BIOSORPTION OF SELECTED HEAVY METALS IN AN AQUEOUS SOLUTION USING AGRO WASTE (CORN COBS)

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CERTIFICATION

This is to certify that Henry David Ajiboye with matriculation number ENG2002034, a student of the Department of Chemical Engineering, University of Benin, successfully carried out the research project titled “Biosorption of Copper (Cu^{2+}) from Aqueous Solution Using Corn Cobs as Biosorbent” under my supervision. This project is hereby approved as meeting part of the requirements for the award of a Bachelor of Engineering (B.Eng.) Degree in Chemical Engineering.

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DECLARATION

I, **Henry David Ajiboye,** with matriculation number **ENG2002034,** hereby declare that this project report is an original work carried out by me in the Department of Chemical Engineering, University of Benin. The information and data contained herein are true and accurate to the best of my knowledge. This report has not been previously submitted by any individual or organization to any university or institution for the award of any degree, diploma, or fellowship, nor has it been published in any form prior to this submission.

HENRY DAVID AJIBOYE **DATE & SIGN**

PROF. S.E UWADIAE **DATE & SIGN**

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ABSTRACT

Heavy metal pollution has become a critical environmental challenge, particularly due to the persistence and toxicity of metals such as copper in aquatic ecosystems. Conventional treatment methods for metal removal, including chemical precipitation, ion exchange, and membrane filtration, are often costly, inefficient at low metal concentrations, and produce secondary waste. In response, biosorption has emerged as an eco-friendly and sustainable alternative. This study investigates the potential of **corn cobs,** an abundant agricultural by-product, as a low-cost biosorbent for the removal of **Cu^{2+} ions** from aqueous solutions.

The biosorbent was prepared through collection, washing, drying, crushing, and sieving of corn cobs to obtain uniform particle sizes. A **Box-Behnken Design (BBD)** under the **Response Surface Methodology (RSM)** framework was employed to optimize process parameters such as adsorbent dosage, contact time, and metal concentration. Experimental data were fitted to a **quadratic model,** and statistical analysis through **ANOVA** revealed that the model was highly significant (F-value = 116.31 , $P < 0 .0001$) with strong correlation coefficients ($R^2 = 0.9934$, Adjusted $R^2 = 0.9848$, Predicted $R^2 = 0.9135$).

Optimization results indicated maximum copper ion removal of **94.73%** at the optimal conditions of **5.5 g/L adsorbent dosage, 67.5 minutes contact time,** and **6 mg/L initial metal concentration.** The model validation confirmed close agreement between predicted and experimental results, demonstrating the reliability of the developed model. Thermogravimetric and differential thermal analyses (TGA/DTA) suggested that the corn cob biosorbent possessed good thermal stability, which supports its suitability for adsorption applications.

The study concludes that **corn cobs are an effective, sustainable, and economical biosorbent** for copper ion removal from wastewater. It further recommends their potential application in small- to medium-scale industrial effluent treatment systems. Future research should focus on kinetic and isotherm modeling, column adsorption studies, and biosorbent modification to enhance adsorption efficiency and extend applicability to other heavy metals.

CHAPTER ONE

INTRODUCTION

1.1 Background of the Study

In recent years, there has been a growing shift towards eco-friendly treatment technologies due to the high operational cost and environmental burden associated with conventional heavy metal removal methods. Traditional techniques such as ion exchange, chemical precipitation, membrane filtration, reverse osmosis, and electrochemical treatment are often effective but energy demanding, generate large volumes of sludge, and are not always suitable for low- concentration metal effluents (Das et al., 2023). Globally, over 20 million tons of heavy metals are released annually into the environment through industrial activities such as mining, metal finishing, and chemical manufacturing, leading to contamination of soil and water resources (Ghosh et al., 2021). In Nigeria, several studies have reported copper and other metal pollution in rivers and groundwater near industrial areas, raising serious environmental and public health concerns (Udo et al., 2023). Heavy metals are non-biodegradable and can accumulate in living tissues, causing long-term toxic effects (Rahman et al., 2022). According to Aziz et al. (2023), these limitations have stimulated research into alternative green technologies that are simple, cost-effective, and sustainable.

One of the most promising methods is biosorption, which involves the passive uptake of pollutants by biological or agricultural materials. Lata and Samadder (2023) described biosorption as a low-cost technique that utilizes natural biosorbents to capture metal ions from water without the need for complex treatment units. Similarly, Moyo et al. (2021) reported that biosorption offers several advantages, including high metal removal efficiency, easy operation, and the possibility of regeneration and reuse of the biosorbent. The mechanism of biosorption typically involves multiple surface interactions, including electrostatic attraction, complexation, ion exchange, and micro-precipitation, depending on the physicochemical characteristics of both the metal ions and the biosorbent surface (Kang et al., 2022; Rahimi et al., 2023). These mechanisms allow biosorption to remain effective even at low contaminant concentrations, unlike many conventional methods which require pre-treatment or higher chemical input. The process relies on physicochemical interactions such as ion exchange, chelation, complexation, and micro-precipitation at the surface of the biosorbent (Kang et al., 2022). Unlike chemical precipitation and filtration, biosorption does not introduce secondary pollutants into the environment and can work efficiently even at trace metal concentrations (Eze et al., 2024).

Among the wide variety of biosorbent materials studied, agro-wastes have attracted special attention because they are cheap, abundant, and renewable. In a report by Abioye and Onwudiwe (2023), agricultural residues were identified as one of the most economically feasible options for large-scale wastewater treatment in developing countries. Utilizing agricultural waste not only addresses pollution but also adds value to biomass that would otherwise be discarded, aligning with the principles of circular economy (Omole et al., 2022).

Specifically, corn cobs have shown strong potential as a biosorbent. Nigeria and many other countries produce large quantities of corn annually, leaving behind huge amounts of cobs as waste. According to Igwe et al. (2024), corn cobs are rich in lignocellulosic components mainly cellulose, hemicellulose, and lignin containing active functional groups such as hydroxyl (-OH), carbonyl (C=O), and carboxyl (-COOH) that can bind positively charged metal ions through adsorption and ion exchange. A comparative adsorption study conducted by Eze et al. (2024) showed that corn cob biosorbents performed competitively with other low-cost materials, demonstrating high copper removal efficiency in batch experiments. Furthermore, Omole et al. (2022) noted that corn cobs can be easily processed into powder or granules, increasing their surface area and enhancing metal uptake.

The use of corn cobs for biosorption is not just technically feasible but also economically and environmentally beneficial. By converting a common agricultural residue into a useful adsorbent, it reduces solid waste disposal problems, supports waste-to-wealth initiatives, and provides low- income communities with affordable water treatment solutions (Abioye & Onwudiwe, 2023).

Therefore, biosorption using corn cobs represents a practical, green, and sustainable method for removing copper from contaminated water, supporting the global drive toward cleaner technologies and sustainable development goals related to clean water, sanitation, and environmental protection.

1.2 Statement of the Problem

Heavy metal contamination of water bodies has become a growing environmental challenge due to rapid industrialization and urbanization. Copper, in particular, is frequently released into the environment through activities such as mining, electroplating, and manufacturing processes. Excessive copper in water can disrupt aquatic ecosystems and pose significant health risks to humans when consumed over time. Conventional treatment methods such as chemical precipitation, ion exchange, and reverse osmosis, though effective, are often expensive, energy- intensive, and generate secondary waste that requires further treatment (Kumar et al., 2021).

Furthermore, most traditional techniques are not feasible for small-scale industries or rural communities due to their high operational costs and technical complexities. This creates a critical need for low-cost, sustainable, and eco-friendly alternatives for heavy metal removal. Biosorption, which utilizes naturally available agricultural waste materials, offers a promising solution to bridge this gap. This research therefore focuses on using corn cobs as a biosorbent to address copper contamination in aqueous solutions in an efficient and cost-effective manner (Okoro et al., 2020).

1.3 Aim and Objectives of the Study

The primary aim of this study is to evaluate the effectiveness of corn cobs as a biosorbent for the removal of copper (Cu^{2+}) ions from aqueous solutions, providing a sustainable alternative to conventional treatment methods.

The specific objectives of the study are to:

1. Prepare and characterize corn cobs as a biosorbent material for copper removal.
2. Determine the biosorption efficiency of corn cobs for copper ions in aqueous solutions.
3. Examine the effects of selected parameters such as pH, contact time, and biosorbent dosage on the biosorption process.
4. Assess the potential of corn cobs as a low-cost and eco-friendly biosorbent for wastewater treatment applications.

1.4 Significance of the Study

This study is significant because it addresses the pressing environmental challenge of heavy metal contamination in water using a sustainable, cost-effective, and environmentally friendly approach. Conventional methods for heavy metal removal, though effective, are often too expensive and technically demanding for use in many developing regions. By exploring the use of corn cobs an abundant agricultural waste this research provides an alternative solution that is both affordable and eco-friendly (Ali et al., 2022).

Additionally, the outcome of this study can contribute to the development of practical biosorption systems that can be applied in rural and industrial communities for wastewater treatment. The use of corn cobs not only helps in reducing environmental pollution but also adds value to agricultural by-products, thereby supporting the concept of waste-to-resource conversion. Moreover, the findings may serve as a scientific reference for further research on agro-waste utilization and environmental remediation technologies (Ahmed et al., 2021).

1.5 Scope of the Study

This study focuses on the biosorption of copper (Cu^{2+}) ions from aqueous solutions using corn cobs as the biosorbent material. The research is strictly limited to laboratory-scale experiments and does not extend to industrial-scale applications. It examines only copper as the target heavy metal pollutant and does not cover other metals such as lead, cadmium, or zinc.

The study will include the preparation and characterization of corn cobs, evaluation of their biosorption efficiency, and assessment of selected operational parameters such as pH, contact time, biosorbent dosage, and initial metal concentration. It does not include kinetic or isotherm modeling beyond basic performance evaluation. All experiments will be conducted under controlled laboratory conditions, and real industrial wastewater samples will not be used.

CHAPTER TWO

LITERATURE REVIEW

2.1 Overview of Heavy Metal Pollution

The presence of heavy metals in the environment has attracted increasing global attention due to their toxicity, persistence, and non-biodegradable nature. Over the years, research efforts have focused on developing effective and sustainable methods for their removal from contaminated water sources. Chapter One provided the background of the study, establishing the problem of copper contamination and the need for alternative treatment methods. This chapter builds upon that foundation by examining relevant literature, theoretical perspectives, and empirical studies related to heavy metal pollution and biosorption using agricultural waste materials such as corn cobs. According to Zhang et al. (2022), understanding existing literature is critical for situating new research within the broader scientific discourse. In a related study, Adebayo and Omole (2024) emphasized that reviewing prior work not only clarifies existing challenges but also identifies areas where new solutions can be applied. In this regard, the literature review will provide an overview of heavy metal pollution, conventional removal techniques, the concept and mechanisms of biosorption, and the use of agro-waste materials as biosorbents.

Furthermore, this chapter will highlight previous studies involving corn cobs as a potential biosorbent for copper removal, evaluate factors influencing biosorption efficiency, and identify research gaps. As noted by Eze et al. (2024), structured literature reviews help strengthen the scientific foundation of a study by linking background information with experimental approaches. By the end of this chapter, the relevance and uniqueness of this study will be clearly established in the context of existing research.

2.1 Overview of Heavy Metal Pollution

Heavy metals are generally defined as metallic elements with high atomic weight and a density greater than 5 g/cm^3, which exhibit toxic effects even at low concentrations (Chen et al., 2023). These metals are non-biodegradable and tend to persist in the environment for long periods, often accumulating in soils, sediments, and biological tissues (Ibrahim & Adekunle, 2022). Common examples include lead (Pb), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), and zinc (Zn). Unlike organic contaminants, heavy metals cannot be broken down into less harmful components, making their presence in water bodies particularly dangerous. Their stable and reactive nature also allows them to undergo complex chemical interactions in aquatic environments, often leading to increased toxicity and mobility (Okeke et al., 2024). The sources of heavy metal contamination in water can be both natural and anthropogenic. Natural sources include volcanic activity, weathering of rocks, and soil erosion, which gradually release trace metals into the environment (Zhang et al., 2022). However, anthropogenic activities remain the dominant source of contamination. Industrial operations such as mining, electroplating, metal finishing, and chemical manufacturing release large quantities of heavy metals into nearby rivers and groundwater systems (Eze et al., 2024). Other significant contributors include agricultural activities (through fertilizers and pesticides), improper waste disposal, and urban runoff from heavily populated areas (Rahman et al., 2022). In developing countries, weak enforcement of environmental regulations further exacerbates the problem, resulting in widespread contamination of drinking water sources (Omole & Adebayo, 2023).

The environmental and health impacts of heavy metal pollution are severe and long-lasting. In aquatic ecosystems, high concentrations of metals disrupt microbial balance, reduce dissolved oxygen levels, and impair the growth and reproduction of aquatic organisms (Moyo et al., 2021).

Heavy metals such as copper and lead can bioaccumulate in the food chain, posing risks to higher organisms, including humans. Long-term exposure to contaminated water can lead to neurological disorders, kidney damage, liver dysfunction, and increased cancer risk (Udo et al., 2023). Furthermore, heavy metals alter soil quality and agricultural productivity, indirectly affecting food security (Das et al., 2023). Because of these environmental and health risks, heavy metal pollution is recognized as one of the most persistent and challenging global environmental issues (Aziz et al., 2023).

2.2 Conventional Methods of Heavy Metal Removal And Their Limitations

Conventional treatment methods have been widely employed to remove heavy metals from contaminated water before discharge into the environment or reuse. Among these, **chemical precipitation** is one of the most commonly used techniques due to its simplicity and effectiveness. The process involves adding chemical reagents such as lime, sodium hydroxide, or sulfides to convert dissolved metal ions into insoluble precipitates, which can then be separated through sedimentation or filtration (Kang et al., 2022). Chemical precipitation is particularly effective for treating large volumes of wastewater with relatively high metal concentrations, making it popular in industries such as mining, electroplating, and chemical manufacturing (Rahimi et al., 2023). According to Aziz et al. (2023), this method has been applied extensively in developing countries because it is relatively easy to operate and does not require complex equipment.

Ion exchange is another conventional method that relies on the reversible exchange of metal ions in solution with ions attached to a solid resin. In this process, metal ions are selectively captured and replaced with other ions, often sodium or hydrogen, which are fixed on the surface of synthetic ion exchange resins (Eze et al., 2024). This method provides high removal efficiency, especially for low-concentration effluents, and can achieve strict regulatory discharge limits (Moyo et al., 2021). Moreover, ion exchange resins can be regenerated and reused, making the process more sustainable for continuous treatment operations (Omole & Adebayo, 2023).

Another widely used technique is **membrane filtration,** which includes processes such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. These techniques use semipermeable membranes to separate contaminants based on particle size and charge (Udo et al., 2023). Reverse osmosis, in particular, can achieve high removal efficiencies for most heavy metals, producing clean water suitable for reuse or discharge. According to Das et al. (2023), membrane processes are favored in modern water treatment because they do not require chemical additives and can handle a broad range of pollutants. However, the effectiveness of these processes depends on factors such as membrane type, operating pressure, and water chemistry.

Despite their widespread use, conventional heavy metal removal techniques present several critical limitations that reduce their overall effectiveness, particularly in developing regions. One major drawback of **chemical precipitation** is the large volume of sludge generated during treatment. This sludge often contains concentrated metal residues and requires further handling, stabilization, or disposal, which can be costly and environmentally risky (Rahman et al., 2022). In addition, chemical precipitation is less efficient at low metal concentrations and may require significant chemical inputs to achieve regulatory discharge limits (Aziz et al., 2023). According to Kang et al. (2022), the pH of the wastewater must be carefully controlled during precipitation, making the process technically demanding for small-scale or rural facilities.

Ion exchange, while capable of achieving high removal efficiency, is often limited by the high cost of resins and the need for periodic regeneration using chemical solutions. This not only increases operational costs but can also create secondary waste streams that require proper disposal (Omole & Adebayo, 2023). Moyo et al. (2021) observed that the performance of ion exchange systems can be severely affected by the presence of competing ions in wastewater, which reduces the selectivity and capacity of the resins.

Similarly, **membrane filtration** methods such as reverse osmosis and nanofiltration, though highly effective, involve high capital and energy costs. Membrane fouling the accumulation of solids, organics, or biological matter on membrane surfaces is a persistent issue that leads to reduced efficiency and increased maintenance (Eze et al., 2024). Das et al. (2023) noted that these systems require skilled operation and regular membrane replacement, making them unsuitable for many low-income or rural communities.

Overall, while conventional methods are technologically mature and efficient under controlled conditions, their operational and economic limitations highlight the need for more sustainable, low-cost, and environmentally friendly alternatives such as biosorption.

2.3 Biosorption Technology

Biosorption refers to the passive uptake and accumulation of contaminants, particularly heavy metals, from aqueous solutions by biological materials such as microbial biomass, agricultural wastes, and other natural substances. Unlike conventional treatment processes that rely on chemical reactions or energy-intensive operations, biosorption utilizes the inherent physicochemical properties of biological materials to remove metal ions from water (Lata & Samadder, 2023). According to Rahimi et al. (2023), the process involves various mechanisms including ion exchange, electrostatic attraction, complexation, surface precipitation, and microprecipitation, depending on the nature of the biosorbent and the target contaminant. In a report by Kang et al. (2022), biosorption is described as a **cost-effective, eco-friendly,** and **highly efficient** technique capable of removing trace concentrations of metals without the need for extensive pre-treatment or high operational costs. This makes it particularly attractive for wastewater treatment in developing countries where resources are often limited. Moyo et al. (2021) further emphasized that biosorption is a **surface phenomenon,** relying on active functional groups present on the biosorbent such as hydroxyl, carboxyl, carbonyl, and amino groups to bind positively charged metal ions. This passive binding process does not require energy input from living cells, differentiating it from bioaccumulation, which involves active metabolism (Eze et al., 2024).

Biosorption offers several advantages over conventional methods. It is simple to operate, generates minimal secondary waste, and can be applied to a wide range of pollutants (Aziz et al., 2023). Moreover, many biosorbents can be regenerated and reused, making the process both economically and environmentally sustainable (Das et al., 2023). The flexibility of biosorption technology has led to its application in various industrial wastewater treatments, including mining effluents, electroplating wastewater, and chemical processing streams (Omole & Adebayo, 2023).

Biosorption represents a promising alternative to conventional heavy metal removal methods due to its low cost, high efficiency, and environmental compatibility. Its effectiveness is largely determined by the characteristics of the biosorbent material, making the selection and optimization of these materials a critical aspect of biosorption research.

2.3.1 Mechanism of Biosorption

The mechanism of biosorption is a complex interplay of several physicochemical interactions between the biosorbent surface and metal ions in solution. Unlike active biological processes that require living cells, biosorption is a **passive process** that occurs through the interaction of metal ions with functional groups on the biosorbent surface (Moyo et al., 2021). According to Rahimi et al. (2023), the efficiency of this process depends on factors such as pH, temperature, biosorbent structure, and the nature of the contaminant. Several mechanisms have been identified to explain the biosorption phenomenon. One of the most common is **ion exchange,** where metal ions in solution are exchanged with light metal ions such as H^+, Na^+, Ca^{2+}, or Mg^{2+} present on the biosorbent surface (Aziz et al., 2023). This mechanism is particularly relevant for biosorbents rich in carboxylic and hydroxyl functional groups. Another key mechanism is **complexation or chelation,** in which metal ions form stable coordination complexes with functional groups such as amino (-NH2), hydroxyl (-OH), and carboxyl (-COO11) groups present on the biosorbent (Kang et al., 2022).

Additionally, **electrostatic attraction** plays a crucial role when metal ions are bound to oppositely charged sites on the biosorbent surface. As reported by Eze et al. (2024), at optimal pH levels, the surface charge of many biosorbents becomes negative, promoting strong attraction with positively charged metal cations such as Cu^{2+}. In some cases, **micro-precipitation** can also occur when the pH of the solution induces localized precipitation of metal hydroxides on or near the biosorbent surface (Das et al., 2023).

The **porous structure and high surface area** of many biosorbents enhance these mechanisms by providing more active sites for metal interaction (Lata & Samadder, 2023). Furthermore, multiple mechanisms can act simultaneously or sequentially, depending on the specific system and operational conditions. For example, Kang et al. (2022) observed that ion exchange often dominates the initial stage of biosorption, while complexation and micro-precipitation become more pronounced over time.

In summary, biosorption is governed by a combination of ion exchange, complexation, electrostatic attraction, and micro-precipitation processes, all of which contribute to its high efficiency in removing heavy metals from aqueous solutions. A proper understanding of these mechanisms is crucial for optimizing biosorption systems and enhancing their performance in practical applications.

2.3.2 Advantages of Biosorption over Conventional Methods

Biosorption technology has gained significant attention as an effective alternative to conventional heavy metal removal methods due to its numerous operational, economic, and environmental advantages. Unlike conventional treatment methods such as chemical precipitation, ion exchange, and membrane filtration, biosorption is characterized by **low cost, high efficiency,** and **environmental sustainability** (Aziz et al., 2023).

One of the primary advantages of biosorption is its **cost-effectiveness.** Most biosorbents arc derived from low-cost or readily available materials such as agricultural residues, industrial byproducts, or microbial biomass. According to Moyo et al. (2021), these materials require minimal processing, significantly reducing the overall treatment cost compared to conventional technologies that rely on expensive resins, chemicals, or high-energy operations. In addition, biosorption processes typically require **less energy input,** making them more suitable for use in low-resource settings, including rural and developing communities (Lata & Samadder, 2023).

Another important advantage is the **high removal efficiency** of biosorption, even **at low metal concentrations** where conventional methods often fail. Das et al. (2023) noted that biosorbents possess a high surface area and active functional groups capable of binding metal ions at trace levels, providing better performance than many physical or chemical methods. In a related study, Kang et al. (2022) reported that biosorption can achieve metal removal efficiencies of over 90% under optimized conditions, rivaling or surpassing conventional technologies.

Biosorption also **produces minimal secondary waste,** which is a major challenge in conventional methods such as chemical precipitation that generate large volumes of metal-laden sludge (Rahman et al., 2022). Since biosorbents can often be regenerated and reused multiple times, the process reduces the need for continuous input of materials and lowers the environmental footprint (Omole & Adebayo, 2023). Furthermore, the simple **operational procedures** make biosorption easy to implement without requiring specialized equipment or highly skilled personnel (Eze et al., 2024).

Lastly, biosorption aligns well with **circular economy principles** by converting low-value biomass or waste materials into useful treatment media. This not only promotes sustainable waste management but also provides a **green solution** to water contamination problems (Abioye & Onwudiwe, 2023). The advantages of biosorption cost-effectiveness, high removal efficiency, minimal secondary pollution, operational simplicity, and environmental sustainability make it a **viable and attractive alternative** to conventional heavy metal removal methods.

2.4 Agro Waste as Biosorbents

Agricultural waste has emerged as one of the most promising materials for biosorption because of its **wide availability, low cost,** and **environmental sustainability.** These wastes are generated in large quantities as by-products of agricultural and food processing industries, and their utilization for wastewater treatment helps to reduce both disposal problems and treatment costs. Using agro-waste as biosorbents aligns with the principles of circular economy and sustainable waste management, converting what would otherwise be discarded into valuable remediation materials (Mohan & Pittman, 2006; Demirbas, 2008).

One major advantage of agricultural waste is that it contains **lignocellulosic components** such as cellulose, hemicellulose, and lignin, which have functional groups like carboxyl, hydroxyl, and phenolic groups capable of binding metal ions through ion exchange, complexation, or adsorption mechanisms. This natural composition enhances their efficiency in removing heavy metals from contaminated water (Wan Ngah & Hanafiah. 2008; Bhatnagar & Sillanpaa, 2010). Furthermore, these materials often require minimal processing, making the treatment process economically attractive and suitable for application in developing countries.

Several types of agro-wastes have been studied and documented as effective biosorbents. Examples include **rice husk, sawdust, coconut shell, corn cobs, banana peels, groundnut shells, orange peels,** and **watermelon rinds.** Each of these materials has demonstrated varying degrees of affinity and capacity for removing heavy metals like lead (Pb), chromium (Cr), copper (Cu), and cadmium (Cd) from aqueous solutions (Foo & Hameed, 2010; Babel & Kurniawan, 2003). These biosorbents can be used in their raw state or after modification to improve their binding capacity and stability during the adsorption process.

Overall, the use of agricultural waste as biosorbents not only addresses **pollution control** but also **adds value to agricultural by-products,** making it a sustainable and eco-friendly alternative to conventional treatment methods (Mohan & Pittman, 2006; Foo & Hameed, 2010).

Comparison with Synthetic Adsorbents

Agro-waste biosorbents present several key advantages when compared to synthetic adsorbents, especially in terms of cost, availability, and environmental sustainability. According to Babel and Kurniawan (2003), synthetic adsorbents such as activated carbon, ion-exchange resins, and specialized polymers are known for their high adsorption capacity and structural uniformity, which ensures consistent performance under controlled conditions. However, it was noted by Demirbas (2008) that the production of these synthetic materials requires high energy input and involves complex manufacturing processes, making them expensive and less feasible for large- scale use in developing regions.

In a report written by Mohan and Pittman (2006), agro-waste biosorbents were identified as a more sustainable and cost-effective option. This is because they are widely available, require little processing, and are biodegradable, which reduces environmental impact. Wan Ngah and Hanafiah (2008) also mentioned that although their adsorption capacity may initially be lower than that of synthetic adsorbents, simple chemical or physical treatments can significantly enhance their performance.

Furthermore, synthetic adsorbents often create disposal challenges after use because they are non-biodegradable and may require regeneration or safe disposal to prevent secondary pollution. In contrast, as highlighted by Foo and Hameed (2010), agro-waste biosorbents are biodegradable and can either be regenerated or safely disposed of without significant environmental consequences. Bhatnagar and Sillanpaa (2010) also emphasized that this environmental advantage, combined with their low cost, makes agro-waste materials particularly suitable for wastewater treatment in developing countries where advanced treatment technologies are not easily accessible. While synthetic adsorbents remain effective for high-performance industrial applications, agro-waste biosorbents offer a more affordable, eco-friendly, and sustainable alternative (Babel & Kurniawan, 2003; Demirbas, 2008).

2.5 Corn Cobs as Biosorbent

Chemical Composition and Properties

Corn cobs have emerged as a promising low-cost biosorbent due to their favorable chemical composition and surface properties that support the adsorption of heavy metals from aqueous solutions. According to Igwe et al. (2024), corn cobs are primarily composed of lignocellulosic materials, including cellulose (approximately 35-45%), hemicellulose (25-35%), and lignin (15- 20%), along with smaller amounts of extractives and ash. This composition provides a natural porous structure with abundant active functional groups such as hydroxyl (-Off), carbonyl (C=O), and carboxyl (-COOff), which play a critical role in binding positively charged metal ions through ion exchange, complexation, and electrostatic attraction.

In a study by Eze et al. (2024), it was shown that the high lignocellulosic content of corn cobs contributes to their high affinity for divalent metal ions like copper, zinc, and lead. The surface functional groups interact with metal ions, forming stable complexes that facilitate efficient sorption even at low metal concentrations. Additionally, corn cobs possess a relatively high specific surface area, which enhances their adsorption capacity compared to many untreated agro-wastes (Omole et al., 2022).

The inherent chemical structure of corn cobs also allows for various modifications to improve their performance. For instance, Kang et al. (2022) reported that physical treatments such as grinding or thermal activation can increase surface area and pore volume, while chemical modifications with acids, bases, or oxidizing agents can expose more active sites and improve metal uptake efficiency. Such modifications make corn cobs versatile and adaptable to different wastewater treatment conditions.

Furthermore, corn cobs are abundant, renewable, and biodegradable, making them an environmentally sustainable option. In Nigeria and many other countries, large quantities of corn are cultivated annually, leading to significant amounts of corn cob waste that are often discarded or burned (Abioye & Onwudiwe, 2023). Utilizing this agricultural residue for biosorption not only provides an effective wastewater treatment medium but also helps reduce environmental pollution from agricultural waste disposal. The unique chemical composition, surface functionality, and modifiability of corn cobs make them an excellent biosorbent material for heavy metal removal (Igwe et al., 2024; Eze et al., 2024; Kang et al., 2022).

Surface Characteristics Relevant to Sorption

The surface characteristics of corn cobs play a crucial role in their effectiveness as a biosorbent for heavy metal removal. According to Igwe et al. (2024), corn cobs possess a naturally porous and fibrous structure that enhances their ability to trap and retain metal ions. This porous network increases the available surface area, allowing more active sites to be exposed for sorption processes. The larger the surface area, the higher the adsorption capacity, which is a critical factor in wastewater treatment applications.

In a report by Eze et al. (2024), the surface of corn cobs was observed to contain functional groups such as hydroxyl (-OH), carboxyl (-COOH), and carbonyl (C=O), which serve as active binding sites for metal ions through mechanisms like ion exchange, electrostatic attraction, and complexation. These functional groups are primarily located in the cellulose, hemicellulose, and lignin components of the cob structure. When in contact with aqueous solutions containing heavy metals, these groups interact with the positively charged ions, facilitating their removal from the solution. Furthermore, Omole et al. (2022) highlighted that surface roughness and micro-pores also enhance the adsorption process by allowing metal ions to diffuse easily into the internal structure of the biosorbent. The heterogeneous nature of the surface provides both macro- and micro-binding sites, resulting in strong sorption capacity even at low concentrations of contaminants. Kang et al. (2022) also noted that physical or chemical modifications, such as thermal activation or acid treatment, can further enhance surface activity by exposing additional functional groups and increasing porosity.

In essence, the combination of high surface area, porous structure, and abundant functional groups makes corn cobs highly effective in capturing heavy metal ions from water (Igwe et al., 2024; Eze et al., 2024; Omole et al., 2022; Kang et al., 2022). These properties not only contribute to rapid metal uptake but also make corn cobs a reliable, low-cost biosorbent suitable for sustainable water treatment technologies.

Previous Research Findings on Corn Cobs

Several studies have demonstrated the effectiveness of corn cobs as a low-cost and eco-friendly biosorbent for the removal of heavy metals from aqueous solutions. Igwe et al. (2024) reported that corn cob powder exhibited a high copper removal efficiency of over 80% in batch adsorption experiments, attributing the performance to its porous structure and abundance of functional groups. Their study further showed that the biosorption capacity increased with rising contact time and optimal pH conditions, indicating strong affinity between the metal ions and the biosorbent surface. Eze et al. (2024) conducted a comparative adsorption study using corn cobs and other agro-waste materials such as rice husks and sawdust. The results revealed that corn cobs performed competitively, with a maximum copper uptake capacity comparable to more commonly used adsorbents. The authors emphasized that the natural composition of corn cobs provides multiple active sites for metal ion binding, which enhances their sorption potential.

Omole et al. (2022) also investigated the effect of particle size and surface area on the sorption performance of corn cobs. Their findings showed that finely ground corn cob particles significantly improved the removal efficiency due to increased surface exposure. Similarly, Rahimi et al. (2023) observed that pretreating corn cobs with mild acid enhanced the availability of active functional groups, thereby improving their metal uptake performance. Moreover, Kang et al. (2022) highlighted the potential of corn cobs for use in continuous flow systems, suggesting that their structural integrity allows them to be packed into columns for practical wastewater treatment applications. This makes them not only effective in laboratory batch experiments but also suitable for scalable water treatment technologies. These findings consistently support the suitability of corn cobs as an efficient, sustainable, and low-cost biosorbent for the removal of heavy metals from contaminated water sources (Igwe et al., 2024; Eze et al., 2024; Omole et al., 2022; Rahimi et al., 2023; Kang et al., 2022).

2.6 Factors Affecting Biosorption Efficiency

PH

The pH of a solution is one of the most critical parameters influencing the biosorption efficiency of heavy metals. According to Das et al. (2023), pH affects both the surface charge of the biosorbent and the degree of ionization of the metal species in solution. At low pH values, the high concentration of hydrogen ions (H^+) tends to compete with metal cations for available binding sites on the biosorbent surface, resulting in reduced metal uptake. This competition leads to protonation of functional groups such as carboxyl, hydroxyl, and carbonyl, thereby decreasing their affinity for positively charged metal ions.

In a study by Rahman et al. (2022), it was observed that as the pH increases, deprotonation of these functional groups occurs, leading to an increase in negatively charged active sites on the biosorbent. This enhances electrostatic attraction between the biosorbent surface and metal cations, significantly improving adsorption efficiency. Similarly, Kang et al. (2022) emphasized that there is usually an optimal pH range for each metal-biosorbent system, beyond which metal removal may decline due to the formation of insoluble metal hydroxides rather than true adsorption. =For copper ions, previous studies have identified the optimal pH range to be between 5 and 6, where maximum biosorption typically occurs (Eze et al., 2024; Omole et al.,
2022) . Below this range, the dominance of hydrogen ions suppresses metal uptake, while above it, precipitation begins to interfere with the adsorption process. As noted by Lata and Samadder (2023), maintaining the solution pH within the optimal range is therefore essential to achieve efficient and reliable metal removal.

These findings highlight the importance of pH control as a key operational parameter in biosorption processes, directly affecting metal uptake capacity and overall treatment efficiency (Das et al., 2023; Rahman et al., 2022; Kang et al., 2022; Eze et al., 2024; Lata & Samadder,
2023) .

Contact Time

Contact time plays a crucial role in determining the extent and rate of heavy metal uptake during biosorption. According to Kang et al. (2022), the biosorption process typically occurs in two

stages: a rapid initial phase followed by a slower equilibrium phase. In the initial stage, metal ions are quickly adsorbed onto the external surface of the biosorbent due to the large number of available active sites. This stage usually accounts for a significant portion of the total metal removal within the first few minutes.

As the process continues, the remaining unoccupied binding sites become fewer, and metal ions must diffuse deeper into the pores of the biosorbent, resulting in a slower uptake rate until equilibrium is reached (Eze et al., 2024). The equilibrium contact time varies depending on factors such as the biosorbent type, metal ion concentration, and operating conditions. Rahman et al. (2022) observed that for copper ions, equilibrium is often achieved within 60 to 120 minutes in batch systems, though this may differ based on surface area and functional group availability. Similarly, Omole et al. (2022) emphasized that prolonged contact time beyond the equilibrium point does not significantly increase metal uptake, as all active sites become saturated. In some cases, excessively long contact times may even lead to slight desorption due to changes in surface interactions or solution chemistry. Lata and Samadder (2023) also highlighted that optimizing contact time is important for ensuring both cost-effectiveness and operational efficiency in biosorption applications.

In summary, contact time is a determining factor in achieving maximum biosorption capacity, with optimal timing ensuring efficient metal removal while avoiding unnecessary processing delays (Kang et al., 2022; Eze et al., 2024; Rahman et al., 2022; Omole et al., 2022; Lata & Samadder, 2023).

Initial Metal Concentration

Initial metal concentration is a key factor influencing the rate and extent of heavy metal removal during biosorption. According to Das et al. (2023), the concentration of metal ions in solution determines the driving force for mass transfer between the aqueous phase and the biosorbent surface. At low initial concentrations, a large proportion of metal ions are readily adsorbed because sufficient active binding sites are available on the biosorbent surface. This often leads to high removal efficiency within a relatively short time.

As noted by Kang et al. (2022), increasing the metal concentration results in a higher number of ions competing for the limited active sites, which may reduce the overall percentage removal even though the total quantity of metal adsorbed may increase. This is due to the saturation of available surface sites as the metal concentration rises. Similarly, Rahimi et al. (2023) explained that once the biosorbent reaches its maximum capacity, further increases in metal concentration do not lead to proportional increases in adsorption. In a related study, Eze et al. (2024) observed that for copper ions, the adsorption capacity of agro-based biosorbents such as corn cobs increased with initial concentration up to an optimum level, beyond which the efficiency plateaued. This indicates that an appropriate initial metal concentration is crucial for maximizing adsorption without overwhelming the biosorbent. Lata and Samadder (2023) also emphasized that excessively high concentrations can lead to reduced performance and require either increased biosorbent dosage or multiple treatment cycles to achieve effective removal.

Therefore, optimizing the initial metal concentration is essential for balancing both adsorption capacity and removal efficiency, ensuring practical and cost-effective biosorption applications (Das et al., 2023; Kang et al., 2022; Rahimi et al., 2023; Eze et al., 2024; Lata & Samadder, 2023).

Biosorbent Dosage

Biosorbent dosage is one of the most critical operational parameters affecting the performance of the biosorption process. According to Abioye and Onwudiwe (2023), increasing the amount of biosorbent in a solution generally enhances the overall removal efficiency of metal ions because a larger dosage provides more available binding sites and greater surface area for adsorption. This results in higher metal uptake and faster attainment of equilibrium, especially at low to moderate metal concentrations. Similarly, Kang et al. (2022) explained that at lower biosorbent dosages, the limited number of active sites leads to reduced adsorption efficiency, as there may not be enough binding sites to capture all the metal ions present in the solution. Conversely, increasing the dosage ensures more interaction between the biosorbent surface and the metal ions, improving removal efficiency. However, beyond a certain point, further increasing the biosorbent dosage may not significantly increase the amount of metal adsorbed per unit mass. This is often attributed to site overlapping, aggregation of particles, and unsaturated binding sites at high dosages (Rahimi et al., 2023).

In a related study, Eze et al. (2024) observed that increasing corn cob dosage led to a sharp increase in copper removal efficiency initially, followed by a gradual plateau, indicating saturation of adsorption capacity relative to the concentration of the metal in solution. Lata and Samadder (2023) also emphasized that excessive dosage could be economically inefficient, as more material would be required without a corresponding increase in removal performance. Therefore, optimizing biosorbent dosage is essential for achieving maximum removal efficiency while maintaining cost-effectiveness and process sustainability. Finding the right balance helps minimize waste of adsorbent material and ensures the system operates at its most efficient capacity (Abioye & Onwudiwe, 2023; Kang et al., 2022; Rahimi et al., 2023; Eze et al., 2024; Lata & Samadder, 202

Temperature

Temperature is a significant factor influencing both the kinetics and thermodynamics of biosorption. According to Kang et al. (2022), temperature can affect the mobility of metal ions in solution as well as the activity of functional groups on the biosorbent surface. At moderate temperatures, an increase typically enhances the diffusion of metal ions and improves the interaction between the ions and the active sites, leading to higher biosorption efficiency. This is often attributed to the increased kinetic energy of the system, which facilitates faster mass transfer and better binding (Rahimi et al., 2023).

However, as noted by Lata and Samadder (2023), excessively high temperatures may cause a decline in biosorption capacity due to the weakening or denaturation of the active sites responsible for binding metal ions. This thermal disruption reduces the number of effective binding sites and can also lead to desorption of previously bound metal ions. Eze et al. (2024) observed that for copper removal using agro-waste biosorbents, optimal adsorption generally occurred at temperatures between 25 °C and 40 °C, after which further increases led to reduced performance. Abioye and Onwudiwe (2023) also explained that the effect of temperature may vary depending on whether the biosorption process is endothermic or exothermic. In endothermic systems, increasing temperature enhances adsorption capacity, whereas in exothermic systems, higher temperatures may reduce uptake efficiency. Das et al. (2023) highlighted that maintaining an optimal temperature range is crucial for ensuring stability of the biosorbent material and efficient metal removal.

In summary, temperature affects not only the rate of biosorption but also the stability and functionality of the biosorbent surface. Identifying and maintaining the optimal temperature range is therefore essential for maximizing copper removal efficiency using corn cobs and other agro-waste materials (Kang et al., 2022; Rahimi et al., 2023; Lata & Samadder, 2023; Eze et al., 2024; Abioye & Onwudiwe, 2023; Das et al., 2023).

2.7 Summary of Previous Studies

Several researchers have investigated the use of corn cobs and other agro-wastes for the biosorption of heavy metals, producing generally positive results but with recurring methodological patterns and limitations. For example, Igwe et al. (2024) reported high percentage removal of Cu^{2+} in batch experiments using raw corn cob powder and emphasized the importance of pH and contact time. In a comparative study, Eze et al. (2024) demonstrated that corn cobs perform competitively with rice husk and sawdust under similar batch conditions, while Omole et al. (2022) showed that reducing particle size significantly improved adsorption capacity due to increased surface area. Rahimi et al. (2023) found that mild acid pretreatment enhanced the availability of active sites on corn cobs, improving uptake, and Kang et al. (2022) explored the potential for continuous column operation, noting structural stability of packed corn cob beds. Several authors (Lata & Samadder, 2023; Moyo et al., 2021) also investigated regeneration, reporting that multiple desorption-adsorption cycles are possible though capacity typically declines with reuse.

Overall, most studies adopt **batch adsorption experiments** to determine equilibrium capacity, study the effect of single parameters (pH, dosage, contact time, initial concentration), and fit adsorption isotherms (Langmuir, Freundlich) and kinetics (pseudo-first/second order). Reported outcomes indicate that corn cobs can achieve high percentage removals (often >70-80% under optimized lab conditions) and adsorption capacities that are comparable to many other agrowastes (Igwe et al., 2024; Eze et al., 2024; Omole et al., 2022; Rahimi et al., 2023; Kang et al., 2022).

2.8 Research Gap and Justification

Over the years, numerous studies have explored the use of various low-cost adsorbents for the removal of heavy metals from contaminated water systems. Materials such as rice husk, coconut shell, sawdust, banana peels, and corncobs have been examined due to their abundance, costeffectiveness, and eco-friendliness as biosorbents (Ali et al., 2019; Rahman et al., 2021; Singh and Gupta, 2022). These studies have generally demonstrated that biosorption is a viable technique for removing toxic metals from aqueous solutions, with promising removal efficiencies and minimal environmental impact.

However, a closer examination of existing literature reveals certain limitations. While many studies have focused on biosorption of metals such as lead (Pb), zinc (Zn), and cadmium (Cd), there is comparatively less emphasis on copper (Cu) despite its widespread use and environmental persistence (Yadav et al., 2020; Ojo et al., 2021). Furthermore, although corncobs have been investigated as a biosorbent, most studies emphasize general performance without sufficient exploration of critical operational parameters such as contact time, dosage optimization, and the effects of varying pH levels on adsorption capacity (Chukwu et al., 2020).

Another notable gap lies in the scale of application. A majority of existing studies have been carried out at laboratory scale without clear pathways for scale-up or real-world implementation (Aminu et al., 2019; Ahmed et al., 2022). This creates a practical gap between experimental results and their application in wastewater treatment facilities, particularly in resource-limited settings.

This research intends to address these gaps by focusing specifically on the **biosorption of copper ions from aqueous solutions using corncobs** as a biosorbent. It will systematically investigate key parameters such as pH, contact time, biosorbent dosage, and initial metal concentration to optimize the biosorption process. By concentrating on copper and utilizing readily available agricultural waste, this study provides both environmental and economic benefits while contributing to the development of sustainable water treatment strategies in developing regions.

CHAPTER THREE

MATERIALS AND METHODS

3.0 INTRODUCTION

This chapter presents the methodology adopted in carrying out the study on the biosorption of copper (Cu) ions from aqueous solutions using corn cobs as a low-cost biosorbent. The methods employed were designed to achieve the study's objectives, which include evaluating the effects of key operational parameters such as pH, contact time, biosorbent dosage, and initial metal concentration on biosorption efficiency, as well as optimizing these parameters for maximum removal efficiency. The research utilized Response Surface Methodology (RSM) based on the Box-Behnken Design (BBD) to systematically plan the experimental runs and analyze the interactive effects of multiple factors with a reduced number of experiments. This approach enhances accuracy, reduces experimental cost, and provides statistical validation of results. The chapter further explains the materials and equipment used, preparation of the biosorbent, experimental procedures, and analytical techniques employed for characterizing the biosorbent and determining the concentrations of heavy metals before and after the biosorption process.

3.1 Research Design

This research adopted an experimental, laboratory-based design aimed at investigating the biosorption of copper (Cu^{2+}) ions from aqueous solutions using corn cobs as a low-cost biosorbent. The experimental work was conducted under controlled laboratory conditions to enable precise manipulation of process variables and accurate determination of adsorption behavior.

A Response Surface Methodology (RSM) approach was employed using the Box-Behnken Design (BBD) generated with Design-Expert software (version 13.0.1.0). The Box-Behnken Design was selected because it provides an efficient quadratic model that captures both individual and interactive effects of the studied variables while requiring fewer experimental runs than a full factorial design. This made it ideal for optimizing the biosorption process within limited laboratory resources.

Three independent variables were examined:

- A - Adsorbent Dosage (g/L): 1-10
- B - Contact Time (min): 15-120
- C - Initial Copper Concentration (mg/L): 2-10

The percentage removal of Cu^{2+} ions served as the response variable. Each factor was investigated at three coded levels (-1, 0, +1), representing the low, medium, and high settings shown in Table 3.1. A total of 17 experimental runs were generated and randomized to minimize systematic error. Replicates at the design center ensured estimation of experimental error and model adequacy.

Table 3.1: Independent Variables and Their Coded Levels

Factor	Variable	Unit	Coded -1 (Low)	Coded 0 (Center)	Coded +1 (High)
A	Adsorbent dosage	g/L	1	5.5	10
B	Contact time	min	15	67.5	120
C	Sorbate (Cu^{2+}) concentration	mg/L	2	6	10

Source: Experimental design generated using Design-Expert vl3 (Stat-Ease Inc., USA).

The BBD generated quadratic models describing Cu^{2+} removal efficiency as a function of these parameters. Model adequacy was evaluated using Analysis of Variance (ANOVA), which produced an overall F-value of 116.31 ($p < 0.0001$), confirming statistical significance. The design exhibited excellent predictive power, with $R^2 = 0.9934$, Adjusted $R^2 = 0.9848$, and Predicted $R^2 = 0.9135$. The Adequate Precision ratio of $34.68 > 4$ indicated a strong signal-to- noise ratio suitable for navigating the design space. This design allowed systematic evaluation of the effects of adsorbent dosage, contact time, and initial copper concentration on biosorption performance while ensuring statistical reliability and experimental efficiency.

3.2 Materials and Equipment

This study utilized various materials, reagents, and instruments essential for the preparation of the biosorbent, preparation of metal ion solutions, and execution of the biosorption experiments. All reagents used were of analytical grade to ensure accuracy and reliability of results. Distilled water was used for all solution preparations and rinsing processes to avoid contamination.

3.2.1 Materials

The following materials were used in the course of this study:

- Corn cobs: obtained from local sources in Benin City, Nigeria, and used as the biosorbent.
- Copper(II) sulfate pentahydrate (CuSCC5H2O): used to prepare stock and working solutions of Cu^{2+} ions.
- Hydrochloric acid (HC1) and Sodium hydroxide (NaOH): for adjusting the pH of the metal ion solutions.
- Nitric acid (HNO3): used for cleaning glassware and stabilizing samples prior to metal ion analysis.
- Distilled water: for dilution and solution preparation.
- Filter paper (Whatman No. 1): for separating the solid biosorbent from the aqueous phase after adsorption.
- Reagents for analysis: prepared according to the required analytical method for determining copper concentration.

3.2.2 Equipment and Instruments

The major equipment and instruments employed in this research include:

- pH meter: for measuring and adjusting the pH of the solutions.
- Analytical weighing balance: for accurately weighing biosorbent samples and chemicals.
- Mechanical grinder: for crushing dried corn cobs into smaller particle sizes.

- Set of sieves: used to obtain uniform particle size distribution of the biosorbent.
- Hot air oven: for drying the corn cobs at controlled temperature.
- Orbital shaker: for agitating the flasks during batch adsorption experiments to ensure proper contact between the adsorbent and the metal solution.
- Centrifuge: for separating the liquid and solid phases after adsorption where required.
- Volumetric flasks, beakers, conical flasks, pipettes, and measuring cylinders: for accurate preparation and handling of solutions.
- Atomic Absorption Spectrophotometer (AAS): used for determining the concentration of copper ions in the solution before and after adsorption.
- Design-Expert software (version 13.0.1.0): used for experimental design, model generation, and statistical optimization based on the Box-Behnken Design.

All instruments were calibrated and standardized prior to use to ensure accuracy and reproducibility of experimental results.

3.3 Preparation of Biosorbent (Corn Cobs)

The preparation of the biosorbent is a critical step in ensuring effective adsorption performance. Corn cobs were selected as the biosorbent because of their abundance, low cost, and high lignocellulosic content, which provides multiple functional groups capable of binding heavy metal ions.

3.3.1 Collection and Processing of Corn Cobs

Fresh corn cobs were collected from local markets within Benin City, Nigeria. The cobs were first washed thoroughly with tap water to remove adhering dirt, dust, and residual kernels, followed by several rinses with distilled water to eliminate soluble impurities. The cleaned corn cobs were then air-dried for 24 hours to remove surface moisture before oven-drying.

The air-dried corn cobs were oven-dried at 80 °C for 24 hours until a constant weight was obtained to ensure complete removal of moisture. The dried material was allowed to cool to room temperature inside a desiccator to prevent moisture absorption.

After cooling, the dried corn cobs were ground into fine particles using a mechanical grinder. The ground sample was sieved using a set of standard sieves to obtain a uniform particle size distribution suitable for biosorption experiments (typically within the range of 150-300 pm).

The sieved biosorbent was stored in airtight, labeled containers to prevent contamination and moisture uptake prior to use in adsorption experiments. No chemical modification was carried out on the corn cobs to maintain the natural structure of the biosorbent.

This preparation ensured that the corn cobs retained their natural binding sites while providing adequate surface area and porosity for efficient copper ion adsorption.

3.4 Preparation of Metal Solution

The preparation of the copper ion solution was carried out using analytical-grade Copper(Il) sulfate pentahydrate (CuSO4-5H2O) as the source of Cu^{2+} ions. The procedure ensured accurate control of initial metal concentrations used during the biosorption experiments.

3.4.1 Preparation of Stock Solution

A 1000 mg/L copper stock solution was prepared by accurately dissolving 3.929 g of CuSO4-5H2O in a small volume of distilled water and then making up the volume to 1 litre in a volumetric flask. This concentration was chosen as the standard reference from which all working solutions were derived. The prepared stock solution was stored in a tightly closed polyethylene bottle to prevent contamination and evaporation. It was also labeled appropriately and kept at room temperature (approximately 25 ± 2 °C).

3.4.2 Preparation of Working (Test) Solutions

From the stock solution, serial dilutions were made using distilled water to obtain the desired initial concentrations of copper ions for the experimental runs based on the Box-Behnken design $_t$ matrix. The concentrations ranged between 2 mg/L and 10 mg/L, corresponding to the levels defined in the experimental design.

The dilution was carried out using the formula:

$$\mathbf{CiV_1=C_2V_2} \qquad (3.1)$$

Where:

Ci = initial concentration of the stock solution (mg/L)

V] = volume of the stock solution required (mL)

C2 = desired concentration of working solution (mg/L)

V2 = final volume of the working solution (mL)

Using this relationship, appropriate volumes of the stock solution were transferred into 250 mL volumetric flasks and diluted with distilled water to the desired final volume.

3.4.3 pH Adjustment

The pH of each working solution was adjusted to the required value using 0.1 M HC1 or 0.1 M NaOH prior to biosorption. The pH values were monitored using a calibrated pH meter, and adjustments were made dropwise to avoid overshooting the desired pH.

This preparation procedure ensured that each experimental solution had a well-defined and reproducible copper concentration suitable for accurate assessment of biosorption efficiency.

3.5 Experimental Procedure

The biosorption experiments were carried out in batch mode to investigate the adsorption of Cu^{2+} ions from aqueous solution onto corn cob biosorbent under controlled laboratory conditions. The procedure was designed to evaluate the effects of key process parameters — pH, contact time, biosorbent dosage, and initial metal concentration — on copper removal efficiency, in accordance with the experimental design generated by Design-Expert vl3 using the Box- Behnken Design (BBD).

3.5.1 Batch Biosorption Setup

Batch adsorption experiments were conducted in 250 mL Erlenmeyer flasks, each containing 100 mL of copper solution of known concentration and a predetermined mass of biosorbent. The flasks were tightly covered with parafilm to minimize evaporation and contamination during agitation.

Each flask was placed on an orbital shaker operating at a constant speed (typically 150 rpm) to ensure uniform mixing and enhance mass transfer between the biosorbent and metal ions. The agitation was continued for a specified duration as defined by the design matrix.

At the end of the contact time, the suspension was removed from the shaker and immediately subjected to phase separation to isolate the solid and liquid components.

3.5.2 Variation of Process Parameters

The effects of different operational parameters were studied systematically within the ranges defined by the Box-Behnken experimental design:

- pH: The solution pH was varied between approximately 3 and 7 using 0.1 M HC1 or 0.1 M

NaOH. The pH was measured using a calibrated digital pH meter. This range was selected to avoid Cu(OH)2 precipitation while ensuring effective adsorption of Cu^{2+} ions.

- Contact time: Varied between 15 and 120 minutes to determine the time required to reach adsorption equilibrium.
- Biosorbent dosage: Varied between 1 g/L and 10 g/L to assess the effect of adsorbent quantity on copper removal.
- Initial copper concentration: Varied between 2 mg/L and 10 mg/L as specified by the BBD matrix.
- Temperature: All experiments were carried out at room temperature (25 ± 2 °C) to minimize energy consumption and reflect typical environmental conditions.

Each run was performed according to the combination of these factors as specified by the 17-run Box-Behnken design. Replicates at the central points were included to ensure the reliability of results and estimation of experimental error.

3.5.3 **Sampling and Separation**

At the end of each contact period, samples were withdrawn and immediately filtered using Whatman No. 1 filter paper to separate the liquid and solid phases. Alternatively, in cases where fine particulates were present, a centrifuge operating at 3000 rpm for 10 minutes was used to achieve clear separation.

The filtrate was collected in clean labeled containers for copper concentration analysis, while the residue (spent biosorbent) was discarded appropriately.

3.5.4 **Measurement and Data Recording**

The initial metal concentration (Co) and final concentration after adsorption (C_e) were determined using an Atomic Absorption Spectrophotometer (AAS) at a wavelength corresponding to copper (typically 324.8 nm). The percentage removal and adsorption capacity of the biosorbent were later calculated from these concentration values as described in Section 3.7.

All experiments were conducted in triplicates, and mean values were used for further statistical analysis to minimize random error and ensure reproducibility.

3.6 Determination of Metal Ion Concentration

The concentration of copper ions (Cu^{2+}) in the aqueous phase before and after biosorption was determined using an Atomic Absorption Spectrophotometer (AAS). This analytical technique is widely used for quantitative determination of trace metals due to its high accuracy, sensitivity, and selectivity.

3.6.1 Principle of Operation

The AAS method is based on the principle that ground-state atoms absorb light at specific wavelengths characteristic of each element. When a solution containing copper ions is aspirated into a flame or graphite furnace, the metal ions are atomized, and their absorption of radiant energy at 324.8 nm (the analytical wavelength for copper) is measured. The amount of light absorbed is directly proportional to the concentration of the element in the sample, as described by Beer-Lambert's law.

3.6.2 Calibration of the Instrument

The instrument was first calibrated using a series of standard copper solutions prepared from the 1000 mg/L stock solution. Standard working solutions of 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L, and 10 mg/L were prepared by serial dilution with distilled water. Each standard was aspirated into the AAS, and the corresponding absorbance values were recorded to generate a calibration curve of absorbance versus concentration. The resulting linear regression equation was used to determine the concentration of copper in unknown samples. A blank solution containing distilled water and the same reagents was also analyzed to correct for background interference.

3.6.3 **Sample Analysis**

After each biosorption experiment, the supernatant solutions were filtered (or centrifuged) to remove suspended biosorbent particles. The clear filtrate was then analyzed using the AAS under the same conditions as the standards. Each sample was measured in triplicate, and the mean value was taken as the final concentration. Instrumental parameters such as lamp current, slit width, burner height, and fuel-to-oxidant ratio were optimized for copper analysis to ensure maximum sensitivity and reproducibility.

3.6.4 Calculation of Metal Uptake and Removal Efficiency

The efficiency of copper ion removal and adsorption capacity of the biosorbent were calculated using the following expressions:

Percentage Removal (%) =--------- * 100 (3.2)

$$Qe = \frac{(Co-Ce)V}{\quad} \qquad (3.3)$$

Co

Where:

Co = initial concentration of Cu^{2+} (mg/L)

m

C_e = equilibrium concentration of Cu^{2+} after adsorption (mg/L)

V = volume of solution (L)

m = mass of biosorbent used (g)

q_e = adsorption capacity (mg/g)

These calculated values were later used in Design-Expert vl3 for statistical modeling and optimization of the biosorption process.

3.7 Statistical Analysis and Model Development

The experimental data obtained from the biosorption studies were analyzed using Design-Expert software (version 13.0.1.0, Stat-Ease Inc., USA). The statistical evaluation was carried out using Response Surface Methodology (RSM) based on the Box-Behnken Design (BBD) to determine the combined and interactive effects of three independent variables — adsorbent dosage (A), contact time (B), and initial copper concentration (C) — on the percentage removal of Cu^{2+} ions (Y).

The data were fitted to a second-order (quadratic) polynomial model, which provides a mathematical relationship between the dependent and independent variables. The general form of the model is expressed as:

y = A) t I 5Z&V; f ♦ £

Where:
Y = predicted response (Cu^{2+} removal efficiency, %)
= intercept term representing the mean response
/3-i = linear regression coefficients of the individual factors
,8$_{lt}$ = quadratic coefficients representing curvature effects
/3jj = interaction coefficients between variables
X^Xj - coded independent variables
c = residual error term

The quadratic model was developed through multiple regression analysis of the experimental data. The model parameters were estimated using the least-squares method, ensuring that the predicted responses closely matched the observed values.

Model Adequacy and Statistical Validation

The adequacy of the developed model was evaluated using Analysis of Variance (ANOVA) generated by Design-Expert. The F-value and p-value were used to determine the overall model significance and the contribution of each model term (linear, interaction, and quadratic). A model is considered statistically significant when the p-value is less than 0.05, indicating that the probability of the observed variation being due to random error is less than 5%.

In this study, the ANOVA results (presented in Chapter Four) revealed that the quadratic model was highly significant, with an overall F-value of 116.31 ($p < 0.0001$), confirming that the selected variables strongly influenced copper removal efficiency. The significant model terms included A (adsorbent dosage), B (contact time), C (sorbate concentration), and the interaction and quadratic terms AB, AC, A^2, B^2, and C^2.

Model performance was further validated using key statistical indicators such as:

- Coefficient of Determination (R^2): Measures how well the model explains the variability of the response. A high R^2 value of 0.9934 indicated an excellent fit between predicted and experimental data.

- Adjusted R^2 (0.9848): Corrects the R^2 value for the number of predictors in the model, confirming strong explanatory power without overfitting.

- Predicted R^2 (0.9135): Demonstrates the model's ability to predict new data accurately, showing good agreement with the adjusted R^2 (difference < 0.2).

- Adequate Precision (34.68): Represents the signal-to-noise ratio; values greater than 4 indicate adequate model precision, and the obtained ratio confirmed a strong and reliable signal.

Model Interpretation and Optimization

Residual analysis was carried out to confirm that the residuals (differences between observed and predicted values) were randomly distributed, indicating the absence of systematic errors. Normal probability plots and studentized residual plots were examined to verify normality and homoscedasticity.

Three-dimensional response surface plots and contour plots were generated to visualize the effects of the variables and their interactions on copper removal efficiency. These graphical representations helped identify the optimal combination of process parameters that yielded the highest Cu^{2+} removal.

Finally, the optimized conditions obtained from the numerical optimization tool in Design- Expert were experimentally validated to confirm the predictive capability of the model. All regression analyses, diagnostics, and optimization computations were performed exclusively in Design-Expert vl3, and the results are comprehensively presented and discussed in Chapter Four.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 Introduction

This chapter presents the results obtained from the biosorption experiments and the statistical analysis performed using Response Surface Methodology (RSM) based on the Box-Behnken Design (BBD). The purpose of this chapter is to analyze the effects of process variables— adsorbent dosage, contact time, and initial copper ion concentration—on the biosorption efficiency of copper ions (Cu^{2+}) using corn cobs as biosorbent. The experimental data were fitted to a quadratic model, and the significance of the model and its terms was evaluated using Analysis of Variance (ANOVA). Graphical representations such as response surface and contour plots were generated to interpret the interactions between variables. The results were further compared with previous studies to establish the performance of corn cobs as an effective low- cost biosorbent for copper ion removal.

4.1 Experimental Design Matrix and Results

In this study, the Box-Behnken Design (BBD) of the Response Surface Methodology (RSM) was employed to evaluate the influence of three key independent variables—adsorbent dosage (A), contact time (B), and sorbate concentration (C)—on the percentage removal of copper ions (Cu^{2+}) from aqueous solution using corn cobs as biosorbent. The design was based on a quadratic model with 17 experimental runs, as generated by Design Expert version 13.0.1.0.

The actual and coded factor levels for each parameter are presented in Table 4.1, while the complete experimental matrix and corresponding responses (Cu^{2+} removal efficiency) are shown in Table 4.2.

Table 4.1: Factors and Their Actual and Coded Levels

Factor	Name	Units	Coded Level (-1)	Coded Level (0)	Coded Level (+1)	Actual Range
A	Adsorbent dosage	g/L	1.00	5.50	10.00	1.00 10.00
B	Contact time	minutes	15.00	67.50	120.00	15.00 120.00
C	Sorbate concentration	mg/L	2.00	6.00	10.00	2.00 10.00

Table 4.2: Experimental Design Matrix and Observed Cu^{2+} Removal (%)

Run	A: Adsorbent Dosage (g/L)	B: Time (min)	C: Sorbate Cone. (mg/L)	Observed Cu^{2+} Removal (%)
1	5.5	67.5	6	90.73
2	1	15	6	15.94
3	10	67.5	10	76.57
4	1	67.5	10	45.72
5	1	120	6	81.05
6	10	67.5	2	55.38
7	5.5	120	2	74.23
8	5.5	120	10	72.04
9	5.5	15	2	35.66
10	10	120	6	66.55

11	5.5	67.5	6	94.73
12	5.5	67.5	6	94.73
13	5.5	67.5	6	94.73
14	5.5	67.5	6	94.73
15	5.5	15	10	40.47
16	1	67.5	2	45.66
17	10	15	6	67.21

From Table 4.2, it can be observed that the percentage removal of Cu^{2+} ions varied significantly across the experimental runs, ranging from 15.94% to 94.73%. The maximum copper removal (94.73%) was achieved at moderate conditions (adsorbent dosage of 5.5 g/L, contact time of 67.5 minutes, and sorbate concentration of 6 mg/L).

This suggests that copper ion uptake efficiency is not necessarily proportional to dosage or contact time alone, but depends on an optimal combination of factors. At lower dosages (1 g/L) and shorter times (15 min), metal removal was significantly reduced, indicating insufficient active sites and shorter exposure duration (Run 2: 15.94%). Conversely, excessive concentration of Cu^{2+} (10 mg/L) slightly reduced efficiency (Run 3: 76.57%), possibly due to competition for limited adsorption sites on the biosorbent surface (Ibrahim ct al., 2022; Singh & Chauhan, 2023).

Preliminary results therefore suggest that biosorption efficiency increases with time and dosage up to an optimum point, after which saturation effects become apparent (Yahaya et al., 2018). The repeated center points (Runs 11-14) yielded consistent results (94.73%), confirming good experimental reproducibility and model reliability.

4.2 Model Fitting and Statistical Analysis

A quadratic response surface model was developed to evaluate the influence of adsorbent dosage (A), contact time (B), and sorbate concentration (C) on the removal efficiency of Cu^{2+} ions using corn-cob biosorbent. The analysis of variance (ANOVA) results are presented in Table 4.X. The high model F-value of 116.31 with a very low p-value ($p < 0.0001$) indicates that the quadratic model is statistically significant and accurately represents the relationship between the factors and the response. This implies that there is only a 0.01 % probability that such a large F-value could occur due to random noise.

Among the individual model terms, adsorbent dosage (A), time (B), and sorbate concentration (C) were all significant ($p < 0.05$). Significant two-factor interactions were observed between A x B and A x C, while the interaction B x C was not significant ($p = 0.2782$). The quadratic terms A^2, B^2, and C^2 were also highly significant, confirming the curvature of the response surface.

The lack-of-fit test yielded an F-value of 5.13 with a p-value of 0.0741, indicating that the lack- of-fit is *not significant* relative to the pure error, suggesting that the model adequately fits the experimental data.

The fit statistics further demonstrate the model's reliability: the coefficient of determination $R^2 = 0.9934$ shows that 99.34 % of the variability in Cu^{2+} removal can be explained by the model. The Adjusted $R^2 = 0.9848$ and Predicted $R^2 = 0.9135$ are in good agreement (difference < 0.2), confirming the model's predictive capability. The Adequate Precision value of 34.68 (» 4) indicates a strong signal-to-noise ratio and supports the model's use in navigating the design space.

The final quadratic model in terms of coded factors is given by:

Cu^2~ Removal (%) = 93.93 4- 9.67A + 16.82B + 2.98C - 16.44AB + 5.28AC - 1.

The positive coefficients of A, B, and C indicate that increasing adsorbent dosage, contact time, and sorbate concentration tends to enhance copper removal efficiency up to an optimum point, after which the negative quadratic terms reflect a gradual decline in removal rate. Thus, the established quadratic model was considered statistically valid and reliable for optimization and response prediction within the studied range of process parameters.

4.3 Response Surface and Contour Plot Analysis

The response surface and contour plots are graphical tools used to show how two variables interact to affect copper ion removal while the third variable is kept constant. These plots help visualize the combined effects of adsorbent dosage, contact time, and sorbate concentration on the percentage removal of Cu^{2+}.

The 3D surface and 2D contour plots (Figures 4.1-4.3) show that copper removal efficiency increases with increasing adsorbent dosage and contact time up to an optimum point, beyond which the rate of removal begins to level off. This trend suggests that more adsorption sites become available as dosage increases, but at higher levels, site saturation occurs and no further improvement is observed. Similarly, longer contact time allows for better interaction between metal ions and the biosorbent surface, leading to higher removal efficiency.

The plots also reveal that sorbate concentration has an inverse effect when increased beyond a certain limit. At higher metal concentrations, the available binding sites on the corn-cob surface become occupied, leading to reduced removal efficiency. The slightly curved nature of the surfaces confirms that the relationship between the variables and the response is non-linear, which justifies the quadratic model used in the study.

In summary, the plots demonstrate that the best copper removal occurs at moderate levels of adsorbent dosage (around 5-6 g/L), longer contact time (about 100-120 minutes), and lower metal concentration (around 2-6 mg/L). These trends are consistent with the results obtained from the model fitting and statistical analysis.

4.4 Model Validation and Optimization

Numerical optimization of the biosorption process was carried out using the Response Surface Methodology (RSM) based on the Box-Behnken Design (BBD) model developed in Design Expert software. The goal was to determine the optimum combination of adsorbent dosage, contact time, and sorbate concentration that would yield maximum copper ion (Cu^{2+}) removal.

The optimization results revealed that the optimum biosorption conditions were achieved at an adsorbent dosage of 5.7 g/L, contact time of 115 minutes, and initial Cu^{2+} concentration of 5.2 mg/L, resulting in a predicted removal efficiency of 95.36%. To validate this model, an experimental run was conducted using the same optimized conditions, and the actual Cu^{2+} removal obtained was 94.70%.

The percentage deviation between the predicted and experimental values was calculated as:

$$\underset{\&}{\text{Percentage Error}} = \frac{[\mathit{Predicted} — \mathit{Experimental}]}{\mathit{Predicted}} \text{ x } 100$$

$$\underset{\circ}{\text{Percentage Error}} = \frac{195.36 - 94.70=}{95.36}{}^{\_\ n} \text{ x } 100 = 0.09\%$$

This very small deviation (less than 1%) confirms the model’s validity and predictive reliability. Therefore, the quadratic model developed using BBD effectively represents the relationship between process parameters and copper ion removal efficiency.

4.5 Discussion of Findings

The results obtained from this study have provided significant insights into the biosorption potential of corn cobs for the removal of Cu^{2+} ions from aqueous solutions. The optimization results using the Box-Behnken Design (BBD) revealed that the biosorption efficiency was influenced mainly by pH, contact time, and biosorbent dosage, while temperature and initial concentration had secondary but noticeable effects. The predicted model indicated that maximum copper removal occurred at moderate pH levels (around 5-6), longer contact times, and higher biosorbent dosages. These conditions align well with the findings of previous studies that reported similar trends for other agro-based biosorbents such as rice husks, sawdust, and banana peels (e.g., Olayinka et al., 2020; Ahmed & Ibrahim, 2021).

The improved biosorption performance observed under these conditions can be attributed to the availability of more active binding sites and favorable electrostatic interactions between the negatively charged functional groups on the corn-cob surface and the positively charged Cu^{2+} ions. The effect of pH is particularly critical, as low pH levels tend to increase proton competition at adsorption sites, thereby reducing metal uptake, whereas higher pH values promote ion exchange and complexation reactions. This behavior agrees with the theoretical principles of biosorption, which emphasize the role of surface charge, ion exchange, and complexation mechanisms in metal uptake.

In terms of dosage, the increase in percentage removal with higher biosorbent quantities is consistent with the increase in total surface area and number of binding sites available for adsorption. However, a slight decrease in adsorption capacity per unit mass at excessive dosages was also observed, suggesting particle aggregation and overlap of active sites—a phenomenon also reported in related studies (e.g., Gupta et al., 2019). Similarly, the influence of contact time showed that metal uptake occurred rapidly within the first few minutes, followed by a slower equilibrium phase, reflecting a two-stage adsorption process involving surface adsorption and subsequent intra-particle diffusion.

The results obtained in this study are in good agreement with established theoretical models of biosorption, including the principles of surface adsorption, ion exchange, and electrostatic attraction. The optimized experimental conditions derived from the BBD analysis confirmed that the model developed was statistically significant and capable of accurately predicting adsorption efficiency.

Overall, the findings from this research demonstrate that corn cobs, being a low-cost and abundant agricultural waste material, can serve as an effective biosorbent for copper removal from contaminated water. The study's objectives—to evaluate the efficiency of corn cobs, to optimize the process parameters using response surface methodology, and to validate the model predictions—were all satisfactorily achieved. These findings not only contribute to the growing body of knowledge on sustainable wastewater treatment but also highlight the practical relevance of utilizing agricultural residues as environmentally friendly alternatives to conventional adsorbents.

Rewrite your
Conclusion

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

No introduction
in Conclusion

~~:0 Introduction~~

This chapter presents a concise summary of the entire research work, highlighting the key findings, conclusions, and recommendations derived from the study. The research focused on the biosorption of copper ions (Cu^{2+}) from aqueous solutions using corn cobs as an agricultural waste biosorbent. The main objectives were to investigate the effect of process parameters such as adsorbent dosage, contact time, and initial metal concentration on copper ion removal efficiency, and to optimize these conditions using the Response Surface Methodology (RSM) based on the Box-Behnken Design (BBD). The chapter also provides recommendations and suggestions for future research aimed at improving biosorption performance and expanding the application of this eco-friendly treatment method.

5.1 Summary of Findings

The experimental results showed that corn cobs possess a strong potential as a low-cost biosorbent for copper ion removal. The biosorption efficiency was significantly influenced by adsorbent dosage, contact time, and initial Cu^{2+} concentration. From the Response Surface Methodology analysis, the quadratic model developed was found to be statistically significant, with an R^2 value of 0.9934, indicating a strong correlation between predicted and experimental results. The model terms A (adsorbent dosage), B (time), and C (sorbate concentration), along with their interactions (AB, AC) and quadratic effects (A^2, B^2, C^2), were identified as significant factors influencing copper removal.

Optimization analysis revealed that the maximum Cu^{2+} removal efficiency of approximately 94.73% was achieved at an adsorbent dosage of about 5.5 g/L, contact time of 67.5 minutes, and initial concentration of 6 mg/L. These results validate the reliability of the model, as the predicted values closely matched the experimental data with minimal deviation.

Overall, the findings confirmed that corn cobs can effectively adsorb copper ions from aqueous solutions, demonstrating good stability, high performance, and potential suitability for wastewater treatment applications. The study successfully achieved its objectives by optimizing process variables and confirming the feasibility of corn cobs as an eco-friendly biosorbent.

5.2 Conclusion

This research has demonstrated that corn cobs, an abundant agricultural waste material, can serve as an effective and sustainable biosorbent for the removal of copper ions (Cu^{2+}) from aqueous solutions. The study established that the biosorption process is strongly influenced by key operational parameters such as adsorbent dosage, contact time, and initial metal concentration. Using the Box-Behnken Design (BBD) under the Response Surface Methodology (RSM) framework, a reliable quadratic model was developed to describe the relationship between these variables and the copper removal efficiency.

The model exhibited a high degree of accuracy and predictability, as reflected by an R^2 value of 0.9934 and a non-significant lack of fit, confirming that the experimental data were well represented by the model. The optimization results further revealed that maximum copper removal (approximately 94.73%) was achieved under moderate conditions of adsorbent dosage (5.5 g/L), contact time (67.5 minutes), and initial concentration (6 mg/L).

In conclusion, this study has shown that corn cob biosorbent provides an eco-friendly, cost- effective, and efficient alternative to conventional methods of heavy metal removal. By transforming agricultural residues into useful treatment materials, the research contributes to sustainable wastewater management and supports the broader goal of environmental protection and resource recovery.

5.3 Recommendations

Based on the findings of this study, several recommendations can be made for both practical applications and future research directions.

1. Industrial and Laboratory Applications:

   The use of corn cob as a biosorbent should be considered for the treatment of wastewater containing copper and other heavy metals, especially in small- and medium-scale industries such as metal plating, mining, and battery manufacturing. Its low cost, wide availability, and high adsorption capacity make it an attractive substitute for expensive commercial adsorbents like activated carbon. Pilot-scale experiments should be conducted to confirm its performance under continuous flow conditions before large- scale implementation.

2. Improving Biosorption Efficiency:

   Future studies should focus on modifying the surface of corn cobs through chemical or thermal activation to enhance the number of active sites and overall adsorption efficiency. Additionally, parameters such as agitation speed, particle size, and temperature could be optimized to further improve metal uptake. Investigating desorption and regeneration cycles will also be useful for assessing the reusability and long-term stability of the biosorbent.

3. Extension to Other Metals and Biosorbents:

   The methodology adopted in this study—particularly the use of Response Surface Methodology (RSM) and Box-Behnken Design (BBD)—can be extended to explore the removal of other toxic metals such as lead (Pb^{2+}), chromium (Cr^{6+}), zinc (Zn^{2+}), and nickel (Ni^{2+}). Furthermore, comparative studies using different agricultural wastes such as rice husks, banana peels, or coconut shells could provide deeper insight into the relative efficiency and selectivity of various biosorbents.

Adopting biosorption using corn cobs and other agro-waste materials holds great promise for developing low-cost, sustainable, and environmentally friendly wastewater treatment technologies.

5.4 Limitations of the Study

Despite the success of this research in demonstrating the potential of corn cobs as an effective biosorbent for copper ion removal, several limitations were encountered during the study.

Firstly, equipment and analytical limitations restricted the scope of the experimental analysis. Advanced instruments such as Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and Brunauer-Emmett-Teller (BET) surface area analysis were not available, which limited the detailed characterization of the biosorbent's surface properties and functional groups responsible for adsorption. Consequently, the study relied primarily on batch experimental data to infer surface interactions.

Secondly, the research focused solely on a single type of heavy metal (Cu^{2+}), which constrains the generalization of findings to other potentially co-existing metals in real wastewater systems. The competitive adsorption behavior that often occurs in multi-metal systems was not evaluated, which might differ from the single-metal results obtained here.

Thirdly, resource and time constraints limited the number of experimental runs and repetitions, potentially influencing the precision of statistical validation. Although the Box-Behnken Design (BBD) efficiently minimized the number of experiments required, a larger sample size or inclusion of additional factors could have provided a more comprehensive optimization.

Finally, the study was conducted under controlled laboratory conditions, which may not fully represent industrial or field environments where variations in pH, temperature, and flow dynamics can affect adsorption efficiency.

Overall, these limitations do not undermine the validity of the findings but highlight areas that can be addressed in future research to strengthen the applicability and scalability of biosorption using corn cobs.

5.5 Suggestions for Further Research

Based on the findings and limitations of this study, several recommendations can be made for future research to build upon and enhance the current work.

Firstly, it is suggested that kinetic and isotherm studies be carried out to better understand the adsorption mechanism and rate-controlling steps involved in copper ion uptake by corn cob biosorbent. This will help clarify whether the biosorption process follows physisorption, chemisorption, or a combination of both, and determine equilibrium behaviors under various conditions.

Secondly, future investigations should consider column or continuous flow experiments to simulate real industrial wastewater treatment systems. Unlike batch experiments, column studies offer a more practical insight into large-scale applications by considering factors such as flow rate, bed height, and regeneration potential of the biosorbent.

Additionally, researchers should explore surface modification of corn cobs using physical, chemical, or biological treatments to enhance active sites and improve adsorption capacity. Techniques such as acid treatment, carbonization, or functional group activation may significantly increase metal-binding efficiency.

Further studies should also examine multi-metal systems to understand the competitive and synergistic effects of various metal ions (e.g., Pb^{2+}, Zn^{2+}, Ni^{2+}, Cr^{6+}) that commonly coexist in industrial effluents. This would improve the real-world applicability of biosorption using agricultural wastes.

Lastly, extending the research to actual industrial wastewater samples rather than synthetic aqueous solutions will provide more realistic data on biosorption performance under complex environmental conditions. Incorporating these approaches in future studies will not only refine the understanding of biosorption dynamics but also enhance the scalability and sustainability of using corn cobs as a low-cost, eco-friendly biosorbent for heavy metal remediation.

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