before and after adsorption. As illustrated in Figure 4.9 (a) the irregular pores of Ca-BBC were observed before adsorption. The surface of Ca-BBC shows a highly porous structure, which enables a suitable diffusion channel for phosphate adsorption. On the other side, as Figure 4.9 (b) demonstrated, an irregular collective surface was observed after adsorption. The external surface of Ca-BBC after adsorption was almost flat, dense, and agglomerated. The SEM images confirmed that pores might be occupied by precipitation of phosphate. This result was comparable agreement with the result reported by Rojas-Mayorga et al., (2016) who studied the application of bone char to heavy metal adsorption in aqueous solution.

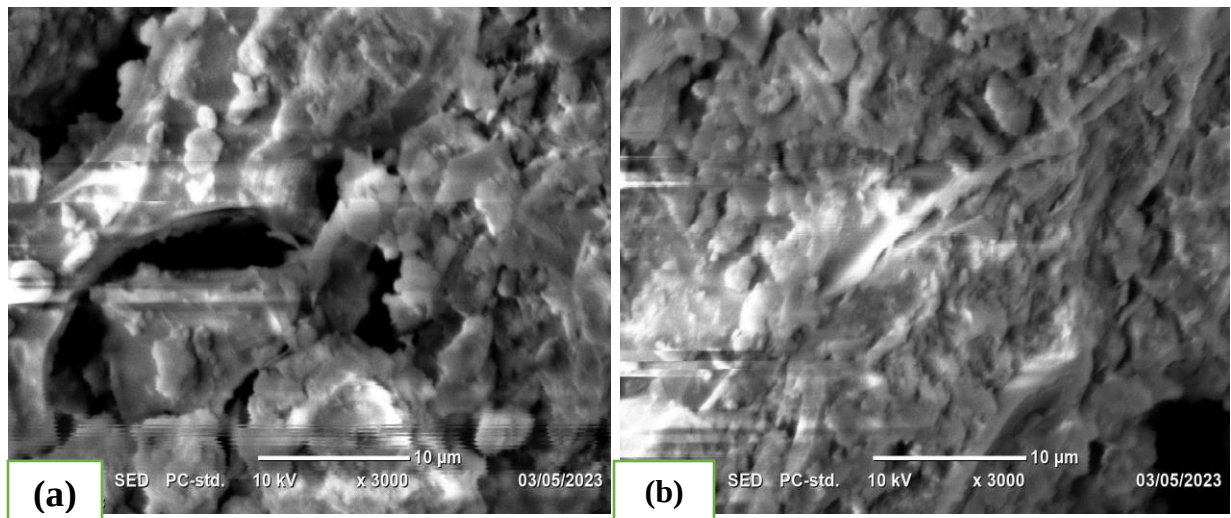


Figure 4.9: SEM image of Ca-BBC before and after adsorption

4.2.5. TGA Analysis of Raw Bone Meal

Thermogravimetric investigations are a useful tool for acquiring a more complete understanding of the thermal behavior of bone (Ellingham et al., 2015). As illustrated in Figure 4.10, the three distinct heating regimes resulted in varied weight losses at temperatures between 100–1100 °C. The initial phase of weight loss (dehydration), which occurred at temperatures ranging from 100 to 250 °C, was primarily due to water evaporation. The second and most severe weight loss phase (decomposition) was attributed to the igniting of organic components, which began the exothermic process of hydroxyapatite re-crystallization. According to Pramanik et al. (2013), the burning of the organic bone components, mainly collagen, triggers the second phase, which occurs between 200 °C and 600 °C. The TGA curve demonstrated that samples did not continue to lose weight between 600–750 °C. These temperatures created favorable conditions for increasing the specific surface area and total pore volume of the bone sample during the adsorption experiment (Rojas-Mayorga et al., 2015). The last organic substances were lost at around 800 °C, which was visible as a slight decrease on the TGA plot, and no further mass loss was observed above 850 °C. According to Mkukuma et al. (2004), the last weight-loss phase (inversion) was mostly caused by the release of CO₂ produced by carbonate breakdown, which is accompanied by the appearance of hydroxide ions.

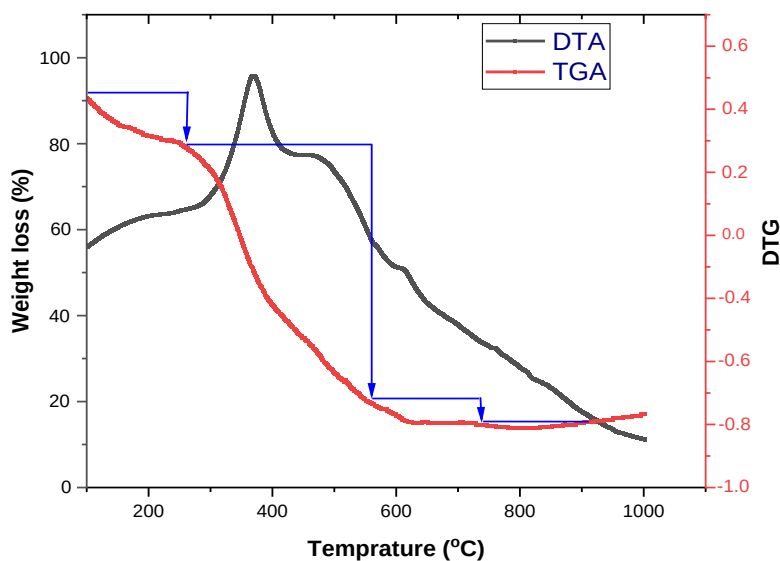


Figure 4.10: Thermogravimetric analysis of raw bone meal

4.3. Design of Experiment Result Analysis

The phosphate removal experiments were conducted according to the CCD design matrix. The removal efficiency (R, %) for observed values of 20 experimental runs was summarized in Table 4.2. These observed experimental results were analyzed using the design-expert version 13. A quadratic polynomial model was used to predict the relationship between the response (i.e. phosphate removal efficiency) and the 3 variables. The predicted R^2 of this model was 0.98, which was in reasonable agreement with the adjusted R^2 of 0.99. The value of initial phosphate concentration was set to 5.1 mg/L targeted to the value of average phosphate concentration in the ASTU wastewater treatment plant to which this adsorbent was expected to apply. Then, an add-in solver was applied to generate the optimum values for the model equation. The optimum values for contact time, adsorbent dosage, and initial solution pH were 12 hr, 3 g/L, and 7.5 respectively. The maximum phosphate removal efficiency of 89.5 % was achieved and this result was comparable with the optimum phosphate removal efficiency value predicted by RSM.

Table 4.2: Experimental result of phosphate removal from aqueous solution

Run	Contact time (min)	pH	Adsorbent Dose (g/250mL)	C _e (mg/L)	Re (%) Actual	Re (%) Predicted
1	1.74	7.5	3	0.96	80.8	80.4
2	3	3	1	1.69	66.2	66.3
3	7	7.5	3	0.79	84.2	84.3
4	7	7.5	3	0.78	84.4	84.3
5	11	12	5	1.21	75.8	75.6
6	12.26	7.5	3	0.52	89.5	89.3
7	3	3	5	1.17	76.5	76.3
8	11	3	5	0.64	87.2	87.5
9	7	7.5	3	0.83	83.4	84.3
10	7	7.5	0.37	1.19	76.2	76.4
11	3	12	5	1.58	68.4	69.0

12	7	7.5	5.63	0.88	82.4	82.0
13	7	13.42	3	1.42	71.6	71.2
14	3	12	1	1.27	74.6	74.4
15	7	1.57	3	1.32	73.6	73.7
16	7	7.5	3	0.77	84.6	84.3
17	11	12	1	1.16	76.8	77.1
18	7	7.5	3	0.76	84.8	84.3
19	7	7.5	3	0.77	84.6	84.3
20	11	3	1	1.29	74.2	73.6

where, C_e = equilibrium concentration of phosphate after adsorption, and Re = Removal efficiency of phosphate. The adsorption was performed by using Ca-BBC as an adsorbent of different factors: contact time, pH, and adsorbent dose with constant initial phosphate concentration of 5.1mg/L, particle size 250-355 μm , stirring speed of 150 rpm and 298k temperature.

4.3.1. Analysis of variance (ANOVA)

Statistical testing of the model was performed by the analysis of variance (ANOVA), which was used to identify the statistical significance of the experimental data, and the results for the coded variable levels are shown in Table 4.3.

Table 4.3: Analysis of variance

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	792.65	9	88.07	349.22	< 0.0001	Significant
A-Contact time	139.44	1	139.44	552.89	< 0.0001	
B-pH	10.62	1	10.62	42.10	< 0.0001	

C-Adsorbent dosage	51.76	1	51.76	205.24	< 0.0001	
AB	10.58	1	10.58	41.95	< 0.0001	
AC	7.60	1	7.60	30.16	0.0003	
BC	117.05	1	117.05	464.11	< 0.0001	
A ²	1.36	1	1.36	5.38	0.0428	
B ²	325.36	1	325.36	1290.10	< 0.0001	
C ²	58.90	1	58.90	233.54	< 0.0001	
Residual	2.52	10	0.2522			
Lack of Fit	1.45	5	0.2894	1.35	0.3762	Not significant
Pure Error	1.07	5	0.2150			
Cor Total	795.17	19				

From the ANOVA indicated in Table, 4.3, the higher F-Value and the lower P-value (<0.0001) indicated the significance of the regression model. As the result demonstrated the model, the F-value of 349.22 implied it was significant. There was only a 0.01% chance that an F-value this large could happen due to noise. The p-value less than 0.05 implied that the model was statistically significant. They were extremely indispensable to understanding the interaction among the independent variables. The result has shown that adsorbent dose (Factor C), pH (Factor B), and contact time (Factor A) were the major important variables in the adsorption process with P-values < 0.0001, < 0.0001, and < 0.0001 respectively. Based on the value both the adsorbent dose, pH, and contact time were the most important factors. From the second polynomial model, B² and C² were significant models with P-values for both models < 0.0001. In the case of interaction effects, AB (contact time and pH), AC (contact time and adsorbent dose), and BC (pH and adsorbent dose) were also significant model terms for phosphate removal (Table 4.3). The lack of fit of the F-value 1.35 implied the lack of fit was insignificant relative to

the pure error. There was about a 37.62 % chance that a lack of fit F-value large could occur due to noise.

The model equations from the ANOVA result could be used to compare the removal efficiency of phosphate within factors and levels. The equation in terms of coded factors could be used to make predictions about the phosphate removal efficiency for the given levels of each factor. The coded equation was useful for identifying the relative impact of the factors by comparing the factor coefficients. The highest coefficients from the equation indicated the most influential factor that affects the adsorption process of phosphate removal. On the other side, the equation in terms of actual factors could be used to make predictions about the removal efficiency of phosphate for given levels of each factor. The levels should be specified in the original units for each factor. This equation should not be used to determine the relative impact of each factor because the coefficients were scaled to accommodate the units of each factor and the intercept was not at the center of the design space.

The Final Coded Equations for phosphate removal from ANOVA result:

$$\text{Removal efficiency} = +84.28 + 3.49*A - 0.9623*B + 2.12*C - 1.15*AB + 0.9750*AC - 3.83*BC + 0.4413*A^2 - 6.83*B^2 - 2.91*C^2 \dots\dots\dots (4.1)$$

Final Equation of Actual Factors:

$$\text{Removal efficiency} = + 42.06002 + 0.599297* A + 6.57009 * B + 7.75782* C - 0.063889 * A* B + 0.121875 * A* C - 0.425000* B* C + 0.027581* A^2 - 0.337448 * B^2 - 0.726835* C^2 \dots\dots\dots (4.2)$$

4.3.2. Model Adequacy

The regression model was found to be significant with the correlation coefficients of determination of R-squared, adjusted R-squared, and predicted R-squared had a value of 0.9968, 0.9940, and 0.9767 respectively as shown in Table 4.3. The goodness fitness of the model was measured by a coefficient of determination R^2 , which measured how well the real experimental data points have been approximated together with the regression model. As the result in Table 4.4, expressed the value of $R^2 = 0.9968$ indicated the better fit of experimental data to that of

predicted one. The value of the larger regression coefficient (R^2) approach to one illustrated, the validity of the model in which it implied an acceptable agreement among the actual and predicted data. It implied that 99.68% of the experimental variable studied attributed to the removal of phosphate. The predicted R^2 of 0.9767 was in reasonable agreement with the adjusted R^2 of 0.9940; i.e. the difference was less than 0.2. Therefore, the result demonstrated that the measured data was very well fitted with a quadratic polynomial model of the predicted value. Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 was desirable. The ratio of 65.625 indicated an adequate signal. This model could be used to navigate the design space.

Table 4.4: Model adequacy measures

Std. Dev.	0.5022	R^2	0.9968
Mean	78.95	Adjusted R^2	0.9940
C.V. %	0.6361	Predicted R^2	0.9767
Press	18.53	Adeq Precision	65.6252

Generally, the smaller the value of the predicted residual sum of squares (PRESS) static obtained 18.53 indicated, the better experimental data points fitted to the model. Moreover, the high R^2 value and p-value as well as the insignificant fit indicate the best prediction of the experiment solution. Therefore, the result in both Table 4.3 and 4.4 proved that, the best performance of the fitness of the model equations.

Figure 4.11 indicates the relationship between actual and predicted values, which could be introduced from the regression model equations of a design expert chart based on predicted and actual percent phosphate removal. The straight line shows the predicted values and the small rectangles represent the actual experimental values. The straight line was very close to the actual values and had a correlation coefficient R^2 equal to 0.9968, which confirmed the accuracy of the model. The result confirmed that all the actual and predicted values were close to the line of perfect fit. Both of them show that good agreement between them.

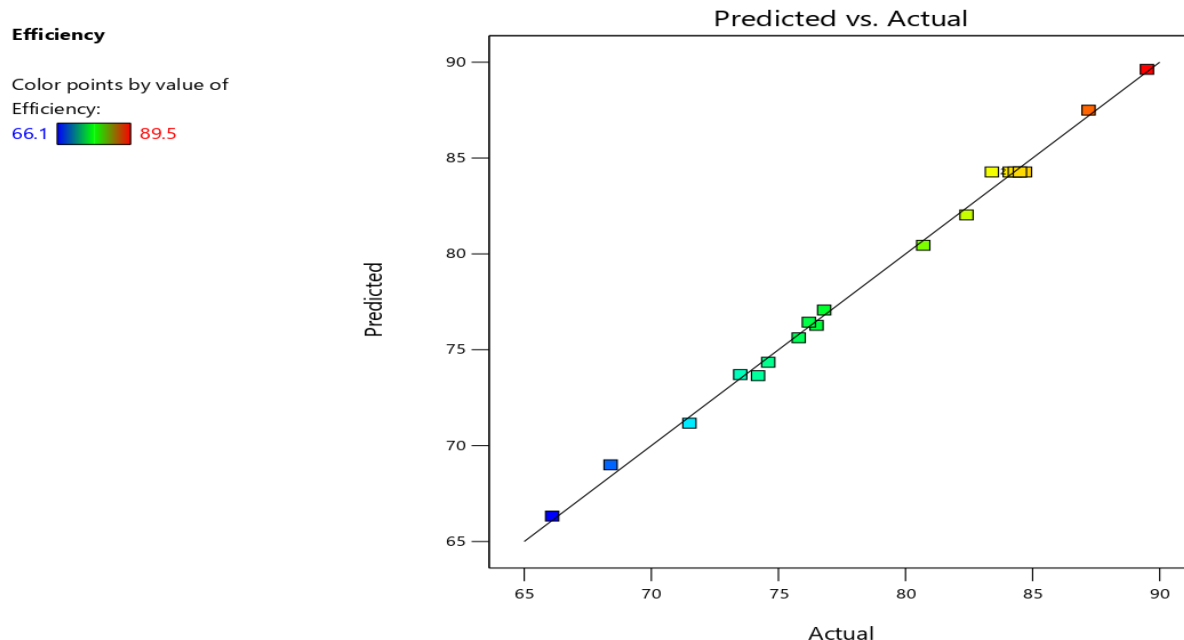


Figure 4.11: Relationship between predicted and actual responses

4.3.3. Factors Affecting Phosphate Adsorption

4.3.3.1. One Factor Effect

i. Effect of contact time

Contact time studies were helpful in understanding how much phosphate was adsorbed by a fixed amount of adsorbent at room temperature (Usman et al., 2022). Adsorptions were said to be complete when the solute in solution and the adsorbent reached equilibrium. However, a certain amount of time was required to maintain the equilibrium contacts and ensure that the adsorption process was completed (Chowdhury & Yanful, 2010). Adsorption tests were performed with fixed adsorbent dosage, pH, and initial concentration for various contact periods. The effect of contact time on the adsorption efficiency of the Ca-BBC with 5 mg/L of initial phosphate concentration, pH=7.5, and contact time (3-12 hr) was presented in Figure 4.12 (a). Results show that the removal of phosphate seemed to take place in two phases. The first phase involved rapid uptake of phosphate within 3-11 hr of contact time and was followed by the subsequent constant uptake. The fast adsorption of phosphate by Ca-BBC adsorbent might be due to external surface adsorption, and phosphate might easily access active adsorption sites, resulting in rapid

phosphate adsorption. However, when the contact time increased, the system achieved a stable state. This was due to, the available active sites were occupied by phosphate (Trinh et al., 2020).

ii. Effect of adsorbent dosage

Adsorbent dosage was observed to affect the phosphate removal efficiency by Ca-BBC. One of the main constraints for the adsorption was adsorbent dosage. An adsorbent with maximum removal efficiency at minimum dosage was desired to make the adsorption process economically viable, however, increasing the adsorbent dose reduces adsorption time (L. Fang et al., 2018). At low adsorbent dosage, all of the adsorbent's active sites were more exposed to phosphate removal. Particle aggregation, interference, and particle-binding site repulsion were the primary causes of active site restriction (R. Liu et al., 2018). Figure 4.12 (b) indicated that the phosphate removal efficiency increased from 79.2% to 84.7% as the Ca-BBC dosage increased from 1 g/L to 3 g/L. Phosphate removal efficiency increased insignificantly as Ca-BBC dosage increased from 3 g/L to 5 g/L, indicating that further increases in adsorbent dosage failed to increase phosphate removal efficiency. This means that the adsorbent's surface has become saturated (J. Liu et al., 2019).

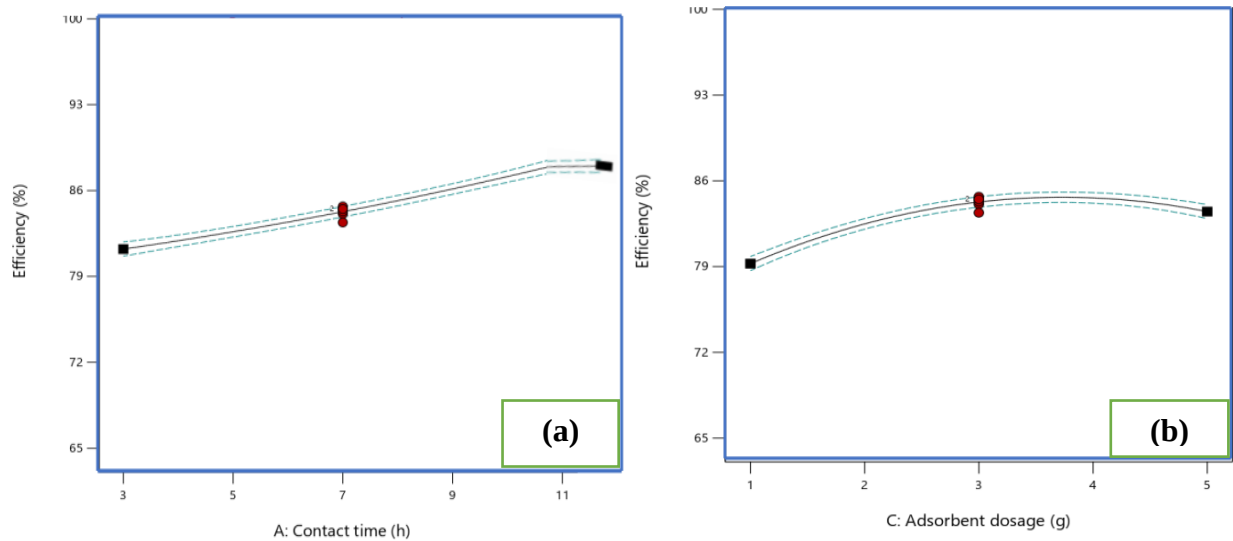
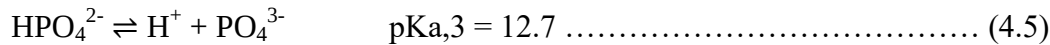
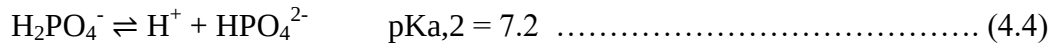
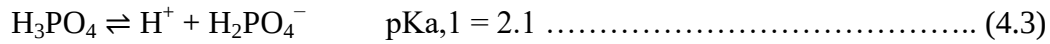


Figure 4.12: Factors affecting phosphate adsorption removal efficiency (R%): (a)-Contact time; (b)- Adsorbent dosage

iii. Effect of pH

The removal efficiency of phosphate by Ca-BBC was pH-sensitive because the performance of phosphate removal depended on the phosphate dissociation equilibrium at various pH levels. The effectiveness of phosphate removal was significantly affected by the pH level of the synthetic wastewater. Figure 4.13 demonstrates that the increased initial pH value from 3 to 7.5 leads to a sharp increase in phosphate removal efficiency. At initial pH equal to 3, only 78.4% phosphate in the wastewater was removed. At a pH higher than 3, the phosphate removal efficiency was increased and reached a maximum value of 84.7% at pH 7.5. However, the pH values after 7.5, the percentage of phosphate removal efficiency gradually decreased.

In this work, the phosphate adsorption on the Ca-BBC was controlled by the solution pH. Phosphate had three different pKa values (2.1, 7.2, and 12.7) and changed its functional groups in different ways depending on the pH. The degree of ionization in phosphate was controlled by the pH of the phosphate solution, which affected adsorption (Cao et al., 2016; Y. Choi et al., 2019; Yao et al., 2011).



Based on the solution pH and pKa value of phosphate in Equation (7)–(9), their major species were H_3PO_4 at pH 2.1, H_2PO_4^- at pH 2.1–7.2, HPO_4^{2-} at 7.2–12.7, and PO_4^{3-} at pH > 12.7, respectively. Since the Ca-BBC had a pH_{PZC} value of 7.8, its surface charge was protonated (positive charge) when the solution pH was lower than its pH_{PZC} value, and negative when it was not.

According to reports similar to this work, phosphate molecules (H_2PO_4^-) had an electrostatic attraction to the positive charge of the Ca-BBC in the pH range (3–7.8). On the other hand, phosphate molecules (HPO_4^{2-}) undergo electrostatic repulsion with the Ca-BBC adsorbents when the pH is between 7.8 and 12. It was shown that at low pH, the positively charged surface of the Ca-BBC and the negatively charged phosphate species would interact primarily by electrostatic attraction, whereas at high pH, phosphate would be precipitated and deposited on the surface of

the Ca-BBC. However, when the adsorption of phosphate onto the Ca-BBC was investigated in the initial pH range of 3 to 7.5, the adsorption increased with an increase of the initial solution pH by a factor of (78.4% removal efficiency at pH 3 and 84.3% removal efficiency at pH 7.5). The results suggested that the precipitation and surface deposition at high pH made a significant contribution to the effective adsorption of phosphate on the Ca-BBC. Many previous studies have shown that raising Ca^{+2} (the growing Ca/P molar ratio) and increasing solution pH could improve HAP precipitation (Hermassi et al., 2015; Leng et al., 2019). $\text{Ca}(\text{OH})_2$ and Ca^{2+} ions placed on the surface of Ca-BBC would rapidly interact with phosphate in water to form Ca-phosphate complexation (Leng et al 2019; Choi et al., 2019; Wang et al., 2018). Taking into account what happens at various pH levels, the following reaction pathways (Equation 4.6 - 4.11) for phosphate adsorption by Ca-BBC were developed:

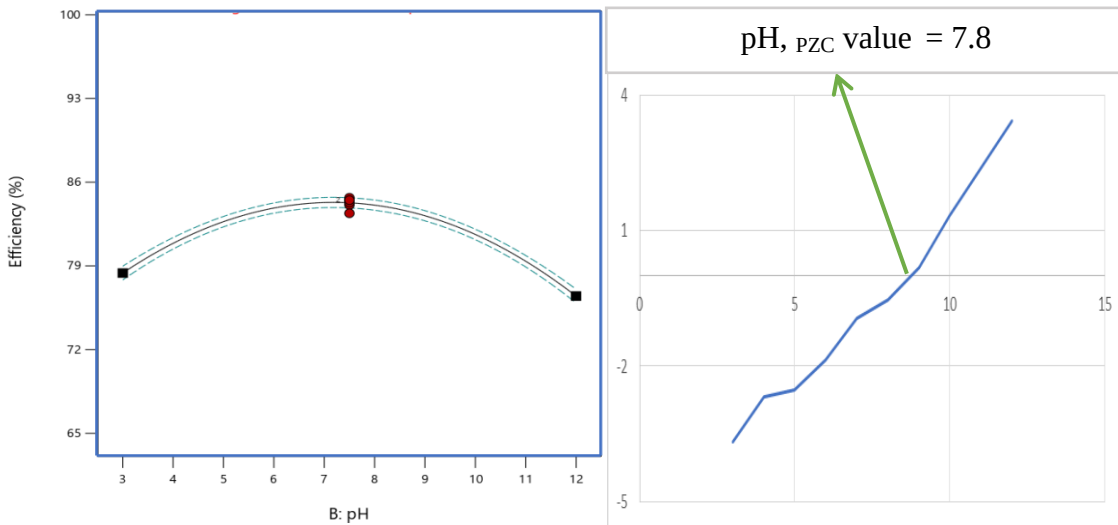
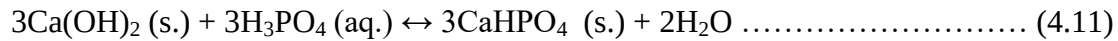
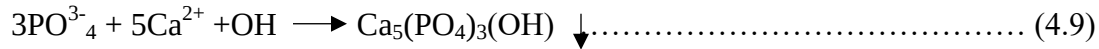
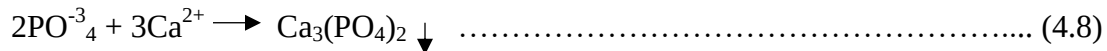
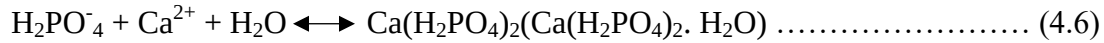


Figure 4.13: Effect of pH on the removal efficiency of phosphate and pH, p_{ZC} value

4.3.3.2. Interaction Effect

i. Effect of Interaction between Contact Time and pH on the Phosphate Removal Efficiency

The response surface curves and contour plots were plotted to understand the interaction effects of adsorption factors on the values of responses, and phosphate removal efficiency (%) of synthesized Ca-BBC adsorbents.

As shown in Figure 4.14, when both adsorbent dosage and initial phosphate concentration remained constant, the increase in contact time and pH of synthetic wastewater influenced the removal efficiency of phosphate positively till it reached its maximum value (84.3%) at a contact time of 7 hr and pH of 7.5. However, the pH started to decline and reached 76.8 % at a pH of 12. This was because, at higher pH levels, the amount of OH^- in the solution increased and was more likely to compete with phosphates for the same adsorption site, resulting in an evident drop. Additionally, at higher pH, the adsorbent surface became more negative, increased repulsion, and lowered phosphate removal. (Berkessa et al., 2019; Usman et al., 2022). When the contact time was raised, the adsorption process accelerated due to the availability of extra active sites, resulting in higher phosphate removal efficiency. However, as time progressed, the adsorption removal efficiency remained constant. Because there were originally available active sites on the surface of Ca-BBC adsorbents, adsorption began faster and was controlled by the transfer of external volume. The decrease in active sites was seen as time increased because most of the active sites of the adsorbents were occupied by phosphate, and hence the adsorption efficiency remained constant (Trinh et al., 2020).

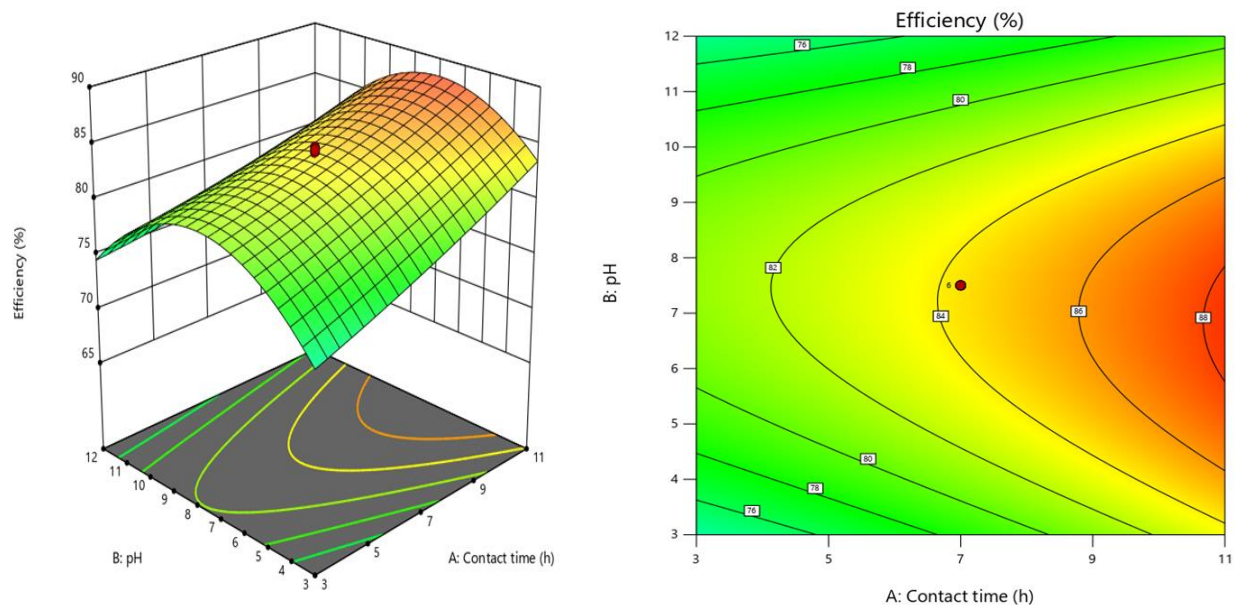


Figure 4.14: Response surface plot shows the effect of the interaction of contact time and pH on the phosphate removal efficiency at constant adsorbent dosage

ii. Effect of Interaction between Adsorbent Dosage and Contact Time on the Phosphate Removal Efficiency

Figure 4.15 illustrates the 3D interaction effect of adsorbent dosage and contact time on phosphate removal efficiency both pH and initial phosphate concentration remained constant. The increase in the adsorbent dose and contact time influenced the phosphate removal efficiency of synthetic wastewater positively up to its maximum value (84.1%) at 7 hr contact time and 3 g/250mL adsorbent dose. Therefore, adsorbent dose and contact time were the main independent variables that affected the adsorption of phosphate from the solution. The presence of a high adsorbent dose in the adsorption process increased the total accessible surface area and adsorption site (Lau & Yeong, 2016). However, the percentage of phosphate removal did not increase with increased adsorbent (> 3 g/L) dosage keeping the initial phosphate concentration constant. This was due to the aggregation of particles in the presence of an excess of adsorbent could decrease the active surface area and active site for the adsorption of phosphate from the solution, leading to a reduction in the adsorption of phosphate (Nguyen, et al., 2020). Whereas as discussed earlier, increments of contact time had a positive impact on the removal efficiency

of phosphate, but it remained constant after 12 hr. This was due to, the available active sites being occupied by phosphate.

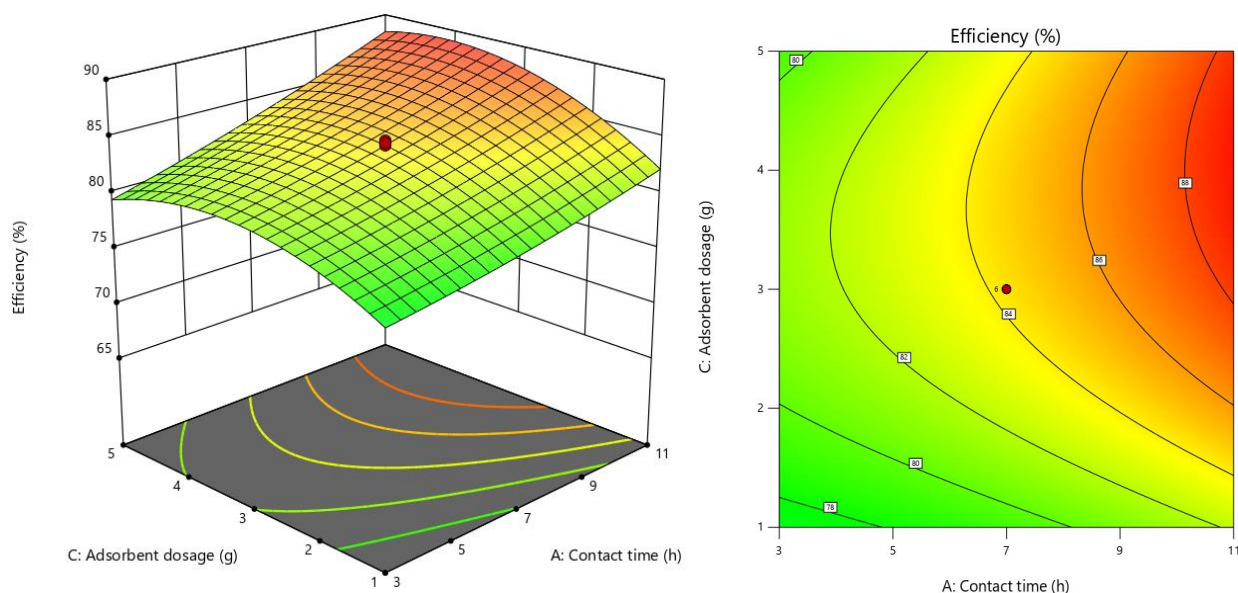


Figure 4.15: Response surface plot shows the effect of the interaction of adsorbent dosage and contact time on the phosphate removal efficiency at constant pH

iii. Effect of Interaction between Adsorbent Dosage and pH on the Phosphate Removal Efficiency

Figure 4.16 explained the 3D interaction effects of adsorbent dosage and pH on phosphate removal efficiency while both contact time and initial phosphate concentration remained constant. The adsorption process was carried out on the molecules and surfaces of the Ca-BBC adsorbents. Therefore, the adsorbent amount and pH had a meaningful effect on the phosphate removal efficiency. Both adsorbent dose and pH had a direct and indirect effect on the process and costs like the other parameters. As it can be observed from the graph, when the adsorbent dosage and pH of synthetic wastewater increased, the phosphate removal efficiency of Ca-BBC adsorbents increased and reached its maximum value (84.7%) at pH 7.5 and 3 g/L adsorbent dosage, then it gradually started to decline and reached 66.1%. Therefore, it could be concluded that the efficiency of phosphate removal was highly dependent on the contact time, pH, and weight of the adsorbent.

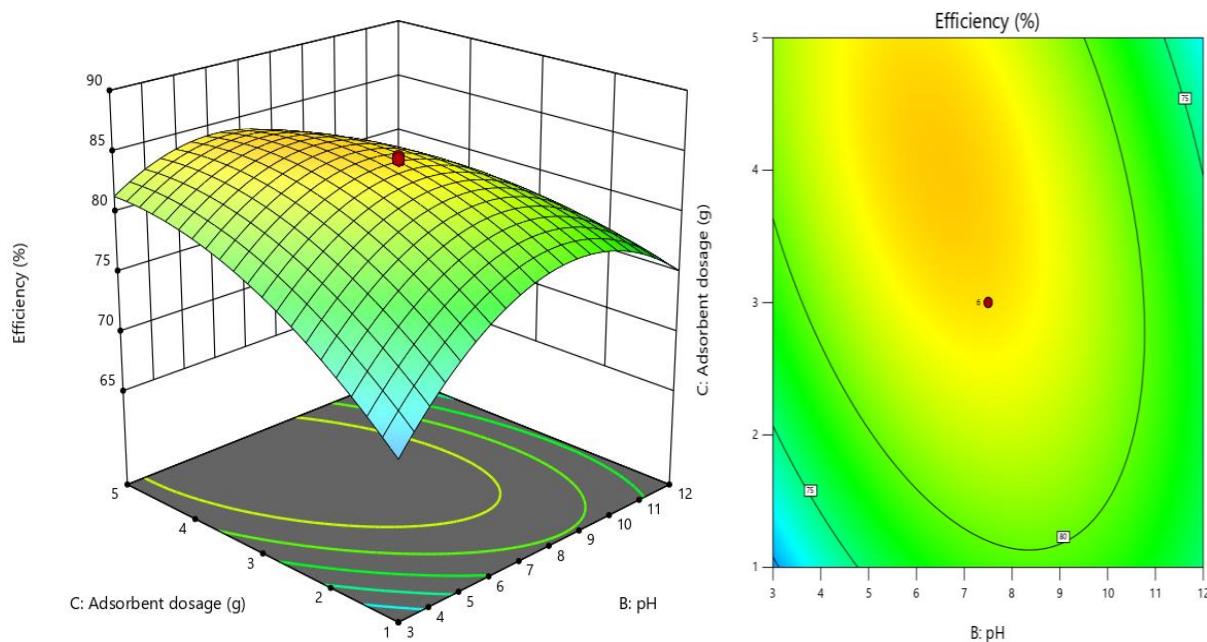


Figure 4.16: Response surface plot shows the effect of the interaction of adsorbent dosage and pH on the phosphate removal efficiency at constant contact time

4.4. Effect of Co-existing Ions

Real wastewater samples always contain co-existing ions that could strongly interfere with the adsorption process of phosphate, resulting in low removal capacity of the adsorbents (Chen et al., 2015; X. Zhang et al., 2017). Therefore, it is critical to evaluate the effect of the competing anions in any adsorption experiment. The effect of common monovalent anions such as fluoride (F^-) and chloride (Cl^-) as well as divalent anions such as carbonate (CO_3^{2-}), sulphate (SO_3^{2-}), and nitrate (NO_3^-) were analyzed for the phosphate removal by synthesized Ca-BBC. As illustrated in Figure 4.17, the effect of nitrate and chloride on the phosphate removal by Ca-BBC was insignificant when compared to the control value. Similar outcomes were seen in previous investigations that used magnetic biochar treated with MgO to remove phosphate from an aqueous solution (J. Liu et al., 2019). In this experiment, the effects of carbonate (CO_3^{2-}), and sulfate (SO_3^{2-}) on the phosphate adsorption onto Ca-BBC were more disruptive. This was due to, an increase in pH might be the reason for the reduction of phosphate adsorption by Ca-BBC that could be bonded with Ca^{2+} ions to form $CaSO_4$ and $CaCO_3$ on the surface of the adsorbent (D. Fang et al., 2018). In addition, fluoride was shown to have the highest impact on the adsorption of phosphate, with a decline in the adsorption range from 89.5 to 69.3 % (25 mg/L F^-

concentration). According to Chatterjee et al. (2018), the fluoride ion had the highest affinity for replacing the hydroxide group in the HAP structure to produce fluorapatite via an ion exchange mechanism. This study observed the effect of coexisting anions on phosphate adsorption by Ca-BBC composite arranged in the following order: fluoride > carbonates > sulfate > nitrate > chloride.

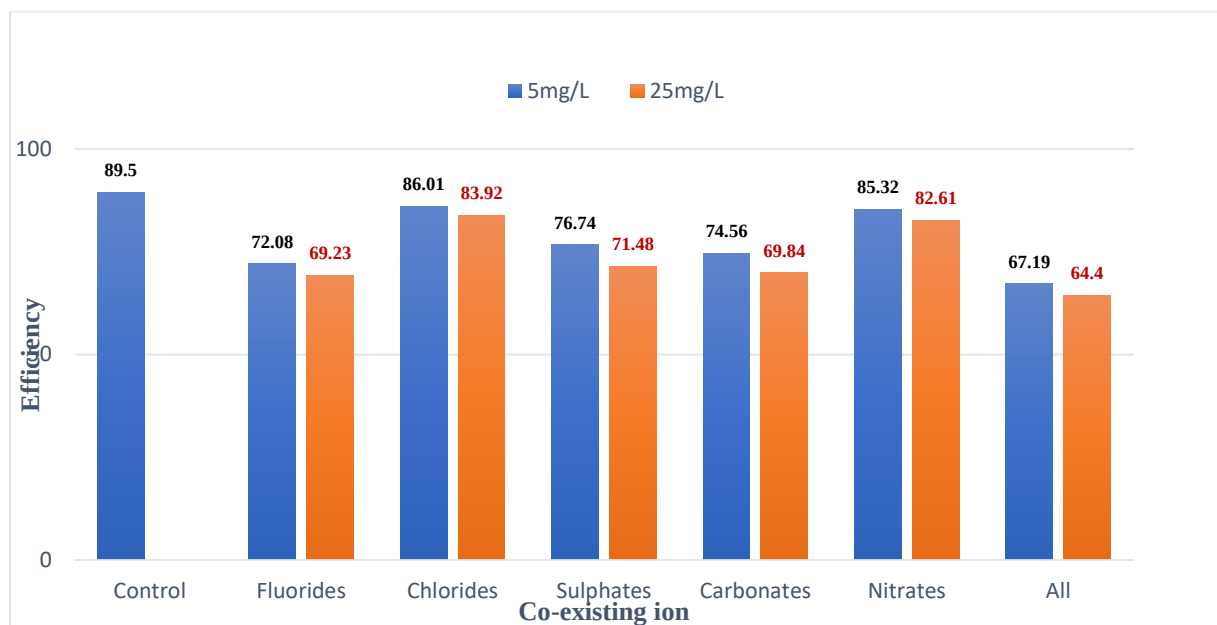


Figure 4.17: Effects of co-existing ions in phosphate removal by Ca-BBC composite

4.5. Adsorption Model

4.5.1. Adsorption Isotherm for Phosphate Adsorption by Ca-BBC Composite

Adsorption isotherm data was generated through a series of experimental procedures that could be used to study the interaction of adsorbate with adsorbent. Modeling the adsorption isotherm data was necessary for forecasting and comparing adsorption performance, which was essential for optimizing adsorption mechanism pathways, expressing adsorbent capacities, and designing effective adsorption systems (Al-Ghouti & Da'ana, 2020). Phosphate ion equilibrium concentration was achieved at optimum conditions computed by the design expert software. The adsorption capacity of Ca-BBC has been examined using Langmuir, Freundlich, and Temkin Isotherms, commonly reported for phosphate removal by various adsorbents. The slope and intercept of the graph for each equation of the isotherms were used to determine their correlation coefficients and constant parameters of phosphate adsorption by Ca-BBC.

4.5.1.1. Langmuir Isotherm

This model assumes that adsorption is homogenous in which monolayer adsorption occurs on the surface of all accessible active sites. The maximum adsorption capacity of Ca- BBC for phosphate removal was determined by studying the concentration of phosphate ions in their respective equilibrium phase at room temperature. The Langmuir model result has shown that the separation factor (R_L) for all initial phosphate concentrations was more than 0 and less than 1, implying that the Langmuir isotherm was favorable (Vadi et al., 2013). The values of R_L were obtained at 0.888, 0.798, 0.725, 0.664, and 0.613 for initial phosphate concentrations of 15, 30, 45, 60, and 75 mg/L, respectively. The intercept of the Langmuir plots of $1/C_e$ vs. $1/q_e$ could be used to determine the maximum adsorption capacity (q_{max}) and energy of adsorption (K_L). The maximum adsorption capacity (q_{max}) and energy of adsorption (K_L) from the Langmuir isotherm model were to be computed as 63.654 mg/g and 0.008 L/mg, respectively. This experimentally determined adsorption capacity was comparable with previous studies using biochar derived from *Rosmarinus officinalis* (Mohammadi et al., 2021) and rice straw (Huang et al., 2022). The correlation factor (R^2) obtained for the Langmuir isotherm was 0.9927.

Table 4.5: Isotherm parameters for the removal of phosphate by Ca-BBC

Isotherm	Parameters	Value
Langmuir	q_{max} (mg/g)	63.654
	K_L (L/mg)	0.008
	R^2	0.9927
Freundlich	n	1.285
	$1/n$	0.778
	k_f (mg/g)(1/mg) ^{1/n}	1.440
	R^2	0.9784
Temkin	β (J/mole)	-0.3475
	b_T	-7129.7
	A_T (L/mg)	0.145
	R^2	0.8784

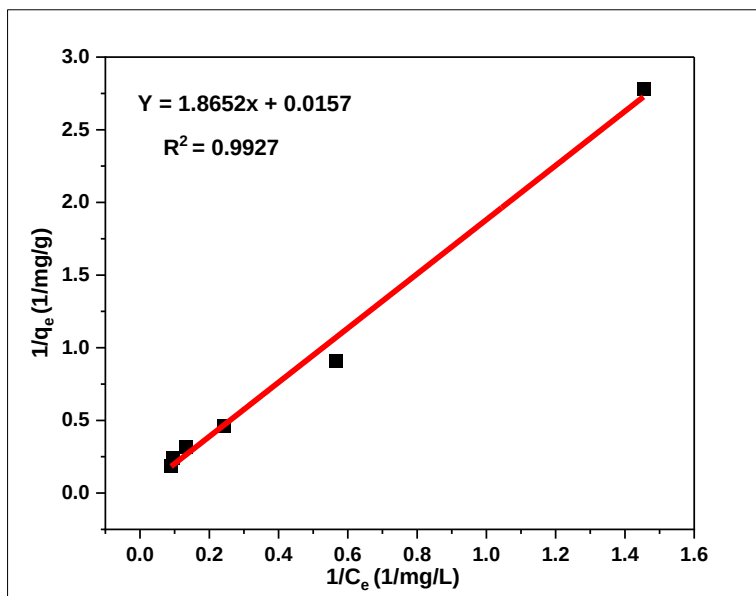


Figure 4.18: Langmuir isotherm model for phosphate adsorption by Ca-BBC

4.5.1.2. Freundlich Isotherm

Unlike the Langmuir isotherm model, this model implied heterogeneous adsorption and could be applied to multilayer adsorption (Al-Ghouti & Da'ana, 2020). The multi-layer adsorption of phosphate on the surface of the Ca-BBC adsorbents was investigated using the linear form of the Freundlich isotherm model from Equation 3.15. The magnitude of the exponent $1/n$ shows the adsorption's favorability (Chen et al., 2015). $1/n$ was a heterogeneous factor that corresponded to the intensity of adsorption or the heterogeneity of the surface. The ratio of $1/n = 0.778$ demonstrated that normal adsorption occurred on the surface of Ca-BBC. The value of n should be in the range of 1 to 10 in order to achieve a favorable adsorption process. Table 4.5 shows that the value of n was 1.285, demonstrating that the adsorption was favorable. The values of constant parameters such as K_f and n were obtained from the Freundlich isotherm model using a linear regression plot of $\ln(C_e)$ vs $\ln(q_e)$. The equilibrium isotherm data well fitted the experimental data from the Freundlich isotherm model, implying that adsorbed phosphate created a multilayer surface coverage on the surface of the Ca-BBC composite and the chemisorption adsorption mechanism occurs. The correlation factor (R^2) obtained for the Freundlich isotherm was 0.9784.

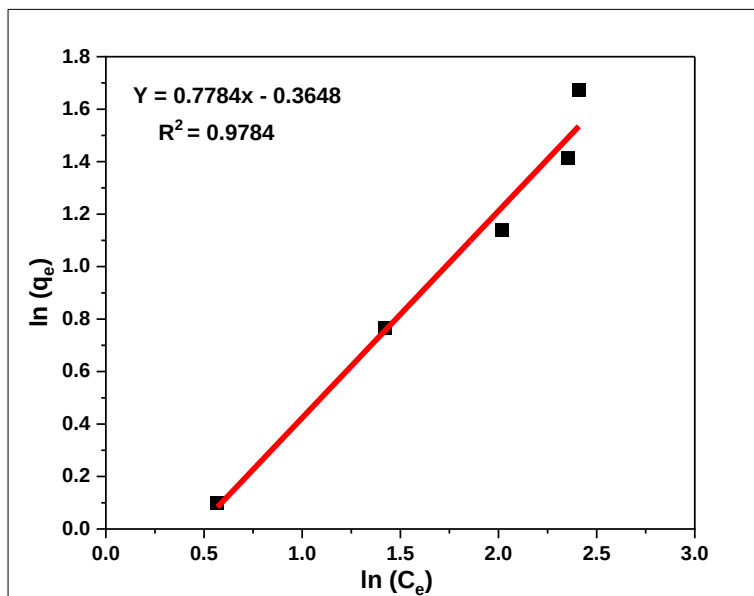


Figure 4.19: Freundlich Isotherm model for phosphate adsorption by Ca-BBC

4.5.1.3. Temkin Isotherm

The Temkin empirical isotherm model was used to offer information about binding energy (A_T), and expressed the heat of adsorption (β) for a specific adsorption experiment (Vadi et al., 2013). The A_T and b_T constants could be obtained by plotting q_e vs. $\ln(C_e)$ as shown in Figure 4.20. The endothermic nature of the adsorption process was indicated by the negative value of β (-0.3475 J/mol). An exothermic process in which the phosphate ion interacted with Ca-BBC would be indicated by a positive β value, while an endothermic activity would be indicated by a negative value. The correlation coefficient (R^2) obtained from this model was 0.8784.

This study found that the fitting of experimental data into the Langmuir isotherm model ($R^2 = 0.993$) and the Freundlich isotherm model ($R^2 = 0.978$), was better than the Temkin isotherm model ($R^2 = 0.878$). According to these results, both the Langmuir isotherm model and the Freundlich isotherm model could generate best-fit experimental data, while the Temkin isotherm model could not. This finding suggested that both monolayer and multilayer adsorption could occur on the surface of Ca-BBC adsorbent. Meanwhile, the values of the correlation factor (R^2) obtained in the Langmuir isotherm model were correspondingly higher than in the Freundlich model. It implied that the phosphate adsorption by Ca-BBC was homogeneous, monolayer and

reversible processes were more dominant. Therefore, by comparison, the order of the isotherm that best fitted the sets of experimental data in this study was in the order of Langmuir > Freundlich > Temkin.

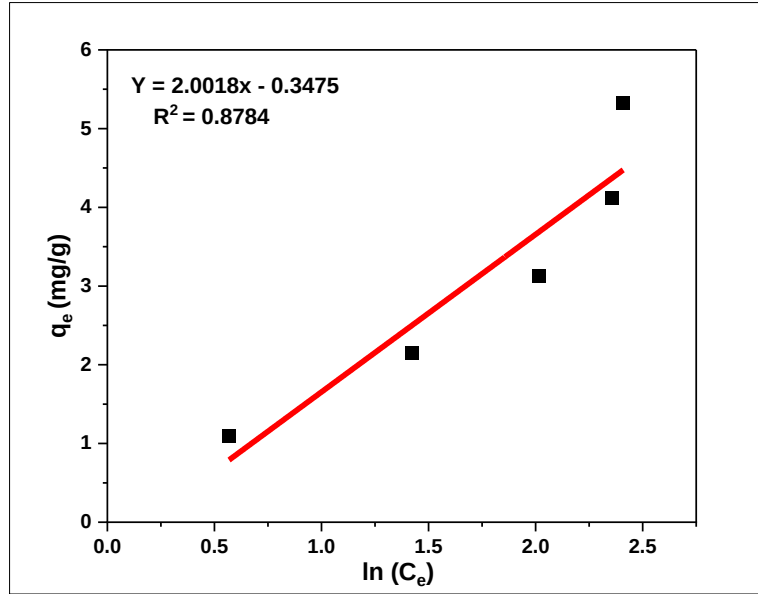


Figure 4.20: Temkin isotherm model for phosphate removal by Ca-BBC

4.5.2. Adsorption Kinetics

Kinetic experiments were investigated to examine the rate of phosphate adsorption on Ca-BBC adsorbent and the time needed to reach equilibrium. The adsorption kinetic research provides information about the adsorption rate, adsorbent performance, time required to reach maximum adsorption capacity, and mass transfer processed (J. Wang & Guo, 2020). In this study, three kinetic models, such as the pseudo-first-order (PFO) model, the pseudo-second-order (PSO) model, and the intra-particle diffusion model have been developed to describe the adsorption kinetic process. The kinetics study time dependence of phosphate removal was investigated from 3 to 15 hours at 5 mg/L initial phosphate concentration, pH of 7.5, adsorbent dosage of 3 g/250 mL, and at room temperature. The slope and intercept of the graph for each equation of the isotherms were used to determine their correlation coefficients and constant parameters of phosphate adsorption by Ca-BBC.

This study found that the fitting of experimental data into the pseudo-first-order (PFO) model ($R^2 = 0.939$), the pseudo-second-order (PSO) model ($R^2 = 0.998$), and the intra-particle diffusion model ($R^2 = 0.973$) were determined. This result suggested that the pseudo-second-order model best described the rate of adsorption equilibrium during phosphate adsorption on the surface Ca-BBC adsorbent. Figure 4.21 shows that the pseudo-second-order rate model had the best agreement with the experimental results, implying that the process was governed by chemical adsorption. According to the pseudo-second-order kinetic model, adsorption behavior involves valence forces via electron exchange between PO_4^{3-} and $\text{Ca}(\text{OH})_2$, as reported by Mitrogiannis et al., (2017). Therefore, the pseudo-second-order kinetic models have been successfully applied for the adsorption of phosphate from aqueous solution. The value of kinetic parameters for three important models were summarized in Table 4.6.

Table 4.6: Kinetics model parameters for Pseudo-first-order, Pseudo-second-order, and Intra-particle diffusion

Kinetics	Parameters	Value
Pseudo-First Order	q_e (mg/g)	0.136
	K_1 (min^{-1})	0.2899
	R^2	0.9399
Pseudo-Second Order	$q_{e \text{ calc}}$ (mg/g)	0.403
	$q_{e \text{ exp}}$ (mg/g)	0.395
	q_e^2	0.162
	K_2 (g/mg.min)	6.980
	R^2	0.9985
Intraparticle Diffusion	K_p ($\text{mg/g.min}^{0.5}$)	0.029
	R^2	0.9733

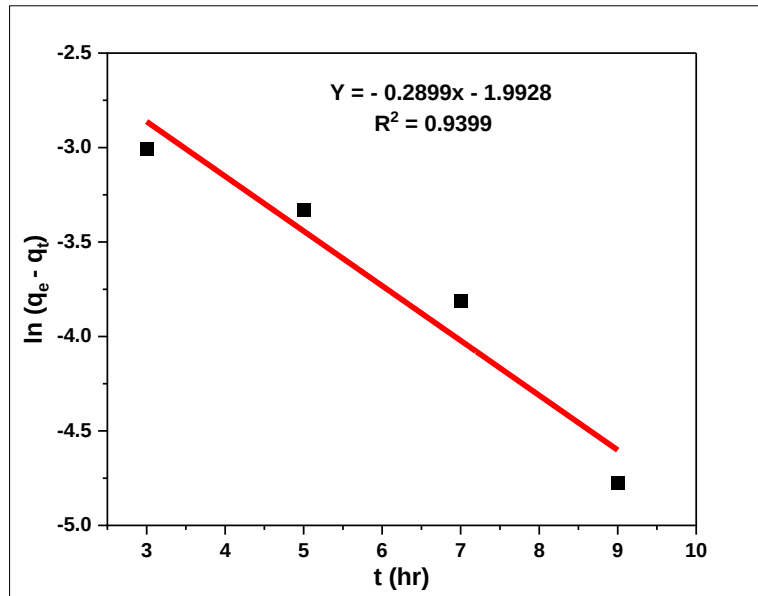


Figure 4.21: Pseudo-first-order kinetics model for adsorption of phosphate ions

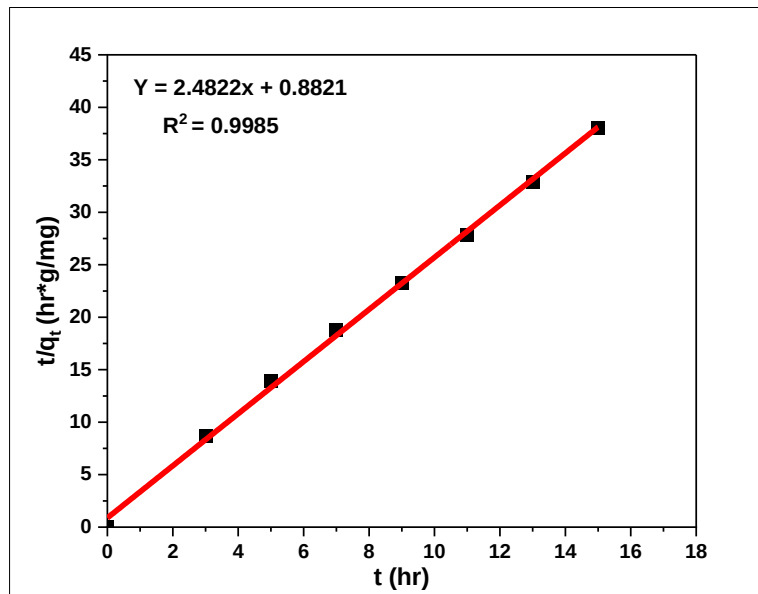


Figure 4.22: Pseudo-second-order kinetics model for adsorption of phosphate ions

Intra-particle diffusion: this model could be used to represent the rate of adsorption, which was determined by the rate at which adsorbate diffused towards the adsorbent. The graph $t^{0.5}$ vs q_t from the adsorption equilibrium data of the intra-particle diffusion model was linear,

demonstrating that this model was involved in the adsorption process. Moreover, the model expressed that intra-particle diffusion was not the only rate-determining step as shown in Figure 4.23, since the graph $t^{0.5}$ versus q_t did not pass through the origin. According to Dada et al., (2021), intra-particle diffusion became not the only rate-limiting step within the adsorption process; the system involved other mass transfer processes.

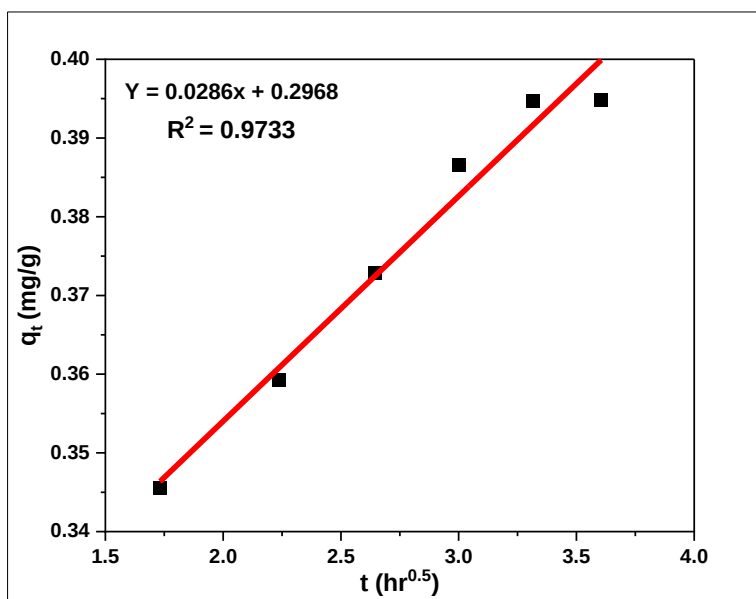


Figure 4.23: Intra-particle diffusion kinetics model for adsorption of phosphate ions

4.6. Adsorption Regeneration Study

Phosphate-saturated Ca-BBC was regenerated for the adsorption of phosphate for five consecutive adsorption-desorption cycles. Thus, this batch desorption of phosphate was carried out at optimum conditions computed by the design expert studies using 200 mL of 0.1M NaOH solutions. The phosphate removal efficiency of the first, second, third, fourth, and fifth cycles were 81.3, 74.5, 62.8, 51.4, and 36.7 %, respectively. As shown in Figure 4.24, the synthesized Ca-BBC could effectively remove phosphate for three cycles without significantly decreasing its adsorption capacity. This result ensured that the prepared Ca-BBC adsorbent could be used to evaluate the adsorption capacity of the regenerated adsorbent for repeated purposes to remove phosphate from wastewater. Hence, Ca-BBC is a promising and economical adsorbent for removing phosphate ions from polluted water effluent. This result was comparable agreement with the previously reported research (Pham et al., 2019).

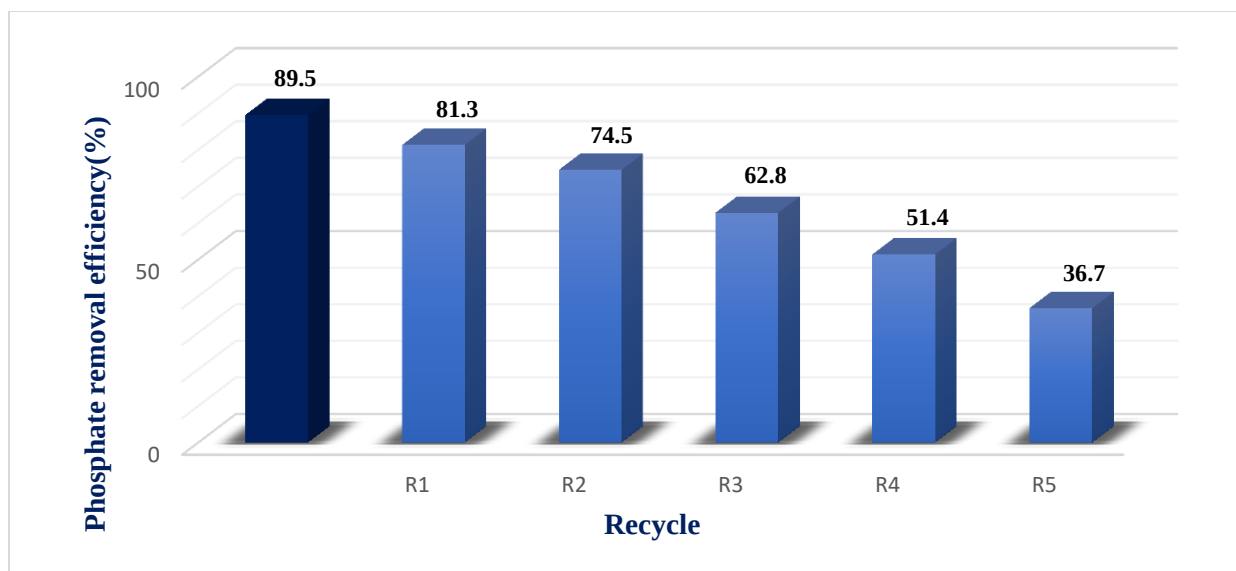


Figure 4.24: Reusability performance of Ca-BBC composite

4.7. Removal of Phosphate from Real Wastewater

The synthesized Ca-BBC was tested to remove phosphate from the ASTU wastewater treatment plant to apply the laboratory experimental result in a practical real-world application. For research purposes, the collected sample at the effluent of the ASTU wastewater treatment plant was filtered using filter paper before the adsorption process. The ASTU wastewater effluents contained phosphate at 5.1 mg/L, nitrate at 62.9 mg/L, sulfate at 70.9 mg/L, and chloride at 21.2 mg/L. The detailed characteristics of ASTU wastewater effluents are listed in Table 4.7. Phosphate adsorption in real wastewater was achieved at optimal parameters determined by the design expert.

The removal efficiency of phosphate on the Ca-BBC adsorbent was found 61.7 %. This result was decreased by about 28% compared to the removal efficiency of synthetic wastewater. This was due to the availability of multiple anions (i.e., sulfate, fluoride, chloride, and nitrate) in ASTU wastewater effluent that could compete with the active sites on synthesized Ca-BBC. Moreover, organic contaminants (COD) competed with phosphate due to hydrophobic and π - π interactions between organic contaminants and the carbon site found on the surface of the adsorbent (Choi et al., 2019).

Table 4.7: Physiochemical analysis result of ASTU wastewater treatment plant effluent.

Parameter	pH	COD	BOD	SO ₄ ²⁻	PO ₄ ³⁻	NO ₃ ⁻	F ⁻	Cl ⁻	Cond.	Alka.	TDS
Unit	-	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/l	µs/cm	mg/L	mg/L
Value	5.65	129.2	22.6	70.9	5.1	62.9	3.87	21.2	690	7.6	57.8

4.8. Comparison Study of Phosphate by Different Adsorbents

The synthesized Ca-BBC composite adsorbent was compared with different adsorbents reported in related works for phosphate removal from wastewater. As Table 4.12 illustrates isotherm model, kinetics models, and $q_{\max}$ were compared for phosphate removal.

Table 4.8: Comparison of phosphate adsorption capacity of different reported adsorbents.

Adsorbents	Kinetic model	Isotherm model	$q_{\max}$ (mg/g)	Reference
Rosmarinus officinalis biochar (BRM)	Second order	Langmuir	65.41	Mohammadi et al., (2021)
Rice straw-derived biochar	PSO	Langmuir	50.0	Huang et al., (2022)
Calcium-decorated sludge carbon	PSO	Langmuir	45.72	Kong et al., (2018)
Calcium-rich sepiolite	PSO	Langmuir	32.0	H. Yin et al., (2011)
Dolomite-modified biochar	PSO	Langmuir	29.18	Li et al., (2019)
Rice husk ash	PSO	Langmuir	0.74	(Mor et al., 2016)
Pg- biochar	PSO	Freundlich	109.0	B. Wang et al., (2020)
MgAl-LDHs/AC	PSO	Freundlich	67.92	Hong et al., (2020)
MBMA	PSO	Langmuir	111	Leng et al., (2019)
Ca-BBC	PSO	Langmuir	63.65	This study

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

This research work focused on the synthesis and characterization of Ca-BBC composite adsorbent from unused bones to remove the phosphate ions from synthetic, and real wastewater effluent. A pyrolysis temperature of 600 °C, pyrolysis time of 2 hr, and mixing ratio of 2:1 was the optimum conditions for the synthesis of Ca- BBC adsorbents. The XRD, FTIR, and SEM result analysis confirmed that phosphate ion was successfully adsorbed by Ca-BBC composite. The specific surface area of Ca-BBC obtained from BET analysis was 331.478 m²/g.

Response surface methodology (RSM) was carried out to assess a model equation that correlates the phosphate removal efficiency (R %) with the factors affecting adsorption such as adsorbent dosage, pH, and contact time (t). The optimum removal efficiency of 89.5% was obtained at pH = 7.5, contact time = 12 hr, and adsorbent dosage of 3 g with initial phosphate concentration was set to 5.1 mg/L targeted to the value of average phosphate concentration in the ASTU wastewater treatment plant to which this adsorbent was expected to apply. The interaction effect of those parameters had a significant effect on the adsorption process.

The removal efficiency of phosphate by Ca-BBC was pH-sensitive because the performance of phosphate removal depended on the phosphate dissociation equilibrium at various pH levels. This study suggested that the precipitation and surface deposition at high pH made a significant contribution to the effective adsorption of phosphate on the Ca-BBC. The effect of coexisting anions on phosphate adsorption by Ca-BBC composite is arranged in the following order: fluoride > carbonates > sulfate > nitrate > chloride. The adsorption isotherm data were best fitted to the Langmuir ($R^2 = 0.993$) with a maximum adsorption capacity of 63.65 mg/g. Moreover, the adsorption kinetics experimental data well fitted to the pseudo-second-order model ($R^2 = 0.999$), implying that chemisorption was the dominant adsorption mechanism for phosphate adsorption on Ca-BBC. The synthesized Ca-BBC was tested for its phosphate removal (R = 61.7%) using real wastewater. Moreover, phosphate-saturated Ca-BBC was regenerated for the adsorption of phosphate for five consecutive adsorption-desorption cycles. The synthesized Ca-BBC could

effectively remove phosphate for three cycles without significantly decreasing its adsorption capacity. According to this study, Ca-BBC is a promising and economical adsorbent for removing phosphate ions from aqueous solution and wastewater effluent.

5.2. Recommendation

For future work, the following recommendations are suggested based on the results obtained from this study.

- ✚ It is recommended that further study on the effects of adsorption parameters such as particle size, temperature, heating rate, agitation speed, as well as adsorption thermodynamics of the system.
- ✚ In this study batch adsorption experiment, equilibrium isotherm, and kinetics were conducted. However, further column adsorption study is recommended for a continuous flow system to optimize process design variables and scale up for practical applications.
- ✚ The regeneration of the adsorbent was investigated by using NaOH only. The determination of the most preferable regenerating solution is a very essential. Thus, further studies on the effectiveness of other regenerating solutions such as H₂SO₄, HCl, NaNO₃, and solvent methods will be recommended.
- ✚ The synthesized BBC, Ca-BBC before and after adsorption was well characterized by using BET, XRD, FTIR, and SEM. However, it needs further characterization for further wastewater engineering applications.

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REFERENCE

- Aibinu, A. M., Folorunso, T. A., Saka, A. A., Ogunfowora, L. A., Iwuozor, K. O., & Ighalo, J. O. (2022). Green synthesis of CuO nanocomposite from watermelon (*Citrullus lanatus*) rind for the treatment of aquaculture effluent. *Regional Studies in Marine Science*, 52. <https://doi.org/10.1016/j.rsma.2022.102308>
- Akram, M., Xu, X., Gao, B., Wang, S., Khan, R., Yue, Q., Duan, P., Dan, H., & Pan, J. (2021). Highly efficient removal of phosphate from aqueous media by pomegranate peel co-doping with ferric chloride and lanthanum hydroxide nanoparticles. *Journal of Cleaner Production*, 292, 125311. <https://doi.org/10.1016/j.jclepro.2020.125311>
- Al-Ghouti, M. A., & Da'ana, D. A. (2020). Guidelines for the use and interpretation of adsorption isotherm models: A review. In *Journal of Hazardous Materials* (Vol. 393). Elsevier B.V. <https://doi.org/10.1016/j.jhazmat.2020.122383>
- Ali, A. F., Atwa, S. M., & El-giar, E. M. (2017). 6 - Development of magnetic nanoparticles for fluoride and organic matter removal from drinking water. In *Water Purification*. Elsevier Inc. <https://doi.org/10.1016/B978-0-12-804300-4/00006-X>
- Alkurdi, S. S. A., Al-Juboori, R. A., Bundschuh, J., Bowtell, L., & McKnight, S. (2020). Effect of pyrolysis conditions on bone char characterization and its ability for arsenic and fluoride removal. *Environmental Pollution*, 262, 114221.
- Alkurdi, S. S. A., Al-Juboori, R. A., Bundschuh, J., & Hamawand, I. (2019). Bone char as a green sorbent for removing health threatening fluoride from drinking water. In *Environment International* (Vol. 127). <https://doi.org/10.1016/j.envint.2019.03.065>
- Almanassra, I. W., Kochkodan, V., Ponnusamy, G., McKay, G., Ali Atieh, M., & Al-Ansari, T. (2020). Carbide Derived Carbon (CDC) as novel adsorbent for ibuprofen removal from synthetic water and treated sewage effluent. *Journal of Environmental Health Science and Engineering*, 18(2), 1375–1390. <https://doi.org/10.1007/s40201-020-00554-0>
- Almanassra, I. W., McKay, G., Kochkodan, V., Ali Atieh, M., & Al-Ansari, T. (2021). A state of the art review on phosphate removal from water by biochars. *Chemical Engineering Journal*, 409(December 2020), 128211. <https://doi.org/10.1016/j.cej.2020.128211>
- American Public Health Association. *Standard Methods for the Examination of Water and Wastewater*. 21st ed. Washington, DC: American Public Health Association, American Water Works Association, Water Environment Federation; 2005.

- Awual, M. R. (2019). Efficient phosphate removal from water for controlling eutrophication using novel composite adsorbent. *Journal of Cleaner Production*, 228, 1311–1319.
- Ayawei, N., Ebelegi, A. N., & Wankasi, D. (2017). Modelling and Interpretation of Adsorption Isotherms. *Journal of Chemistry*, 2017. <https://doi.org/10.1155/2017/3039817>
- Azeem, M., Ali, A., Arockiam Jeyasundar, P. G. S., Bashir, S., Hussain, Q., Wahid, F., Ali, E. F., Abdelrahman, H., Li, R., Antoniadis, V., Rinklebe, J., Shaheen, S. M., Li, G., & Zhang, Z. (2021). Effects of sheep bone biochar on soil quality, maize growth, and fractionation and phytoavailability of Cd and Zn in a mining-contaminated soil. *Chemosphere*, 282. <https://doi.org/10.1016/j.chemosphere.2021.131016>
- Bacelo, H., Pintor, A. M. A., Santos, S. C. R., Boaventura, R. A. R., & Botelho, C. M. S. (2020). Performance and prospects of different adsorbents for phosphorus uptake and recovery from water. In *Chemical Engineering Journal* (Vol. 381).
- Bektaş, T. E., Kıvanç Ugürluoğlu, B., & Tan, B. (2021). Phosphate removal by ion exchange in batch mode. *Water Practice and Technology*, 16(4). <https://doi.org/10.2166/wpt.2021.072>
- Berkessa, Y. W., Mereta, S. T., & Feyisa, F. F. (2019). Simultaneous removal of nitrate and phosphate from wastewater using solid waste from factory. *Applied Water Science*, 9(2). <https://doi.org/10.1007/s13201-019-0906-z>
- Bhattacharya, S. (2021). Central Composite Design for Response Surface Methodology and Its Application in Pharmacy. In *Response Surface Methodology in Engineering Science*. <https://doi.org/10.5772/intechopen.95835>
- Braun, J. C. A., Borba, C. E., Godinho, M., Perondi, D., Schontag, J. M., & Wenzel, B. M. (2019). Phosphorus adsorption in Fe-loaded activated carbon: Two-site monolayer equilibrium model and phenomenological kinetic description. *Chemical Engineering Journal*, 361. <https://doi.org/10.1016/j.cej.2018.12.073>
- Cao, D., Jin, X., Gan, L., Wang, T., & Chen, Z. (2016). Removal of phosphate using iron oxide nanoparticles synthesized by eucalyptus leaf extract in the presence of CTAB surfactant. *Chemosphere*, 159. <https://doi.org/10.1016/j.chemosphere.2016.05.080>
- Chagtmi, R., Trabelsi, A. B. H., Haddad, K., Maaoui, A., Lopez, G., Santamaria, L., Cortazar, M., Khedira, H., Chaden, C., & Olazar, M. (2022). Biochar derived from animal bone waste as an alternative bioadsorbent for an industrial tannery dye removal. *Biomass Conversion and Biorefinery*. <https://doi.org/10.1007/s13399-022-03459-0>

- Chen, L., Li, Y., Sun, Y., Chen, Y., & Qian, J. (2019). La(OH)₃ loaded magnetic mesoporous nanospheres with highly efficient phosphate removal properties and superior pH stability. *Chemical Engineering Journal*, 360, 342–348. <https://doi.org/10.1016/j.cej.2018.11.234>
- Chen, L., Zhao, X., Pan, B., Zhang, W., Hua, M., Lv, L., & Zhang, W. (2015). Preferable removal of phosphate from water using hydrous zirconium oxide-based nanocomposite of high stability. *Journal of Hazardous Materials*, 284, 35–42.
- Cheung, C. W., Porter, J. F., & McKay, G. (2001). Sorption kinetic analysis for the removal of cadmium ions from effluents using bone char. *Water Research*, 35(3).
- Choi, Y., Jang, H. M., Kan, E., Wallace, A. R., & Sun, W. (2019). Adsorption of phosphate in water on a novel calcium hydroxide-coated dairy manure-derived biochar. 24(3), 434–442.
- Choi, Y. K., Jang, H. M., Kan, E., Wallace, A. R., & Sun, W. (2019). Adsorption of phosphate in water on a novel calcium hydroxide-coated dairy manure-derived biochar. *Environmental Engineering Research*, 24(3), 434–442. <https://doi.org/10.4491/EER.2018.296>
- Chowdhury, S. R., & Yanful, E. K. (2010). Arsenic and chromium removal by mixed magnetite-maghemite nanoparticles and the effect of phosphate on removal. *Journal of Environmental Management*, 91(11). <https://doi.org/10.1016/j.jenvman.2010.06.003>
- Dada, A. O., Adekola, F. A., Odebunmi, E. O., Ogunlaja, A. S., & Bello, O. S. (2021). Two–three parameters isotherm modeling, kinetics with statistical validity, desorption and thermodynamic studies of adsorption of Cu(II) ions onto zerovalent iron nanoparticles. *Scientific Reports*, 11(1), 1–15. <https://doi.org/10.1038/s41598-021-95090-8>
- Daudzai, Z., Dolphen, R., & Thiravetyan, P. (2021). Simultaneous removal of phosphate and nitrate from synthetic and real wastewater by *Meretrix lusoria* as an efficient and novel material. *Water, Air, & Soil Pollution*, 232(5), 186.
- Delgadillo-Velasco, L., Hernández-Montoya, V., Cervantes, F. J., Montes-Morán, M. A., & Lira-Berlanga, D. (2017). Bone char with antibacterial properties for fluoride removal: Preparation, characterization and water treatment. *Journal of Environmental Management*, 201. <https://doi.org/10.1016/j.jenvman.2017.06.038>
- Deng, Z., Gu, S., Cheng, H., Xing, D., Twagirayezu, G., Wang, X., Ning, W., & Mao, M. (2022). Removal of Phosphate from Aqueous Solution by Zeolite-Biochar Composite: Adsorption Performance and Regulation Mechanism. *Applied Sciences (Switzerland)*, 12(11). <https://doi.org/10.3390/app12115334>

- Dong, S., Wang, Y., Zhao, Y., Zhou, X., & Zheng, H. (2017). La³⁺/La(OH)₃ loaded magnetic cationic hydrogel composites for phosphate removal: Effect of lanthanum species and mechanistic study. *Water Research*, 126. <https://doi.org/10.1016/j.watres.2017.09.050>
- Ellingham, S. T. D., Thompson, T. J. U., & Islam, M. (2015). Thermogravimetric analysis of property changes and weight loss in incinerated bone. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 438, 239–244. <https://doi.org/10.1016/j.palaeo.2015.08.009>
- Fang, C., Zhang, T., Li, P., Jiang, R., & Wang, Y. (2014). Application of Magnesium Modified Corn Biochar for Phosphorus Removal and Recovery from Swine Wastewater. 9217–9237. <https://doi.org/10.3390/ijerph110909217>
- Fang, D., Huang, L., Fang, Z., Zhang, Q., Shen, Q., Li, Y., Xu, X., & Ji, F. (2018). Evaluation of porous calcium silicate hydrate derived from carbide slag for removing phosphate from wastewater. *Chemical Engineering Journal*, 354. <https://doi.org/10.1016/j.cej.2018.08.001>
- Fang, L., Wu, B., Chan, J. K. M., & Lo, I. M. C. (2018). Lanthanum oxide nanorods for enhanced phosphate removal from sewage: A response surface methodology study. *Chemosphere*, 192, 209–216. <https://doi.org/10.1016/j.chemosphere.2017.10.154>
- Fang, L., Zeng, W., Xu, L., & Huang, L. Z. (2020). Green rusts as a new solution to sequester and stabilize phosphate in sediments under anoxic conditions and their implication for eutrophication control. *Chemical Engineering Journal*, 388.
- Ferro-García, M. A., Rivera-Utrilla, J., Bautista-Toledo, I., & Mingorance, M. D. (1990). Removal of lead from water by activated carbons. *Carbon*, 28(4).
- Flores-Cano, J. V., Leyva-Ramos, R., Carrasco-Marin, F., Aragón-Piña, A., Salazar-Rabago, J. J., & Leyva-Ramos, S. (2016). Adsorption mechanism of Chromium(III) from water solution on bone char: effect of operating conditions. *Adsorption*, 22(3), 297–308. <https://doi.org/10.1007/s10450-016-9771-3>
- Ghorai, P., & Ghosh, D. (2022). Sustainable Approach for Insoluble Phosphate Recycling from Wastewater Effluents BT - Environmental Degradation: Monitoring, Assessment and Treatment Technologies (I. Haq, A. S. Kalamdhad, & S. Dash (eds.); pp. 77–86). Springer International Publishing. https://doi.org/10.1007/978-3-030-94148-2_7
- Gizaw, A., Zewge, F., Chebude, Y., Tesfaye, M., & Mekonnen, A. (2022a). Phosphate abatement using calcium silicate hydrate synthesized from alum factory solid waste residue. *Separation Science and Technology (Philadelphia)*, 57(11).

- Gizaw, A., Zewge, F., Chebude, Y., Tesfaye, M., & Mekonnen, A. (2022b). Phosphate abatement using calcium silicate hydrate synthesized from alum factory solid waste residue. *Separation Science and Technology (Philadelphia)*, 57(11), 1669–1687.
- Guaya, D., Jiménez, R., Sarango, J., Valderrama, C., & Cortina, J. L. (2021). Iron-doped natural clays: Low-cost inorganic adsorbents for phosphate recovering from simulated urban treated wastewater. *Journal of Water Process Engineering*, 43.
- He, J., Yang, Y., Wu, Z., Xie, C., Zhang, K., Kong, L., & Liu, J. (2020). Review of fluoride removal from water environment by adsorption. In *Journal of Environmental Chemical Engineering* (Vol. 8, Issue 6). Elsevier B.V. <https://doi.org/10.1016/j.jece.2020.104516>
- Hermassi, M., Valderrama, C., Dosta, J., Cortina, J. L., & Batis, N. H. (2015). Evaluation of hydroxyapatite crystallization in a batch reactor for the valorization of alkaline phosphate concentrates from wastewater treatment plants using calcium chloride. *Chemical Engineering Journal*, 267. <https://doi.org/10.1016/j.cej.2014.12.079>
- Huang, J., Zhu, C., Kong, Y., Cao, X., Zhu, L., Zhang, Y., Ning, Y., Tian, W., Zhang, H., Yu, Y., & Zhang, J. (2022). Biochar Application Alleviated Rice Salt Stress via Modifying Soil Properties and Regulating Soil Bacterial Abundance and Community Structure. *Agronomy*, 12(2). <https://doi.org/10.3390/agronomy12020409>
- Iftekhhar, S., Ramasamy, D. L., Srivastava, V., Asif, M. B., & Sillanpää, M. (2018). Understanding the factors affecting the adsorption of Lanthanum using different adsorbents: A critical review. In *Chemosphere* (Vol. 204).
- Jia, Z., Zeng, W., Xu, H., Li, S., & Peng, Y. (2020). Adsorption removal and reuse of phosphate from wastewater using a novel adsorbent of lanthanum-modified platanus biochar. *Process Safety and Environmental Protection*, 140. <https://doi.org/10.1016/j.psep.2020.05.017>
- Jiang, D., Chu, B., Amano, Y., & Machida, M. (2018). Removal and recovery of phosphate from water by Mg-laden biochar: Batch and column studies. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 558.
- Jung, K. W., Jeong, T. U., Hwang, M. J., Kim, K., & Ahn, K. H. (2015). Phosphate adsorption ability of biochar/Mg–Al assembled nanocomposites prepared by aluminum-electrode based electro-assisted modification method with MgCl₂ as electrolyte. *Bioresource Technology*, 198, 603–610. <https://doi.org/10.1016/J.BIORTECH.2015.09.068>

- Karthikeyan, P., & Meenakshi, S. (2019). Synthesis and characterization of Zn–Al LDHs/activated carbon composite and its adsorption properties for phosphate and nitrate ions in aqueous medium. *Journal of Molecular Liquids*, 296.
- Kasim, N. Z., Abd Malek, N. A. A., Hairul Anuwar, N. S., & Hamid, N. H. (2020). Adsorptive removal of phosphate from aqueous solution using waste chicken bone and waste cockle shell. *Materials Today: Proceedings*, 31. <https://doi.org/10.1016/j.matpr.2020.09.687>
- Kong, L., Han, M., Shih, K., Su, M., Diao, Z., Long, J., Chen, D., Hou, L., & Peng, Y. (2018). Nano-rod Ca-decorated sludge derived carbon for removal of phosphorus. *Environmental Pollution*, 233. <https://doi.org/10.1016/j.envpol.2017.10.099>
- Kudela, R. M., Bickel, A., Carter, M. L., Howard, M. D. A., & Rosenfeld, L. (2015). The Monitoring of Harmful Algal Blooms through Ocean Observing: The Development of the California Harmful Algal Bloom Monitoring and Alert Program. In *Coastal Ocean Observing Systems*. <https://doi.org/10.1016/B978-0-12-802022-7.00005-5>
- Kuwahara, Y., & Yamashita, H. (2017). Phosphate removal from aqueous solutions using calcium silicate hydrate prepared from blast furnace slag. *ISIJ International*, 57(9). <https://doi.org/10.2355/isijinternational.ISIJINT-2017-123>
- Lau, Y. L., & Yeong, Y. F. (2016). Optimization of Nitrate Removal from Aqueous Solution by Amine-functionalized MCM-41 Using Response Surface Methodology. *Procedia Engineering*, 148. <https://doi.org/10.1016/j.proeng.2016.06.485>
- Lee, C. G., Alvarez, P. J. J., Kim, H. G., Jeong, S., Lee, S., Lee, K. B., Lee, S. H., & Choi, J. W. (2018). Phosphorous recovery from sewage sludge using calcium silicate hydrates. *Chemosphere*, 193. <https://doi.org/10.1016/j.chemosphere.2017.11.129>
- Lee, S. Y., Choi, J. W., Song, K. G., Choi, K., Lee, Y. J., & Jung, K. W. (2019). Adsorption and mechanistic study for phosphate removal by rice husk-derived biochar functionalized with Mg/Al-calcined layered double hydroxides via co-pyrolysis. *Composites Part B: Engineering*, 176. <https://doi.org/10.1016/j.compositesb.2019.107209>
- Lencha, S. M., Tränckner, J., & Dananto, M. (2021). Assessing the water quality of lake hawassa Ethiopia—Trophic state and suitability for anthropogenic uses—applying common water quality indices. *International Journal of Environmental Research and Public Health*, 18(17). <https://doi.org/10.3390/ijerph18178904>

- Leng, L., Zhang, J., Xu, S., Xiong, Q., Xu, X., Li, J., & Huang, H. (2019). Meat & bone meal (MBM) incineration ash for phosphate removal from wastewater and afterward phosphorus recovery. *Journal of Cleaner Production*, 238. <https://doi.org/10.1016/j.jclepro.2019.117960>
- Li, J. H., Lv, G. H., Bai, W. B., Liu, Q., Zhang, Y. C., & Song, J. Q. (2016). Modification and use of biochar from wheat straw (*Triticum aestivum* L.) for nitrate and phosphate removal from water. *Desalination and Water Treatment*, 57(10).
- Li, J., Li, B., Huang, H., Lv, X., Zhao, N., Guo, G., & Zhang, D. (2019). Removal of phosphate from aqueous solution by dolomite-modified biochar derived from urban dewatered sewage sludge. *Science of the Total Environment*, 687, 460–469.
- Liao, T., Li, T., Su, X., Yu, X., Song, H., Zhu, Y., & Zhang, Y. (2018). La(OH)₃-modified magnetic pineapple biochar as novel adsorbents for efficient phosphate removal. *Bioresource Technology*, 263. <https://doi.org/10.1016/j.biortech.2018.04.108>
- Liu, J., Jiang, J., Aihemaiti, A., Meng, Y., Yang, M., Xu, Y., Gao, Y., Zou, Q., & Chen, X. (2019). Removal of phosphate from aqueous solution using MgO-modified magnetic biochar derived from anaerobic digestion residue. *Journal of Environmental Management*, 250(July), 109438. <https://doi.org/10.1016/j.jenvman.2019.109438>
- Liu, R., Chi, L., Wang, X., Sui, Y., Wang, Y., & Arandiyana, H. (2018). Review of metal (hydr)oxide and other adsorptive materials for phosphate removal from water. In *Journal of Environmental Chemical Engineering* (Vol. 6, Issue 4).
- Loganathan, P., Vigneswaran, S., Kandasamy, J., & Bolan, N. S. (2014). Removal and recovery of phosphate from water using sorption. *Critical Reviews in Environmental Science and Technology*, 44(8). <https://doi.org/10.1080/10643389.2012.741311>
- Medellin-Castillo, N. A., Padilla-Ortega, E., Tovar-García, L. D., Leyva-Ramos, R., Ocampo-Pérez, R., Carrasco-Marín, F., & Berber-Mendoza, M. S. (2016). Removal of fluoride from aqueous solution using acid and thermally treated bone char. *Adsorption*, 22(7), 951–961. <https://doi.org/10.1007/s10450-016-9802-0>
- Mezener, N. Y., & Bensmaili, A. (2009). Kinetics and thermodynamic study of phosphate adsorption on iron hydroxide-eggshell waste. *Chemical Engineering Journal*, 147(2–3), 87–96. <https://doi.org/10.1016/J.CEJ.2008.06.024>
- Mitrogiannis, D., Psychoyou, M., Koukoulas, N., Tsoukalas, N., Palles, D., Kamitsos, E., Pantazidis, A., Oikonomou, G., & Baziotis, I. (2018). Phosphate recovery from real fresh

- urine by $\text{Ca}(\text{OH})_2$ treated natural zeolite. *Chemical Engineering Journal*, 347.
- Mittelstet, A. R., Storm, D. E., & White, M. J. (2016). Using SWAT to enhance watershed-based plans to meet numeric water quality standards. *Sustainability of Water Quality and Ecology*, 7, 5–21. <https://doi.org/10.1016/j.swaqe.2016.01.002>
- Mkukuma, L.D., Skakle, J.M.S., Gibson, I.R., Imrie, C.T., Aspden, R.M., Hukins, D.W.L., 2004. Effect of the proportion of organic material in bone on thermal decomposition of bone mineral: an investigation of a variety of bones from different species using thermogravimetric analysis coupled to mass spectrometry, high-temperature X-ray diffraction, and Fourier transform infrared spectroscopy. *Calcif. Tissue Int.* 75, 321–328.
- Mohammadi, R., Hezarjaribi, M., Ramasamy, D. L., Sillanpää, M., & Pihlajamäki, A. (2021). Application of a novel biochar adsorbent and membrane to the selective separation of phosphate from phosphate-rich wastewaters. *Chemical Engineering Journal*, 407.
- Mokrzycki, J., Fedyna, M., Marzec, M., Szerement, J., Panek, R., Klimek, A., Bajda, T., & Mierzwa-Hersztek, M. (2022). Copper ion-exchanged zeolite X from fly ash as an efficient adsorbent of phosphate ions from aqueous solutions. *Journal of Environmental Chemical Engineering*, 10(6). <https://doi.org/10.1016/j.jece.2022.108567>
- Mor, S., Chhoden, K., & Ravindra, K. (2016). Application of agro-waste rice husk ash for the removal of phosphate from the wastewater. *Journal of Cleaner Production*, 129. <https://doi.org/10.1016/j.jclepro.2016.03.088>
- Nakarmi, A., Kim, J., Toland, A., & Viswanathan, T. (2019). Novel reusable renewable resource-based iron oxides nanocomposites for removal and recovery of phosphate from contaminated waters: Removal of phosphate from contaminated waters using reusable renewable resource-based nanocomposites. *International Journal of Environmental Science and Technology*, 16(8). <https://doi.org/10.1007/s13762-018-2058-3>
- Naushad, M., Sharma, G., Kumar, A., Sharma, S., Ghfar, A. A., Bhatnagar, A., Stadler, F. J., & Khan, M. R. (2018). Efficient removal of toxic phosphate anions from aqueous environment using pectin based quaternary amino anion exchanger. *International Journal of Biological Macromolecules*, 106. <https://doi.org/10.1016/j.ijbiomac.2017.07.169>
- Nigri, E. M., Cechinel, M. A. P., Mayer, D. A., Mazur, L. P., Loureiro, J. M., Rocha, S. D. F., & Vilar, V. J. P. (2017). Cow bones char as a green sorbent for fluorides removal from

- aqueous solutions: batch and fixed-bed studies. *Environmental Science and Pollution Research*, 24(3), 2364–2380. <https://doi.org/10.1007/s11356-016-7816-5>
- Novais, S. V., Zenero, M. D. O., Barreto, M. S. C., Montes, C. R., & Cerri, C. E. P. (2018). Phosphorus removal from eutrophic water using modified biochar. *Science of The Total Environment*, 633, 825–835. <https://doi.org/10.1016/J.SCITOTENV.2018.03.246>
- Nsenga Kumwimba, M., Dzakpasu, M., & Li, X. (2020). Potential of invasive watermilfoil (*Myriophyllum* spp.) to remediate eutrophic waterbodies with organic and inorganic pollutants. *Journal of Environmental Management*, 270, 110919.
- Okano, K., Miyamaru, S., Kitao, A., Takano, H., Aketo, T., Toda, M., Honda, K., & Ohtake, H. (2015). Amorphous calcium silicate hydrates and their possible mechanism for recovering phosphate from wastewater. *Separation and Purification Technology*, 144.
- Okano, K., Uemoto, M., Kagami, J., Miura, K., Aketo, T., Toda, M., Honda, K., & Ohtake, H. (2013). Novel technique for phosphorus recovery from aqueous solutions using amorphous calcium silicate hydrates (A-CSHs). *Water Research*, 47(7).
- Patel, A., Lee, H. O., Jawerth, L., Maharana, S., Jahnel, M., Hein, M. Y., Stoyanov, S., Mahamid, J., Saha, S., Franzmann, T. M., Pozniakovski, A., Poser, I., Maghelli, N., Royer, L. A., Weigert, M., Myers, E. W., Grill, S., Drechsel, D., Hyman, A. A., & Alberti, S. (2015). A Liquid-to-Solid Phase Transition of the ALS Protein FUS Accelerated by Disease Mutation. *Cell*, 162(5), 1066–1077. <https://doi.org/10.1016/J.CELL.2015.07.047>
- Peng, G., Jiang, S., Wang, Y., Zhang, Q., Cao, Y., Sun, Y., Zhang, W., & Wang, L. (2020). Synthesis of Mn/Al double oxygen biochar from dewatered sludge for enhancing phosphate removal. *Journal of Cleaner Production*, 251. <https://doi.org/10.1016/j.jclepro.2019.119725>
- Peng, Y., Sun, Y., Fan, B., Zhang, S., Bolan, N. S., Chen, Q., & Tsang, D. C. W. (2021). Fe/Al (hydr)oxides engineered biochar for reducing phosphorus leaching from a fertile calcareous soil. *Journal of Cleaner Production*, 279. <https://doi.org/10.1016/j.jclepro.2020.123877>
- Pramanik, S., Hanif, A.S.M., Pingguan-Murphy, B., Osman, N.A.A., 2013. Morphological change of heat treated bovine bone: a comparative study. *Materials* 6, 65–75.
- Pham, T. H., Lee, K. M., Kim, M. S., Seo, J., & Lee, C. (2019). La-modified ZSM-5 zeolite beads for enhancement in removal and recovery of phosphate. *Microporous and Mesoporous Materials*, 279. <https://doi.org/10.1016/j.micromeso.2018.12.017>

- Pimentel, J. S. M., & Giani, A. (2014). Microcystin production and regulation under nutrient stress conditions in toxic *Microcystis* strains. *Applied and Environmental Microbiology*, 80(18), 5836–5843. <https://doi.org/10.1128/AEM.01009-14>
- Preisner, M., Neverova-Dziopak, E., & Kowalewski, Z. (2020). An Analytical Review of Different Approaches to Wastewater Discharge Standards with Particular Emphasis on Nutrients. *Environmental Management*, 66(4), 694–708. <https://doi.org/10.1007/s00267-020-01344-y>
- Qin, J., Zhang, C., Chen, Z., Wang, X., Zhang, Y., & Guo, L. (2022). Converting wastes to resource: Utilization of dewatered municipal sludge for calcium-based biochar adsorbent preparation and land application as a fertilizer. *Chemosphere*, 298.
- Qiu, B., & Duan, F. (2019). Synthesis of industrial solid wastes/biochar composites and their use for adsorption of phosphate: From surface properties to sorption mechanism. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 571.
- Ramola, S., Belwal, T., Li, C. J., Liu, Y. X., Wang, Y. Y., Yang, S. M., & Zhou, C. H. (2021). Preparation and application of novel rice husk biochar–calcite composites for phosphate removal from aqueous medium. *Journal of Cleaner Production*, 299, 126802.
- Rashid, M., Price, N. T., Gracia Pinilla, M. Á., & O’Shea, K. E. (2017). Effective removal of phosphate from aqueous solution using humic acid coated magnetite nanoparticles. *Water Research*, 123. <https://doi.org/10.1016/j.watres.2017.06.085>
- Razanajatovo, M. R., Gao, W., Song, Y., Zhao, X., Sun, Q., & Zhang, Q. (2021). Selective adsorption of phosphate in water using lanthanum-based nanomaterials: A critical review. In *Chinese Chemical Letters* (Vol. 32, Issue 9). <https://doi.org/10.1016/j.cclet.2021.01.046>
- Ren, J., Li, N., Li, L., An, J. K., Zhao, L., & Ren, N. Q. (2015). Granulation and ferric oxides loading enable biochar derived from cotton stalk to remove phosphate from water. *Bioresource Technology*, 178. <https://doi.org/10.1016/j.biortech.2014.09.071>
- Rojas-Mayorga, C. K., Bonilla-Petriciolet, A., Aguayo-Villarreal, I. A., Hernández-Montoya, V., Moreno-Virgen, M. R., Tovar-Gómez, R., & Montes-Morán, M. A. (2013). Optimization of pyrolysis conditions and adsorption properties of bone char for fluoride removal from water. *Journal of Analytical and Applied Pyrolysis*, 104.
- Rojas-Mayorga, C. K., Bonilla-Petriciolet, A., Silvestre-Albero, J., Aguayo-Villarreal, I. A., & Mendoza-Castillo, D. I. (2015). Physico-chemical characterization of metal-doped bone

- chars and their adsorption behavior for water defluoridation. *Applied Surface Science*, 355. <https://doi.org/10.1016/j.apsusc.2015.07.163>
- Rojas-Mayorga, C. K., Silvestre-Albero, J., Aguayo-Villarreal, I. A., Mendoza-Castillo, D. I., & Bonilla-Petriciolet, A. (2015). A new synthesis route for bone chars using CO₂ atmosphere and their application as fluoride adsorbents. *Microporous and Mesoporous Materials*, 209. <https://doi.org/10.1016/j.micromeso.2014.09.002>
- Rojas-Mayorga CK, Mendoza-CastilloDI, Bonilla-PetricioletA, Silvestre-AlberoJ (2016) Tailoring the adsorption behavior of bone char for heavy metal removal from aqueous solution. *Adsorption Sci Technol* 34:368–387.
- Sabzehmeidani, M. M., Mahnaee, S., Ghaedi, M., Heidari, H., & Roy, V. A. L. (2021). Carbon based materials: A review of adsorbents for inorganic and organic compounds. In *Materials Advances* (Vol. 2, Issue 2). <https://doi.org/10.1039/d0ma00087f>
- Samanta, A., Chanda, D. K., Das, P. S., Ghosh, J., Mukhopadhyay, A. K., & Dey, A. (2016). Synthesis of Nano Calcium Hydroxide in Aqueous Medium. *Journal of the American Ceramic Society*, 99(3), 787–795. <https://doi.org/10.1111/jace.14023>
- Schaefer, D., & Cheung, W. M. (2018). Smart Packaging: Opportunities and Challenges. *Procedia CIRP*, 72. <https://doi.org/10.1016/j.procir.2018.03.240>
- Shaheen, S. M., Natasha, Mosa, A., El-Naggar, A., Faysal Hossain, M., Abdelrahman, H., Khan Niazi, N., Shahid, M., Zhang, T., Fai Tsang, Y., Trakal, L., Wang, S., & Rinklebe, J. (2022). Manganese oxide-modified biochar: production, characterization and applications for the removal of pollutants from aqueous environments - a review. In *Bioresource Technology* (Vol. 346). <https://doi.org/10.1016/j.biortech.2021.126581>
- Sun, C., Cao, H., Huang, C., Wang, P., Yin, J., Liu, H., Tian, H., Xu, H., Zhu, J., & Liu, Z. (2022). Eggshell based biochar for highly efficient adsorption and recovery of phosphorus from aqueous solution: Kinetics, mechanism and potential as phosphorus fertilizer. *Bioresource Technology*, 362, 127851. <https://doi.org/10.1016/J.BIORTECH.2022.127851>
- Taffese, T., Tilahun, S., & Steenhuis, T. (2014). Phosphorus Modeling, in Lake Tana Basin, Ethiopia. *Journal of Environment and Human*, 2014(2), 47–55.
- Taweekarn, T., Wongniramaikul, W., & Choodum, A. (2022). Removal and recovery of phosphate using a novel calcium silicate hydrate composite starch cryogel. *Journal of Environmental Management*, 301. <https://doi.org/10.1016/j.jenvman.2021.113923>

- Trinh, V. T., Nguyen, T. M. P., Van, H. T., Hoang, L. P., Nguyen, T. V., Ha, L. T., Vu, X. H., Pham, T. T., Nguyen, T. N., Quang, N. V., & Nguyen, X. C. (2020). Phosphate Adsorption by Silver Nanoparticles-Loaded Activated Carbon derived from Tea Residue. *Scientific Reports*, 10(1). <https://doi.org/10.1038/s41598-020-60542-0>
- Trinh, V. T., Pham, T. T. H., Van, H. T., Trinh, M. V., Thang, P. Q., Vu, X. H., Nguyen, V. Q., & Dang, T. T. (2020). Phosphorus Removal from Aqueous Solution by Adsorption using Silver Nanoparticles: Batch Experiment. *Journal of Hazardous, Toxic, and Radioactive Waste*, 24(4), 1–7. [https://doi.org/10.1061/\(asce\)hz.2153-5515.0000529](https://doi.org/10.1061/(asce)hz.2153-5515.0000529)
- Usman, M. O., Aturagaba, G., Ntale, M., & Nyakairu, G. W. (2022). A review of adsorption techniques for removal of phosphates from wastewater. In *Water Science and Technology* (Vol. 86, Issue 12, pp. 3113–3132). IWA Publishing. <https://doi.org/10.2166/wst.2022.382>
- Vadi, M., Mansoorabad, A. O., Mohammadi, M., & Rostami, N. (2013). Investigation of langmuir, freundlich and temkin adsorption isotherm of tramadol by multi-wall carbon nanotube. *Asian Journal of Chemistry*, 25(10). <https://doi.org/10.14233/ajchem.2013.14786>
- Vikrant, K., Kim, K. H., Ok, Y. S., Tsang, D. C. W., Tsang, Y. F., Giri, B. S., & Singh, R. S. (2018). Engineered/designer biochar for the removal of phosphate in water and wastewater. *Science of the Total Environment*, 616–617(November), 1242–1260.
- Wang, B., Lian, G., Lee, X., Gao, B., Li, L., Liu, T., Zhang, X., & Zheng, Y. (2020). Phosphogypsum as a novel modifier for distillers grains biochar removal of phosphate from water. *Chemosphere*, 238. <https://doi.org/10.1016/j.chemosphere.2019.124684>
- Wang, B., Ma, Y., Lee, X., Wu, P., Liu, F., Zhang, X., Li, L., & Chen, M. (2021). Environmental-friendly coal gangue-biochar composites reclaiming phosphate from water as a slow-release fertilizer. *Science of the Total Environment*, 758, 143664.
- Wang, J., & Guo, X. (2020). Adsorption kinetic models: Physical meanings, applications, and solving methods. *Journal of Hazardous Materials*, 390(January), 122156.
- Wang, S., Kong, L., Long, J., Su, M., Diao, Z., Chang, X., Chen, D., Song, G., & Shih, K. (2018). Adsorption of phosphorus by calcium-flour biochar: Isotherm, kinetic and transformation studies. *Chemosphere*, 195, 666–672.
- Wang, Z., Shen, D., Shen, F., & Li, T. (2016). Phosphate adsorption on lanthanum loaded biochar. *Chemosphere*, 150. <https://doi.org/10.1016/j.chemosphere.2016.02.004>

- Xiao, J., Hu, R., & Chen, G. (2020). Micro-nano-engineered nitrogenous bone biochar developed with a ball-milling technique for high-efficiency removal of aquatic Cd(II), Cu(II) and Pb(II). *Journal of Hazardous Materials*, 387. <https://doi.org/10.1016/j.jhazmat.2019.121980>
- Xu, K., Lin, F., Dou, X., Zheng, M., Tan, W., & Wang, C. (2018). Recovery of ammonium and phosphate from urine as value-added fertilizer using wood waste biochar loaded with magnesium oxides. *Journal of Cleaner Production*, 187, 205–214.
- Yaashikaa, P. R., Kumar, P. S., Varjani, S., & Saravanan, A. (2020). A critical review on the biochar production techniques, characterization, stability and applications for circular bioeconomy. In *Biotechnology Reports* (Vol. 28).
- Yagub, M. T., Sen, T. K., Afroze, S., & Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption: A review. In *Advances in Colloid and Interface Science* (Vol. 209). <https://doi.org/10.1016/j.cis.2014.04.002>
- Yami, T. L., Du, J., Brunson, L. R., Chamberlain, J. F., Sabatini, D. A., & Butler, E. C. (2015). Life cycle assessment of adsorbents for fluoride removal from drinking water in East Africa. *International Journal of Life Cycle Assessment*, 20(9), 1277–1286.
- Yang, F., Zhang, S., Sun, Y., Tsang, D. C. W., Cheng, K., & Ok, Y. S. (2019). Assembling biochar with various layered double hydroxides for enhancement of phosphorus recovery. *Journal of Hazardous Materials*, 365. <https://doi.org/10.1016/j.jhazmat.2018.11.047>
- Yao, Y., Gao, B., Inyang, M., Zimmerman, A. R., Cao, X., Pullammanappallil, P., & Yang, L. (2011). Biochar derived from anaerobically digested sugar beet tailings: Characterization and phosphate removal potential. *Bioresource Technology*, 102(10), 6273–6278. <https://doi.org/10.1016/J.BIORTECH.2011.03.006>
- Yin, H., Yun, Y., Zhang, Y., & Fan, C. (2011). Phosphate removal from wastewaters by a naturally occurring, calcium-rich sepiolite. *Journal of Hazardous Materials*, 198. <https://doi.org/10.1016/j.jhazmat.2011.10.072>
- Yin, Q., Ren, H., Wang, R., & Zhao, Z. (2018). Evaluation of nitrate and phosphate adsorption on Al-modified biochar: Influence of Al content. *Science of The Total Environment*, 631–632, 895–903. <https://doi.org/10.1016/J.SCITOTENV.2018.03.091>
- Zare, K., Gupta, V. K., Moradi, O., Makhlouf, A. S. H., Sillanpää, M., Nadagouda, M. N., Sadegh, H., Shahryari-ghoshekandi, R., Pal, A., Wang, Z. jun, Tyagi, I., & Kazemi, M. (2015). A comparative study on the basis of adsorption capacity between CNTs and

- activated carbon as adsorbents for removal of noxious synthetic dyes: a review. In *Journal of Nanostructure in Chemistry* (Vol. 5, Issue 2). <https://doi.org/10.1007/s40097-015-0158-x>
- Zhang, L., Li, M., Gao, Y., Liu, J., & Xu, Y. (2016). Performance and mechanism study on phosphate adsorption onto activated carbon fiber loading lanthanum and iron oxides. *Desalination and Water Treatment*, 57(10). <https://doi.org/10.1080/19443994.2014.992976>
- Zhang, P., He, M., Huo, S., Li, F., & Li, K. (2022). Recent progress in metal-based composites toward adsorptive removal of phosphate: Mechanisms, behaviors, and prospects. In *Chemical Engineering Journal* (Vol. 446). <https://doi.org/10.1016/j.cej.2022.137081>
- Zhang, X., Gao, B., Creamer, A. E., Cao, C., & Li, Y. (2017). Adsorption of VOCs onto engineered carbon materials: A review. In *Journal of Hazardous Materials* (Vol. 338). <https://doi.org/10.1016/j.jhazmat.2017.05.013>
- Zhang, Y., Liu, H., Yan, S., Wen, X., Qin, H., Wang, Z., & Zhang, Z. (2019). Phosphorus removal from the hyper-eutrophic lake caohai (China) with large-scale water hyacinth cultivation. *Environmental Science and Pollution Research*, 26(13), 12975–12984.
- Zhang, Z., Wang, X., Wang, H., & Zhao, J. (2018). Removal of Pb(II) from aqueous solution using hydroxyapatite/calcium silicate hydrate (HAP/C-S-H) composite adsorbent prepared by a phosphate recovery process. *Chemical Engineering Journal*, 344.
- Zheng, Q., Yang, L., Song, D., Zhang, S., Wu, H., Li, S., & Wang, X. (2020). High adsorption capacity of Mg–Al-modified biochar for phosphate and its potential for phosphate interception in soil. *Chemosphere*, 259. <https://doi.org/10.1016/j.chemosphere.2020.127469>
- Zhou, Q., Wang, X., Liu, J., & Zhang, L. (2012). Phosphorus removal from wastewater using nano-particulates of hydrated ferric oxide doped activated carbon fiber prepared by Sol-Gel method. *Chemical Engineering Journal*, 200–202. <https://doi.org/10.1016/j.cej.2012.06.123>

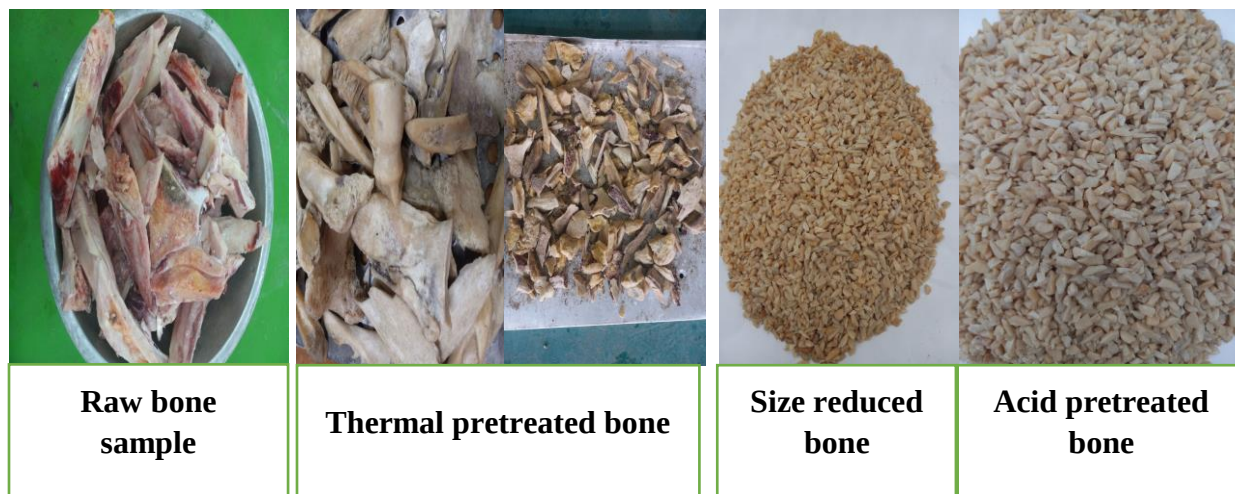
APPENDIX

Appendix A: The effect of three factors on the removal efficiency of phosphate as a preliminary investigation to select the levels of factors.

Run	Factor 1: Adsorbent dosage (g/L)	Factor 2: pH	Factor 4: Contact time (hr)	Response: Removal efficiency (%)
1	1	3	3	49.7±1.5
2	2	3	3	51.2±2.8
3	3	3	3	53.8±1.3
4	4	3	3	54.1±3.7
5	5	3	3	51.9±4.8
6	4	4	3	56.5±2.4
7	4	6	3	57.8±1.2
8	4	8	3	61.3±4.6
9	4	10	3	60.5±2.7
10	4	12	5	53.6±3.4
11	4	8	3	61.2±2.9
12	4	8	5	64.7±1.4
13	4	8	7	67.4±1.9
14	4	8	9	73.6±2.8
15	4	8	11	75.6±1.2
16	4	8	13	75.6±4.3

Note: value = mean ± SD

Appendix B: Pretreatment of bone

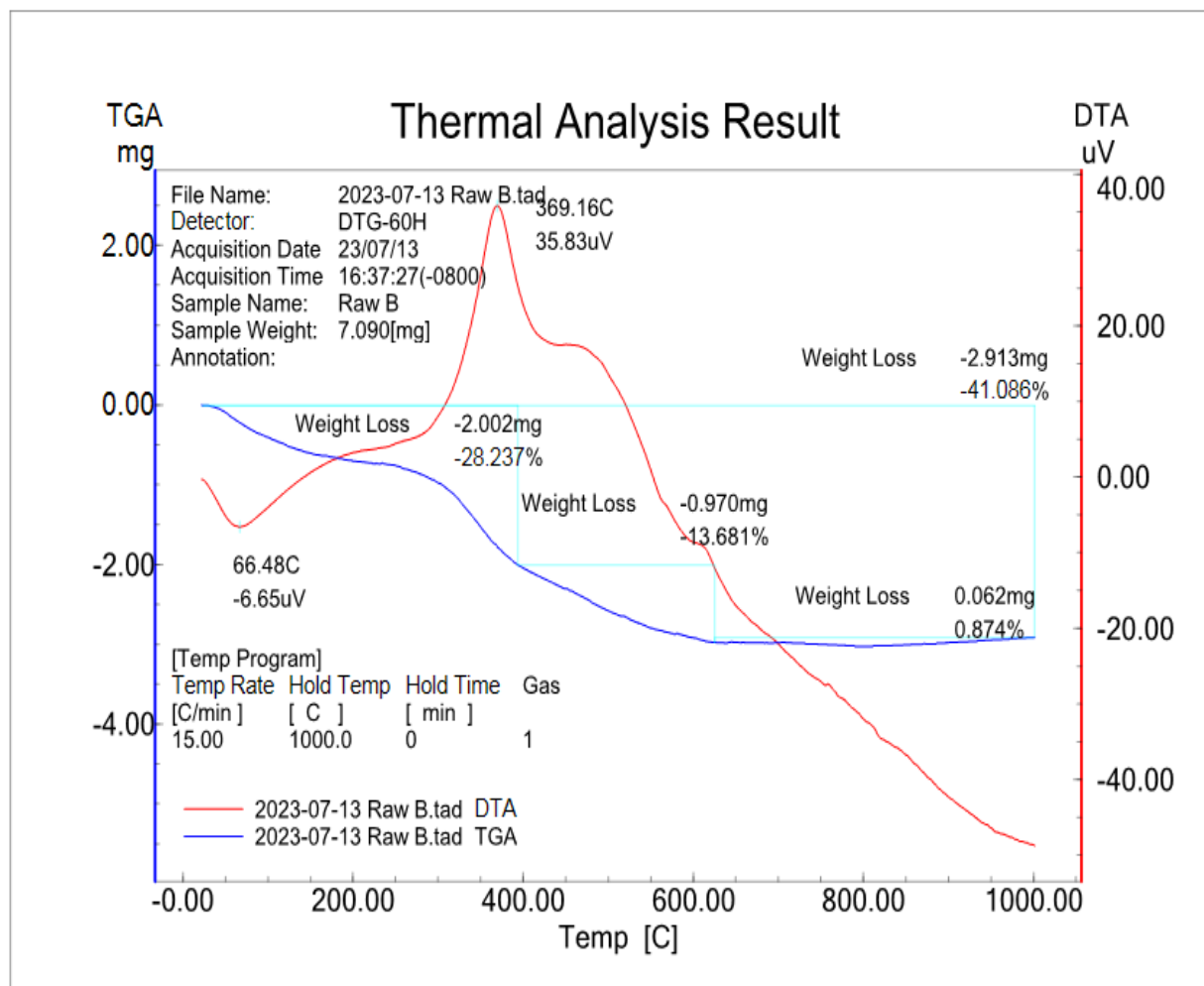


Appendix C: BET-specific surface area analysis of BBC and Ca-BBC

Quantachrome NovaWin - Data Acquisition and Reduction for NOVA instruments ©1994-2010, Quantachrome Instruments version 11.0			
Analysis		Report	
Operator:alex	Date:2007/01/01	Operator:alex	Date:7/20/2023
Sample ID: Ca-BBC b	Filename:	C:\QCdata\Physisorb\dc a.qps	
Sample Desc: sample	Comment:	TEST	
Sample weight: 0.08 g	Sample Volume: 0.02051 cc	Sample Density:3.9 g/cc	
Outgas Time: 8.0 hrs	OutgasTemp: 300.0 C		
Analysis gas: Nitrogen	Bath Temp: 77.3 K		
Press. Tolerance:0.100/0.100 (ads/des)Equil time: 60/60 sec (ads/des) Equil timeout: 240/240 sec (ads/des)			
Analysis Time: 63.8 min	End of run: 2007/01/01 2:52:39	Instrument:	Nova Station B
Cell ID: 2	F/W version: 0.00		
Adsorbate Nitrogen	Temperature 77.350K		
Molec. Wt.: 28.013 g	Cross Section: 16.200 Å²	Liquid Density: 0.808 g/cc	
Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]	
P/Po	cc/g		
5.02960e-02	28.4639	1.4887e+00	
1.33617e-01	48.7230	2.5326e+00	
1.96634e-01	63.1651	3.1004e+00	
2.81483e-01	82.8285	3.7843e+00	
3.45630e-01	98.1061	4.3077e+00	
BET summary			
Slope =		9.347	
Intercept =		1.159e+00	
Correlation coefficient, r =		0.994526	
Surface Area =		331.478 m²/g	

Quantachrome NovaWin - Data Acquisition and Reduction for NOVA instruments ©1994-2010, Quantachrome Instruments version 11.0			
Analysis		Report	
Operator:alex	Date:2007/01/01	Operator:alex	Date:7/20/2023
Sample ID: BBC	Filename:	C:\QCdata\Physisorb\ac sirn.qps	
Sample Desc: sample	Comment:	TEST	
Sample weight: 0.08 g	Sample Volume: 0.020513 cc	Sample Density:3.9 g/cc	
Outgas Time: 8.0 hrs	OutgasTemp: 300.0 C		
Analysis gas: Nitrogen	Bath Temp: 77.3 K		
Press. Tolerance:0.100/0.100 (ads/des)Equil time: 60/60 sec (ads/des) Equil timeout: 240/240 sec (ads/des)			
Analysis Time: 56.9 min	End of run: 2007/01/01 4:10:50	Instrument:	Nova Station B
Cell ID: 2	F/W version: 0.00		
Adsorbate Nitrogen	Temperature 77.350K		
Molec. Wt.: 28.013 g	Cross Section: 16.200 Å²	Liquid Density: 0.808 g/cc	
Relative Pressure	Volume @ STP	1 / [W((Po/P) - 1)]	
P/Po	cc/g		
5.50100e-02	24.7597	1.8811e+00	
1.20808e-01	40.4990	2.7147e+00	
2.08261e-01	60.4349	3.4825e+00	
2.83883e-01	77.6483	4.0848e+00	
3.47379e-01	92.3699	4.6107e+00	
BET summary			
Slope =		9.127	
Intercept =		1.501e+00	
Correlation coefficient, r =		0.99601	
Surface Area =		327.675 m²/g	

Appendix D: Thermal analysis result (TGA) raw bone sample



Appendix E: Proximate Analysis of raw Bone and bone-derived biochar (BBC) at 600 °C.

Material	Proximate analysis	Value
Raw bone	Moisture content, %MC	2.33 ± 0.49
	Percentage volatile matter, %VM.	42.16 ± 1.53
	Percentage ash content, %Ash.	50.32 ± 1.78
	Percentage fixed carbon content, %FC.	5.18 ± 0.67

Ca-BBC at 600 °C	Moisture content, %MC	1.32 ± 0.18
	Percentage volatile matter, %VM.	12.91 ± 1.86
	Percentage ash content, %Ash.	78.64 ± 3.13
	Percentage fixed carbon content, %FC.	7.14 ± 2.54

Note: value = mean ± SD

Appendix F: The values of R_L at various initial phosphate concentrations

Co (mg/L)	R_L
15	0.888
30	0.798
45	0.725
60	0.664
75	0.613

Appendix G: Isotherm data for the removal of phosphate by Ca-BBC composite

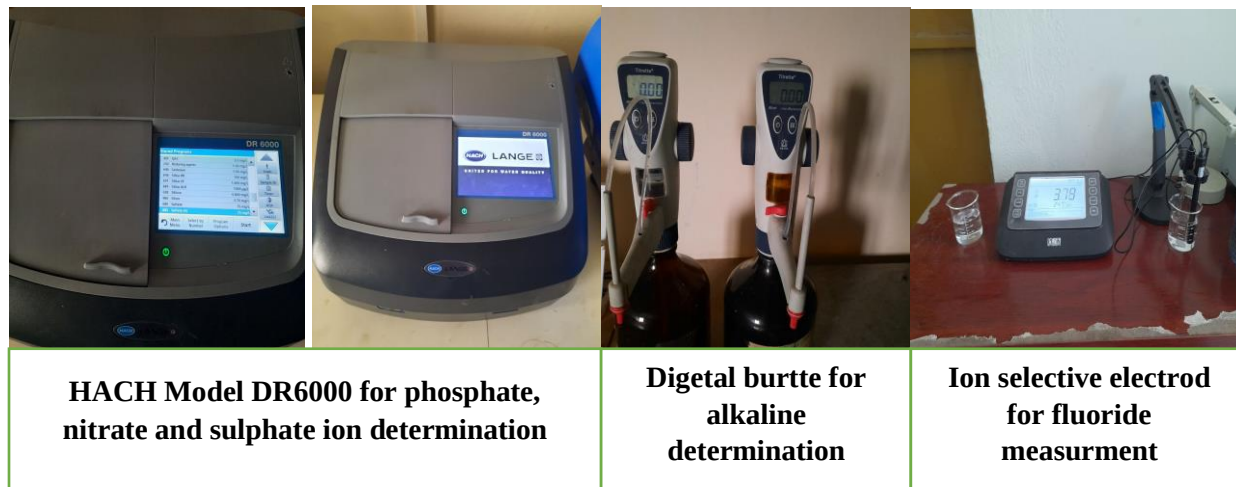
C_o (mg/L)	C_e (mg/L)	$1/C_e$	$\ln(C_e)$	q_e (mg/g)	$1/q_e$	$\ln(q_e)$	C_e/q_e
5	0.688	1.453	-0.374	0.359	2.782	-1.023	1.915
15	1.765	0.566	0.568	1.103	0.907	0.098	1.600

30	4.147	0.241	1.422	2.154	0.464	0.768	1.925
45	7.519	0.133	2.017	3.123	0.320	1.139	2.407
60	10.548	0.095	2.356	4.121	0.243	1.416	2.559
75	11.125	0.089	2.409	5.323	0.188	1.672	2.090

Appendix H: Pseudo-first order, pseudo-second order, and intra-particle diffusion kinetics data and its constant values

Time (hr)	C _o (mg/L)	C _e (mg/L)	q _t (mg/g)	q _e (mg/g)	ln(q _e -q _t)	t/q _t (g.min/mg)	t ^{0.5} (hr ^{0.5})
0	0	0	0	0	0	0	0
3	5	0.854	0.346	0.395	-3.008	8.683	1.732
5	5	0.689	0.359	0.395	-3.331	13.918	2.236
7	5	0.525	0.373	0.395	-3.813	18.771	2.646
9	5	0.361	0.386	0.395	-4.778	23.281	3
11	5	0.263	0.395	0.395	-	27.866	3.317
13	5	0.262	0.395	0.395	-	32.925	3.606
15	5	0.262	0.395	0.395	-	37.990	3.873

Appendix I: Instrument for Systematic Analysis of Competitive Ion



Appendix J: Standard calibration curve of phosphate removal

