PINE NEEDLES AS GREEN MATERIAL FOR REMOVAL OF METAL IONS AND DYES FROM WASTEWATER

A

PROJECT REPORT

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of

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HIMACHAL PRADESH, INDIA

MAY, 2024

DECLARATION

I hereby declare that the work presented in the Project report entitled **"PINE NEEDLES AS GREEN MATERIAL FOR REMOVAL OF METAL IONS AND DYES FROM WASTEWATER"** submitted for partial fulfillment of the requirements for the degree of Bachelor of Technology in Civil Engineering at **Jaypee University of Information Technology, Waknaghat** is an authentic record of my work carried out under the supervision of **Dr. Rishi Rana.** This work has not been submitted elsewhere for the reward of any other degree/diploma. I am fully responsible for the contents of my project report.

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CERTIFICATE

This is to certify that the work which is being presented in the project report titled **“PINE NEEDLES AS GREEN MATERIAL FOR REMOVAL OF METAL IONS AND DYES FROM WASTE WATER”** in partial fulfillment of the requirements for the award of the degree of Bachelor of Technology in Civil Engineering submitted to the Department of Civil Engineering, **Jaypee University of Information Technology, Waknaghat** is an authentic record of work carried out by **Dechen Wangmo (201605)** during a period from January 2024 to May 2024 under the supervision of **Dr. Rishi Rana** (Assistant Professor, Senior Grade), Department of Civil Engineering, Jaypee University of Information Technology, Waknaghat.

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ABSTRACT

According to the United Nations World Water Development Report, the industrial sector uses 22% of freshwater and an estimated 380 billion cubic meters of wastewater are generated globally, but only 24% of this is treated before disposal or reuse. With the increasing growth of the population and industrial activities, waste water generated is also increasing which potentially contributes to increase in the pollutants present in the environment. There is a lot of conventional methods like coagulation-flocculation, membrane filtration, reverse osmosis, chemical precipitation, ion-exchange, electrochemical treatment, solvent extraction, etc. which are being employed to remove the pollutants from the wastewater in the world. But it has its limitations, whereby there is an increase in the demand for effective and environmentally friendly solutions for the management of the resources we have and treat wastewater using the concept of circular economy so that in long run we won't be facing resource shortages.

As a result, it has prompted us to explore other techniques and employ sustainable materials to manage our resources and treat wastewater in order to lessen the strain on the environment. The study will provides a valuable insight into the application of natural materials like pine needles in water remediation, fostering the integration of sustainable practices in environmental management. The current research will study the characteristics of pine needles which affect the absorbance of the pollutants like metal ions and dyes, specifically methylene blue dye and cobalt metal ion. It also involves the collection and preparation of different pine needle biochar, followed by the activation methods implied on it. We will also be conducting batch experiments to obtain optimum parameters like dosage, temperature and time for maximum removal of the pollutants. On further research we will be using pine needle biochar is practical situations and check the effectiveness of the biochar on the wastewater like sewage and textile wastewater. To enhance its sustainability we can explore the potential for reusability and regeneration of the adsorbent. The outcomes of this research will contribute to the development of a green and economically viable solution for the removal of dye and metal ions, addressing both environmental and economic concerns associated with wastewater treatment.

Keywords: wastewater treatment, biochar, pine needles, sustainability, waste management

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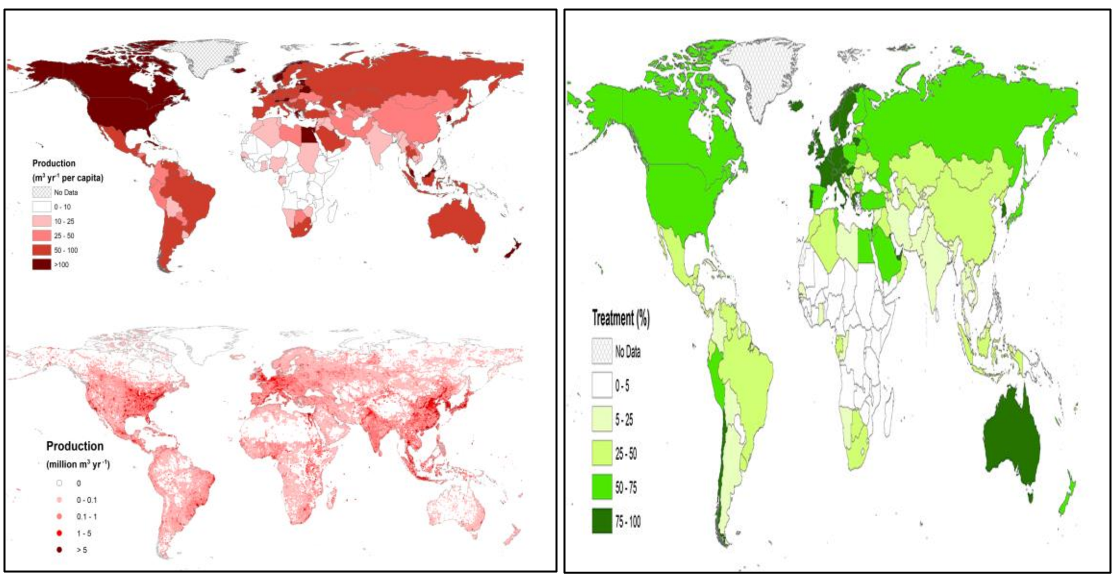
LIST OF ACRONYMS AND ABBREVIATION

APB	Activated pine needle biochar
PNB	Native pine needle biochar
BOD	Biological oxygen demand
COD	Chemical oxygen demand
TSS	Total suspended solid
TDS	Total dissolved solid
TS	Total solid
UV	Ultraviolet
JUIT	Jaypee University of Information Technology
MLD	Mega liters per day
KLD	Kilo liters per day
ASTM	American Society for Testing and Materials

CHAPTER 1
INTRODUCTION

1.1 GENERAL

It is estimated that more than 2.6 billion people in developing countries lack access to clean water for personal hygiene or drinking. According to the United Nations World Water Development Report, the industrial sector uses 22% of freshwater, with high-income countries using 59% and low-income countries using 8%. An estimated 380 billion cubic meters of wastewater are generated globally, but only 24% of this is treated before disposal or reuse [23]. As for India, 38,354 MLD of wastewater is generated daily and the treatment plant has a capacity to treat only 11,786 MLD [11]. Many development activities, such as urbanization, caused by population growth and lifestyle changes, also increase wastewater volumes and represent a major issue of the 21st century: ensuring access to clean and sufficient water for all. The Figure 1.1 below shows the production and the percentage of wastewater treated in the world.



[a] [b]

Figure 1.1: (a) Production of wastewater and (b) % of the treatment [23]

It is a well-known fact that the world's water resources are suffering from continuous degradation due to the release of various organic and inorganic pollutants, such as heavy metals, dyes, pharmaceuticals, pesticides, and personal care products, into water bodies by industries and municipalities [32]. These pollutants are highly persistent and difficult to remove, causing harm to ecosystems. To address this issue, conventional technologies such as coagulation-flocculation, adsorption, membrane filtration, reverse osmosis, chemical precipitation, ion-exchange, electrochemical treatment, solvent extraction, and flotation are used worldwide [12]. However, these methods have limitations such as inefficiency, high energy and chemical consumption, process complexity, and high maintenance costs. To overcome these limitations, research into environmentally friendly materials and sustainable wastewater treatment methods proves to be a promising approach to address the pressing wastewater pollution problem. Green materials such as pine needles are easily available as forest waste and can be converted into a carbonaceous material called biochar, which has natural properties such as surface chemistry and porous structure which provides an effective means of adsorption. Due to their low cost, renewable nature and natural affinity for pollutants, they are a sustainable alternative to traditional treatment technologies [5]. Previous research articles have also demonstrated its effectiveness in treating wastewater to meet the environmental and financial requirements of sustainable development.

1.2 WASTEWATER POLLUTION

As communities expand and industrial activities intensify, wastewater pollution poses serious challenges to environmental sustainability and public health worldwide [7]. Wastewater production has skyrocketed, posing a major threat to ecosystems, water resources, and human well-being and understanding the scope and implications of wastewater pollution is paramount for devising effective mitigation strategies and safeguarding our shared environment.

The impacts of wastewater pollution are diverse and involve different dimensions, underscoring its critical importance in current environmental debates. In essence, wastewater pollution poses a profound threat to the integrity of aquatic ecosystems, disrupting fragile ecological balances and endangering biodiversity [13]. When untreated or inadequately treated wastewater is discharged into waterways, a variety of pollutants are produced, including organic matter, heavy metals, and synthetic chemicals. These pollutants can have harmful effects on aquatic life, from fish and amphibians to macro-invertebrates and aquatic plants. Wastewater contaminants can disrupt biological processes, impair reproductive success, weaken immune systems, lead to population declines and changes in species composition [46]. Furthermore, the accumulation of contaminants in sediments and food webs may have long-term ecological consequences, affecting ecosystem resilience and stability.

In addition to ecological impacts, the discharge of untreated or inadequately treated wastewater can degrade water quality and render it unusable for human, recreational and agricultural purposes [43]. The Figure 1.2 below shows the sources and the impacts of wastewater. Wastewater contaminants can contaminate drinking water sources, pose a threat to public health, and worsen waterborne diseases. Exposure to pathogens, toxins and chemical contaminants in contaminated water can lead to gastrointestinal illness, skin infections and respiratory problems, especially in communities lacking clean water and sanitation. Additionally, contaminated waters can become unsuitable for recreational activities such as swimming, boating and fishing, depriving communities of valuable recreational opportunities and harming local economies that rely on tourism and outdoor recreation [49]. Additionally, irrigating crops with contaminated water can introduce contaminants into the food chain, posing risks to food safety and human health.

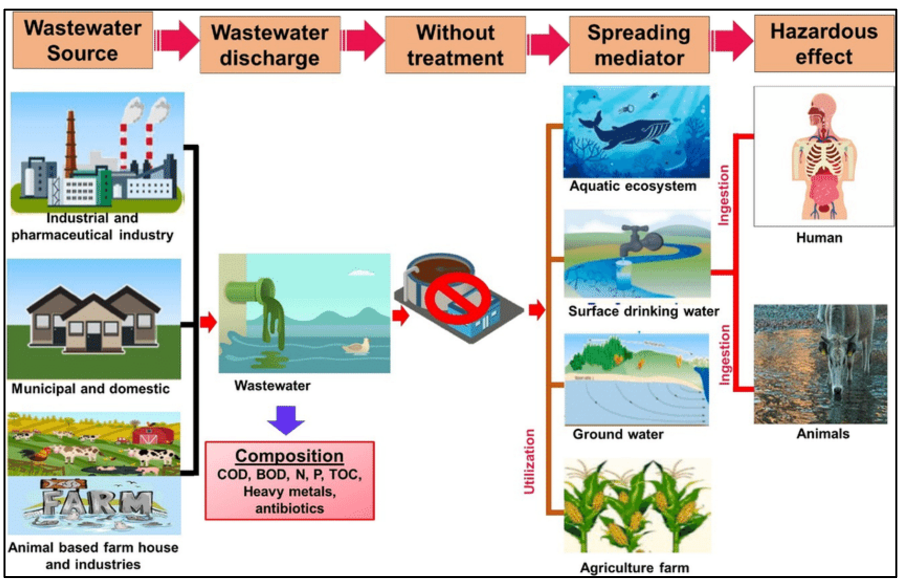


Figure 1.2: wastewater sources [12]

1.2.1 SOURCES AND TYPES OF POLLUTANTS

Wastewater contains a variety of pollutants and originates from residential, industrial, agricultural, and commercial activities [4]. These pollutants are classified into different types based on their origin and nature. The most common sources and types of contaminants in wastewater include:

1. Residential Source:

- ✓ Organic matter: Domestic wastewater contains organic pollutants such as human waste, food debris, and cleaning products.
- ✓ Nutrients: Household wastewater can contain nutrients such as nitrogen and phosphorus, primarily from detergents, cleaning products and human waste.
- ✓ Pathogens: Human and animal feces in wastewater can introduce pathogens such as bacteria, viruses and parasites, posing a threat to public health [12].

2. Industrial sources:

- ✓ Heavy metals: Industry releases heavy metals such as lead, mercury, cadmium and chromium into wastewater through processes such as metal plating, mining and manufacturing.
- ✓ Chemical compounds: Industrial activities produce a variety of chemical pollutants, including solvents, pesticides, dyes, and pharmaceuticals, that can contaminate wastewater.
- ✓ Oil and grease: Industries such as food processing, petrochemicals and manufacturing release oil, grease and other hydrocarbons into wastewater through processes such as cleaning, refrigeration and equipment maintenance.

3. Agricultural sources:

- ✓ Fertilizers and pesticides: Agricultural runoff transports excess nutrients from fertilizers (such as nitrogen and phosphorus) and chemical pesticides into water bodies, causing eutrophication and ecological imbalance.
- ✓ Animal manure: Animal farms release organic pollutants, pathogens and nutrients from animal manure into water bodies through runoff and direct discharges [13].

4. Commercial Sources:

- ✓ Chemical Contaminants: Commercial activities such as dry cleaning, vehicle maintenance, and photo processing can introduce hazardous chemicals like solvents, degreasers, and photographic chemicals into wastewater.
- ✓ Pharmaceuticals and Personal Care Products: Commercial establishments like hospitals, pharmacies, and beauty salons discharge pharmaceuticals, cosmetics, and personal care products into wastewater, contributing to emerging contaminants in water bodies.

5. Storm water Runoff:

- ✓ Sediments: Storm water runoff carries sediments, soil particles, and debris from urban and rural landscapes into water bodies, contributing to turbidity and sedimentation.
- ✓ Urban Pollutants: Storm water runoff can contain pollutants from urban areas, including heavy metals, oil and grease, litter, and contaminants from roads, parking lots, and construction sites [35].

Overall, wastewater is a complex mixture of pollutants originating from various sources and activities. Managing and treating wastewater effectively require comprehensive strategies to address the diverse range of pollutants and mitigate their adverse impacts on water quality, public health, and the environment.

1.3 CONVENTIONAL TREATMENT METHODS

Conventional wastewater treatment encompasses a diverse range of technologies and processes designed to effectively remove pollutants and contaminants from wastewater [18]. Some common conventional technologies used in wastewater treatment include:

1. Coagulation-Flocculation: Involves the addition of coagulants such as alum or ferric chloride to wastewater to destabilize and aggregate suspended particles [21]. Flocculants are then added to form larger, settleable flocs, which can be easily removed by sedimentation or filtration.

2. Membrane Filtration**:** Employed in processes such as microfiltration, ultra-filtration, nano-filtration, and reverse osmosis to physically separate suspended solids, pathogens, and dissolved substances from wastewater using semi-permeable membranes. Membrane filtration processes can produce high-quality effluent suitable for reuse or discharge.

3. Reverse Osmosis (RO): Utilizes pressure to force water molecules through a semi-permeable membrane, effectively removing dissolved salts, organic compounds, and other contaminants from wastewater. Reverse osmosis is particularly effective for desalination and producing high-purity water.

4. Chemical Precipitation: Involves the addition of chemicals such as lime, soda ash, or coagulants to wastewater to induce the formation of insoluble precipitates, which trap and remove dissolved metals, phosphorus, and other contaminants from the water [21].

5. Ion Exchange: Utilizes ion exchange resins to remove dissolved ions such as heavy metals, nitrates, and hardness minerals from wastewater by exchanging them with ions of similar charge attached to the resin.

6. Electrochemical Treatment: Involves the use of electrical current to induce chemical reactions that degrade organic pollutants, disinfect pathogens, and remove heavy metals from wastewater. Electrochemical treatment processes include electro-coagulation, electro-oxidation, and electro-chlorination [24].

Overall, these conventional technologies play a crucial role in wastewater treatment by providing effective means to remove pollutants and contaminants, ensuring the protection of public health and the environment.

1.3.1 CHALLENGES OF CONVENTIONAL TREATMENT METHODS

Conventional wastewater treatment methods, while effective to a certain extent, are not without their limitations and challenges [45]. Here, we delve into some of the key issues associated with traditional treatment approaches, including chemical coagulation, sedimentation, and biological treatment:

1. Cost: One of the primary challenges of conventional treatment methods is their often high capital and operational costs. Chemical coagulation, for instance, requires the procurement and handling of expensive chemicals such as aluminum sulfate or ferric chloride [8]. Additionally, the energy-intensive nature of some treatment processes, such as aeration in biological treatment systems, contributes to increased operational expenses.

2. Energy Consumption: Many conventional treatment methods rely on energy-intensive processes such as aeration, pumping, and mechanical mixing. Biological treatment, in particular, requires significant energy inputs to maintain optimal conditions for microbial activity. The reliance on fossil fuels for energy generation in wastewater treatment plants contributes to greenhouse gas emissions and environmental degradation.

3. Generation of Sludge: Conventional treatment methods often produce large volumes of sludge as a byproduct, which requires further treatment and disposal [10]. Sludge handling and disposal present significant challenges in terms of cost, logistics, and environmental impact. Improper management of sludge can lead to contamination of soil and water resources, as well as emissions of greenhouse gases and odorous compounds.

4. Secondary Pollutants: Some conventional treatment methods may inadvertently generate secondary pollutants during the treatment process. For example, chemical coagulation can result in the formation of disinfection byproducts (DBPs) when chlorine is used for disinfection [25]. DBPs, such as trihalomethanes and haloacetic acids, are known carcinogens and pose risks to human health.

Addressing these challenges requires a concerted effort towards innovation and the adoption of sustainable practices in wastewater treatment. Exploring alternative treatment technologies, such as green materials-based approaches, holds promise for overcoming the limitations of conventional methods while promoting environmental stewardship and resource efficiency.

1.4 EMERGING TRENDS IN GREEN MATERIALS FOR WASTEWATER TREATMENT

In recent years, there has been a notable shift towards utilizing green materials for wastewater treatment, driven by the increasing awareness of environmental sustainability and the limitations of conventional treatment methods. Several emerging trends in this area include:

1. Natural Adsorbents: Natural materials such as agricultural residues (e.g., rice husks, coconut shells), biomasses (e.g., algae, fungi), and plant-based materials (e.g., activated carbon derived from bamboo or palm shells) are being explored for their adsorption capacity. These materials offer advantages such as renewable sourcing, biodegradability, and cost-effectiveness compared to synthetic adsorbents [32].

2. Biofiltration and Phytoremediation: Biofiltration systems, which utilize microorganisms or plants to treat wastewater, are gaining traction as sustainable alternatives to traditional treatment processes [33]. Constructed wetlands and vegetated swales are examples of biofiltration systems that harness the natural filtration capabilities of plants and soil microbes to remove pollutants from wastewater through processes such as adsorption, absorption, and microbial degradation.

3. Advanced Oxidation Processes (AOPs) with Green Catalysts: Advanced oxidation processes, such as photocatalysis and ozonation, are being combined with green catalysts derived from natural sources (e.g., clay minerals, metal oxides, and plant extracts) to degrade organic pollutants and disinfect wastewater [43]. These green catalysts offer advantages such as low toxicity, high reactivity, and compatibility with renewable energy sources.

4. Biosensors and Bioreporters: The development of biosensors and bioreporters based on living organisms or biomolecules is enabling real-time monitoring of water quality and the detection of specific pollutants in wastewater [1]. These innovative technologies provide rapid, sensitive, and cost-effective solutions for identifying and quantifying contaminants, thereby facilitating timely intervention and remediation efforts.

5. Circular Economy Approaches: Integrated wastewater treatment systems that emphasize resource recovery and reuse are becoming increasingly prevalent. By incorporating technologies such as anaerobic digestion, biochar production, and nutrient recovery, these systems aim to extract value from wastewater by recovering energy, nutrients, and water for agricultural, industrial, or municipal applications, thus promoting a circular economy and reducing environmental impact [45].

Overall, the emerging trends in green materials for wastewater treatment reflect a growing emphasis on sustainability, efficiency, and holistic approaches to water management. By harnessing the natural capabilities of green materials and innovative technologies, researchers and practitioners are working towards more environmentally friendly and resilient solutions for addressing the challenges of wastewater pollution.

1.5 PINE NEEDLES AS A GREEN MATERIAL

Pine needles are very thin, sharp leaves that grow on pine trees. They are the adult leaves, bundled in clusters called fascicles [3]. The figure of pine needles is given in Figure 1.3. Pine needles, often overlooked as mere forest debris, hold remarkable potential beyond their natural habitat. From crafting eco-friendly mulch to brewing fragrant teas, these slender green appendages of pine trees offer a myriad of practical uses. In sustainable agriculture, they serve as invaluable organic mulch, enriching soil with nutrients as they decompose. Their high resin content also deters pests, making them a natural and chemical-free solution for gardeners. Beyond the garden, pine needles find purpose in traditional medicine, where their antioxidant-rich extracts are believed to alleviate respiratory ailments and promote overall well-being [7]. Moreover, their fibrous nature lends itself to creative endeavors, such as weaving baskets or crafting rustic decor. Even in the realm of environmental conservation, pine needles play a crucial role, acting as a natural filter in erosion control and watershed protection projects. Thus, amidst their humble appearance, pine needles embody a wealth of versatility and sustainability, serving as a testament to the ingenuity of nature's offerings.

Figure 1.3: Pine needle [3]

Pine needle is utilized as a green material for the following reasons:

1. Abundant and renewable: Pine needles are abundant in nature and renewable, making them a sustainable choice for wastewater treatment. Unlike some synthetic adsorbents, pine needles do not deplete finite resources and can be continuously replenished through natural processes.

2. Low cost: Pine needles are often readily available at low or no cost, especially in areas where pine trees are prevalent. This makes them a cost-effective option for wastewater treatment, particularly in regions with limited financial resources for environmental remediation.

3. Biodegradable and Environmentally Friendly: After use, pine needles can be disposed of or undergo natural degradation without causing harm to the environment [16]. This contrasts with some synthetic adsorbents, which may persist in the environment and pose long-term risks.

4. Natural Adsorbent Properties: Pine needles contain various organic compounds such as lignin and cellulose, which possess adsorbent properties. These compounds have the ability to attract and bind with molecules of dyes and metal ions present in wastewater, effectively removing them from the water.

5. Potential for Regeneration: In some cases, pine needles can be regenerated and reused multiple times for wastewater treatment [18]. Processes such as washing or desorption can help recover adsorbed contaminants from the pine needles, allowing them to be reused, thereby extending their lifecycle and enhancing cost-effectiveness.

1.5.1 CHARACTERISTICS OF PINE NEEDLES

Pine needles, the evergreen leaves of pine trees, boast distinctive characteristics that contribute to their resilience and versatility. Their tough, waxy outer coating helps to minimize water loss and protect against environmental stressors, making them well-suited for thriving in diverse climates, from temperate forests to arid landscapes [24]. Pine needles have found practical applications across various domains, one of which is to treat wastewater. It has been reported that it has physical and chemical characteristics that contribute to the effectiveness in removal of its pollutants especially metal ions and dyes.

1.5.1.1 PHYSICAL CHARACTERISTICS

The physical characteristics of pine needles play a crucial role in their adsorbance of dyes and metal ions from wastewater. Here are some key physical attributes that influence this process:

1. Surface Area: The surface area of pine needles, which is determined by factors such as needle length, diameter, and surface roughness, directly impacts their adsorption capacity [27]. A larger surface area provides more sites for adsorption to occur, thereby enhancing the efficiency of pollutant removal.

2. Pore Structure: Pine needles possess a hierarchical pore structure consisting of micropores, mesopores, and macropores. This pore structure contributes to their high surface area and facilitates the diffusion of pollutants into the interior of the needles, where adsorption can take place.

3. Surface Roughness: The surface of pine needles is not perfectly smooth but rather exhibits varying degrees of roughness due to natural features such as stomata, trichomes, and epidermal cells [36]. This roughness increases the contact area between the needles and the pollutants in wastewater, promoting adsorption.

4. Hydrophobicity: Pine needles are inherently hydrophobic due to the presence of natural resins and waxes on their surface [33]. This hydrophobicity can affect the adsorption of hydrophobic pollutants, such as certain dyes, by facilitating their partitioning onto the surface of the needles.

5. Flexibility and Porosity: Pine needles are flexible and porous, allowing them to conform to the shape of the adsorbate molecules and provide access to adsorption sites. This flexibility enables effective interaction between the needles and pollutants, leading to efficient adsorption.

By considering these physical characteristics, researchers and engineers can optimize the use of pine needles as an adsorbent for the removal of dyes and metal ions from wastewater, leading to more efficient and sustainable wastewater treatment processes. The Table 1.1 below shows the physical characteristics of pine needles.

Table 1.1: Physical characteristics [8]

Characteristics	Value
Length	170 to 250 mm
Diameter	0.7 to 1.31 mm
Color(when dried)	Brown

1.5.1.2 CHEMICAL CHARACTERISTICS

The chemical characteristics of pine needles that influence their adsorbance of dyes and metal ions primarily stem from their composition and surface properties. Here are some key factors:

1. Presence of Functional Groups: Pine needles contain various functional groups such as hydroxyl (-OH), carboxyl (-COOH), and phenolic groups (-C_6H_4OH) within their organic compounds, including lignin and cellulose [19]. These functional groups offer sites for chemical interactions with dye molecules and metal ions through processes like hydrogen bonding, ion exchange, and complexation.

2. Surface Area and Porosity: The porous structure of pine needles provides a large surface area for adsorption to occur [11]. This increased surface area enhances the contact between the adsorbent (pine needles) and adsorbate (dyes and metal ions), improving the efficiency of adsorption.

3. pH-Dependent Adsorption: The pH of the solution can significantly affect the adsorption capacity of pine needles. The presence of acidic functional groups on pine needles may lead to enhanced adsorption of positively charged metal ions at lower pH values due to electrostatic attraction. Conversely, at higher pH values, the surface charge of pine needles may become negative, favoring the adsorption of negatively charged dye molecules [15].

4. Redox Activity: Certain components of pine needles, such as polyphenols and terpenoids, possess redox-active properties. These compounds can participate in redox reactions with metal ions, influencing their adsorption behavior by forming complexes or undergoing oxidation-reduction reactions.

5. Natural Resins and Extractives: Pine needles contain natural resins and extractives, including terpenes and phenolic compounds, which contribute to their adhesive and hydrophobic properties. These substances may interact with hydrophobic dye molecules and metal ions, facilitating their adsorption onto the surface of pine needles [13].

Understanding these chemical characteristics is essential for optimizing the use of pine needles as an adsorbent for the removal of dyes and metal ions from wastewater, as it enables researchers and engineers to tailor adsorption processes for maximum efficiency and effectiveness.

In summary, the sources and types of contaminants that cause wastewater contamination have been discussed in this chapter. Its effects, the conventional treatments employed, and the difficulties associated with such techniques. Next, we discussed the growing trends in the application of green materials for wastewater treatment and the rationale for our project's usage of pine needles as a green material.

This study will provide a thorough analysis of the characteristics of pine needle biochar, which change in response to changes in the temperature during pyrolysis, affecting their capacity to absorb metal ions and dyes. Additionally, the report will underscore the importance of distinguishing between the efficacy of native and activated pine needle biochar. It will delve into the application of pine needle biochar in wastewater treatment and evaluate its effectiveness in this context.

CHAPTER 2

LITERATURE REVIEW

2.1 GENERAL

This chapter includes a critical analysis of various articles, books, and journals about the removal of metal ions and dyes from wastewater. Different literature has been evaluated, which helped us understand different methods and techniques used for the removal of metal ions and dyes. In this chapter, we could also identify the research gaps and objectives of our study. A summary of a few other research papers is also provided below.

Pandey et al. investigated that the pine needle can be used to remove methylene blue dye. It was also concluded that the acid modified biochar has more efficiency than the native pine needle biochar. It was found from the batch experiments that the removal efficiency for native pine needle biochar increased from 8% to 32% on increasing the biochar amount from 0.015 g to 0.05 g, while the removal efficiency of strong and weak acid-treated biochar increased from 15% to 76% and from 11% to 37%, respectively [11].

Joshil et al. investigated about the removal of malachite green dye from wastewater. It was found that the absorbance of malachite green dye increased with an increase in temperature, and pH 7 was found to be the best equilibrium pH for maximum removal of the dye [13]. It was also observed that the quasi-steady state equilibrium was achieved after 12 hours, and after 12 hours there was a negligible increase in the adsorbed amount of malachite green onto biochar.

Li et al. investigated the removal of rhodamine B dye by pine needle biochar and traditional peat. It was found that pine needle biochar has a higher carbon and hydrogen content than traditional peat. Through comparison, it was seen that the manufactured pine needle biochar takes longer to attain equilibrium than the purchased peat. This result could be explained by the fact that peat has smaller pores and surface area than pine needle biochar. However, it was found that the adsorption of rhodamine blue dye was best done by pine needle biochar [15].

Anastopoulos et al. investigated the removal of caffeine from aqueous solution using oxidized biochar obtained from pine needles. It was shown that absorbance rose with extended contact durations, that equilibrium was attained after 150 minutes, and that pH 4 was ideal for eliminating caffeine. It was also shown that the absorption increases dramatically between 298 and 313 K, and then drops around 323 K. The rise was explained by the expanding of the internal structure of the carbon due to warmth, which made it possible for more molecules of caffeine to enter the carbon [34].

Park et al. investigated the removal of cadmium using various pine tree residues and pyrolysis temperature. It was observed that the pine residue biochar prepared at 550°C was the optimum temperature for the pyrolysis, as it showed maximum absorbance for the pine needle biochar. On comparing the 3 biochars at the same temperature [550 °C], pine needle biochar was found to be more effective than pine cone biochar and pine bark biochar. But on the contrary, the pine cone biochar and pine bark biochar prepared at 600°C showed maximum absorbance, so the optimum pyrolysis temperature was concluded to be 600°C. The Figure 2.1 below represents that pine bark biochar absorbs the Cd metal ion more than pine cone biochar and pine needle biochar. All the pine residue biochars achieved equilibrium after 2 hours of reaction [46].

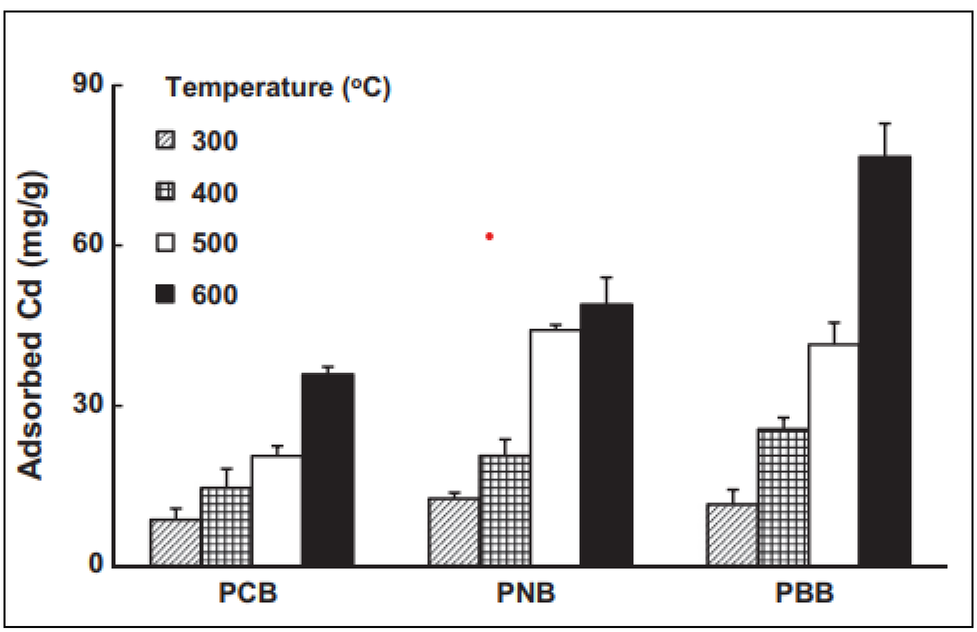


Figure 2.1: Amounts of Cd adsorbed by biochars derived from different pine tree residues and temperature (PCB: Pine cone biochar; PNB: Pine needle biochar, and PBB: Pine bark biochar)

Singh et al. investigated the removal of lead and cadmium from aqueous solutions using magnetic biochar. It was seen that the adsorbent surface became negatively charged at a basic pH, which made it easier for the metal ions to be adsorbed [12]. The Figure 2.2 shows how the magnetite binds onto biochar and its bonding mechanism with heavy metal ions. Compared to a high pH (basic medium), the removal efficiency was lower in a low pH (acidic medium). Heavy metal ions were bonded to the functional group of biochar via reduced oxygen and to magnetite nanoparticles via cation exchange in the host matrix.

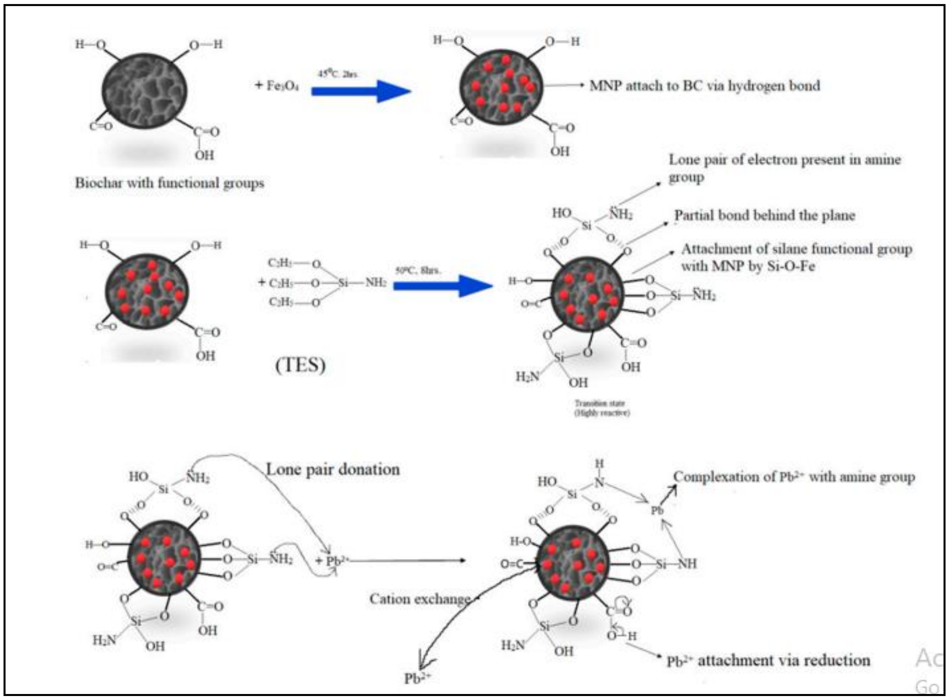


Figure 2.2: Binding model of magnetite onto biochar, its functionalization process, and the bonding mechanism with heavy metal ions [12]

Choudary et al. investigated the removal of lead by using pine needles biochars produced at different pyrolysis temperature. Pine needle biochar produced at 550 °C was chosen for adsorptive lead removal in batch and column experiments. Increasing the pyrolysis temperature increased lead sorption up to 550 °C. Lead adsorption increased dramatically as pH increased from 2 to a maximum of pH 5 and above [11].

Gulati et al. investigated that pine needles can be used as a green material for removal of metal ions and dyes. The study mainly focused on removal of hexavalent chromium and rhodamine B dye and it was seen that with Rhodamine B, the maximum adsorption was at pH 4 with a contact time of 30 min on the addition of 0.2 g of adsorbent, where as pine needles yielded a maximum adsorption for Cr(VI) at pH 1 on addition of 0.4 g of adsorbent with contact duration of 180 min [21].

Enaime et al. studied the various conversion technologies and applications of biochar and how it can be used as a material for wastewater treatment. This paper provides a systematic analysis of adsorption mechanisms towards organic and inorganic contaminants, and the physico-chemical properties of biochar, which are influenced by the type of beginning feedstock, the thermal conversion method, and the preparation circumstances, which are directly related to its ability to remove contaminants from aqueous solutions. The proposed mechanisms for the removal of organic and inorganic contaminants by biochar are given in Figure 2.3. It has been noted that the surface functional groups of biochar can be altered through physical and chemical activation processes, which also increases the amount of oxygen-containing surface functional groups [25].

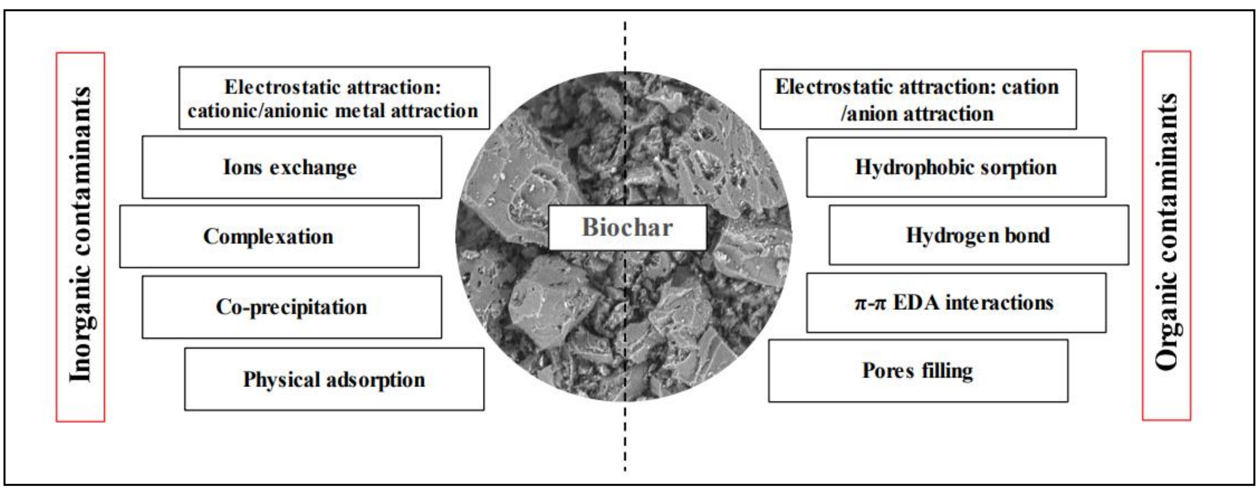


Figure 2.3: The proposed mechanisms for the removal of organic and inorganic contaminants by biochar [25]

Tomczyk et al. studied the biochar physicochemical properties and how it is being affected by pyrolysis temperature and feedstock kind effects. The physicochemical properties (pH, specific surface area, pore size, CEC, volatile mater, ash and carbon content) of biochar were considered while doing the study. The study show that CEC and volatile matter decreased with increasing pyrolysis temperature, where as pH, specific surface area, ash and carbon content, pore volume increased with the increase in pyrolysis temperature. Increasing temperature also decreased the number of acidic functional groups, especially carboxylic functional groups, and caused appearance of basic functional groups [23].

Ambaye et al. studied the mechanisms and adsorption capacities of biochar to remove inorganic and organic pollutants from industrial wastewater. This study showed that biochar has a great potential to adsorb inorganic and organic pollutants involving various mechanisms such as pore-filling, electrostatic interactions, ion exchange, precipitation, and surface adsorption, which are dependent upon the interactions and ion physiochemical characteristics of biochar, such as biochar dosage, pyrolysis temperature, and the pH of the treated matrix [31]. Also, it was reported that biochar decreases the bioavailability, toxicity, and mobility of organic and inorganic pollutants and is found to be beneficial for the removal of contaminants at high concentrations.

Mostafa et al. studied the concept and current pollutant removal technologies in textile industries. The research paper explains the need to recover water from wastewater for use in production processes in the textile industry by the use of individual or combination advanced treatment methods [28]. The advanced techniques can also be used to reuse chemicals and water in order to comply with strict environmental or regulatory standards. Furthermore, it also explains the efficient use of materials and energy can be enhanced by the use of strategic, all-encompassing preventive measures and cutting-edge manufacturing technologies. We can also lessen and completely eradicate the production of waste and its emissions, the overuse of resources, and the hazards it poses to both the environment and people.

Silvana et al. studied the methods for wastewater treatment in textile industry. According to the research paper, high-quantity of water is heavily consumed in the textile manufacturing processes, particularly in the wet treatments and finishing (finishing, dyeing, printing, etc.) of textile materials. Large volumes of contaminated water are released as a result of these different processes. As a result of extreme variety of textile processes and products, it is impossible to develop a realistic concept for an effective treatment of wastewater without a detailed analysis of the actual situation in the textile plant [35]. Therefore it is important to characterize the textile process effluent to develop strategies for water treatment and reuse.

Chandran et al. investigated the treatment of sewage wastewater by using dried pine needles. According to the research article, pine needles may be used to remediate wastewater from residential as well as commercial premises. When wastewater was exposed to pine needles, it was seen that some metrics altered, including total dissolved solids, chemical oxygen demand, and biological oxygen demand [5]. The effectiveness of this application was discovered when it was utilized in the river. It was observed that the calcium concentration of the water in the rivers had decreased, which would undoubtedly lower the prevalence of kidney stones.

Cha et al. studied the production and utilization of biochar. It was seen that there was many processes used to produce biochar, including pyrolysis, torrefaction, gasification, and hydrothermal carbonization. It described the numerous elements that influence the various processes and the intended outcomes. It also describes the ways of modification that we may apply to increase the effectiveness of the biochar [47]. It infers that the alteration was made via a chemical and physical process. The article also outlines the various environmental uses for biochar as well as what lies ahead for research.

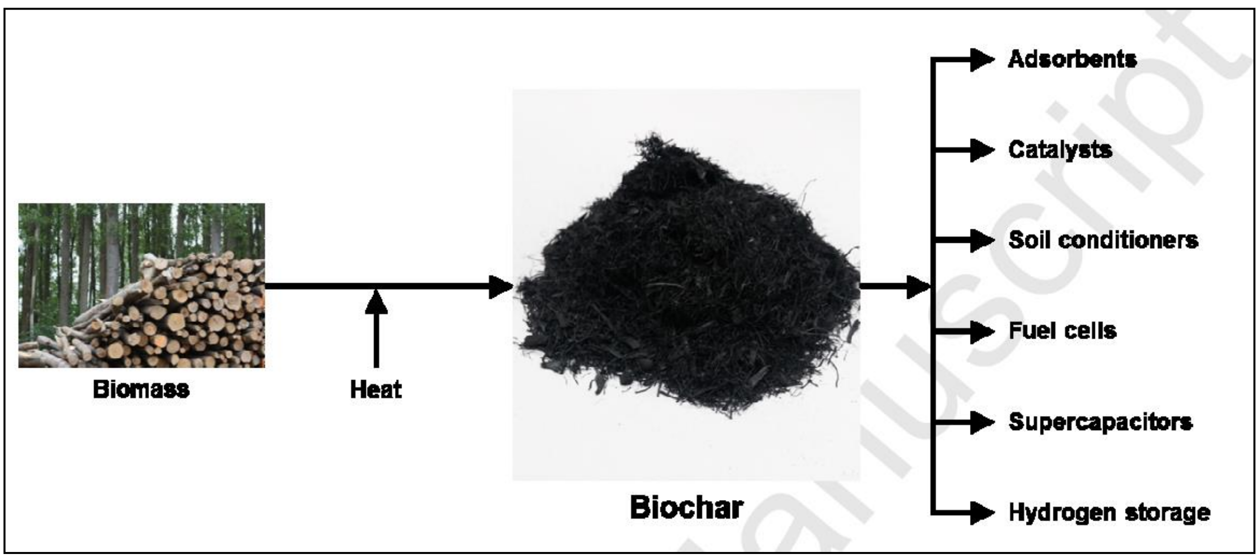


Figure 2.4: Graphical abstract [47]

2.2 NEED OF THE STUDY

The study of pine needles as a green material for the removal of metal ions and dyes from wastewater in Himachal Pradesh is important for several reasons:

1. Availability of Pine needles: Himachal Pradesh is a region with vast forests, and pine needles are one of the most abundant and underutilized forest residues available in the region. Utilizing pine needles as an adsorbent can help in the proper management of this waste material [2].

2. Environmental concerns: The discharge of industrial wastewater containing heavy metals and dyes is a major environmental concern in Himachal Pradesh. The use of pine needles as a green material for the removal of these pollutants can provide a sustainable and eco-friendly solution to this problem.

3. Economic benefits: Pine needles are a low-cost material that can be easily collected from the forests of Himachal Pradesh. The use of pine needles as an adsorbent can provide an affordable and effective solution for the treatment of wastewater, which can benefit the local industries [4].

4. Efficiency of Pine needles: Pine needles have been reported to have a high adsorption capacity for various pollutants, including heavy metals and dyes. Therefore, utilizing pine needles as an adsorbent for the treatment of wastewater can provide a highly efficient solution for the removal of these pollutants [6].

There is a lack of studies on the use of pine needles as a green material for the removal of metal ions and dyes from wastewater in Himachal Pradesh. Hence, conducting research in this area can contribute to the development of a sustainable and cost-effective method for wastewater treatment in the region.

In particular, the study of pine needles as a green material for the removal of metal ions and dyes from wastewater in Himachal Pradesh can provide a sustainable, cost-effective, and eco-friendly solution for the treatment of wastewater in the region.

2.3 RESEARCH GAP

There have been several studies conducted on the use of pine needles as a green material for the removal of metal ions or dyes from wastewater. However, there are still some research gaps in this area that need to be addressed. Most studies have focused on the use of raw pine needles or modified pine needles as adsorbents for metal ions or dyes. However, there is a need for optimization of pine needle-based adsorbents in terms of their properties and performance. For example, the effect of pine needle particle size, pH, and contact time on adsorption capacity should be investigated to improve the efficiency of the adsorbents [3]. The effectiveness of pine needles in real-world scenarios, such as industrial wastewater or contaminated water bodies, has not been thoroughly investigated. Therefore, our present research is focused on the utilization of pine needles biomass, to synthesize green cost-effective adsorbent for dyes and metal ions through techniques to improve its properties via simple acid treatment and then using that efficient biochar on the wastewaters and checking its parameters.

Overall, there are still research gaps in the use of pine needles as a green material for the removal of metal ions or dyes from wastewater. Addressing these gaps can help to improve the efficiency and practicality of pine needle-based adsorbents for water treatment applications.

2.4 RESEARCH OBJECTIVES

1. To study the characteristics of pine needles and how they affect the adsorbance of pollutants.
2. To do a comparative study for the use of native pine needle biochar and acid activated pine needle bochar.
3. To use the pine needle biochar for remediating wastewater and identify the pollution parameters of polluted water which can be improved using pine needle biochar.
4. To develop a prototype for the treatment of wastewater using pine needle biochar.

CHAPTER 3

METHODOLOGY

3.1 GENERAL

The framework given below in Figure 3.1 will mainly describe the workflow of our study. Firstly, we have done some research on the topic and identified our research objectives. Then we have collected our pine needles, and they're further pyrolyzed into biochar. The characteristics of the biochar are then determined, and then it's used in batch experiments and treating wastewater.

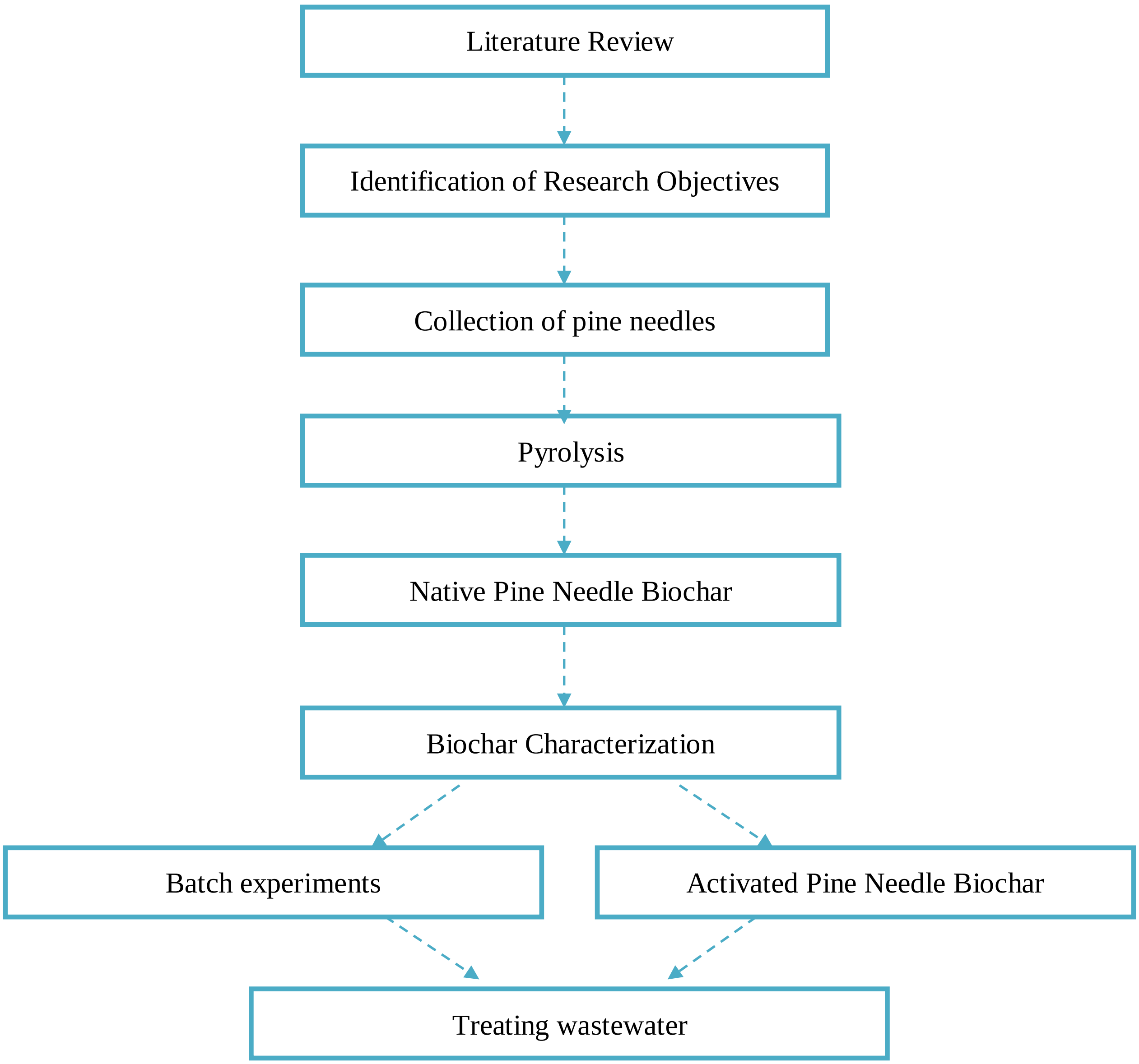


Figure 3.1: Framework of the study

3.2 MATERIALS REQUIRED

Pine needles, Beaker, Conical flask, Distilled water, Muffle Furnace, Oven, Weighing machine, Centrifuge tubes, Methylene Blue dye, Cobalt sulphate, Nitric acid, Sulphuric acid, UV-Visible spectrophotometer, Measuring cylinder, Jar test Apparatus, pH meter, DO meter, COD digester, Incubator shaker, Centrifuge, Crucible, Mortar and pestle

Figure 3.2: Materials Required [1] UV Spectrophotometer, Methylene blue dye, muffle furnace [2] Cobalt metal ion, pH meter, BOD probe [3] COD digester, BOD incubator, Oven From left to right respectively

3.3 STUDY AREA

The Himalayan region was the primary focus of the study since there is where pine needles are most common. Thus, among the several Indian states, we have selected Himachal Pradesh—more in particular, Jaypee University Campus [29]. The map view of the study and the campus location is given in Figure 3.3 and 3.4 respectively. The institution is situated three kilometres off of National Highway 22, which travels from Kalka to Shimla, India. The campus is located on the green slopes of Waknaghat and spans 25 acres (100,000 m^2) [35].

Figure 3.3: Map view of the study area [24]

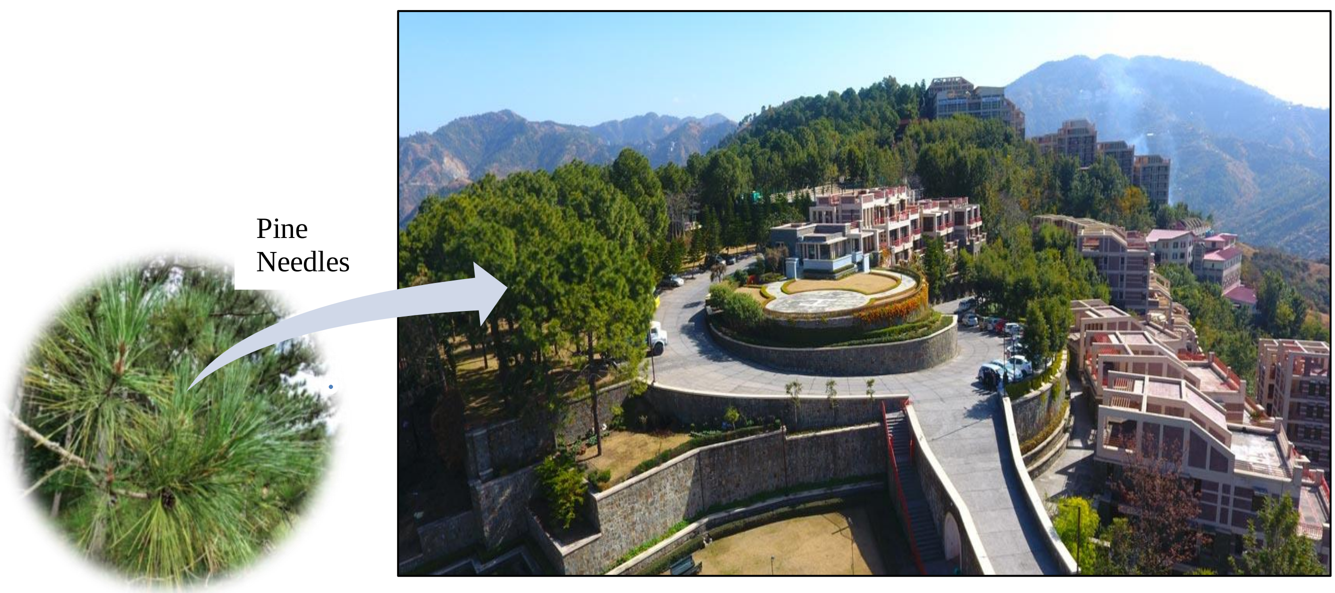


Figure 3.4: JUIT Campus [29]

3.4 METHODOLOGY

The pine needles collected were pyrolyzed into biochar, and a series of batch experiments were conducted on methylene blue dye and cobalt metal ions to check the efficiency of the biochar using UV spectrophotometer. The biochar was further used in sewage wastewater and textile wastewater to check the parameters that are affected by it.

3.4.1 PYROLYSIS

Pyrolysis is a process of decomposing organic materials thermally under limited oxygen condition in the temperature range, 300-900℃ [13]. The biomass's cellulose, hemicellulose, and lignin go through several reaction pathways during thermal breakdown, such as cross-linking, depolymerization, and fragmentation at different temperatures, to produce solid, liquid, and gaseous products. Char and bio-oil are the terms for the solid and liquid byproducts, respectively, while syngas is the term for the gaseous mixture that contains CO, CO_2, H_2, and C_1–C_2 hydrocarbons. The properties of the raw biomass sources and the customised pyrolysis processes determine the yields of the pyrolysis products [16].

The residence time, heating rate, and reaction temperature are the factors that affect the pyrolysis processes' end products. Generally speaking, when the pyrolysis temperature rises, the production of syngas increases and the output of biochar falls. Additionally, it was also reported that the biomass produced more ash and had a lower volatile matter content when the heating rate was increased [37]. The biochar yield dropped with longer residence times at the same pyrolysis temperature, indicating that residence time has an impact on the product composition in pyrolysis processes. The figure of the pyrolysis process for pine needles biomass is give below in Figure 3.5.

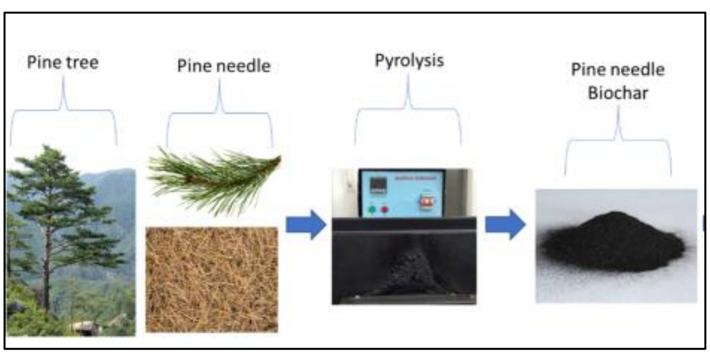


Figure 3.5: Pyrolysis process [16]

3.4.2 NATIVE PINE NEEDLE BIOCHAR

Pine needles were collected from the campus of Jaypee University, which is located in the foothills of Himachal Pradesh. After being cleaned with water to get rid of any dirt, it was dried for 24 hours at 70°C. After the dried biomass had been cut into small pieces, pyrolysis was carried out in a furnace with a limited amount of oxygen. The pictorial representation of the process is given in Figure 3.6. To create pine needle biochar, biomass was placed in a crucible and burned at distinct temperatures, 450°C and 550°C, for a residence time of 2 minutes. After allowing the biochar to cool, it was crushed into smaller pieces in a mortar and sieved through a 40-micrometer sieve. It was then kept for subsequent use in a sealed container. The biochar obtained is named *native pine needle biochar* as it directly originates from pine needles without any modification. These two different biochars are named 450 PNB and 550 PNB. The two biochars are then first characterized and used in the batch experiments conducted on methylene blue dye and cobalt metal ions to check which one is more efficient.

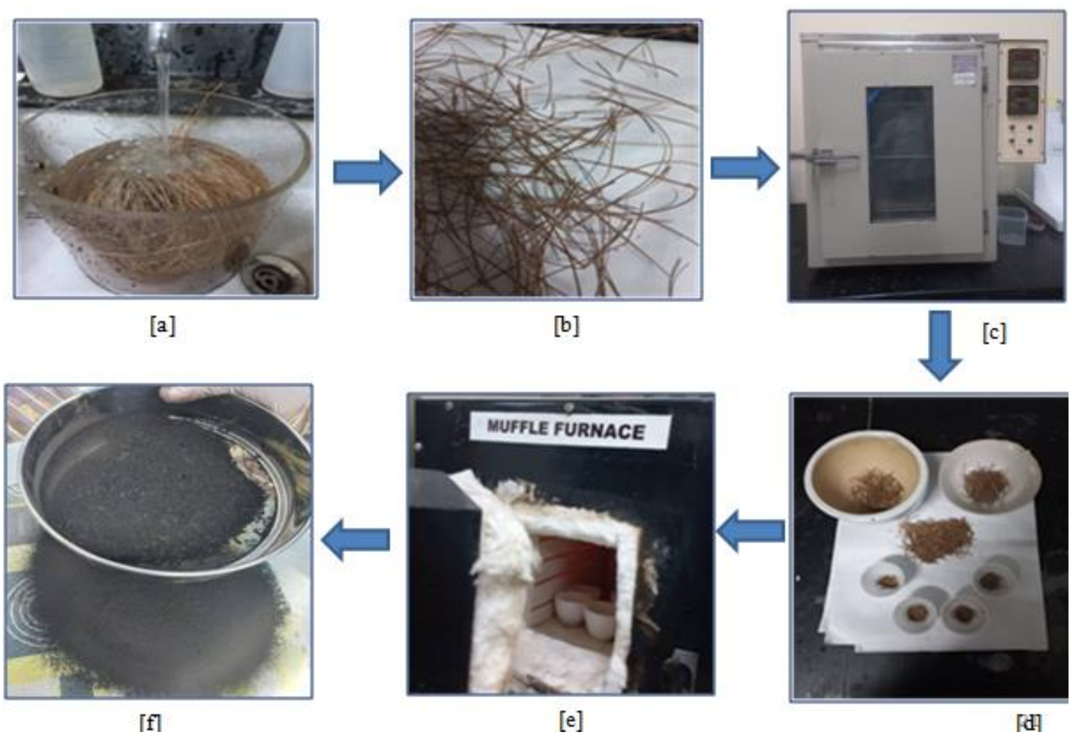


Figure 3.6: Biochar production process [a] Washing pine needles [b] Drying in air [c] Drying in oven [d] Crushing into smaller pieces [e] Burning in muffle furnace [f] Biochar obtained

3.4.3 BIOCHAR CHARACTERIZATION

The Greek word "bios" (meaning life) and "char" (relating to charcoal made by carbonising organic materials) are the sources of the phrase "biochar," which was first used in the late 1900s. Biochar is a type of charcoal that plays an active role in various biological processes that occur in soil, water bodies, and even animal digestive systems [17].

Biochar is defined by the international biochar initiative as “the solid material obtained from the thermo chemical conversion of biomass in an oxygen-limited condition.” Biochar, which is an eco-friendly and cost-effective material made from organic wastes like agricultural and municipal wastes, has gained increasing attention due to its use in various environmental applications [18]. Biochar has enhanced properties like high carbon content, surface area, cation/anion exchange capacity, and stable structure, making it efficient in removing contaminants like pathogenic organisms, heavy metals, and organic dyes. However, information on the design and optimization of biochar-based systems for cleansing of drinking water and wastewater treatment is still largely lacking. Biochar's ability to remove pollutants is dependent on its adsorption capacity, which varies with physico-chemical properties like elemental composition, surface area, pore size distribution, surface functional groups, and cation/anion exchange capacity [15]. For our study, the proximate analysis parameters like moistire content, volatile matter, and ash content were measured as per ASTM methods and the physical and chemical characteristics of our three different biochars, including their colour, odour, and pH, were measured using our senses and pH meter respectively.

3.4.3.1 PROXIMATE ANALYSIS PARAMETERS

ASTM D1762-84 ‘Standard Test Method for Chemical Analysis of Wood Charcoal’ was used to determine the proximate parameters.

The proximate analysis parameters for biochar typically include the following:

1. Moisture content

The moisture content of biochar refers to the percentage of water present in the biochar material relative to its total weight. It is a measure of the amount of water retained within the pores and surface of the biochar after it has been produced through pyrolysis [1]. Moisture content can significantly affect the physical and chemical properties of biochar, including its porosity, surface area, and adsorption capacity.

Moisture content is measured by briefly drying 1 gram biochar in an oven at 105°C for 2 hours.

Note: The sample is considered sample shall be considered oven-dry when the decrease in weight of consecutive weight is 0.0005 g or less. Succeeding drying periods shall be not less than 1 h [1].

2. Volatile matter

The volatile matter of biochar refers to the proportion of combustible materials that are released as gases or vapors when the biochar is heated under specific conditions. The volatile matter content is an important parameter that influences the properties and quality of biochar, including its stability, porosity, surface area, and reactivity [1].

Volatile matter is measured by heating the moisture removed sample in a furnace at 950 °C for 10 minutes with a closed lid and the percent weight loss before and after treatment was measured.

3. Ash content

The ash content of biochar refers to the proportion of inorganic mineral residue left behind after the organic components of the biomass feedstock have been pyrolyzed or burned off. Ash content in biochar mainly consists of minerals such as silica, calcium carbonate, potassium, magnesium, phosphorus, and trace elements present in the original biomass feedstock [3].

Ash content is measured by heating the volatile removed sample at 750 °C for 6 hours in open lid condition and the percent weight after combustion with respect to weight before combustion was measured as ash content.

4. Biochar yield

The yield of biochar refers to the quantity or percentage of biochar obtained from a given amount of biomass feedstock subjected to pyrolysis. The biochar yield can vary depending on several factors, including the type of biomass feedstock, pyrolysis conditions (such as temperature, heating rate, and residence time), and the presence of additives or catalysts [23].

Biochar yield was calculated as the weight percentage of biochar obtained after pyrolysis to the dry biomass before pyrolysis.

5. pH

The pH of biochar refers to the measure of acidity or alkalinity of the biochar material. It indicates the concentration of hydrogen ions (H^+) in the biochar solution, which influences its ability to interact with other substances and its suitability for various applications [35].

For pH measurement, 1 gram biochar was added to 20 ml of distilled water and allowed to stand for 30 minutes. pH readings of the solution were taken with the help of a pH meter.

3.4.3.2 MODIFICATION OF BIOCHAR

In order to improve its specific surface area and pore fraction or to create functional groups before usage, the biochar obtained from thermal treatment methods can be activated. Physical activation and chemical activation are the two categories of activation techniques [36]. The kind and quantity of biomass and activating gas used to create the activated biochar affect its pore fraction and pore size distribution. As for our study we have used chemical activation method.

3.4.3.2.1 PHYSICAL ACTIVATION

Gases like steam, CO_2, and ozone are used in physical activation, also known as gas activation, to activate temperatures higher than 700°C. Physical activation consists of two stages. First, the tiny holes enclosed in the carbon structure are expanded, increasing the interior surface area, while the unstructured portions of the carbonized material are selectively destroyed. The activation processes during the second phase deplete the crystalloid carbon, which contains carbonized material or carbon with fine holes, generating bigger pores [46]. The process of pore creation during physical activation and the reduction of carbon via reactions are closely related.

3.4.3.2.2 CHEMICAL ACTIVATION

In chemical activation, biochar is treated with a chemical agent and micro pores are formed by subsequent dehydration and oxidation. Chemical activation provides better activation efficiency than physical activation, despite a number of disadvantages, including corrosion of the equipment by chemicals, challenging chemical recovery, and expensive chemical costs [38]. Representative chemical agents employed for the chemical activation of biochar include basic chemicals like KOH, NaOH, NH_3, K_2CO_3, and $ZnCl_2$, as well as acids like H_3PO_4, H_2SO_4, HNO_3 and HCl. For our study we have used two strong acids; H_2SO_4 and HNO_3.

3.4.4 ACTIVATED PINE NEEDLE BIOCHAR

For this process, the effective biochar from 450 PNB and 550 PNB was utilised. Acid activation of biomass was performed using two different combinations of acids (5 molars each): a mixture of strong acids containing sulphuric acid and nitric acid in 1:1 ratio. The acid treatment was carried out by adding a 125ml acid mixture to 5g pine needle biochar in a 250ml conical flask. The mixture was stirred using hand and kept for 24 hours. The suspension was washed with water to remove excess acid mixture. The acid functionalized were dried at 80 °C in an oven for 24 hours and stored in a sealed container for subsequent use. The activated pine needle biochar was then further characterized using the same method for native pine needle biochar.

Acid activated biochar = 5 g biochar + 62.5 mL Sulphuric acid + 62.5 mL Nitric acid

3.4.5 BATCH EXPERIMENTS

A series of batch experiments were conducted to find the optimum wavelength, temperature, dosage, and time for the removal of methylene blue dye and cobalt metal ion [1]. The experiments were conducted using incubator shaker to maintain constant temperature and rotation and UV spectrophotometer was used to measure the absorbance of the biochar.

Note: Make a working solution of 50mg/l for both substances.

3.4.5.1 TO DETERMINE THE OPTIMUM WAVELENGTH

To determine the optimum wavelength of a particular substance, we have to take 50 ml of solution with a fixed amount of biochar. After 24 hours, the absorbance of the sample is taken using a UV spectrometer, and the maximum absorbance for the particular wavelength is taken as the optimum wavelength.

3.4.5.2 TO DETERMINE THE BEST BIOCHAR FROM 450 PNB AND 550 PNB

To determine the best biochar, we have to take the same amount of solution in two conical flasks, with a fixed amount of biochar in both solutions. After 24 hours, we take the absorbance reading and see which one has a higher absorbance value.

3.4.5.3 TO DETERMINE THE OPTIMUM TEMPERATURE

To determine the optimum temperature, first at 30 °C, the absorbance of the biochar was measured after 24 hours with the same amount of biochar as in the first two experiments. Then, at 25 °C and 35 °C, with the same amount of biochar as at 30 °C, we take the absorption reading and compare the three results.

3.4.5.4 TO DETERMINE THE OPTIMUM TIME

We have to take measurements of the biochar-containing solution at regular intervals to ascertain the ideal length of time or equilibrium period. The absorbance value will eventually either begin to gently climb or slightly decrease. We will then use that amount of time as our equilibrium time.

3.4.5.5 TO DETERMINE THE OPTIMUM DOSAGE

To determine the optimum dosage, we have to take different amounts of biochar for the same duration and temperature. After the equilibrium time is reached, the absorbance of the different amounts of biochar is measured, and when the value seems to vary by a slight amount, the dosage is then taken as the optimum dosage for the solution.

3.4.5.6 TO DRAW COMPARISON BETWEEN NPB AND ACID APB

To draw a comparison between the two biochars, we have to take the same amount of biochar for the same amount of solution and time. After that, the readings are taken and compared to see which one has the better absorbance.

3.5 ADSORPTION MECHANISM

During adsorption, the adsorbate attaches itself to the surface of the adsorbent until a state of balance is reached. This process involves two steps: physical adsorption where the adsorbate settles on the surface of the adsorbent, and pore filling where the adsorbate is condensed into the pores of the adsorbent. The process is divided into three stages, with the first being the clean zone where no adsorption occurs. The second stage is called the mass transfer zone where the adsorption takes place, while the third and last stage is the exhausted zone where equilibrium is reached. As the process continues, the exhausted zone increases while the clean zone decreases. The increase in the adsorbate's concentration affects the mass transfer zone, but otherwise, it remains unaffected. This trend continues until the breakthrough point where the adsorbent is saturated [18]. The Figure 3.7 shows how the pores in the biochar that makes adsorption possible.

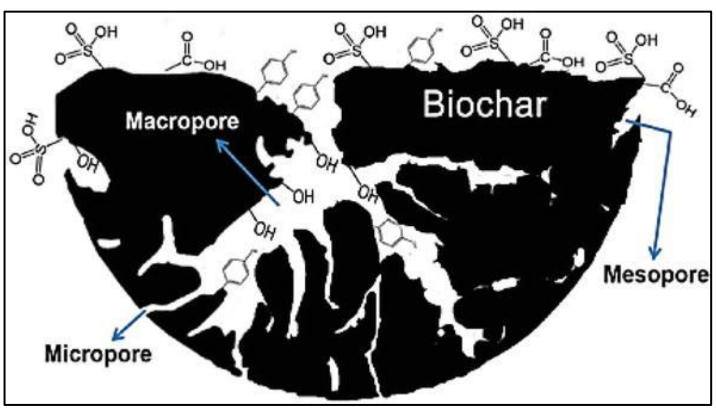


Figure 3.7: Adsorption Mechanism [18]

3.6 TREATING WASTEWATER

Firstly wastewater was collected from the treatment plants and the parameters like BOD, COD, pH, Oil and grease, TSS, TS and TDS were checked for the inlet and outlet of both the wastewater treatment plant. The efficient biochar obtained from the above batch experiment were used to treat both the sewage wastewater and textile wastewater [27]. For the treatment process a series of batch experiments were conducted on both the wastewater simultaneously. Then the results for the pine needle biochar treated wastewater and conventional treated wastewater were compared. The results obtained from these comparative experiments provided valuable insights into the potential of biochar as a sustainable and cost-effective alternative for wastewater treatment, paving the way for further research and development in this field.

Wastewater source

1. Sewage wastewater was collected from the sewage treatment plant located in Jaypee University of Information Technology. The treatment plant has a capacity to treat 300KLD of wastewater. The Figure 3.8 is the figure of the sewage wastewater source.

Figure 3.8: Sewage wastewater source

2. The textile wastewater was collected from the textile mill located in Pilkhuwa, Uttar Pradesh. It is a common effluent treatment plant for about 50 textile mills located in that region.

Figure 3.9: Textile wastewater source

3.6.1 PARAMETERS

It is crucial to regularly monitor and analyse the wastewater parameters at the treatment systems' input and output levels for a number of important reasons. First of all, it is a vital instrument for evaluating the effectiveness and efficiency of wastewater treatment procedures. Operators can determine the degree of pollution removal or mitigation by comparing the parameters at the inlet, which represents the raw, untreated wastewater, with those at the outflow, which indicates the treated effluent [49]. In addition, this monitoring protects against possible fines and penalties for exceeding allowable limits by guaranteeing adherence to strict regulatory criteria controlling wastewater discharge. Beyond regulatory compliance, monitoring helps protect human health and the environment by ensuring that harmful pollutants and contaminants are effectively removed before discharge, thereby mitigating risks to aquatic ecosystems, soil quality, and public health. Furthermore, by analyzing inlet and outlet parameters, treatment plant operators can identify inefficiencies, troubleshoot problems, optimize treatment processes, and make data-driven decisions to enhance overall treatment performance and resource utilization [51].

3.6.1.1 BIOLOGICAL OXYGEN DEMAND

Biochemical Oxygen Demand for wastewater is a measure of the amount of dissolved oxygen consumed by microorganisms during the biochemical degradation of organic matter present in the wastewater over a specific period of time [17]. It is a key parameter used to assess the organic pollution or strength of wastewater, indicating the level of biodegradable organic compounds that can exert an oxygen demand when discharged into water bodies.

BOD is typically measured by incubating a sample of wastewater in the dark at a controlled temperature (usually 20°C) for a specified period (commonly 5 days) and then determining the decrease in dissolved oxygen concentration in the sample. The difference in dissolved oxygen concentration before and after incubation provides a measure of the oxygen consumed by microorganisms during the degradation of organic matter in the wastewater [19]. BOD is expressed in milligrams of oxygen per liter of water (mg/L), indicating the amount of oxygen required for microbial respiration to break down the organic material present in the wastewater.

3.6.1.2 CHEMICAL OXYGEN DEMAND

Chemical Oxygen Demand for wastewater is a measure of the amount of oxygen required to chemically oxidize or break down organic and inorganic compounds present in the wastewater. It quantifies the total concentration of both biodegradable and non-biodegradable organic matter, as well as some inorganic substances, that can be oxidized by strong chemical oxidizing agents.

The determination of COD typically involves the introduction of an excess of the dichromate ion (usually in the form of potassium dichromate, $K_2Cr_2O_7$) into the wastewater sample. After the reaction is completed, any excess dichromate remaining in the solution is then titrated with a reducing agent, such as ferrous ammonium sulfate ($Fe(NH_4)_2(SO_4)_2$), which acts as an indicator of the amount of dichromate that has reacted with the organic matter in the sample [9]. The volume of titrant required to reach the endpoint of the titration is proportional to the amount of excess dichromate present, which in turn correlates to the concentration of organic compounds in the wastewater sample. The COD value is expressed in milligrams per liter (mg/L), indicating the mass of oxygen consumed per liter of solution during the oxidation reaction

3.6.1.3 pH

pH for wastewater refers to the measure of acidity or alkalinity of the water-based solution containing various pollutants, contaminants, and dissolved substances [34]. pH is a fundamental parameter that quantifies the concentration of hydrogen ions (H^+) in the wastewater solution, thereby indicating its level of acidity or alkalinity.

The pH scale ranges from 0 to 14, with pH 7 considered neutral. pH values below 7 indicate acidic conditions, with lower values indicating greater acidity. Conversely, pH values above 7 indicate alkaline or basic conditions, with higher values indicating greater alkalinity.

3.6.1.4 TOTAL SUSPENDED SOLID, TOTAL SOLID AND TOTAL DISSOLVED SOLID

Total Suspended Solids in wastewater refers to the concentration of solid particles that are suspended in the water and can be trapped by a filter [27]. These solids include organic and inorganic matter such as silt, sediment, plant matter, and microorganisms.

Total Dissolved Solids in wastewater refers to the concentration of all solid particles that are dissolved in the water and cannot be trapped by a filter. These solids include minerals, salts, metals, and organic compounds that are dissolved in the water phase.

Total Solids in wastewater refers to the sum of all dissolved and suspended solids present in the water. This includes both the Total Suspended Solids and the Total Dissolved Solids.

3.6.1.5 OIL AND GREASE

Oil and grease in wastewater refer to organic compounds that are insoluble in water and can float on the surface or be suspended in the water. Oil refers to substances that are liquid at room temperature, while grease typically refers to semi-solid or solid fats. In wastewater treatment, oil and grease pose challenges as they can coat equipment, interfere with biological processes, and cause environmental pollution if discharged untreated [34]. Therefore, effective removal of oil and grease is essential in wastewater treatment processes to ensure compliance with environmental regulations and protect water quality.

3.6.2 BATCH EXPERIMENTS

For both the wastewaters a varying amount of biochar was added to 500 ml of the wastewater. The duration was increased to 24 hours because the optimum temperature required was not met during the practical experiments. The experiment was conducted on the jar test apparatus with a speed of 120 revolutions per minute for 2 hours. Due to the jar test apparatus's inflexibility, the 8-hour mixing period was shortened to 2 hours. The figure of a Jar test apparatus is given below in Figure 3.10. After the treatment the parameters were checked and compared with the outlet of the treatment plant. The same procedure was followed for textile wastewater as well.

Figure 3.10: Jar Test Apparatus

3.7 DEVELOPING PROTOTYPE MODEL

The main reason why I chose to develop a prototype model is to give a clear idea of how to effectively use pine needle biochar in the treatment of wastewater. It was clear that it is hard to maintain temperature when we treat the wastewater in the practical field, so we propose this idea keeping in mind the limitations of the conventional treatment method. Our Pine needle biochar based wastewater treatment plant model will mainly explain the steps you need to follow to remove the pollutants effectively. The detailed steps in given in the Figure 3.11.

To check the efficiency of pine needle biochar we can try for different amount of biochars at different flow rates and detention time so that we can optimize it and reduce the energy and cost required for the treatment.

Figure 3.11: Wastewater treatment Plant

1. Receiving tank

A receiving tank is a primary storage facility designed to collect and temporarily hold incoming wastewater. The following Figure 3.12 is the picture of the receiving tank. This tank regulates the flow and quality of wastewater entering subsequent treatment stages, helping to manage variations in wastewater volume and composition.

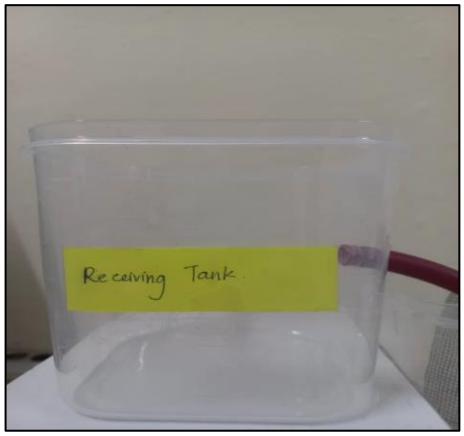


Figure 3.12: Receiving Tank

2. Screening

A screening tank, often referred to simply as a "screen," is a structure equipped with screens or sieves designed to capture and remove large solids, debris, and other coarse materials from wastewater. The following Figure 3.13 is the picture of the screening tank. These materials can include rags, sticks, plastics, and other refuse that could clog or damage downstream treatment equipment.

Figure 3.13: Screening Tank

3. Pine needle biochar treatment

In the third section, we will be making a layer of pine needle biochar, and the wastewater will be allowed to pass through it. The following Figure 3.14 is the picture of the pine needle biochar treatment tank. In order to increase the adsorption efficiency, rotation should be provided in the form of aeration tools or mixing blades in the tank for a specific period of time. Rate of flow also plays an important role to increase the contact time between the biochar and pollutants.

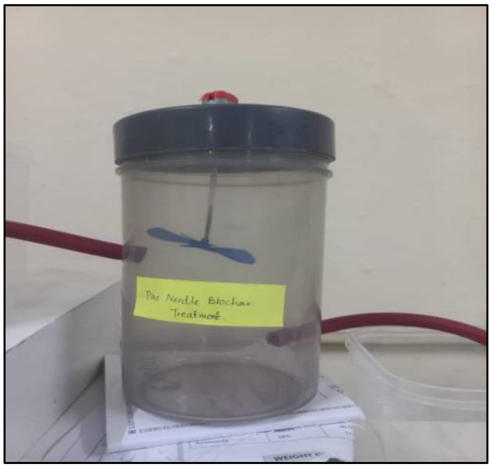


Figure 3.14: Pine needle biochar treatment

4. Sedimentation tank

A sedimentation tank is a basin or tank in which treated wastewater by pine needle bicohar is held for a period to allow suspended solids to settle out by gravity. The following Figure 3.15 is the picture of the sedimentation tank. This process helps to clarify the water before it undergoes further treatment.

Figure 3.15: Sedimentation Tank

5. Filtration

A filtration tank is a vessel or series of vessels where wastewater is passed through a filter medium to remove fine particles, residual solids, and other impurities. The filter medium can vary but typically includes materials like sand, gravel, activated carbon, etc. The following Figure 3.16 is the picture of the filtration tank. For our prototype model we can use filters with micrometer size, activated carbon, or biochar enhanced sand filters. The primary goal of the filtration tank is to produce effluent with reduced turbidity and contaminant levels, making it suitable for discharge or further use.

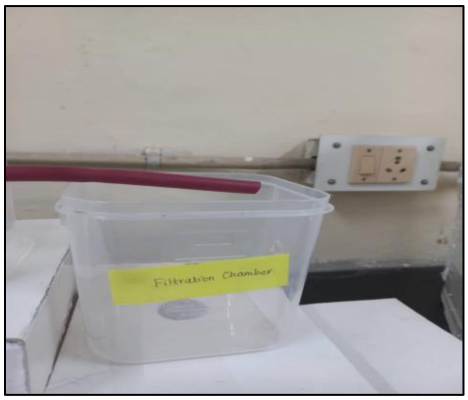


Figure 3.16: Filtration Tank

6. Distribution chamber

A distribution tank also referred to as an effluent distribution tank or post-treatment equalization tank is a structure designed to collect and distribute treated wastewater to various end points. The following Figure 3.12 is the picture of the distribution chamber. These end points can include discharge to water bodies, reuse systems, or additional treatment processes like advanced filtration or disinfection.

Figure 3.17: Distribution chamber

CHAPTER 4

RESULTS AND DISCUSSION

4.1 GENERAL

The result and analysis chapter of this study is aimed at representing and interpreting the findings obtained from the experimental investigation. In this chapter, we will provide a detailed account of the tests conducted on the biochars, batch experiments performed on the methylene blue dye and cobalt metal ion, and the results obtained from treating wastewater using the pine needle biochars.

4.2 BIOCHAR CHARACTERIZATION

Colour: During the prolysis process the biomass was burned at two different temperatures. The end product of the pyrolysis process gives us the black coloured charcoal which is known as biochar. The figure of pine needle biochar is given below in Figure 4.1. Its fragrance, upon analysis, was reminiscent of burned charcoal. Our findings have been validated by other study articles, and they too are similar to what we have found [11].

Figure 4.1: Biochar

Biochar yield is obtained from a given amount of feedstock subjected to pyrolysis. It can vary depending on several factors, including the type of biomass feedstock, pyrolysis conditions (such as temperature, heating rate, and residence time), and the presence of additives or catalysts [23]. It is calculated as the weight percentage of biochar obtained after pyrolysis to the dry biomass before pyrolysis. The biochar yield of the pine needle biomass is given in Table 4.1.

Table 4.1: Biochar yield

	450 PNB	550 PNB
W1(Dry Biomass)	0.5117 g	0.5107 g
W_2 (Biochar obtained)	0.2214 g	0.0994 g
Biochar yield= W_2/W_1	= **43.27%**	= **19.46%**

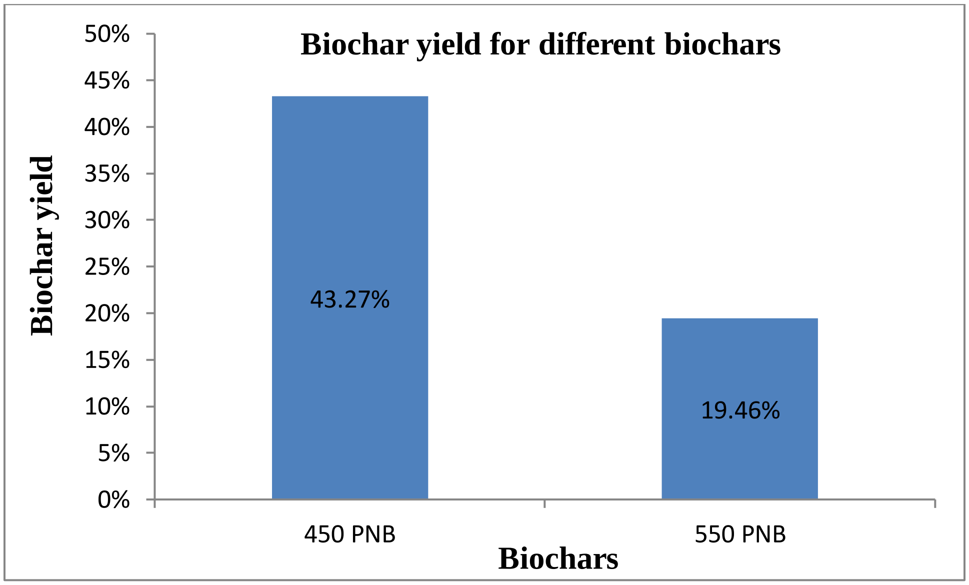


Figure 4.2: Biochar yield for Different biochars

As we can see, the biochar yield decreases with an increase in temperature from 450 to 550 °C. This is because at higher temperatures, there is greater decomposition of organic matter present in the biomass feedstock. Lignin and cellulose, which are major components of biomass feed stocks, undergo thermal decomposition at higher temperatures. This results in the breakdown of complex organic polymers into simpler compounds, including volatile gases and liquids. As a result, less solid residue is left behind to form biochar. The same can be deduced from the Figure 4.2 presented above. Our findings have been validated by other study articles, and they too fall within the range [12].

The measurement of the biochar material's acidity or alkalinity is called its pH. It shows the amount of hydrogen ions (H^+) in the biochar solution, which affects the substance's capacity to interact with other compounds and the usefulness of the biochar solution for different purposes. Thirty minutes were given for the addition of one gramme of biochar to twenty millilitres of distilled water in order to measure the pH. A pH metre was used to get the solution's pH measurements. The pH of the pine needle biochar is given in Table 4.2.

Table 4.2: pH

Description of sample	450 PNB	550 PNB	550 APB
pH Value	**9.90**	**10.3**	**4.91**

The increase in pH for pine needle biochar with increase in temperature attributed to the reduction of organic functional groups, such as –COOH and -OH. As the temperature increases, more organic acids and acidic functional groups are volatilized and released as gases. This results in a reduction of acidic functional groups in the biochar, leading to an increase in pH. As for APB there is decreases in its pH because its subjected to strong acids which contribute to the increase in the acid functional groups on the biochar.

The moisture content of biochar refers to the percentage of water present in the biochar material relative to its total weight. It is a measure of the amount of water retained within the pores and surface of the biochar after it has been produced through pyrolysis [1].

Moisture content is measured by briefly drying 1 gram biochar in an oven at 105°C for 2 hours. The moisture content of the pine needle biochar is given in Table 4.3.

Table 4.3: Moisture content

	450 PNB	550 PNB	550 APB
W_1 Before heat treatment	1.0141 g	1.0156 g	1.0376 g
W_2 After heat treatment	0.9921 g	0.9861 g	0.9921 g
Miosture content $=(W_1 - W_2) \div W_1 * 100$	2.904%	2.16%	2.38%

The moisture content of the biochar decreases with the increase in temperature as when the temperature rises, more heat is applied to the biomass feedstock, leading to greater evaporation of moisture and volatile organic compounds. As a result, the moisture content of the biomass decreases, and the remaining solid residue becomes drier. As for APB since it is washed with water during its manufacturing process the moisture content increases a little.

The volatile matter of biochar refers to the proportion of combustible materials that are released as gases or vapors when the biochar is heated under specific conditions. Volatile matter is measured by heating the moisture removed sample in a furnace at 950 °C for 10 minutes with a closed lid and the percent weight loss before and after treatment was measured. The volatile matter of the pine needle biochar is given in Table 4.4.

Table 4.4: Volatile matter

	450 PNB	550 PNB	550 APB
W_1 Before heat treatment	0.9921 g	0.9861 g	0.9921 g
W_2 After heat treatment	0.2266g	0.2980 g	0.1982 g
Volatile Matter	77.15%	69.96%	79.9%

As the temperature increases during pyrolysis, the thermal energy applied to the biomass causes the breakdown of complex organic molecules into simpler compounds, such as gases and volatile organic compounds. These volatile components, including water vapor, tars, and gases like methane and carbon monoxide, are released from the biomass as gases during heating. Therefore, the decrease in volatile matter content with increasing temperature during pyrolysis is a result of the thermal decomposition and volatilization of organic compounds, leading to the production of biochar with a higher carbon content and reduced volatile content. As for APB there is increase in the volatile matter content as acid activation introduces acidic functional groups, such as carboxyl (-COOH) and phenolic (-OH) groups, onto the surface of the biochar. At higher temperatures, these acidic groups may undergo thermal decomposition or dehydration reactions, leading to the release of volatile byproducts such as water vapor (H_2O), carbon dioxide (CO_2), and carbon monoxide (CO) [26]. This can contribute to the increase in volatile matter content observed with increasing temperature.

The ash content of biochar refers to the proportion of inorganic mineral residue left behind after the organic components of the biomass feedstock have been pyrolyzed or burned off. Ash content in biochar mainly consists of minerals such as silica, calcium carbonate, potassium, magnesium, phosphorus, and trace elements present in the original biomass feedstock [3].

Ash content is measured by heating the volatile removed sample at 750 °C for 6 hours in open lid condition and the percent weight after combustion with respect to weight before combustion was measured as ash content. The ash content of the pine needle biochar is given in Table 4.5.

Table 4.5: Ash Content

	450 PNB	550 PNB	550 APB
W_1 Before heat treatment	0.2266g	0.2980 g	0.1982 g
W_2 After heat treatment	0.0267g	0.0398 g	0.0127 g
Ash content	11.78%	13.35%	6.4%

As we can see that the ash content increases with increase in pyrolysis temperature. At higher temperatures, there is greater thermal decomposition of organic compounds present in the biomass feedstock. This results in increased volatilization of volatile organic compounds, such as water, tars, and gases, leaving behind a higher proportion of non-volatile ash constituents in the biochar. As for APB the ash content decreased due to the removal of trapped inorganic constituents as a result of acid treatment.

Table 4.6: SUMMARY OF BIOCHAR CHARACTERIZATIONS

Characteristics	Results		
Colour	Black		
Odour	Burned Charcoal smell		
	450 PNB	550 PNB	550 APB
Biochar yield	43.27%	19.46%	
pH	9.90	10.3	4.91
Moisture content	2.16%	2.904%	4.38%
Volatile Matter	77.15%	69.96%	79.9%
Ash content	11.78%	13.35%	6.4%

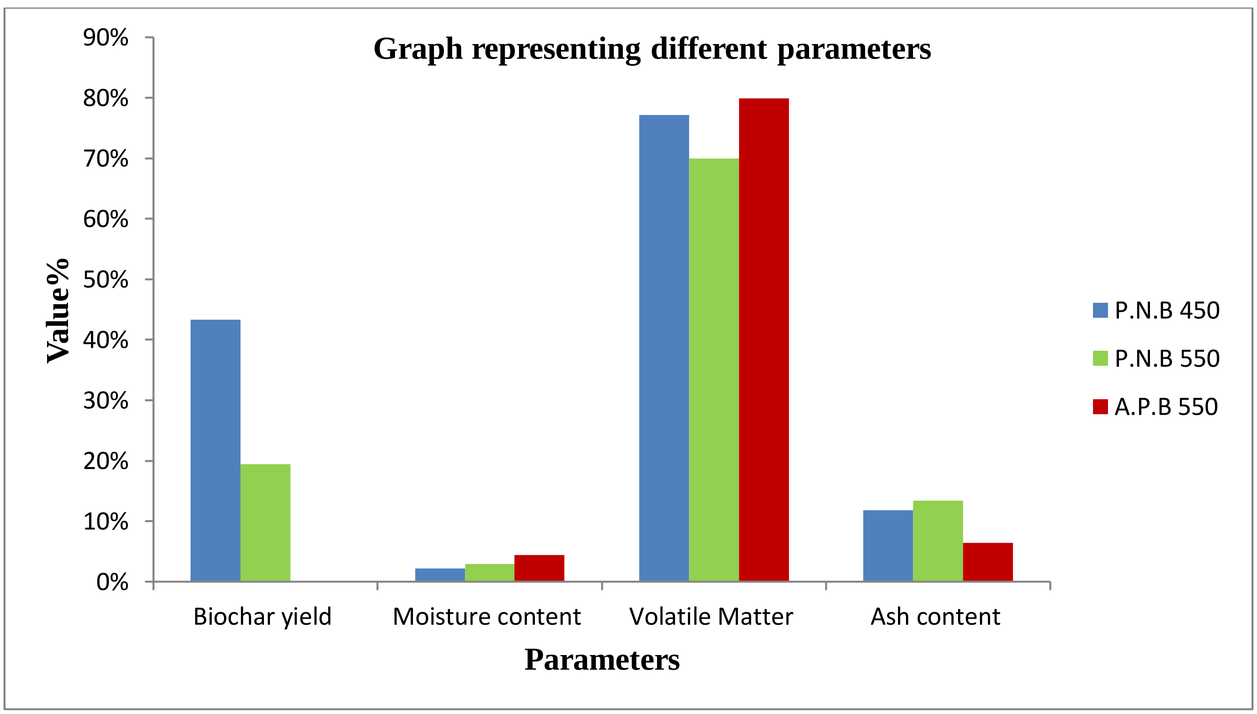


Figure 4.3: Graph representing different parameters

4.3 BATCH EXPERIMENTS FOR METHYLENE BLUE DYE

a. To determine the optimum wavelength of methylene blue dye

Table 4.7: Absorbance of methylene blue dye

Wavelength (nm)	Adsorbent Dosage (0.05g)
300	0.097
400	0.104
500	0.144
600	**0.162**
700	0.073
800	0.077

It is clear from the Table 1.1 given above that 600 nm was determined to be the ideal wavelength for the absorbance of methylene blue dye. It is evident that the highest value attained was 0.162 for a wavelength of 600nm. The optimal wavelength for methylene blue bye absorption is around 630 nm, as per the findings of our mother study article. So, we can say that our result validate the optimum wavelength for methylene blue dye.

b. To determine the best biochar from 450 PNB and 550 PNB

The absorbance of different biochar is given in Table 4.8 below.

Table 4.8: Absorbance of different biochar

Wavelength (nm)	450 PNB (0.05g)	550 PNB (0.05g)
600	0.165	0.232

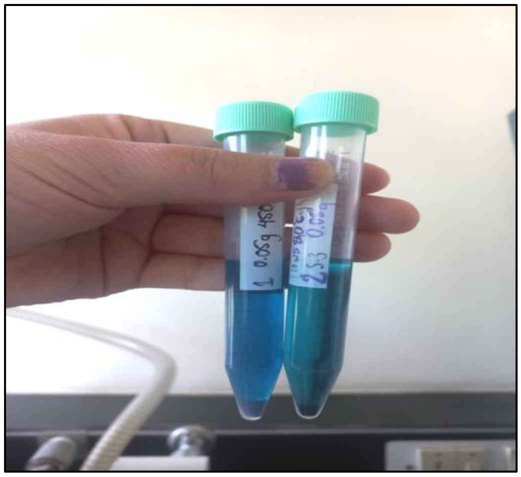


Figure 4.4: 450 PNB and 550 PNB respectively

With the increase in pyrolysis temperature the pore structure of the pine needle biochar gets larger whereby we can see that the absorbance for 550 PNB is more than 450 PNB. When we calculate the percentage increase for the absorbance of the two native pine needle biochar, it was found to increase by 40.6061%. So, we can conclude that 550 PNB is more effective then 450 PNB and for further experiments we will be using 550 PNB as our efficient biochar. The Figure 4.4 also depicts the difference in the colour of the methylene blue solution. Similar results were also obtained in other research papers as well.

c. To determine the optimum temperature

The absorbance with varying temperature is given in Table 4.9 below.

Table 4.9: Absorbance with varying temperature

Wavelength [nm]	Absorbance Sample[0.05g]		
	25°C	30°C	35°C
600	0.156	0.232	0.134

The values in the table represents that the biochar absorption decreases with increase in temperature because its properties like pore structure gets destroyed when it is subjected to higher temperature. As the temperature drops, methylene blue dye absorbance lowers as well. This is because optimal conditions must be reached for the dye to open up its pores and undergo better absorption. It can be also drawn from the table that when the temperature drops there is 32.75% decrease in the absorbance and similarly there is a decrease of 42.24% when the temperature is increased. Therefore, it can be concluded that 30°C is an optimum temperature for better absorption.

d. To determine the optimum duration with varying time

The absorbance with increase in contact time is given in Table 4.9 below.

Table 4.10: Absorbance with increase in contact time

Wavelength [nm]	Absorbance Sample[0.05g]		
	4 hrs	8hrs	24hrs
600	0.232	0.312	0.311

With the increase in contact time from 4 hours to 8 hours the absorbance for methylene blue dye increased by 34.4828%. It can be concluded that at 600nm with temperature 30°C the absorption increases with contact time because the pores open up for the dyes and metal ions to get attached to the functional groups. As the duration increased from 8hrs to 24 hrs there was a slight decrease in the absorbance so the experiment was stopped and the duration of 8hrs was taken as the optimum duration required by 550 PNB to absorb the methylene blue dye.

e. To determine the optimum dosage with varying dosage

The absorbance with increase in dosage is given in Table 4.9 below.

Table 4.11: Absorbance with increase in dosage

Wavelength [nm]	Sample 1 [0.015 g]	Sample 2 [0.025 g]	Sample 3 [0.05 g]	Sample 4 [0.1g]	Sample 5 [0.25g]	Sample 6 [0.3g]
600	0.162	0.172	0.232	0.356	0.456	0.458

Figure 4.5: Sample 4, sample 5 and sample 6 respectively

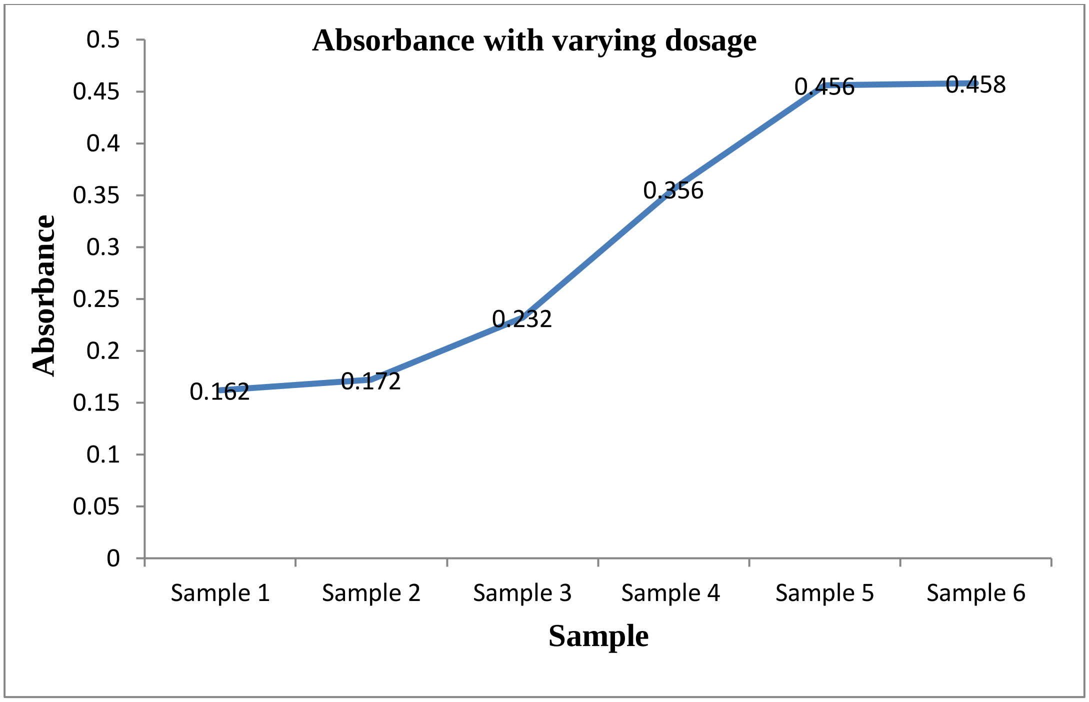


Figure 4.6: Absorbance with varying dosage

When a varying amount of pine needle biochar was added into the methylene blye dye, which was then incubated at a temperature of 30°C for 8hrs. It was found that the absorbance increase with increased in dosage from 0.015g to 0.25g, but slightly increased from 0.25g to 0.3g. It is due to increase in the site available for the bond between the dye and the biochar. We can conclude from the above experiment that the optimum dosage for removal of 50mg/l dye solution to be 0.25g. The same can be deduced from the Figure 4.6 given above.

4.4 BATCH EXPERIMENTS FOR COBALT METAL ION

a. To determine the optimum wavelength of cobalt metal ion

Table 4.12: Absorbance of Cobalt metal ion

Wavelength (nm)	Adsorbent Dosage (0.05g)
300	0.076
400	0.088
500	**0.146**
600	0.058
700	0.064
800	0.109

It is clear from the Table 4.12 given above that 500 nm was determined to be the ideal wavelength for the absorbance of cobalt metal ion. It is evident that the highest value attained was 0.146 for a wavelength of 500nm. The optimal wavelength for cobalt metal ion absorption is around 510 nm, as per the findings of our mother study article. So, we can say that our result validate the optimum wavelength for cobalt metal ion.

b. To determine the best biochar from 450 PNB and 550 PNB

The absorbance of different biochar is given in Table 4.13 below.

Table 4.13: Absorbance of different biochar

Wavelength (nm)	450 PNB (0.05g)	550 PNB (0.05g)
500	0.147	0.176

With the increase in pyrolysis temperature the pore structure of the pine needle biochar gets larger whereby we can see that the absorbance for 550 PNB is more than 450 PNB. When we calculate the percentage increase for the absorbance of the two native pine needle biochar, it was found to increase by 19.72%. So, we can conclude that 550 PNB is more effective then 450 PNB and for further experiments we will be using 550 PNB as our efficient biochar. Similar results were also obtained in other research papers as well.

c. To determine the optimum temperature

The absorbance with varying temperature is given in Table 4.14 below.

Table 4.14: Absorbance with varying temperature

Wavelength [nm]	Absorbance Sample[0.05g]		
	25°C	30°C	35°C
500	0.136	0.176	0.132

The values in the table represents that the biochar absorption decreases with increase in temperature because its properties like pore structure gets destroyed when it is subjected to higher temperature. As the temperature drops, cobalt metal ion absorbance lowers as well. This is because optimal conditions must be reached for the metal ion to diffuse into its pores and undergo better absorption. It can be also drawn from the table that when the temperature drops there is 22.72% decrease in the absorbance and similarly there is a decrease of 25% when the temperature is increased. Therefore, it can be concluded that 30°C is an optimum temperature for better absorption.

d. To determine the optimum duration with varying time

The absorbance with increase in contact time is given in Table 4.15 below.

Table 4.15: Absorbance with increase in contact time

Wavelength [nm]	Absorbance Sample[0.05g]		
	4 hrs	8hrs	24hrs
500	0.232	0.236	0.235

With the increase in contact time from 4 hours to 8 hours the absorbance for methylene blue dye increased by 1.72%. It can be concluded that at 500nm with temperature 30°C the absorption increases with contact time because the pores open up for the metal ions to get attached to the functional groups. As the duration increased from 8hrs to 24 hrs there was a slight decrease in the absorbance so the experiment was stopped and the duration of 8hrs was taken as the optimum duration required by 550 PNB to absorb the cobalt metal ion.

e. To determine the optimum dosage with varying dosage

The absorbance with increase in dosage is given in Table 4.9 below.

Table 4.16: Absorbance with increase in dosage

Wavelength [nm]	Sample 1 [0.015 g]	Sample 2 [0.025 g]	Sample 3 [0.05 g]	Sample 4 [0.1g]	Sample 5 [0.25g]
500	0.144	0.152	0.176	0.184	0.185

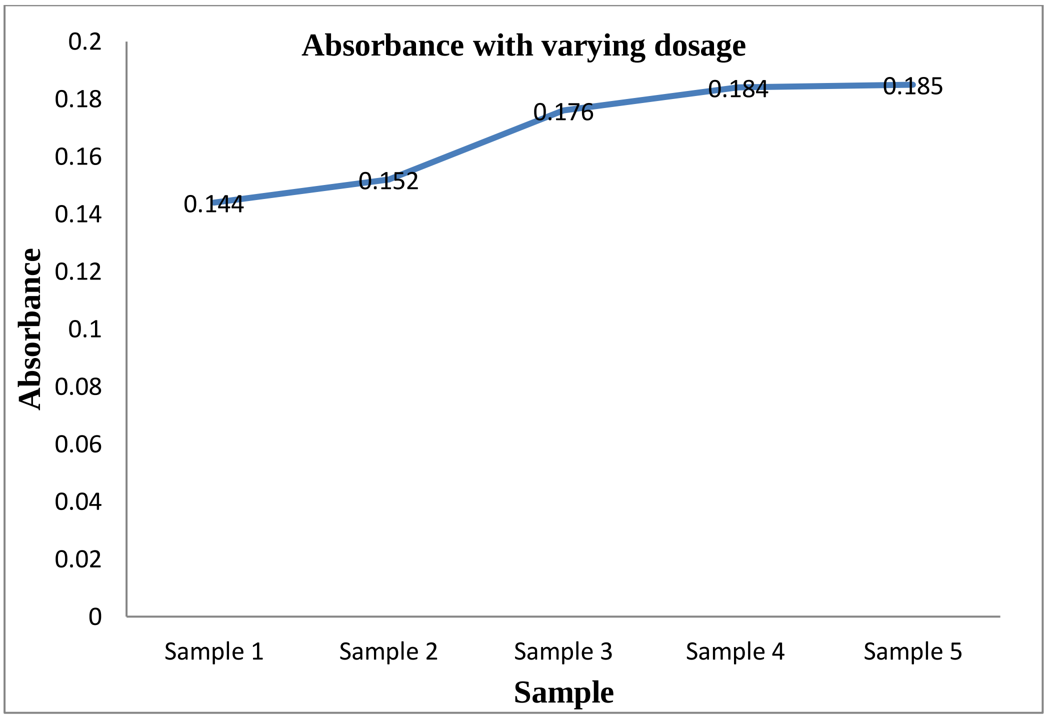


Figure 4.7: Absorbance with varying dosage

When a varying amount of pine needle biochar was added into the cobalt ion solution, which was then incubated at a temperature of 30°C for 8hrs. It was found that the absorbance increases with increase in dosage from 0.015g to 0.1g, but slightly increased from 0.1g to 0.25g. It is due to increase in the site available for the bond between the metal ion and the biochar. We can conclude from the above experiment that the optimum dosage for removal of 50mg/l cobalt metal ion solution to be 0.1g. The same can be deduced from the graph presented above.

4.5 BATCH EXPERIMENTS FOR ACID ACTIVATED PINE NEEDLE BIOCHAR

The absorbance for activated pine needle biochar is given in Table 4.17 below.

Table 4.17: Absorbance for Activated pine needle biochar

Wavelength[nm]	Sample 1[0.05g]
600	0.312
500	0.198

The table above represents the absorbance value for a dosage of 0.05g for both methylene blue dye and cobalt metal ion. The acid activated biochar showed a absorbance value of 0.312 and 0.198 respectively for methylene blue dye and cobalt metal ion. It can be also drawn that the acid activated pine needle biochar is more effective for dye molecules then metal ions. The following Table 4.18 gives the comparison between PNB and APB.

Table 4.18: Comparison table for PNB and APB

Wavelength[nm]	PNB	APB
600	0.232	0.312
500	0.176	0.198

The comparison table provided above illustrates the contrast between pine needle biochar and activated pine needle biochar. From the information provided, it can be inferred that the activated pine needle biochar has a greater absorption capacity than the regular pine needle biochar at the most effective wavelength by 34.48% and 12.5% increase for methylene blue dye and cobalt metal ion respectively. The summaries for the batch experiments is given in Table 4.9 below

Table 4.19: SUMMARIES FOR THE BATCH EXPERIMENTS

Parameters	Methylene Bue Dye	Cobalt metal ion
Optimum Wavelength	600	500
Optimum Temperature	30°C	30°C
Optimum Dosage	0.25g	0.1g
Optimum Duration	8hrs	8hrs

4.6 TREATING WASTEWATER

From the above experiment, it was deduced that if your wastewater contains methylene blue dye and cobalt metal ions, we can use the optimum dosage to remove the pollutants, provided that the optimum temperature and duration are met. As for the treatment of our sewage wastewater and textile wastewater, we have deduced from the above experiment that since we are conducting our experiment in a practical situation where the temperatures are hard to maintain, we concluded that using the biochar amount more than the optimum will be better for efficient removal of the pollutants.

4.6.1 SEWAGE WASTEWATER

The parameters such as pH, BOD, DO, TSS, TDS and TS were checked for the sewage wastewater before and after treatment of pine needle biochar. A varying amount of biochar was added to the wastewater and its parameters were checked after 24 hours. The parameters for before and after treatment of sewage waste water are given in Tables 4.20 and 4.21, respectively.

Table 4.20: Before Treatment [Raw Sewage wastewater]

Parameters	Inlet	Outlet
pH	6.85	6.91
BOD	273mg/l	12mg/l
COD	664mg/l	38mg/l
TDS	366mg/l	290mg/l
TS	755mg/l	330mg/l
TSS	389mg/l	40mg/l

Table 4.21: Treatment using pine needle biochar

Parameters	5g 550 PNB	10g 550 PNB	**15g 550 PNB**	15g 550 APB
pH	7.8	8.1	**8.2**	4.6
BOD	153mg/l	45mg/l	**28mg/l**	48mg/l
COD	360mg/l	110mg/l	**103mg/l**	188mg/l
TDS	506mg/l	730mg/l	**940mg/l**	975mg/l
TS	748mg/l	1052mg/l	**1373mg/l**	1431mg/l
TSS	242mg/l	322mg/l	**433mg/l**	456mgl

Figure 4.8: Experiments on Sewage wastewater

We can see that the parameters for 15 g of biochar were found to be more effective than the other amount of biochar. The parameter BOD, which is of most importance when considering the sewage wastewater, was found to be the least when we used 15g of PNB. The BOD value of 38 mg/l is not up to the standard limit for a drinking water but can be discharged into the water bodies as its BOD is less than the required value of 80 mg/l. We can see that there is a vast difference in the BOD of the sewage wastewater before and after treatment. Even though the other parameters like TDS, TSS, and TS are lower for 5g and 10g, its BOD is decreased by 120 mg/l and 228 mg/l respectively, unlike for 15 g of pine needle biochar, where the difference is 245 mg/l, which is huge. When the activated pine needle biochar was used its BOD slightly increased by 10mg/l then the native pine needle biochar. It may be due to the presence of nitrogen in the nitric acid which provides an additional nutrient source for microbial growth, potentially increasing BOD indirectly. So, we can conclude that for practical removal of pollutant, native pine needle biochar is more effective than the activated. Even though its BOD and other parameters are up to the standard limit for disposal and irrigation but the suspended solid should be lesser than 100mg/l for disposal so in order to reduce the suspended solid we have to use uncrushed pine needle biochar. The Figure 4.8 depicts the experiments conducted on sewage wastewater.

The Comparison table for the outlet of the treatment plant and PNB treated wastewater is given in Table 4.22 below.

Table 4.22: Comparison between outlet of treatment plant and PNB treated

Parameters	PNB Treated	Outlet
pH	8.5	6.91
BOD	28mg/l	12mg/l
COD	103mg/l	38mg/l
TDS	940mg/l	290mg/l
TS	1373mg/l	330mg/l
TSS	433mg/l	40mg/l

On comparing the results, we can see that the pH of our treated wastewater is much better than the pH of the pH of the outlet of the treatment plant. We can see that the other parameters are much better for the outlet of the sewage treatment plant, but with better treatment come the expensive cost of the treatment. If the wastewater is treated to just dispose of it in the water bodies, we use our pine needle biochar, which is more cost-effective than the conventional treatment method.

4.6.2 TEXTILE WASTEWATER

The parameters such as pH, BOD, COD, DO, TSS, TDS and oil and grease were checked for the textile wastewater before and after treatment of pine needle biochar. A varying amount of biochar was added to the wastewater and its parameters were checked after 24 hours. The parameters for before and after treatment of sewage waste water are given in Tables 4.23 and 4.24, respectively.

Table 4.23: Before Treatment [Raw Textile wastewater]

Parameters	Inlet	Outlet
pH	7.38	7.12
BOD	171mg/l	31mg/l
COD	640mg/l	70mg/l
Oil and grease	4.2 mg/l	4.9 mg/l
TDS	1967.4mg/l	1753mg/l
TS	2122.4mg/l	1784.6mg/l
TSS	155mg/l	31.6mg/l

Table 4.24: Treatment using pine needle biochar

Parameters	5g 550 PNB	**10g 550 PNB**	15g 550 PNB	10g 550 APB
pH	7.9	**8.3**	8.9	5.2
BOD	160mg/l	**95mg/l**	165.5mg/l	116mg/l
COD	236mg/l	**220mg/l**	696mg/l	465mg/l
Oil and grease	4.6mg/l	**4.5mg/l**	4.3mg/l	4.6mg/l
TDS	2386mg/l	**2567mg/l**	2834mg/l	2578mg/l
TS	2553mg/l	**2810mg/l**	3380mg/l	2843mg/l
TSS	167mg/l	**243mg/l**	546mg/l	265mg/l

Figure 4.9: Experiments on textile wastewater

We can see that the parameters for 10 g of biochar were found to be more effective than the other amount of biochar. The parameter COD, which is of most importance when considering the textile wastewater, was found to be the least when we used 10g of PNB. The COD value of 220 mg/l is not up to the standard limit for a drinking water but it is below the permissible limits of 250mg/l to 500mg/l. We can see that there is a vast difference in the COD of the textile wastewater before and after treatment. Even though the other parameters like TDS, TSS, and TS are lower for 5g , its COD is decreased by 404mg/l, unlike for 10 g of pine needle biochar, where the difference is 420 mg/l, which is huge. When the 10g activated pine needle biochar was used its COD increased by 245mg/l then the native 10g pine needle biochar. It may be due to the presence of ions in the acids used in the activation which potentially increases the chemical oxygen demand. So, we can conclude that for practical removal of pollutant, native pine needle biochar is more effective than the activated pine needle biochar. Even though the COD of the wastewater is lowered but its TSS is more than the permissible limit so we can use uncrushed pine needle biochar to decrease the TSS. The Figure 4.9 depicts the experiments conducted on textile wastewater.

The Comparison table for the outlet of the treatment plant and PNB treated wastewater is given in Table 4.25 below.

Table 4.25: Comparison between outlet of treatment plant and PNB treated

Parameters	PNB Treated	Outlet
pH	8.3	7.12
BOD	95mg/l	31mg/l
COD	220mg/l	70mg/l
Oil and grease	4.5mg/l	4.9 mg/l
TDS	2567mg/l	1753mg/l
TS	2810mg/l	1784.6mg/l
TSS	243mg/l	31.6mg/l

On comparing the results of both treated wastewater it was seen that the conventional treatment method for textile wastewater was more effective than our pine needle biochar. The reasons can be due to the chemical reactions occurring between the chemical present in pine needle biochar and the textile wastewater which contributes to the increase in demand of active sites for absorption. But it was also seen that on further increase of dosage the parameters started to increase rather than decrease, it can be due to the reason stated above.

4.6.3 UNCRUSHED PINE NEEDLE BIOCHAR

The pine needle bicohar obtained was washed and not grinded in the mortar. It was dried at 70 °C for 24 hours. Then it was used in the wastewaters for the treatment.

Table 4.26: Treatment using uncrushed pine needle biochar

Parameters	Sewage WW [15g]	Textile WW [10g]
pH	7.7	7.9
BOD	26mg/l	86mg/l
COD	97mg/l	160mg/l
Oil and grease		4.4mg/l
TDS	569mg/l	1567mg/l
TS	667mg/l	1780mg/l
TSS	98mg/l	213mg/l

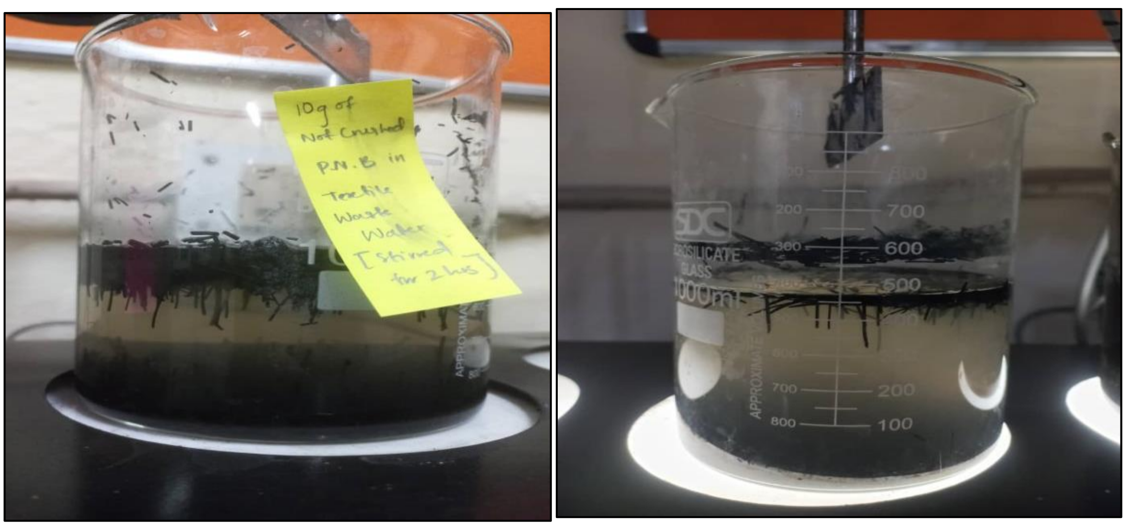


Figure 4.10: Uncrushed pine needle biochar in textile and sewage wastewater respectively

From the Table 4.26 we have finally concluded that use of uncrushed pine needle biochar will have better effect on the treatment of wastewater. We can see that the TSS parameter which was more in the case of crushed pine needle biochar was both decreased when we use uncrushed pine needle biochar. The Figure 4.10 depicts the aftermath of the treatment of PNB. The parameters are also up to the standard limit for the use in irrigation and disposal to the water bodies.

CHAPTER 5
CONCLUSION

The project aimed at using an eco-friendly and sustainable material like pine needles for the treatment of wastewater. Firstly, the pine needles were pyrolyzed into two different native biochars, and their characteristics were determined using proximate analysis methods. To test if the biochars work effectively or not, we conducted batch experiments on a specific dye and metal ion, and the efficiency was known accordingly. After that, the biochar was activated using strong acids, and its effectiveness was also compared with respect to the native pine needle biochar. The best biochar obtained was then used in the treatment of wastewater in practical situations where it is hard to maintain a constant value for any parameter.

Through batch experiments and analysis on methylene blue dye and cobalt metal ion, it was observed that the use of pine needle biochar in the removal of methylene blue dye and cobalt metal ion was possible. The optimum dosage, time, and temperature for both of the pollutants were measured and observed as 0.25 g, 8 hours, 30 °C, and 0.1g, 8 hours, 30 °C, respectively, for methylene blue dye and cobalt metal ions. Moreover, the use of activated pine needle biochar increased the absorbance by 34.48% and 12.5%, respectively, for methylene blue and cobalt metal ions.

From the study, we have concluded that activated pine needle biochar produced by nitric acid and sulfuric acid helps in the removal of metal ions and dyes more than native pine needle biochar. But the limitation of the activated biochar was that the cost of its manufacture was higher than that of the native pine needle biochar. So, a series of batch experiments were first conducted using the best native pine needle bicohar, and then, after determining the optimum dosage of 15g and 10g for sewage and textile wastewater, respectively, the activated biochar of the same amount was used in the wastewater and the parameters were checked. It was found that the native pine needle biochar, when added to both wastewaters, reduced the pollution parameters to the extent that we could either dispose of it in water bodies or use it for irrigation. But, on the contrary, activated pin needle biochar increased those parameters because of the chemical reactions occurring between the chemicals in the wastewater and activated biochar. It can also be deduced that, due to the nitrogen present in nitric acid, it contributed to the growth of bacteria, which potentially increased the parameters.

In conclusion, the use of pine needles as a green material for the treatment of wastewater is a promising approach that can help address the challenges of water pollution and water scarcity in developing countries and areas with limited access to conventional treatment methods. Further research and development in this area can help to promote the sustainable use of natural resources for water management and contribute to the achievement of the United Nations Sustainable Development Goals.

FUTURE SCOPE

1. The work can proceed with the use of biochar pyrolyzed at a higher temperature to check and compare its efficiency.

2. A different method of activation can be used, or different acids and bases can be used to activate the biochars and do a comparative analysis.

3. The biochar used in the treatment can be further regenerated or checked for reusability efficiency so that the cost can be reduced.

The findings of this study suggest that increasing the pyrolysis temperature increases the removal efficiency of pollutants, and while using acids to activate pine needle biochar, we have to use acids that will not contribute to bacterial growth and that will not react with the chemicals in the wastewater. The future scope of this study can involve further investigation into using other sustainable materials to remove pollutants.

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