Preparation and characterization of activated Teff (*Eragrostis*) straw Biochar for Methylene Blue Adsorption

By Mekonnen Tega Birhane

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Mekonnen Tega Birhane

Advisor(s)

Dr.Zelalem Tumsa

The Department of Chemical Engineering

School of Mechanical, Chemical and Material Engineering

Office of Graduate Studies

Adama Science and Technology University

Adama

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Advisor approval Sheet

We have that the recommendation and suggestions given by the proposal review committed are appropriately incorporated in to the final thesis proposal entitled "preparation and characterization of activated Teff (Eragrostis) straw Biochar for Methylene Blue adsorption "by Mekonnen Tega

Dr.Zelalem Tumsa _____ _____

Advisor /Supervisor/ Signature Date

Declaration

I declare that this MSc/MA Thesis / Dissertation entitled "Preparation and characterization of activated Teff (Eragrostis) straw Biochar for Methylene Blue adsorption "For MSc Degree at the university of Adama science and technology university. Herby submitted me and has not been submitted for Degree at this or any other university, and that all sources of material used for this thesis/ dissertation have been duly acknowledged.

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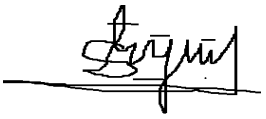
Dr.Sintayehu Mekuria		
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LIST OF ACRONYMS AND ABBREVIATIONS

ABC	Activated Biochar
AC	Activated Carbon
AOP	Advanced Oxidation Processes
ATSB	Activated Teff Straw Biochar
ASTM	American Society of Testing Materials
BC	Biochar
BET	Braeuer-Emmett-Teller
CCD	Central Composite Design
EDA	Electron Donor Acceptors
HTC	Hydro Thermal Carbonization
FC	Fixed Carbon
FTIR	Fourier Transform Infrared
NA	Not Available
NRA	Not Readily Available
SEM	Scanning Electron Microscope
VM	Volatile Matter

Abstract

An activated biochar adsorbent obtained from Teff (*Eragrostis)* straw was prepared using two-step" carbonization and activation technique and its performance was evaluated for the adsorption of MB. The activated biochar also characterized by Scanning electron microscopy (SEM), FT-IR and BET. The effects of ratio (KOH/biochar: w/w), temperature, and time of carbonization on the removal of methylene blue by ATSB biochar were evaluated to determine the optimum treatment conditions to come up with best performance. The adsorption performance for the removal of methylene blue (MB) was deeply investigated. The effects of pH, initial dye concentration, contact time, adsorbent dosage, and temperature on the adsorption of MB onto ATSB were also investigated. SEM results shows that the ATSB were porous and also the BET result shows surface area of ATSB became 259.21 m^2/g which is much higher than raw BC surface area which was 4.628 m^2/g. The best operating conditions to make activated biochar were KOH/Teff *(Eragrostis)* straw ratio 2:1, activation temperature 450°C, and 2 hours of holding time in the activation chamber. The study conducted on the adsorption kinetics indicated that Pseudo-first-order kinetics (R^2=0.967) guided the adsorption process. The Langmuir model (R^2=0.99) was shown to be the best fit for the experimental adsorption isotherm, meaning that MB adsorption by porous biochar occurred as a monolayer adsorption with a maximal monolayer adsorption capacity of 59.17 mg/g. Gibbs free energy, enthalpy, and entropy were determined as thermodynamic parameters. The positive value of ΔH^0 (13.65) showed that the nature of adsorption process was endothermic. The positive value of ΔS^0(0.99) indicated an increase in the randomness at the solid/solution interface during the adsorption of the MB dye on teff straw biochar. ΔG^0(-15.69) has negative value and which indicate that the process is spontaneous The ATSB has a presentable recyclability, according to the regeneration analysis. The ATSB developed in this study has the potential to treat dye wastewater in real applications due to its strong adsorption ability.

Keywords: Activated biochar (KOH), Adsorption, methylene blue, Teff *(Eragrostis)* straw

CHAPTER ONE

1. Introduction

1.1 Background

Today, the global population is growing at an annual rate of 83 million people. By 2050, it is expected to reach 9.8 billion people(Abhishek Pokharel 2021). As a result of industrial development and population growth, environmental pollution has become one of the most serious threats to human health. The pollution of water resources with synthetic dyes and pigments is a significant aspect of this pollution. Textiles, leather, cosmetics, and food industries all use dyes and pigments to color their products (Gemici, Ozel, and Ozel 2021).

The rising demand for dyes in many industries exacerbates dye wastewater discharge as well as their hazardous effects on the environment and organisms, causing widespread worry among society. Dye wastewater discharged into forests or fields, for example, would have a direct impact on soil productivity, while dyes in water can impair light penetration and photosynthesis in aquatic plants. (Ying et al. 2021) As a result, eliminating dye from wastewater is a must if it is not to be discharged into the environment (Zhu et al. 2018).

Methylene blue (MB) is the most widely used dyeing agent for cotton, wood, and silk. MB can cause eye burns, which can result in irreversible damage to humans and animals' eyes. It can cause short periods of rapid or difficult breathing when inhaled, and it can also cause nausea, vomiting, intense sweating, and mental confusion when consumed through the mouth. Because of the negative effects on receiving water, the treatment of wastewater containing such dye is of importance (Ahmed and Dhedan 2012).

In the last few decades, interest has grown for the use of lignocellulosic materials for different applications. Lignocellulosic biomass consists cellulose, hemicellulose and lignin which when separated can be used for different applications (Srivastava 2016).

Teff (*Eragrostis*) a lignocellulosic biomass is one of the major food crops used in Ethiopia, and its annual yield is estimated to be about 15.5 million tones/year. Teff has very high amount of calcium content and is an excellent source of vitamin C. In the literature, a number of agricultural residues have been tested as adsorbent for chromium removal (Coker et al. 2023).

Adsorption technology has grown in popularity as a reliable and widely used wastewater treatment process that is also ecologically benign, efficient, and cost-effective (Wu et al. 2021).

Because of increased environmental concerns and the demand for cost-effective competitive adsorbent goods, biomass has lately gained popularity as a source of carbonaceous product due to its availability, practicality, and biodegradability in nature (Workie et al. 2019).

Biochar is a carbon-based solid product produced through thermochemical transformations of biomass, such as pyrolysis, gasification, torrefaction, and hydrothermal carbonization. Wood and agricultural wastes, rice husks and straw, leaves, food waste, paper sludge, bagasse, and a variety of other materials are also potential biochar feedstocks (Gargiulo et al. 2018).

Biochar's adsorption capacity is determined by its physiochemical properties, which include surface area, pore size distribution, functional groups, and cation exchange capacity. These qualities vary depending on the preparation circumstances. Many academics are studying biochar to see how effective it is at removing various impurities (Yaashikaa et al. 2020).

Biochar is a low-cost, environmentally friendly adsorbent that can be used to remove dye from wastewater. It is primarily made up of amorphous carbon with a highly functionalized surface, making it reactive to a wide range of chemicals, both inorganic and organic. (Kalinke et al. 2017)

The increase in micropore volume caused by the elimination of volatile organic compounds at high temperatures results in biochar with a larger surface area and carbon content (Wang and Wang 2019a).

Biochar can have various environmental benefits in addition to reducing the amount of greenhouse gases in the atmosphere. It has the ability to improve soil quality, water quality, soil fertility, and agricultural productivity (Srivastava 2016).

As the industry seeks to minimize its reliance on petroleum-based products, there is a growing need to discover alternative ecologically friendly materials with improved qualities and long-term sustainability to replace the existing ones. As a result, this work attempted to determine the efficacy of teff straw as a biochar for MB adsorption.

Only few studies have been reported on use of teff straw as an adsorbent because of its less familiarity in scientific research world (Wassie and Srivastava 2016) used raw teff straw without

any chemical modification and also with sodium hydroxide, phosphoric acid and zinc chloride modification for Cr(VI) removal (Srivastava 2016). Temesgen and Abeto Amibo used Novel Lanthanum Doped Magnetic Teff Straw Biochar Nanocomposite for DE fluoridation of Groundwater (Amibo, Beyan, and Damite 2021).

The ultimate goal of this research is to develop low-cost and efficient activated biochar for MB adsorption in order to prevent contaminated waste from industry into the environment. KOH activated biochar from agricultural waste biomass, teff straw (*Eragrostis),* using a slow pyrolysis approach at 300, 400, and 600 ℃, and its MB adsorption ability was also evaluated.

1.2 Statement of the Problem

Dyes such as methylene blue which contaminate water sources from various industries such as textiles, leather, paper printing and cosmetics. Vast discharge of these organic materials is of great concern in water treatment since they are carcinogenic, show allergic reactions and gives water bad appearance. It is a fact that dye removal in the treatment of wastewater requires sophisticated processes which is costly and not so easy to carry out. Various methods have been developed to remove dyes from wastewaters, including chemical oxidation, biodegradation, electro coagulation, photo degradation, solvent extraction, and adsorption. most of the methods used for the removal of dye are costly and the disposal of the large amount of concentrated sludge causes problems. But the adsorption technique is the most favorable method for dyes removal. carbonaceous adsorbents bio mass based adsorbent is preferable due to low cost and availability of the material. Now a day, the high cost and sophisticated and installation of waste treatment process in several industry have directed to increasing interest in the possible use of other locally accessible materials for MB adsorption. Even though most of these traditional biomass materials are low cost compared to other MB adsorbent, they are subjected to factors such as geographical location and cultivated land yield, so the cost of large-scale recycling is quite high.it is necessary to use agricultural waste biomass to produce low-cost MB adsorbents. Teff (*Eragrostis)* is an indigenous lignocellulose material in Ethiopia, and it is residual waste obtained after the seeds of Teff were removed. Use of teff straw biochar for the removal of dyes could reduce health problems associated with water contamination with toxic dyes or reduce cost of purification of water.

1.3 Significance of the study

To the best knowledge of the researcher, there is no research report on removal of Methylene blue by using teff straw biochar. This study has a valuable significance to prepare activated biochar from Bio-based adsorbents Teff (*Eragrostis*) straw. Since teff straw fiber is cheap, locally available and byproducts using it as biochar can minimize the production costs of adsorbent to remove MB from industrial waste.

1.4 general and specific objectives

1.4.1 General Objective

- ✓ The general objective of this study is to prepare, characterize and evaluate KOH activated Teff (*Eragrostis*) biochar adsorbent for MB adsorption.

1.4.2 Specific Objectives

- ✓ Produce Teff straw derived biochar and characterize its physicochemical properties.
- ✓ Investigate the individual and interaction effects of parameters for biochar treatment to enhance its adsorption performance and conduct statistical parameter optimization.
- ✓ Evaluate the efficiency of the adsorbent.
- ✓ Study adsorption Isotherms and kinetics of MB onto the biochar.
- ✓ Study the regeneration capacity for reusability of the biochar purpose.

1.5 Scope of the study

The scope of this study is to prepare and characterize activated biochar adsorbent from Teff (*Eragrostis)* straw for MB adsorption. The *teff (Eragrostis)* straw used to produce biochar is collected from specific farm (Bishoftu, Oromia) and white teff species. Since the mineral contents of the soil, geographical area and variety of the teff have an impact on morphological structure and chemical compositions, it would have been deeper study if it was collected from different species and geographical location. To study the adsorption performance of teff straw deeply including factors which may affect the adsorption performance like temperature, pH, MB concentration, adsorbent dosage and contact time. kinetics of adsorption, isotherm, thermodynamics, regeneration and reusability of ATSB adsorbent were studied.

CHAPTER TWO

2. Literature review

2.1 General

Clean water is essential for the survival of all living beings. Water consumption has increased as a result of technological advancements, as indicated by fast industrialization, modernization, and population growth, with around 70%, 22%, and 8% being used in the agricultural, industrial, and home sectors, respectively. Because of the increasing demand for water, a great amount of wastewater is produced, which contains a variety of pollutants including medications, poisons, pharmaceuticals, pesticides, herbicides, surfactants, chlorophenols, heavy metals, and dyes. Dye effluents, which come from the textile sector, are an ever-increasing source of contaminants in receiving water streams. Uncontrolled dye emission at concentrations of mg/L or below have had negative consequences for the environment and human health (Marrakchi, Hameed, and Bouaziz 2020).

Industry (coal and steel industry, non-metallic minerals industry) produces a considerable volume of wastewater every day. This has a significant environmental impact. As a result, advanced oxidation processes (AOPs), reverse osmosis, adsorption, ion exchange, ozonation, precipitation, filtration with coagulation, and the coagulation process have all been used to treat industrial wastewater. However, the majority of these processes come at a high cost of operation and capital. This has been cited as the primary impediment to their use in both developed and developing countries for the abatement/removal of potentially harmful pollutants from polluted waters (Biochar 2015).

Textile, leather, cosmetics, paper, dye synthesis, food processing, pulp mills, pharmaceuticals, and plastics sectors all emit dye pollutants that pollute the environment.(Yaashikaa et al. 2020) Methylene blue (MB) is a cationic dye that is commonly used in industry. Cotton, wool, silk, and nylon are among the most common materials dyed using it. (Ambaye, Vaccari, van Hullebusch, et al. 2021) MB has a wide range of applications, making it a common contaminant or ingredient in color effluents (Biochar 2015).

Biochar is a solid made by pyrolyzing biomass at temperatures below 700°C in the absence or low presence of oxygen. The resultant solid is high in carbon and has good adsorption properties, thus it can remove organic and inorganic pollutants from wastewater. Various waste items, such as straw, faces, and sludge, have been evaluated as biochar source materials (Biochar 2015).

2.2 Nature of dyes

Dyes are complex organic compounds which are widely used in textile, printing, leather, cosmetic and paper industries and hence produce large amount of dye bearing liquid effluents. Today, more than 100,000 commercial dyes are known with a total yearly production of 7×10^5 tons per year. The high solubility of dyes in water effluents possesses serious risks to crop, aquatic life and human health (Dawood, Sen, and Phan 2016).

Dyes have hazardous, deleterious and chromogenic nature. it has complex aromatic structure resistant to biodegradation or structural modification on exposure to light, temperature or common oxidizing agents (Isotherms and Analysis 2020).

Methylene blue (MB) a cationic dye has been studied as dye pollution not only because of its toxicity but its color as well. MB has very wide applications which make it one of the common pollutants or constituent of color effluents (Biochar 2015).

2.3 Dye pollution and health risks

Methylene blue (MB) is the most commonly used substance for dying cotton, wood, and silk. MB can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. The non- degradability of azo dyes leads to bioaccumulation in organisms and could be responsible for various dysfunctional observations (Isotherms and Analysis 2020). On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, profuse sweating, and mental confusion. Therefore, the treatment of effluent containing such dye is of interest due to its harmful impacts on receiving water. Due to the structural stability and complexity of dye molecules, they represent a real threat to the environment and human health.(Biochar 2015) Therefore, the effective removal of dye from wastewater and preventing it from polluting the

environment is a significant challenge for industrial production that requires an urgent solution (Ying et al. 2021).

2.4 Dye removal methods

Various methods have been developed to remove dyes from wastewaters, including chemical oxidation, biodegradation, electro coagulation, photo degradation, solvent extraction, ultra-filtration, and adsorption. Biological methods and physical-chemical methods have often been used to remove dyes from wastewater. Biological methods, such as membrane separation for dye wastewater treatment, technology, anaerobic process, and aerobic process are frequently utilized (Isotherms and Analysis 2020).

Due of dyes' physicochemical thermal optical stability, these procedures are ineffective. Advanced oxidation, son lysis, photo-catalysis, and electrochemical oxidation are examples of physical-chemical techniques that need extremely effective oxidative catalysts and the inclusion of oxidative agents (Nartey and Zhao 2014).

Because of its ability to remove hazardous contaminants from aquatic systems, adsorption, which is an environmentally acceptable and cost-effective operation, is usually recognized as the most efficient way among these strategies (Kaya, Yıldız, and Ceylan 2018).

Table 2. 1 Classification of dye effluent treatment methods (Nartey and Zhao 2014)

Biological	Chemical	Physical
Aerobic biological processes	Coagulation-flocculation and precipitation	Adsorption: adsorption with activated carbon, adsorption with activated alumina and other metal oxides, biosorption adsorption with biochar
Anaerobic biological treatment process Electrocoagulation	Electrocoagulation	irradiation
	Oxidative processes: Ozonation, oxidative processes with hydrogen peroxide, oxidative process with sodium hypochlorite, photochemical oxidation process, and electrochemical oxidation processes. (Bautista)	Membrane processes: reverse osmosis, micro-filtration, bio-filtration, ultra-filtration, Nano-filtration**.**

2.5 Methylene Blue dye

Methylene Blue is a monovalent cationic dye with the chemical formula $C_3H_{18}ClN_3S$ with a molecular weight of 319.85 g/mol. Methylene blue (MB) is a common dye used in sectors such as paper coloring, hair dye, cotton dyeing, and wool dyeing, among others. MB has a wide range of applications, making it a common contaminant or ingredient in color effluents (Biochar 2015).

To living organisms, MB (a thiazine cationic dye) can cause a variety of health problems, including breathing difficulties, retching, nausea, gastritis, and diarrhea (Gargiulo et al. 2018).

Table 2.2 Details of the dye used (Gemici, Ozel, and Ozel 2021)

Dyestuff	Basic Blue 9 (BB 9)
IUPAC name	Methylthionine chloride 3.7 Bis (dimethyl amino) phenothiazinium chloride, Tetra methylthionine chloride
Commercial name	Methylene Blue (MB)
C.I Number	52015
Appearance	Dark green crystalline powder
Empirical Formula	$C_{16}H_{18}ClN_3S$
Molecular weight	319.85g/mol
λ_{max}	664nm

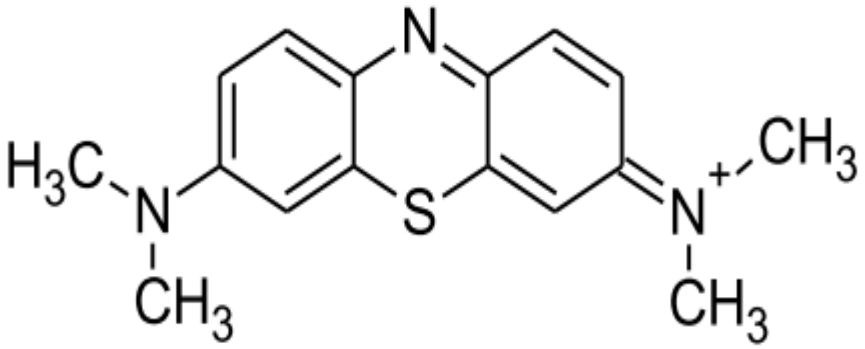

Figure 2.1 molecular structure of MB

2.6 Biochar (BC)

Biochar (BC) is a carbon-rich substance that is produced when biomass, such as wood, manure, or leaves, is burned. Biomass is a complex biological organic or inorganic solid substance obtained organically from live or recently living organisms. Animal dung, waste paper, sludge, and a variety of industrial wastes are just a few examples (Tripathi, Sahu, and Ganesan 2016).

Biochar made from wood, on the other hand, will be more stable over time. Higher fire temperatures will result in more micro porosity and adsorptive capacity, and hence a better adsorption potential (L. Liu and Li 2019).

Because to its greater surface area and microporosity, biochar produced at a higher pyrolysis temperature is superior for removing nonpolar organic molecules. Biochar made at temperatures below 500°C, on the other hand, includes more O- and H-containing functional groups, making it more likely to bind to polar chemical molecules. Biochar with more O- and H-functional groups (<400°C) showed increased sorption of aromatic cat- ionic dyes like methyl-violet and methyl-blue (Biochar 2015).

Because of its unique properties, including as adsorption capacity, specific surface area, microporosity, and ion exchange capacity, biochar offers a wide range of uses in water and wastewater treatment. Biochar has been utilized for a variety of environmental applications, including improving soil quality, removing emerging pollutants from soil and water, reducing greenhouse gas emissions, and producing electricity (Qian et al. 2015).

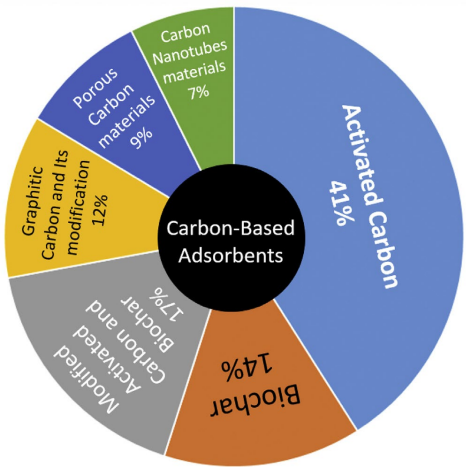

Figure 2.2 Research of carbon adsorbents for the removal of methylene blue

The interactions of various contaminants with various properties of biochar, which are dependent on pyrolysis temperature and feedstock type, determine their removal methods. The temperature at which biochar is pyrolyzed has a significant impact on its characteristics (Kalinke et al. 2017).

2.7 Biochar production technique

Biochemical conversion and thermochemical conversion are the two types of bioenergy conversion strategies. Biochemical conversion uses biological catalysts and living organisms to generate energy from biomass, whereas thermochemical conversion uses heat and a chemical catalyst to generate energy from biomass. Combustion, gasification, and pyrolysis are the three types of thermochemical conversion techniques (Tripathi, Sahu, and Ganesan 2016).

Biochar is a porous carbonaceous material made by thermochemically converting organic matter in an oxygen-depleted environment (Dulanja et al. 2019).

Depending on the technology (e.g., torrefaction (a pyrolytic process primarily at low temperatures), slow pyrolysis, inter-mediate pyrolysis, fast pyrolysis, gasification, hydrothermal carbonization (HTC), or flash carbonization) used for its production, carbonized organic matter can have essentially different physical and chemical properties (Nartey and Zhao 2014)(Nartey and Zhao 2014).

The technologies used to extract energy from biomass are known as bioenergy conversion technologies. Bioenergy conversion of biomass can yield a variety of energy-dense products. Biochemical conversion and thermochemical conversion are the two broad categories of bioenergy conversion processes.

Biochemical conversion uses biological catalysts and living organisms to generate energy from biomass, whereas thermochemical conversion uses heat and a chemical catalyst to generate energy from biomass. Carbonization methods such as pyrolysis, gasification, and hydrothermal carbonization can be used to transform feedstock into char (Tripathi, Sahu, and Ganesan 2016).

2.8 Type of thermochemical biochar production process

2.8.1 Combustion

Combustion is a method of obtaining chemical energy stored in biomass in the form of heat by burning it directly in the presence of oxygen/air. Combustion guarantees that the biomass is completely oxidized. Biomass is burned at temperatures between 800 and 1000 degrees Celsius (Ahmed and Dhedan 2012).

2.8.2 Gasification

Gasification is a thermochemical process in which the carbonaceous content of biomass is transformed into a gaseous fuel in the presence of a gaseous medium such as oxygen, air, nitrogen, carbon dioxide, steam, or a mixture of these gases at temperatures ranging from 700 to 900 degrees Celsius (Tripathi, Sahu, and Ganesan 2016).

2.8.3 Pyrolysis

Pyrolysis is one of the most successful and efficient methods for extracting energy from biomass in the form of char. Pyrolysis creates a variety of bio-oil and other value-added products in addition to charcoal. Pyrolysis is a thermochemical process in which biomass is thermally decomposed into its chemical constituents in the presence of inert or extremely low stoichiometric oxygen. The solid, liquid, and gas products are generated during the pyrolysis process. Pyrolysis comes in a variety of forms. Pyrolysis can be divided into five subclasses based on the operating conditions. Each type of pyrolysis has its own set of benefits and drawbacks (Tripathi, Sahu, and Ganesan 2016).

Table 2.3

Process	Temperature (°C)	Residence time (s/h/min/days)	Char yield (wt.%)
Slow pyrolysis	300-600	min to days	20-40
Fast pyrolysis	400–600	~s	10-20
Gasification	800-1000	5-20s	~10S
Hydrothermal carbonization	180-250	1-12h	30-60

Typical char yield from thermochemical processes

The traditional kind of pyrolysis is slow pyrolysis, which is characterized by a slow heating rate and a long residence duration. Slow pyrolysis involves heating biomass to temperatures in the range of 400–500 °C at a rate of about 0.1 to 1 °C/s over a period of 5 to 30 minutes. The development of char is favored by slow pyrolysis (Tripathi, Sahu, and Ganesan 2016).

Table 2. 4 Biomass feedstock products of different types of pyrolysis (Dantas et al. 2011)

Process	Liquid biooil) %	Solid (BC) %	Gas (syngas) (%)
Fast pyrolysis: moderate temperature (600℃), short hot vapor residence time	75	12	13
Intermediate pyrolysis: low moderate temperature, moderate hot vapor residence time	50	25	25
Slow pyrolysis: low moderate temperature, long residence time	30	35	35
Gasification: high temperature (>700℃), long vapor residence time	5	10	85
Hydrothermal carbonization: elevated temperature (200–250℃) and elevated pressure	NAR	NAR	NAR
Flash carbonization: (350–650℃), residence time below 30 minutes, at elevated pressure (1–3MPa)	NAR	50	50

∗NAR = not readily available

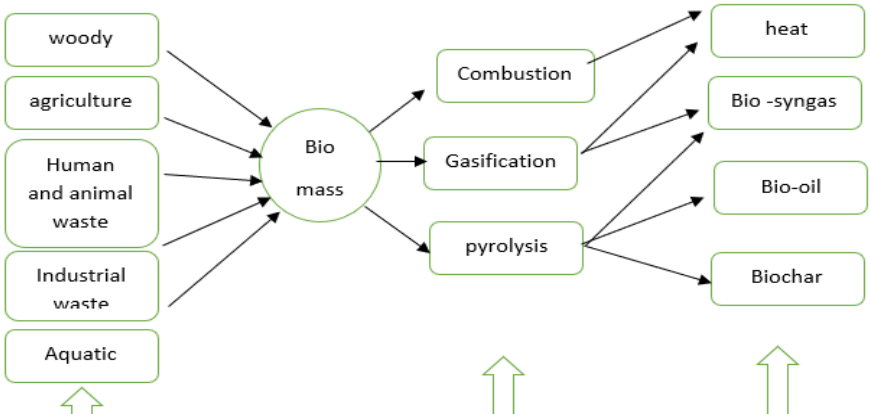

Figure 2.3 Conversion techniques of biomass obtained from different sources and their products

The pyrolysis solid residue (char) is a carbonaceous substance that is primarily employed as a fuel, adsorbent, and soil treatment. Char is a solid porous structure that forms when the hydrogen and oxygen that were previously present in the biomass leave it due to high temperatures.

It also offers a lot of potential in soil treatment, soil water improvement, carbon sequestration, and adsorption-based water pollution reduction (Tripathi, Sahu, and Ganesan 2016).

2.9 Chemical properties of biochar

The adsorption of MB onto the biochar surface is also affected by the chemical properties of the biochar such as alkalinity, mineral, composition, presence of surface functional groups, hydrophobicity, and non-polarity. The MB adsorption capacity of biochar can be enhanced by increasing the alkalinity of the biochar surface (Dulanja et al. 2019).

2.9.1 Basic functional groups

Functional groups, primarily oxygen-containing groups such as carboxylic, hydroxyl, phenolic (hydroxyl), carbonyl, lactone, carboxylic acid anhydride, and cyclic peroxide, are intimately related to the properties of BC and the reaction mechanisms of the charring processes (Sajjadi, Chen, and Egiebor 2019). Because they contribute to surface basicity, which increases biochar's affinity for MB, basic surface functional groups play a key role in MB adsorption (Qian et al. 2015).

2.9.2 Alkaline and alkaline earth metals

Biochar's MB adsorption capacity may be enhanced by the presence of alkaline metals and alkaline earth metals. Alkali metals and alkaline earth metals (e.g., Na, K, Ca, Mg, and Li) can

promote the creation of basic sites with a large affinity for MB, which is acidic (Dulanja et al. 2019).

2.9.3 Hydrophobicity, polarity, and aromaticity

Because most porous materials have a high affinity for H_2O, studies have shown that the MB adsorption capacity may be lowered in humid settings. Biochar with hydrophobic and non-polar properties may improve MB adsorption capability by reducing H_2O molecule competition. Low H/C and O/C ratios (<0.2) indicate a high degree of aromaticity and chemically stable fixed carbon (Dulanja et al. 2019).

2.10 Process parameters and biochar production

2.10.1 Process temperature

The biochar yield is affected by increasing the pyrolysis temperature because high temperatures produce thermal cracking of heavy hydrocarbons, resulting in an increase in liquid and gas products and a decrease in solid products. Higher fire temperatures result in more micro porosity and adsorptive capacity, which means more potential for hazardous chemical adsorption and soil rehabilitation (Sakhiya, Anand, and Kaushal 2020).

2.10.2 Heating rates

Pyrolysis is classified as quick, flash, slow, or intermediate depending on the heating rate. The heating rate has an impact on the biochar's physicochemical qualities as well as its yield.

Higher heating rates and reaction temperatures yield more bio-oil and gas, whereas slower heating rates and lower temperatures yield more charcoal (Yaashikaa et al. 2020).

2.10.3 Biomass type

Lignin, cellulose, hemicellulose, and a small number of inorganic materials are the three main components of biomass. The content of biomass has a significant impact on the yield of pyrolysis products. Biochar can be made from biomass with a higher lignin content.

The yield of the product is determined by a variety of operational conditions, but in general, low temperatures and long residence times promote char production (Yaashikaa et al. 2020).

On pyrolysis, cellulose mostly creates tar, which is a mixture of discrete ketones, aldehydes, organic liquids, and char, whereas lignin largely produces char and a tiny amount of water.

Biochar production is enhanced by both cellulose and lignin present in the biomass; however, biochar production is higher in biomass with more lignin than cellulose (Dantas et al. 2011). Biomass with a moisture content greater than 30% is not appropriate for pyrolysis. The use of dry biomass is recommended for a higher char production. Another parameter for biomass selection is the amount of lignin and cellulose in the biomass. The thermal decomposition of cellulose begins at a low temperature. It involves two sorts of reactions. At low temperatures, breakdown and charring take place gradually, whereas at high temperatures, fast volatilization takes place (Tripathi, Sahu, and Ganesan 2016).

The lignocellulosic material's chemical makeup has a significant impact on fiber characteristics. Because hemicelluloses soften in the wet state and lignin provides wet stiffness and resistance to strength development after refining, cellulose is the major component that produces strength. The rate of cellulose elimination is significantly influenced by the lack of physical protection provided by lignin and hemicelluloses.

2.10.3.1 Teff (*Eragrostis Teff*)

Teff straw is a plentiful and indigenous lignocellulose material in Ethiopia, and it is a residual waste obtained after the seeds of Teff were removed. Ethiopia is a significant producer of Teff in the globe, presently producing a considerable amount of Teff annually in various locations, and Teff accounted for roughly 24% of all grain-cultivated land in Ethiopia in 2017. Teff straw was freely available in all regions of Ethiopia once Teff seeds were removed, and Teff straw was considered a waste (Amibo, Beyan, and Damite 2021).

Table 2.5 Chemical composition teff straw and other materials

Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Extractives (%)	Reference
Wheat straw	43.2	28.5	21.12	5.3	Singh et al., 2011 kumar et al
Rice straw	32	24	18	NA	Goyal & Ray, 1989
Bagasse	42	28.45	20.3	1.73	Dutt, 1994
Teff straw	39.4	29.6	14	NA	Maria et al., 2011
Hardwood	38-48	NA	23-30	NA	Ward et al., 2008

Softwood	40-45	NA	26-34	NA	Ward et al., 2008

2.10.4 Particle size

Biomass particle size is an essential parameter that affects the pyrolysis product yield. The smaller particle size is heated uniformly and releases more volatile matter, which leads to higher bio-oil and gas yield. large particle size favors higher biochar yield (Biochar 2015).

2.10.5 Effect of carrier gas flow rate Carrier

During the pyrolysis of biomass, a large number of vapors are produced, and if these vapors are not purged, they can cause secondary reactions and alter the nature and composition of the pyrolysis products. Nitrogen, argon, and water vapors have all been employed as carrier gases, but nitrogen is the most widely used since it is inert, less expensive than the other inert gases, and more generally available.

There are numerous publications that discuss the impact of carrier gas flow rate on pyrolysis product distribution. When the nitrogen flow rate was increased from 1.2 to 4.5 L/min, Zhang et al. saw a minor decrease in biochar yield from 24.4 to 22.6 percent. Increasing the nitrogen flow rate from 50 to 400 mL/min lowered the biochar yield from 28.48 % to 27.21 %, according to Erts and Alma. Haidari and colleagues (Dulanja et al. 2019).

2.11 Physical properties of biochar

BC is a carbon dominant product which is obtained when biomass feedstocks are heated at elevated temperature in a closed reactor with little or no oxygen present. The quality characteristics of BCs will change along several dimensions according to final pyrolysis temperature as well as the heating rate and residence time, and the type of raw materials. For example, the yield, surface area, pore volume, ash, elemental composition, viscosity, calorific value, and water content of BCs vary with pyrolysis temperature.

2.11.1 Specific surface area

Biochar has a favorable link between its specific surface area and its MB adsorption capacity. More active sites for MB adsorption by physical adsorption are available with a higher surface area. BC feedstock, pyrolysis temperature, and the activation process all have an impact on surface area and porosity (Sajjadi, Chen, and Egiebor 2019). More active sites for MB adsorption

by physical adsorption will be available with a higher surface area (Dulanja et al. 2019). Biochar made from plant-based biomass such as corn stove, oak wood, and pine needles had much greater surface areas than biochar made from animal-based biomass. With increasing pyrolysis temperature and residence time, the surface area of the biochar increases, probably due to the release of volatile materials, which expands the pore volume (Dulanja et al. 2019).

2.11.2 Total pore volume and pore size

Adsorption is influenced by the pore volume and pore size. The creation of porous structures in biochar is caused by the release of volatile organic matter from the feedstock, and a larger overall pore volume provides more active sites for interaction between MB and the biochar (Qian et al. 2015).

A study that looked at the effect of pyrolysis temperature on pore volume found that when the temperature went from 400 to 500 °C, the micropore volume and overall pore volume of the biochar increased (Dulanja et al. 2019).

2.12 Modified (activation) biochar for adsorption Biochar

Biochar has been modified using a variety of techniques. Chemical and physical alteration are two of the most prevalent approaches (Wang and Wang 2019a).

Chemical modification, physical modification, impregnation with elements, and grafting are all methods for activating biochar. Biochar can be activated to increase surface attributes like surface area and pore characteristics (Sakhiya, Anand, and Kaushal 2020).

2.12.1 Acid modification

The major goal of acid modification is to remove contaminants like metals from the surface of biochar and introduce acid functional groups. Hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, oxalic acid, and citric acid are some of the most prevalent acids.

Acidic chemical reagents such as H_3PO4 and H_2SO_4 are often employed in chemical activation, although they have drawbacks such as high activation energy consumption, pollution, and non-recyclability. $ZnCl_2$ and KOH activators, on the other hand, have the benefit of a low activation temperature and a high biochar production (C. Liu et al. 2020).

2.12.2 Alkaline modification

Alkaline modification's main goal is to increase surface area and oxygen-containing functional groups. Potassium hydroxide and sodium hydroxide are two popular alkaline agents.

Chemical activation improved pore size and adsorption capacity by using zinc ($ZnCl_2$) and potassium hydroxide (KOH) as activating agents, which are both dehydrating agents capable of promoting carbonaceous material decomposition, inhibiting structure contraction, and serving as a template for developing micro porosity (Benedetti et al. 2019).

The activation of biochar with KOH or NaOH dissolves ash and other components such as lignin and cellulose, increasing the biochar's carbon content and surface basicity. The BET surface area of KOH-activated biochar was found to be larger, as well as the volume of ultra-micropores and super-micropores. Chemical activation involves impregnating a raw material with an activating reagent such as $ZnCl_2$, H_3PO_4, KOH, or other reagent and heating the impregnated material in an inert atmosphere (Dulanja et al. 2019).Chemical activation is chosen over physical activation because of its greater yield, simplicity, lower temperature and shorter activation time, and superior porous structure development (Ahmed and Dhedan 2012).

2.12.3 Oxidizing-agents modification

Activation using oxidizing agents can increase the content of oxygen-containing functional groups on the biochar. Hydrogen peroxide modification can increase the oxygen- containing functional groups, especially carboxyl groups (Wang and Wang 2019b).

2.12.4 Metal salts or metal oxides modification

Adsorption, catalysis, and magnetic properties can all be altered by utilizing metal salts or metal oxides Metal salts or metal oxides modified biochar was developed for three reasons.

a) To enhance the adsorption of targeted pollutants.

b) To recycle biochar. Due to the small size of biochar, it is difficult to recycle biochar from the water when applying biochar for the removal of pollutants in water and waste- water.

c) To enhance the catalytic characteristic of biochar

2.13 Physical and chemical characterization of biochar

Biochar characterization is performed to determine the ability to remove pollutants or other applications.

2.13.1 Physical characterization of biochar

The ASTM (American Society for Testing and Materials) standard were utilized to establish the proximate analysis for moisture content, ash content, volatile matter were examined to estimate the fixed carbon content in Teff straw biomass (Amibo, Beyan, and Damite 2021).

2.13.2 chemical characterization of biochar

Biochar can be characterized by different techniques which include X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), BET, Scanning Electron Microscope (SEM) analysis and UV visible spectroscopy (Adams 2015).

2.13.2.1 Braeuer-Emmett-Teller Analysis (BET)

Surface area of the adsorbent is an important factor which influences its efficiency. Surface areas of activated carbons are usually measured using the Braeuer-Emmett-Teller (BET) methods. The study of surface area is important because this property of biochar is mainly responsible for pollutant removal from soil and aqueous environment (Yaashikaa et al. 2020).

2.13.2.2 Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy is a vibrational technique for investigating the functional groups present on the surface of biochar (Adams 2015)(Amibo, Beyan, and Damite 2021).

2.13.2.3 X-ray diffraction (XRD)

X-ray diffraction is a broadly relevant strategy to determine the crystallinity and structure of biochar. In XRD (Amibo, Beyan, and Damite 2021)(Yaashikaa et al. 2020).

2.13.2.4 Scanning electron microscopy (SEM)

The surface structures of biochar identified by SEM. SEM pictures of biochar demonstrated that various procedures and temperatures caused generous changes in the surface morphology of the first particles (Yaashikaa et al. 2020)(Adams 2015).

2.14 Environmental application of biochar

Biochar is a carbonaceous substance that is inexpensive. It has a lot of feedstocks, a lot of surface area, microporosity, and ion exchange capacity, and it has a lot of environmental applications. Biochar is a cost-effective carbonaceous material. It has abundance in feedstock, high surface area, micro-porosity and ion exchange capacity and it has extensive application prospect in the environment.

2.14.1 Soil amendment

Biochar is advised as a soil addition to improve fertility and hold water for longer periods of time, lowering the frequency of irrigation in the field. Biochar has been used to improve soil qualities due to its organic origin, increased surface area, and usefulness (Sakhiya, Anand, and Kaushal 2020).

2.14.2 Adsorbent for soil and water pollutants

By eliminating pollutants from soil and water, biochar can aid in the mitigation of environmental difficulties. Biochar has been shown to be a good sorbent for a variety of pollutants in soils.

Biochar is being used to remove organic contaminants from soil and water in a variety of applications (Yaashikaa et al. 2020).

2.14.3 Biochar as gas adsorbents

The capture and storage of CO_2 is one of the promising strategies to reduce CO_2 emissions (Wang and Wang 2019b).

2.14.4 Biochar as a raw material for making activated carbon

The two primary phases in the production of activated carbon from char are (a) carbonization of the raw material (such as farm residue) in an inert or low-oxygen environment to form char, and (b) chemical or physical activation of the char (Qian et al. 2015).

2.14.5 Biochar as a catalyst

solid biochar catalyst used in the transesterification and esterification process of waste cooking oil for biodiesel production.

2.14.6 Biochar as fuel alternatives

The better way is to pyrolyze the biomass at elevated temperatures to obtain energy-rich and value-added products. Many researchers produced biochar from different agriculture residues for fuel applications (Dantas et al. 2011).

Table 2.6 Advantages and limitations of different applications of biochar (Yaashikaa et al. 2020)

Applications	Aim	Benefit	Limitations
Catalyst	Act as supporting materials for direct catalysis	Low cost, more functional groups, large surface area Low	Limitations Efficiency may be less References
Adsorbents	Removal of organic and inorganic pollutants in soil and aqueous system	Low cost and more oxygen groups present in biochar enhances adsorption of pollutants	Contamination of heavy metals and poly aromatic hydrocarbons may persist
Soil amendment	Enhancing soil fertility and quality and carbon sequestration	Low cost, minimize emission of greenhouse gases, helps to retain nutrients and water, controls nutrient loss	Removal efficiency of pollutants is undetermined and heavy metals retains in soil

2.15 Biochar adsorption mechanism

Because of its operational simplicity and capacity to treat a wide range of contaminants, the adsorption approach has been a promising method for treating dye wastewater (Shu et al. 2019). Electrostatic interaction, ion exchange, pore filling, and precipitation can all be used to explain how biochar removes organic and inorganic contaminants. This is dependent on the biochar's physiochemical properties, such as dosage, pyrolysis temperature, and medium/ effluent pH.

Through the surface action of the adsorbent, the adsorption method of bleaching absorbs and eliminates the colors and contaminants in the oil. The electrostatic interaction, ion exchange, pore filling, and precipitation mechanisms used by biochar to remove organic and inorganic contaminants work by combining physical and chemical adsorption (Shu et al. 2019).

Through the surface action of the adsorbent, the adsorption method of bleaching absorbs and eliminates the colors and contaminants in the oil. The electrostatic interaction, ion exchange, pore filling, and precipitation mechanisms used by biochar to remove organic and inorganic contaminants work by combining physical and chemical adsorption (Ambaye, Vaccari, van Hullebusch, et al. 2021).

2.15.1 Physical adsorption

Physical adsorption, which occurs frequently during low-temperature bleaching processes and relies on intermolecular forces between the adsorbent and pigment surface groups to form single- and multilayer selective mixed adsorption with low activation energy, is used to form single- and multilayer selective mixed adsorption.

2.15.2 Chemical adsorption

This is common in high-temperature procedures.the asymmetry of the gravitational force on the surface of the adsorbent is caused by the unevenness of the atoms on the surface of the adsorbent, and thus the surface molecules have a certain free energy, leading the free energy to decrease. Selective and monolayer adsorption is used to produce shared electrons or transfer electrons between adsorbates. (C. Liu et al. 2020)

Nonetheless, due of its simple design, ease of operation, and relatively simple regeneration, the adsorption approach remains the most preferred method for dye removal. Because of their huge surface area, microporous nature, and high adsorption capacity, activated carbons are the most extensively utilized adsorbents for dye removal from wastewaters. (Ahmed and Dhedan 2012)

Because of its enormous surface area and great surface reactivity, activated carbon (AC) adsorption is one of the most successful dye removal procedures. AC manufacturing has a high related cost, which limits its widespread use. a result, research has concentrated on using a low-cost, renewable source as well as easily available agricultural and forest by-products as alternative AC precursors (Marrakchi, Hameed, and Bouaziz 2020).

Biochar, unlike activated carbon, can be made from a variety of materials, including industrial waste, agricultural by-products, livestock manure, sludge, and other trash. Wide pores, a large surface area, and a variety of surface functional groups are all advantages of biochar. In the adsorption process, rich surface functional groups are far more significant than high porosity. carbon-based adsorbents are rated according to the advantages of relatively low cost, easy regeneration and generally stable cyclic performance. Biochar (BC) has potential for the physical adsorption because of its highly developed micro-porosity and large surface area (Nguyen and Lee 2016).

The physicochemical properties of biochar, such as surface area, pore size, pore volume, basicity of biochar surface, presence of surface functional groups, presence of alkali and alkali earth metals, hydrophobicity, polarity, and aromaticity, all influence its adsorption capacity, which is the amount of adsorbent adsorbed per unit weight of biochar. The type of feedstock used and the thermochemical conditions of biochar production are closely related to the physical and chemical properties of biochar (C. Liu et al. 2020).

2.16 Mechanisms of biochar adsorption

The steps involved in the adsorption process include:

(a) physical adsorption in which the adsorbate settles on the adsorbent's surface;

(b) precipitation and complexation in which the adsorbate deposits on the adsorbent's surface; and (c) pore filling in which the adsorbate is condensed into the pore of the adsorbent.

The process is divided into three stages, each of which qualifies one of three zones: the first is the clean zone, in which no adsorption occurs. The mass transfer zone is the second step, where the adsorption is taking place. The tired zone is the final step, where equilibrium is attained (Ambaye, Vaccari, van Hullebusch, et al. 2021).

2.16.1 Mechanism of the adsorption of toxic metals

Surface sorption, ion exchange, electrostatic interaction, precipitation, and complexation are some of the mechanisms involved in harmful metal elimination.

2.16.1.1 Surface sorption

It is a physical process in which chemical bonds are formed by the diffusion of metal ions via the pores of the sorbent. The carbonization temperature affects the volume of pores and the surface area of the sorbent (biochar).

2.16.1.2 Electrostatic interaction of metals on biochar

This mechanism involves the electrostatic interaction between the charged biochar and metals ions to limit the mobilization of potentially toxic metals.

2.16.1.3 Cation/ion exchange capacity

The primary basis of this action is the exchange of protons and ionized cations with dissolved salts on the biochar's surface. The adsorption capacity of biochar to remove heavy metals is determined by the polluted size and surface functional group (Rizwan et al. 2016). According to Ali et al. (2017), the higher the biochar's cation exchange capacity, the greater the metal adsorption.

2.16.1.4 Precipitation

It entails the production of mineral precipitates in the solution or on the surface of the sorbing material, particularly in the case of biochar, which is made from cellulose and hemicelluloses degraded at temperatures greater than 300°C and has an alkaline property.

2.16.1.5 Complexation

Which includes the arrangement of multi-atom formation through the interaction of specific metal ligands to form complex (Ambaye, Vaccari, Hullebusch, et al. 2021).

2.16.2 The mechanism involved in the adsorption of organic pollutants

The different mechanism involved in the organic pollutants' adsorption is pore filling, hydrophobic interaction, partitioning, electrostatic interaction and electron donor–acceptor (EDA) interaction.

2.16.2.1 Partitioning

The adsorbate material diffuses into the pores of the non-carbonized component of the biochar during this phase. This part can easily interact with the organic adsorbate, causing it to bind to it. This part can easily interact with the organic adsorbate, causing it to bind to it. However, the properties of non-carbonized biochar (crystalline or amorphous carbon) as well as the carbonized

crystalline and graphene fractions of the biochar affect the adsorption of organic pollutant chemicals. When the biochar has a high volatile matter content and a high concentration of organic pollutants, the partitioning process is more evident and efficient (Ambaye, Vaccari, van Hullebusch, et al. 2021).

2.16.2.2 Pore filling

The pore filing mechanism is determined by the organic contaminant's polarity, as well as the composition of the biochar. The biochar must have a minimal quantity of volatile matter and occur at low concentrations of organic pollutants to have a high efficiency of this pore filling process (Ambaye, Vaccari, van Hullebusch, et al. 2021).

2.16.2.3 Electrostatic interaction

Electrostatic interaction is the most essential mechanism, which involves the adsorption of ionizable organic molecules to the biochar's positively charged surface via electrostatic interaction.

The pH and ionic strength of the aqueous solution determine its ability to attract or repel contaminants.

2.16.2.4 Electron donor and acceptor interaction

The adsorption of aromatic chemicals on biochar with a graphene-like structure uses the electron donor and acceptor interaction process.

2.16.2.5 Hydrophobic interaction

This mechanism can be used for the adsorption of hydro- phobic and neutral organic compounds through partitioning and hydrophobic interaction processes (Ambaye, Vaccari, Hullebusch, et al. 2021).

2.17 Factors affecting adsorption of contaminate onto the biochar

PH, adsorbent dosage, temperature, initial dye concentration and contact time will affect adsorption capacity.

2.17.1 Effect of the pH of the medium

The sorption of pollutants onto biochar is influenced by the pH of the aqueous solution.

This has to do with the pH-dependent oxygen-containing functional groups. As a result, the surface charge and ionization of biochar are pH-dependent, resulting in varied adsorption capacities for removing pollutants (Creamer, Gao, and Zhang 2014).

2.17.2 Adsorbent dosage

The amount of biochar used has an impact on the adsorption capacity. When the biochar concentration was increased from 0.5 to 5 g/L, the adsorption effectiveness of hazardous metals improved. The rise in the amount of biochar was related to an increase in the number of active sites and surface area (Ambaye, Vaccari, van Hullebusch, et al. 2021)(Matseh et al. 2018).

2.17.3 Temperature

The percentage of MB dye removed increases as the temperature rises. This could be due to the dye molecules in the solution diffusing faster as the temperature rises. Because the diffusion process from the bulk to the surface controls adsorption. Adsorptive interactions may be improved by strengthening the bonds between dye molecules and binding sites that are active at higher temperatures of the sorbent (Kaya, Yıldız, and Ceylan 2018).

2.17.4 Initial dye conc

For a successful adsorption process, the initial concentration of the adsorbate must be taken into account. The initial dye concentration acts as a powerful driving factor in overcoming dye mass transfer resistance between the aqueous and solid phases (Kaya, Yıldız, and Ceylan 2018).

2.17.5 Contact time

In the adsorption treatment process, the contact time for adsorbate exchange from solution to adsorbent is a critical element. Due to the abundance of unoccupied surface sites, species absorption was initially rapid, but when adsorption achieved equilibrium, the rate of uptake slowed (Srivastava 2016).

2.18 Adsorption Studies

To investigate the porous biochar's removal characteristics, methylene blue was employed as the adsorbate. The mass balance equation was used to quantify the methylene blue adsorption capacity of porous biochar per unit mass (Biochar 2015).

Batch Adsorption Studies: Using the batch adsorption method, the effects of MB starting concentration and adsorbent dosage on MB adsorption using untreated and treated biochar's were investigated. Equation 2.1 calculated the amount of MEB removed at equilibrium qe (mg/g), equation 2.2 calculated the percentage MEB (percent) adsorbed by ARHB, and equation 2.3 calculated the quantity of MEB adsorbed by biochar at time t qt(mg/g) (Isotherms and Analysis 2020).

$$q_e = (c_0 - c_i) \times \frac{v}{m} \tag{2.1}$$

$$\text{MB removal efficiency} = \frac{C_i - C_o}{C_i} \times 100 \tag{2.2}$$

$$q_t = (c_0 - c_i) \times \frac{v}{m} \tag{2.3}$$

2.19 Equilibrium Adsorption Isotherms

Adsorption isotherms are used to show the relationship between the adsorbed and dissolved concentrations at equilibrium, as well as to characterize a specific interaction between the adsorbent and the adsorbate in a given environment. Adsorption isotherms are crucial in defining the maximal capacity and the sort of adsorption front that is obtained. By determining the value of correlation coefficients, R^2, the relevance of Langmuir and Freundlich isotherms equations were compared (Hasana, Wahi, and Yusof 2021).

2.20 Kinetics of adsorption

Adsorption rate is described by adsorption kinetics which is an important characteristic for evaluating the adsorption process. In this study, pseudo-first-order and pseudo-second-order models were applied (Srivastava 2016).

Analyzing experimental data to investigate the mechanism of the adsorption process, which may include mass transfer or chemical reaction, is required to establish an acceptable kinetic model (Ding and Liu 2020).

At a specific initial adsorbate pressure and constant temperature, adsorption kinetics can provide useful information on the adsorption rate and mechanism of the process. The determination

coefficient (R^2) is used to assess whether the predicted values of models are confirmed by experimental data (determination coefficient value close to or equal to 1), with R^2 values closer to unity indicating the best match to the particular kinetic model (Cen et al. 2012).

Table 2.7 Equations of linear and nonlinear isotherm and kinetics models

	Non linear	linear	Reference
	Isotherm		
Langmuir	$q_e = \frac{q_m k_1 c_e}{1 + k_1 c_e}$	$\frac{c_e}{q_e} = \frac{1}{k_L q_m} + \frac{c_e}{q_m}$	(Nh, Wahi, and Yusof 2021)(Talbi et al. 2014)
Freundlich	$q_e = k_f c_e^{1/n}$	$\ln q_e = \ln k_F + \frac{1}{n_F} \ln c_e$	(Mallakpour and Tabesh 2019)(Talbi et al. 2014)
	kinetics		
Pseudo-first-order	$q_t = q_e\left(1 - \exp\left(-k_1 t\right)\right)$	$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t$	(Srivastava 2016)(Talbi et al. 2014)
Pseudo-second-order	$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	(Srivastava 2016)(Mallakpour and Tabesh 2019)

For isotherm

Where q_e is the adsorption capacity at equilibrium on the adsorbent, C_e is the equilibrium concentration (mg/l) q_m is the maximum amount of MB that will be adsorbed, K_1 is a constant k_f and 1/n are constant which indicates the capacity and intensity of the adsorption, respectively

For kinetics equations Where $q_t\ (\mathrm{mg.g^{-1}})$ and $q_e\ (\mathrm{mg.g^{-1}})$ are the MB adsorption concentrations at time t and at equilibrium, respectively. $k_1(\mathrm{g.mg^{-1}.s^{-1}})$ and $k_2\ (\mathrm{g.mg^{-1}.s^{-1}})$ is the first and second-order adsorption rate constants respectively**.**

Table 2. 8 Comparison of adsorption capacities of various adsorbents for removal of MB dye

Adsorbents	q_{max} (mg/g)	Refs.
EB bio-char	104.2	(Dawood, Sen, and Phan 2016)
Banana Peels	111,111	(Talbi et al. 2014)
Salix alba (white willow)	35.46	(Gemici, Ozel, and Ozel 2021)
Salix Babylonia (weeping willow)	42.74	(Gemici, Ozel, and Ozel 2021)
graphite/Fe_3O_4 composite	79.051	(Wu et al. 2021)
Wheat straw	62.5	(Ying et al. 2021)
Carbon nanotubes	35	(Fu et al. 2015)
Coconut husk based activated carbon	66	(Srivastava 2016)
Poly(cyclotriphosphazene-co-4,40-sulfonyldiphenol) nanotubes	69.16	(Srivastava 2016)
$ZnCo_2O_4$ microspheres Palm	79.1	(Srivastava 2016)
kernel fiber	237.4	
Citric acid modified mixed hardwoods powder	95.4	(Srivastava 2016)

PDA microsphere	90.7	(Srivastava 2016)
activated rice husk biochar	356.99	(Isotherms and Analysis 2020)
hazelnut shell biochar	3.785	(Kaya, Yildiz, and Ceylan 2018)
Water Hyacinth based biochar	44.13	(Mathew, Desmond, and Caxton 2016)

2.21 Regeneration of exhausted biochar

Desorption investigations have been carried out to elucidate the adsorption mechanism and adsorbent renewal (Dawood, Sen, and Phan 2016). Adsorption is reversed in the biochar regeneration process. Adsorbate desorption and adsorbate decomposition are the two principles of regeneration. As a result of the repeated sorption-desorption cycle, a competitive adsorbent should be reusable and recyclable for industrial applications, lowering the cost of charcoal sorbents significantly. (Dai et al. 2019) The progressive drop in dye adsorption effectiveness could be due to the loss of adsorbents in the trials or a decrease in active sites after each cycle (Marrakchi, Hameed, and Bouaziz 2020).

The adsorbate can be recovered during biochar regeneration using the breakdown and desorption concept. The adsorption process is made more cost-effective by the regeneration of the adsorbent. The use of water for regeneration, on the other hand, is ineffective. Chemical regeneration should be taken into account. NaOH and other chemicals are used. It can also be done by changing the pH of the adsorbent to desorb non-reactive compounds such as aniline and colors. Thermal regeneration is one of the most effective ways to regenerate biochar. In comparison to the original pores of the used biochar, it allows for the development of small pore diameters. (Srivastava 2016)

A simple and cost-effective regeneration process can drastically lower transportation costs as well as the amount of discarded contaminant-loaded adsorbent (M. B. Ahmed et al. 2016).

Biochar regeneration and cost reduction can be done by using different technologies to handle different types of biochar (Tesfaw and Tizazu 2021).

2.21.1 Thermal regeneration Thermal

One of the most successful strategies for achieving desorption is thermal regeneration. At high temperatures, adsorbate is carbonized and degraded, resulting in molecules that are smaller than the pore size of biochar and finally escape. Thermal treatment was found to be effective in removing dissolved organic carbon in a study.

2.21.2 Solvent regeneration

The equilibrium relationship between biochar, solvent, and adsorbate is used in solvent regeneration to break the adsorption equilibrium by changing the temperature and pH value of the solvent. Solvent regeneration is a good method to be considered (Sakhiya, Anand, and Kaushal 2020).

2.21.2.1 Regeneration of inorganic chemical

It is called acid-base regeneration and use inorganic acids (like hydrochloric acid and sulfuric acid) or alkali as sodium hydroxide and other chemicals to remove adsorbate (Mathew, Desmond, and Caxton 2016).

2.21.2.2 Organic solvent regeneration

The adsorbents adsorbed on activated carbon were extracted from organic solvents such as benzene, acetone and methanol (Dai et al. 2019). Biochar and composite, organic solvent such as ethanol and acetone is suitable to remove methylene blue from adsorbent (Lesbani et al. 2020).

2.21.3 Microwave irradiation regeneration Microwave

The microwave irradiation approach involves using microwave to induce dipole polarization in polar material molecules in biochar. At the same time, thermal energy can be converted from the electromagnetic field. The heated and volatilized organic substance trapped in the pore is released (Dai et al. 2019).

2.21.4 Reusability of Biochar

The adsorbent reusability technique was used to assess the performance of the adsorbent for methylene blue adsorption. Methylene blue is removed from the adsorbent using ethanol. The explanation for this is most likely due to the like and dissolve concept. The adsorbent was desorbed, rinsed multiple times with water, and dried at 100 °C so that it could be utilized in the next cycle (Lesbani et al. 2020).

2.22 Possible Removal Mechanism of Methylene Blue by Biochar

The main mechanisms for MB removal by adsorbent or biochar involve physical interaction, ion exchange, electrostatic interaction, $\pi - \pi$ stacking, hydrogen bonding and pore filling. The dominant mechanisms depend on the physicochemical properties of biochar and specific environmental conditions in the solution (L. Liu and Li 2019).

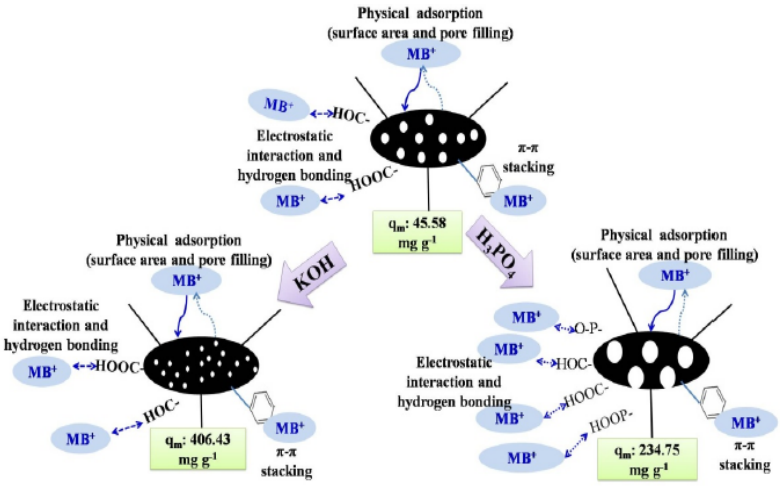

Figure 2.4 Schematic diagram of removal mechanism between CSBC, KOH-CSBC,H3PO4-CSBC and MB(Biochar 2015)

CHAPTER THREE

3. Materials and Methods

3.1 Materials

The equipment and tools used throughout the experiments to achieve the objective of the study were: ball mill, A laboratory test sieve (BS 410-1Endecotts Ltd., England), Whatman number-42 filter paper for gravity filtration purposes. Electronic Time clock (1049496, China), Digital balance (Mettler Toledo 1118330367, 2000, Switzerland), Erlenmeyer flasks and beakers, magnetic stirrer, Silica crucibles used to hold the weighed sample both in oven and muffle Furnace, Electrical oven (300oC max, Netaji Subhash Marg, Darya Ganj, New Delhi-2, India) and muffle furnace (Bibby Stuart R000100002, 2000W, U.K) pipet burette, desiccator, separating funnel, UV-visible spectrophotometer (Cary 50 Varian Australia PTY LTD, Australia), pH meter Jetway 3510 (Barloworld scientific Ltd. Dunmow, Essex, CM6 3LB, UK), heater and mechanical shaker. BET Horiba Instruments, Inc. SA-9600 Series Surface Area Analyzer, FTIR -Jasco 6600typeA SEM JCM-6000Plus.

(a)Muffle Furnace | (b)Mechanical shaker | (c) Oven

Figure 3.1 char production process materials muffle furnace and oven mechanical shaker and desiccator

3.2 Chemicals and reagents

Materials and chemicals used for the experiments were collected teff straw from local farm land of Bishoftu area, distilled water, potassium hydroxide KOH (98.08% pure) The adsorbate, methylene blue (MB) 0.5 w/v % and HCl (35.4 Purity), Sodium hydroxide, NaOH (98.08% pure)

and ethanol 90 % purity will be purchased from chemical suppliers. All chemicals used throughout this study were attaining the analytical reagent grade, maximum purity and commercially available.

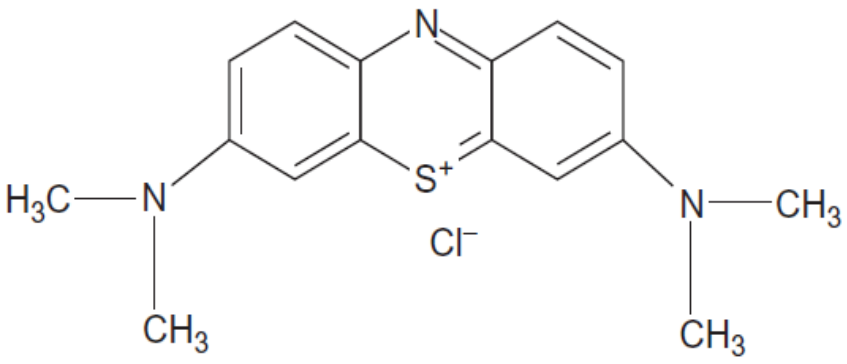

Figure 3.2 molecular structure of MB.

Table 3. 1 Properties and characteristics of MB

Dyestuff	Basic blue 9 (BB9)
Generic name	Methylene blue
Chemical formula	$C_{16}H_{18}ClN_3S_3H_2O$
Molecular weight (g/mol)	319.85
λ max (nm)	664

3.3 Methods

3.3.1 Method for activated biochar preparation

Biochar samples were made from Teff straw using a method proposed by C. Kalinke and colleagues, with the following calcination conditions: To remove any contaminants, the biomass samples were washed with deionized water and then dried with air for 12hr and then dry in oven for 6 hrs. at 105 ℃ . The dried sample was crushed and sieved to a fineness of less than 250 micrometers. Surface treatment of precursor biochar with chemical activation was used to

increase the amount of surface functional groups and improve the material's adsorptive capacity (Kalinke et al. 2017). At varying KOH/biomass weight ratios of 0, 1, 2, 3, and 4, the powdered sample and solid KOH were completely mixed. The mixes were then carbonized in a muffle furnace at various temperatures (300°C, 450 and 600°C) for 1, 2 and 3 hours. The solid powdered activated biochar was rinsed with 1M HCl to completely remove potassium residues, then washed with deionized water until the pH reached around 7. Finally, wet black solid powders containing activated biochar were dried for 6 hours at 95 degrees Celsius in an oven (S. Mangrich et al.2017).

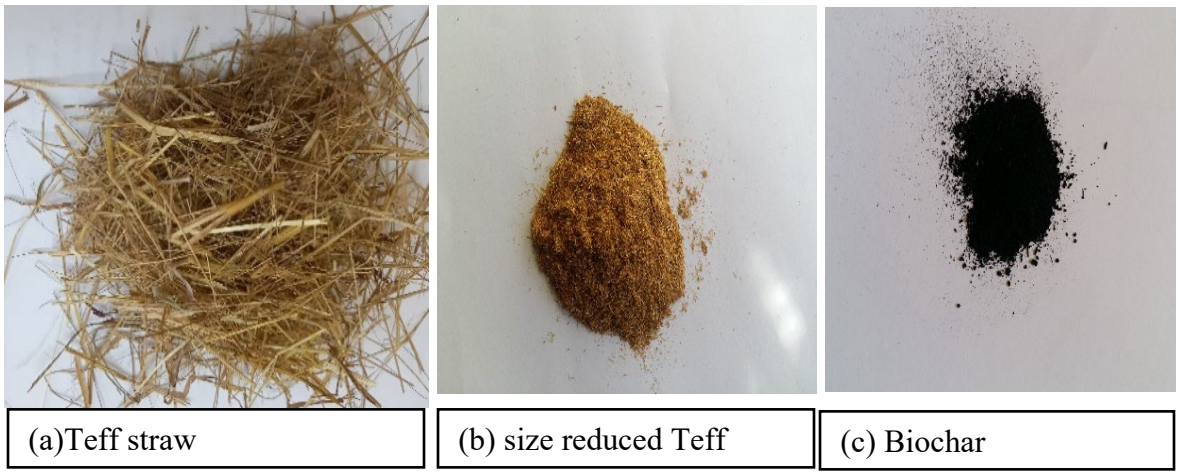

Figure 3.3 raw material preparation and biochar production

The yield of biochar can be calculated using

$$\text{Biochar yield} = \frac{\text{the amount of biochar collected for a certain batch}}{\text{total amount of biomass in that batch}} \times 100 \quad (3.1)$$

3.3.2 Characterization of Teff Straw Biochar

The following characteristic properties of teff straw biochar were studied.

3.3.2.1 Proximate Analysis

ASTM defines proximate analysis as the determination by prescribe methods of moisture, volatile matter, ash content, volatile matter content and bulky density. The proximate analysis Moisture Content, Ash Content, Volatile matter content and Fixed carbon content of the KOH activated teff straw biochar was done using the following procedure.

3.3.2.1.1 Determination of Moisture Content

The crucible was filled with 15 grams of finely powdered Teff straw, which was then covered with a lid and weighed using a weighing balance. The crucible was dried in a hot air oven at 105°C for 1 hour and 30 minutes with the lid removed. The crucible was removed, covered with the lid right away, cooled in a desiccator, and weighed. Equation was used to compute the moisture content (ASTM -E1755-01).

$$MC(\%)=\frac{(B - F)}{(B-G)}\times 100 \tag{3.2}$$

where B is the weight of crucible and original sample, F weight of crucible and dried sample, G weight of crucible and M percentage moisture.

3.3.2.1.2 Determination of Ash Content

Ash content, was done using standard by muffle furnace incineration gravimetric method. 10 g of the processed Teff straw was measured into a crucible. Finley, powdered Teff straw in the crucible was heated without lid in a muffle furnace at a temperature of 750°C for 30 minutes. Afterward, the crucible was taken out, then transferred to desiccator, and weighed. Accordingly, weight of crucible + weight of Teff straw before heating was given as weight of crucible + weight of Teff straw after heating. Finally, weight of ash (weight of sample + weight of crucible) − weight of crucible (ASTM E871-82).

$$\text{Ash content } (\%) = \frac{w_1 - w_2}{w_1}\times 100$$

(3.3)

where W_1 is the initial weight of sample before burning and W_2 is the final weight of sample after burning.

3.3.2.1.3 Volatile Matter content

Total volatile matter is the weight loss obtained on heating. Known mass of Teff straw in the crucible was covered with a lid, placed in muffle furnace maintained at 900 ℃ for 10 minutes to avoid toxic matters. After 10 minutes, the crucible was cooled in air; then it was kept into

desiccator and weighed. therefore, weight of Teff straw before heating could be total weight − weight of crucible; at the same time, weight of Teff straw after heating was (weight of sample + weight of crucible) weight of crucible. Finally, total weight loss of moisture Teff straw was weight loss due to volatile matter + moisture. Weight loss due to volatile matter equals total weight loss of moisture ASTM (E-872).

$$\mathrm{VM}(\%) = \frac{\text{weight loss due to volatile matter}}{\text{weight of Teff straw}} \times 100$$

(3.4)

Where VM is volatile matter

3.3.2.1.4 Fixed Carbon

The FC of Teff straw can be determined as in the following equation:

$$FC(\%) = 100 - (VM + Ash + MC)\%$$

(3.5)

where VM is the volatile matter and MC is the moisture content.

3.3.2.1.5 Bulk density

Bulk density is defined as the weight of a material per unit volume. It is mostly used for material powders. This bulk density test indicates the flow uniformity and solid sample package quantity. unit of measurement is kilograms per cubic meter (kg/m^3). To begin, determine the mass of the measuring cylinder utilized in this experiment. The activated biochar sample was then inserted into this cylinder and reweighed. It was then moved to an aluminum plate and oven dried for 60 minutes at 105 °C. The weight of the dry sample was measured after it had dried. Equation 3.6 was used to calculate the bulky density (Dantas et al. 2011).

$$\text{Bulky density}, \rho_b = \frac{W_2 - W_1}{V} \tag{3.6}$$

Where W_1 is the mass of measuring cylinder in grams, W_2 is mass of measuring cylinder and its contents and volume of the measuring cylinder in liters.

3.3.2.2 The Brunauer–Emmett–Teller (BET)

The surface area and average pore size will be calculated by using the Brunauer–Emmett–Teller (BET)(Workie et al. 2019) BET Horiba Instruments, Inc. SA-9600 Series Surface Area Analyzer instrument was used to determine the specific surface area of Teff straw biochar. (BET) technique was used to calculate the volume of adsorbed nitrogen gas based on the adsorption and desorption of various gas concentrations at atmospheric pressure and ambient temperature. The two samples were first treated for 1 hour at 230°C to eliminate air and water molecules from the pore. Finally, the samples were tested (Amibo, Beyan, and Damite 2021).

3.3.2.3 SEM

The surface morphology of biochar adsorbents will be analyzed by the Scanning Electron Microscope SEM JCM-6000 Plus instrument at 1000 and 1500 μm magnification.(Workie et al. 2019) Morphology of adsorbents is typically analyzed using the Scanning Electron Microscopy which uses a beam of electrons to scan the surface of a specimen and makes possible the direct observation of its surface features at the micro and submicron levels. Scanning Electron Microscopy (SEM) gives morphological examination with direct visualization (Marrakchi, Hameed, and Bouaziz 2020).

3.3.2.4 Fourier Transform Infrared Spectroscopy (FTIR)

FT-IR -Jasco 6600 type A spectroscopy is used as vibrational technique for investigating the functional groups present on the surface of biochar (Yaashikaa et al. 2020). Fourier Transform Infrared Spectroscopy (FTIR) used to identify the chemical composition of char by recording the infrared spectrum of respective samples. By analyzing the spectra with relative intensities, which indicate different functional groups, the compositions of the sample can be identified (Workie et al. 2019).

3.3.1.5 UV–vis spectroscopic analysis

For all types of characterization activated raw teff straw biochar and activated teff straw biochar that produced with different temperature, biomass/activator ratio samples will be analyzed. UV–vis spectroscopic measurements were carried out using UV-visible spectrophotometer (Cary 50 Varian Australia PTY LTD, Australia) to determine the concentrations of MB left in supernatant solutions referring to the standard curve of MB at the maximum wavelength (664 nm) of MB dye (Fu et al. 2015).

3.4 Methylene blue Adsorption and Response Surface Methodology Analysis.

3.4.1 Batch Adsorption Experiments

To determine the applicability of produced activated biochar as an adsorbent for water treatment, the batch adsorption experiments will be performed using MB dye as the adsorbate. The dye stock solution (300 mg/l) will be prepared by dissolving accurately weighed quantity of the dye in distilled water and all working solutions for the dye sorption experiments were obtained by diluting the stock solution with distilled water to the desired concentration which is 300mg/l.

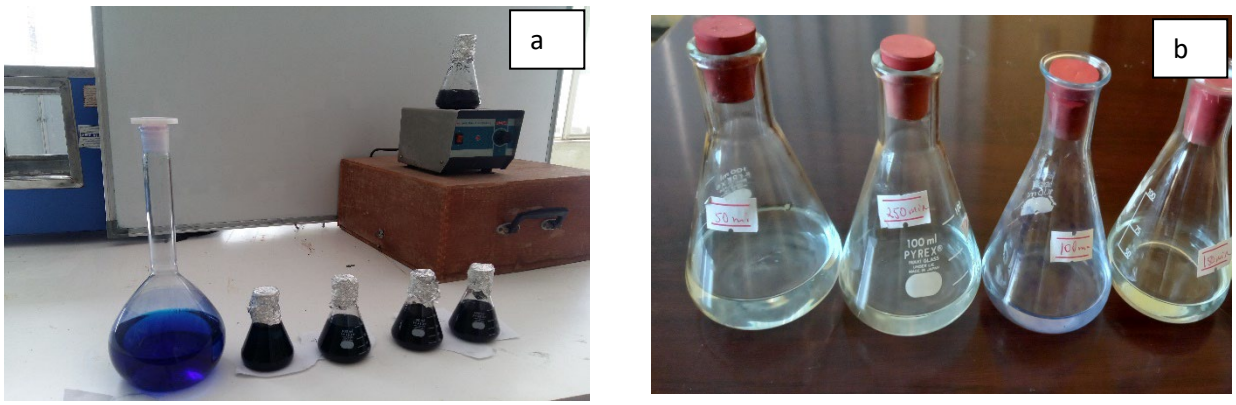

Figure 3. 4 (a) prepared MB solution with ATSB before adsorption and (b) ATSB) after adsorption.

Batch equilibrium adsorption studies performed using 100 mL of dye solutions.

Parameters affecting the adsorption process such as pH (2-10), adsorbent dosage (0.1-0.4 g/100ml), initial dye concentration (50-300 mg/l), contact time (0- 300 min) and temperature (25-40°C) will be studied in a batch system. pH of the solutions was adjusted by 0.1M HCl and 0.1M NaOH solutions.

For the optimization study 100 ml of 300mg/l of MB solution and 0.5 g of biochar selected according to KOH/Biomass ratio, calcination time and temperature.

In each adsorption experiment, the samples mixtures were agitated in a mechanical shaker and were collected at predetermined time of 8 hr. and adsorbent separated from the samples by filtering. The filtrate will be analyzed by a UV-visible spectrophotometer at λ max (664 nm) to determine the residual dye concentration. Based on the acquired values, the amount of dye

adsorbed per unit mass of the adsorbent (qe) was calculated according to the following Equation (1) and the adsorption yield was calculated by using the Equation (2).

$$q_e = (c_0 - c_i) \times \frac{v}{m} \tag{3.7}$$

$$\text{MB removal efficiency} = \frac{C_i - C_o}{C_i} \times 100 \tag{3.8}$$

where q_e is the amount of adsorbed dye per gram of adsorbent (mg/g), Co and C are the initial and final dye concentration in solution phase, respectively (mg/l), V is the volume of dye solution (l) and m is the weight of adsorbent (g).

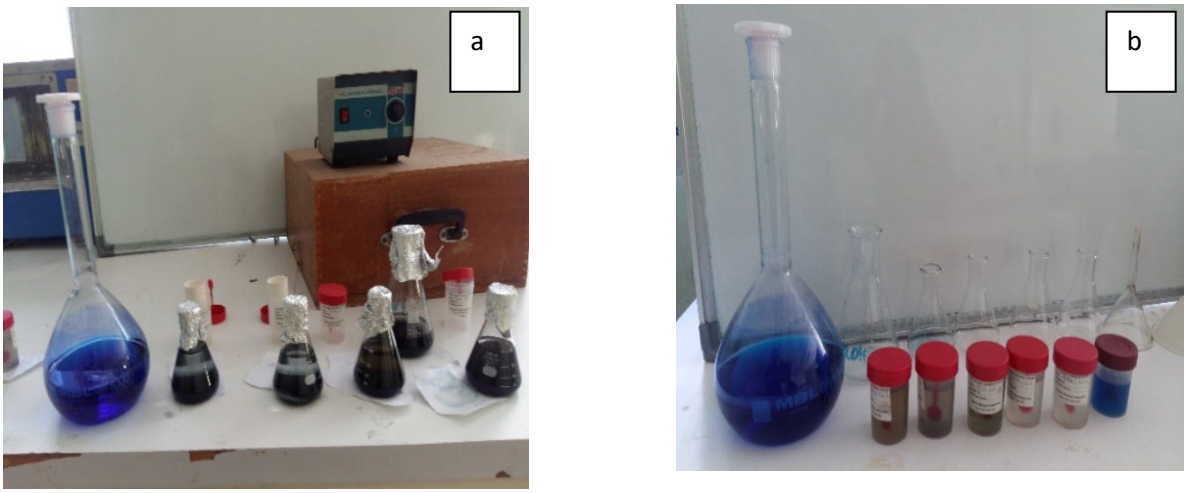

Figure 3. 5 (a) sample after adsorption complete and (b) samples after centrifuge and filtered

3.4.1.1 Effect of initial dye concentration on MB adsorption

Set of 100 ml volumetric flasks containing various initial concentrations of 50 mg/l; 100mg/l; 200 mg/l; 250 mg/l and 300 mg/l prepared and 0.5 g of KOH activated teff straw biochar was added to each bottle and agitated, kept at room temperature, 25 ºC, on mechanical shaker set at 150 rpm for 8 hours. The concentration of methylene blue in the filtrate solution after adsorption were determined using a UV-Vis spectrophotometer at maximum wavelength of 664 nm. The contents of the reagent bottles were filtered through Whatman No 42-filter paper after

centrifugation. The filtrates were placed in cuvettes and their absorbance and concentrates were measured in a UV-Vis spectrophotometer.

3.4.1.2 Effect of contact time on MB adsorption

Effect of contact time was investigated with optimum conditions of pH, concentration and bio-sorbent. 300 mg/l of 100 ml methylene blue solution was set at fixed pH of 7 and then mixed with 0.5 g of KOH activated teff straw biochar adsorbent. The mixture was agitated using shaker at 150 rpm for 50,100,150,200 and 250 minutes. The contents of bottles were centrifuge for 30 minute and filtered through Whatman No 1 filter paper. The filtrates were placed in cuvettes and their absorbance and concentrates were measured in a UV-Vis spectrophotometer at the maximum wavelength of 664 nm.

3.4.1.3 Effect of adsorbent dosage

Various amounts of adsorbent were used to investigate the effect of adsorbent dosage on dye adsorption. 100 ml solutions of methylene blue dye at initial concentration of 300 mg/l were mixed with 0.1 g, 0.2 g, 0.3 g and 0.4 g of activated teff biochar at optimum pH of 7. Mixtures were agitated at 150 rpm at room temperature and the dye uptake was determined using a UV-Vis spectrophotometer at the maximum wavelength of dye 664 nm.

3.4.1.4 Effect of pH

The effect of pH on adsorption of methylene blue was investigated. 100 ml of 300 mg/l of methylene blue was filled into 100 ml reagent bottles. Solutions of dyes in 100 ml reagent bottles were set at pH 2,4,6,8 and 10. The pH was maintained by adding required amounts 0, 1 M NaOH solutions and 0, 1 M HCl acid which were added using micro-pipettes. A Checker pH meter was used to measure the pH of the mixtures. 0.5 g of biochar was placed into each of the reagent bottles. Solutions were agitated with a mechanical shaker set at 150 rpm at room temperature. The contents of the reagent bottles were filtered through Whatman No 42-filter paper after centrifugations. The filtrates were placed in cuvettes and their absorbance and concentrations were measured in a UV-Vis spectrophotometer at the maximum wavelength of 664 nm.

3.4.1.5 Effect of Temperature on MB adsorption capacity of ATSB

The effect of different dye solution temperatures of 25, 30, 35 and 40 °C on the adsorption kinetic was studied to determine the optimum solution temperature and the thermodynamic behavior of MB dye adsorption on KOH activated teff biochar

3.5 Experimental Design and data analysis

Design of experiment software is a tool for management and optimization of a set of experiments will be used through a face centered central composite design (CCD) using Design Expert 12.0 software to obtain an optimal condition for activated biochar preparation by the pyrolysis process. Experimental design involved three independent variables, including the pyrolysis temperatures (X_1) of 300℃–600℃, KOH/Biomass ratio (X_2) 0:1-4:1 and time(X_3) 1-3hr, was studied. two extreme points (highest and lowest) used for each factor. The dependent variable which is adsorption capacity of the activated teff straw biochar was taken as the response. A total of 19 different combinations were chosen in random order according to CCD configuration for the three factors with five center point.

Table 3.2 Independent variable and their levels of experiment

Factor	Name	Units	Minimum	Maximum	-alpha	+alpha
A	Temperature	℃	300	600	-1	1
B	KOH/Biomass	Ratio	0	4	-1	1
C	Time	hr.	1	3	-1	1

Table 3.3 Central composite design layout for MB Adsorption using teff straw biochar

Std	Run	Factor 1 A: Temperature ℃	Factor 2 B: KOH/Biomass ratio	**Factor 3 C: Time hr.**	**Response Adsorption Capacity(mg/g)**
17	1	450	2	2	
4	2	600	4	1	
19	3	450	2	2	
13	4	450	2	1	
16	5	450	2	2	
15	6	450	2	2	
6	7	600	0	3	
11	8	450	0	2	
5	9	300	0	3	
10	10	600	2	2	
18	11	450	2	2	
12	12	450	4	2	
8	13	600	4	3	
2	14	600	0	1	
14	15	450	2	3	
7	16	300	4	3	
1	17	300	0	1	
9	18	300	2	2	
3	19	300	4	1	

3.6 Determination of Adsorption Capacity of ATSB

The removal of methylene blue (MB) from aqueous solution was investigated using ATSB with the highest surface area (259.21 m^2/g) carbonized at 450 °C. In adsorption, comparable consequences of various parameters influencing the dye removal process from aqueous solution

is an important. Therefore, batch experiments were carried out to determine the effect of pH, initial dye concentration, contact time, adsorbent dosage and temperature in this study.

3.7 Adsorption Isotherm

Isotherm analysis is one of the important adsorption models in determining the relationship between adsorbent and adsorbate, interpreting the adsorption mechanism and obtaining the adsorption capacity of the adsorbent (Qian et al. 2015).

To determine the suitable isotherm model, the experimental data obtained at different initial MB concentration for MB removal from aqueous solutions were examined using Langmuir and Freundlich isotherms. Each of the two models makes use of a parameter q_e (i.e., adsorption capacity per unit mass of the adsorbent at equilibrium) in mg/g.

The Langmuir model is based on the assumption that adsorption is localized on a monolayer and all adsorption sites at the adsorbent are homogeneous. Whereas the Freundlich isotherm presumes that the multilayer of the adsorption process occurs on a heterogeneous surface (Fu et al. 2015).

Langmuir model is based on the assumption that adsorption occurs on a surface with homogeneous

sites, where each molecule of the adsorbate occupies an adsorption site, and maximum adsorption occurs with the formation of the complete monolayer, in which there is migration of the adsorbate molecules on the surface of the adsorbent (Guar, Moreno-pirajan, and Giraldo 2018).

The adsorption isotherm is an equation that describes the relationship between the amount of solute adsorbed onto the solid and the equilibrium concentration of the solute in solution at a given temperature. In order to optimize the design of a sorption system on biochar, the appropriate isotherm model for equilibrium curves must be established. Langmuir and Freundlich are two equilibrium models that will be looked at here. After sample screening, the adsorption equilibrium, adsorbent surface characteristics, and adsorbate distribution on the adsorbent will be determined using the desorption isotherm on the biochar with the highest adsorption capability (Cen et al. 2012).

The Langmuir isotherm model states that the active sites of the adsorbent have equal adsorption energy, that one adsorption site is filled by one adsorbate molecule, that there is no interaction between adsorbed molecules, and that the adsorption is complete when the monolayer is created.

The Freundlich model, on the other hand, states that the energy of the adsorption sites is not equal, resulting in the formation of a multilayer (S. Mallakpour and F. Tabesh 2019).

Freundlich model is described by an empirical equation used for systems with a high degree of heterogeneity. In this model, it is assumed that adsorption occurs at different sites and the formation of multilayers occurs with different adsorption energies. This leads to an exponential decrease in energy as the coverage of the surface originates (Guar, Moreno-pirajan, and Giraldo 2018).

Langmuir model $$q_e = \frac{q_m k_1 c_e}{1 + k_1 c_e}$$

(3.9)

Where q_e is the adsorption capacity at equilibrium on the adsorbent, C_e is the equilibrium concentration (mg/l) q_m is the maximum amount of MB that will be adsorbed, K_1 is a constant.

The linear form of Langmuir model $$\frac{c_e}{q_e} = \frac{1}{k_L q_m} + \frac{c_e}{q_m}$$

(3.10)

Freundlich model $$q_e = k_f c_e^{1/n}$$

(3.11)

The linear form of Freundlich model $$\ln q_e = \ln k_F + \frac{1}{n_F} \ln c_e$$

(3.12)

Where k_f and 1/n are constant which indicates the capacity and intensity of the adsorption, respectively

3.8 Adsorption equilibrium

The kinetics data of MB removal should be obtained to predict the ability of an adsorbent to adsorb a certain component. MB adsorption equilibrium will be determined by plotting (C_e/q_e) versus (C_e) (Sumatera, Energy, and Utara 2018).

3.9 Adsorption Kinetics

Analyzing experimental data to investigate the mechanism of the adsorption process, which may include mass transfer or chemical reaction, is required to establish an acceptable kinetic model (Amibo, Beyan, and Damite 2021).

At a specific initial adsorbate pressure and constant temperature, adsorption kinetics can provide useful information on the adsorption rate and mechanism of the process. The determination coefficient (R^2) is used to assess whether the predicted values of models are confirmed by experimental data (determination coefficient value close to or equal to 1), with R^2 values closer to unity indicating the best match to the particular kinetic model (Cen et al. 2012).

Two different kinetic models, including

1. Pseudo-first order and
2. Pseudo-second order,

Will be studied to assess the MB adsorption rate. The differential form of pseudo- first order can be written as below as described in (Creamer, Gao, and Zhang 2014) (Adams 2015).

Nonlinear $$q_t = q_e\left(1-\exp\left(-k_1 t\right)\right) \quad (3.13)$$

linear $$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \quad (3.14)$$

The pseudo-second order rate equation is shown as below

Nonlinear $$q_t = \frac{q_e^2 k_2 t}{1+q_e k_2 t}$$

(3.15)

linear $$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3.16)$$

Where $q_t\ (\mathrm{mg.g^{-1}})$ and $q_e\ (\mathrm{mg.g^{-1}})$ are the MB adsorption concentrations at time t and at equilibrium, respectively. $k_1(\mathrm{g.mg^{-1}}.s^{-1})$ and $k_2\ (\mathrm{g.mg^{-1}}.s^{-1})$ is the first and second-order adsorption rate constants respectively (Creamer, Gao, and Zhang 2014).

3.10 Thermodynamic model

To explain the nature of adsorption, it is important to determine the thermodynamic parameters, including Gibbs free energy of adsorption(ΔG°), enthalpy of adsorption (ΔH°), and entropy of adsorption (ΔS°), examined by a series of experiments when the ΔH is less than 25 kJ·mol^{-1}, the acting force is Van der Waals' force and can be attributed to physical adsorption.(Dawood, Sen, and Phan 2016)

$$k_d = \frac{q_e}{c_e} \times 1000 \tag{3.17}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{3.18}$$

$$\Delta G = -RT \ln K_d \tag{3.19}$$

where R (8.314 J/mol K) is the universal gas constant and T (K) is the absolute solution temperature. The values of ΔH° and ΔS° were determined from the slope and intercept of the Van's Hoff plot of ln Kd versus 1/T.

3.11 Regeneration and reusability

Desorption investigations have been carried out to elucidate the adsorption mechanism and adsorbent renewal. The adsorbent reusability technique was used to assess the performance of the adsorbent for methylene blue adsorption.(Li et al. 2018) A simple and cost-effective regeneration process can drastically minimize transportation costs as well as the amount of discarded contaminant-loaded adsorbent (M. B. Ahmed et al.2016)(Coker et al. 2023).

All the regeneration studies were performed in 100 ml Erlenmeyer flask. The MB loaded ATSB was separated from dye solution by centrifugation, washed using deionized water and dried. After dried the adsorbent was agitated with 90% ethanol and 0.1M NaOH with 9:1 ratio for 4 hrs. Then, the regenerated ATSB was again placed in the flask for adsorption, with the adsorption–regeneration process occurring in six cycles (Fu et al. 2015).

3.12 Possible Removal Mechanism of Methylene Blue by Biochar

The main mechanisms for MB removal by adsorbent or biochar involve physical interaction, ion exchange, electrostatic interaction, π–π stacking, hydrogen bonding and pore filling. The dominant mechanisms may depend on the physicochemical properties of biochar and specific environmental conditions in the solution (Biochar 2015)(Talbi et al. 2014).

CHAPTER FOUR

4. Result and discussion

4.1 Proximate analysis

Proximate Analysis of Raw Teff Straw (*Eragrostis Tef*) was analyzed to determine the fixed carbon contents of Teff straw by investigating the ash content, moisture content, and volatile matter content which were mandatory to determine the fixed carbon content in Teff straw. The proximate analysis of teff straw presented in Table 4.1 From the total bases, including ash content, moisture content, and volatile matter, the yield of biochar produced from Teff straw was 12 %, while from fixed carbon, the yield was around 88.8 percent. And this result was obtained at a temperature of 450°C for 2hr.

Table 4.1 Proximate analysis of teff straw samples

analysis	Experimental result	From (Amibo, Beyan, and Damite 2021)
Moisture content, CM (%)	6.8	6-8
Ash Content (%)	3.7	3-6
Volatile Matter Content, VM (%)	76	70-80
Fixed Carbon, FC (%)	13.5	12-17

Bulk density of raw teff straw was, $\rho = 0.43$ after activation with KOH the bulk density of ATSB found to be 0.99 g/ml provided that a perceptive regarding the floatability property of the adsorbent. It suggests that if the activated biochar is added to water, it will sink and that will result in better contact with the adsorbate and thereby leading to effective adsorption process.

4.2 FTIR Analysis

In the FTIR spectra of the ATSB, the broad absorption peak around 3431 cm^{-1} is attributed to the O–H stretching in the –COOH functional group. Which may be attributed to the presence of moisture, phenol or hydroxyl groups. After adsorption of MB, the peak around 3445cm^{-1} caused by O–H stretching vibration was broadened and the peak intensity was enhanced, indicating that

the hydroxyl groups on the ATSB surface and $–CH_2$ of MB formed hydrogen bonds, and MB were adsorbed to ATSB under the action of hydrogen bonding.

The peaks in the range of 800 to 1400 cm^{-1} suggest the presence of lignin and the pick in the rage of 1900 to 3400 cm^{-1} suggest the presence of cellulose. The absorption peak at 900-700 and 1600-1500 cm^{-1} found in the lignin spectra of all char and biomass, correspond to aromatic C-H stretch, and C=C in the aromatic ring, respectively. the peak at 2616 cm^{-1} and 2605 are due to the stretching vibrations of OH of carboxylic acids. A small peak of 2358 cm^{-1} suggests the presence of C≡C stretching band. The sharp peak at 1793 and 1643 cm^{-1} reflects the C=O bond stretching vibration while the broad strong absorption peak around 1103 cm-1 is an anti-symmetric stretching vibration of the C–O–C bond on the surface of the material. The C=O peak at 1103 cm^{-1}became weaker after adsorption of MB but almost unchanged, this may be attributed to the higher affinity of the C=O functions towards MB.

Peaks such as 780 cm^{-1} of ATSB disappeared after the adsorption of MB dye while other peaks at 1,631 and 1,055 cm^{-1} shifted to 1,643 and 1,103 cm^{-1}, respectively, which suggest the aggregation of MB molecules with their functional groups of ATSB and also suggests that carboxyl group took part in the adsorption processes.

These observations clearly showed that the MB molecules were adsorbed on the surface of the ATSB and that the active functional groups of the biomass that participated in the binding of the MB molecules were –OH, CO, C=O and –COO– representing, respectively, hydroxyl group, inorganic carbonates, and cyclic anhydride and carboxylic groups.

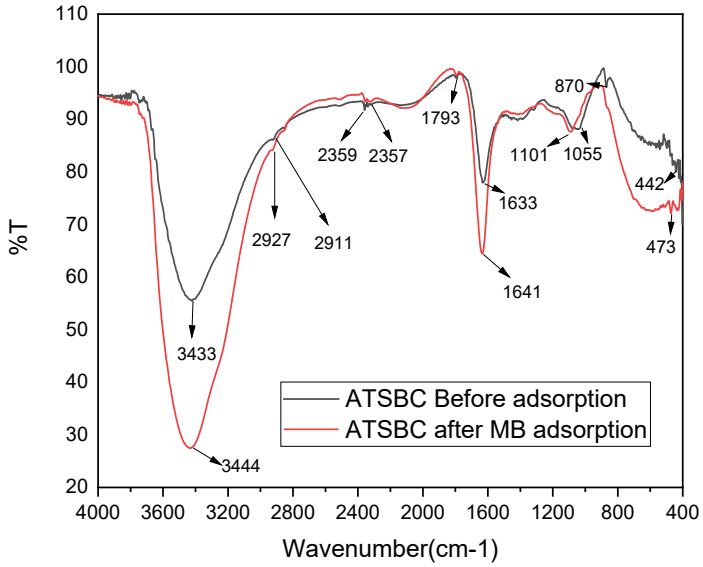

Figure 4.1 FTIR Analysis of ATSB before and after MB adsorption

4.3 The Braeuer–Emmett–Teller (BET)

The BET surface area experiments were done and reported in the following table The BET results (Table 4.2) indicated the specific surface areas for raw biochar at 450 °C and activated biochar calcinated 450°C were 4.628 m^2/g and 259.21 m^2/g, respectively. From the above results, it can be seen that the BET surface area of activated biochar was higher than of non-activated biochar. These results show that KOH activation can significantly increase the BET surface area.

Table 4.2 BET result of raw and activated teff biochar

Sample	BET surface area m^2/g
Raw Teff straw biochar at 450 ℃	4.628
Activated Teff straw biochar at 450℃	259.21

4.4 SEM Analysis

SEM analysis has been employed to observe the changes in surface texture and morphology of both untreated and chemically modified adsorbent. The SEM images of raw teff straw biochar

and chemically modified Teff straw biochar are given in Figure (4.2) and Figure 4.3. The untreated Teff straw and teff straw biochar shows a relatively smooth surface (Figure 4.2 a and b). After KOH modification, the presence of pores and cracks made the surface of Teff straw more uneven and irregular (Figure 4.3), which may be more helpful for adsorption. KOH modified biochar shows significant surface modification (Figure 4.3) that develop honeycomb, rough surfaces, non-uniform pores and cavities. These were happened due to the remove of lignin and hemicellulose structure during reaction between KOH and ester bonds.

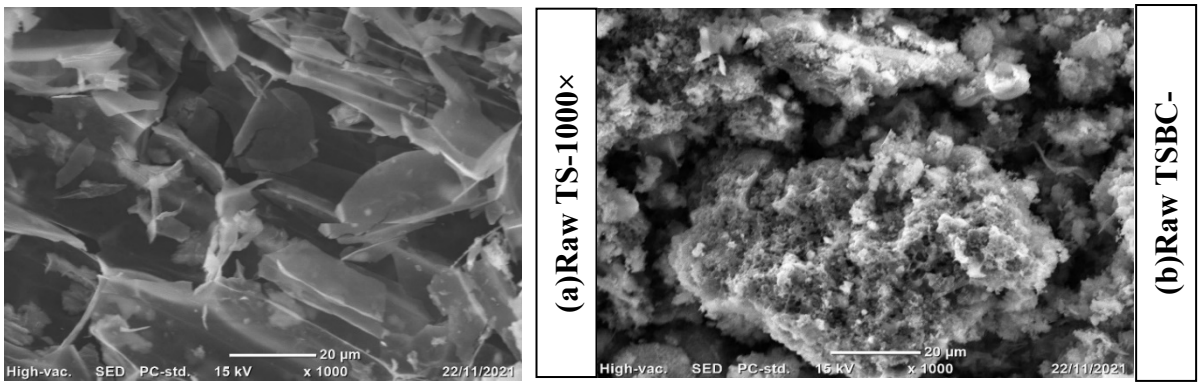

Figure 4.2 SEM image of (a) raw teff straw(b) raw teff straw biochar at 300 ℃ for 2hrs.

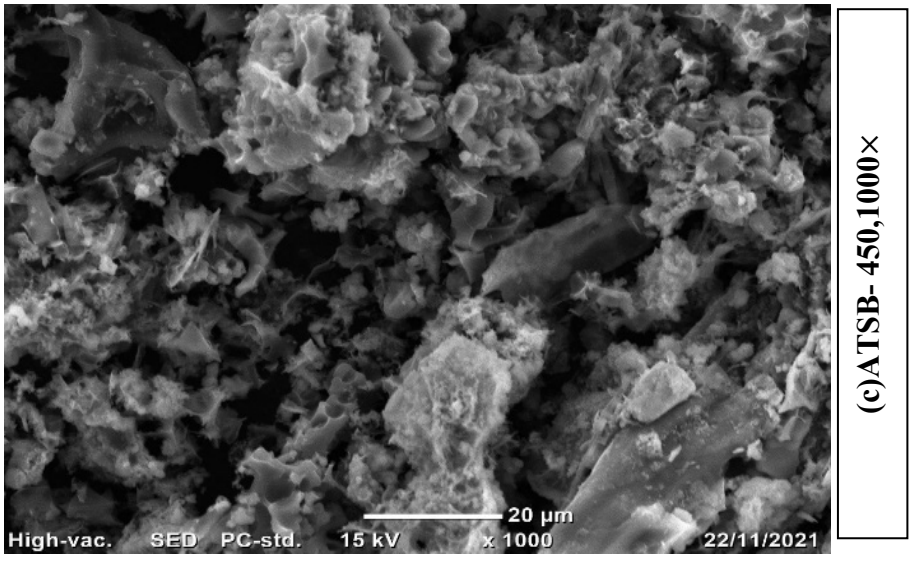

Figure 4.3 SEM image of KOH modified teff straw biochar carbonated at 450 ℃ for 2 hrs. and KOH: Teff straw ratio of 2.

4.5 Experimental design and optimization

The statistical analysis of the model was represented by the analysis of variance (ANOVA) at a significance level of 0.05. ANOVA was not only used to check the model validity but also used to signify the relationship between the model and actual results. The fitness of the models was assessed from the coefficient of determination (R^2), and the adjusted R^2

Table 4.3 Central composite design layout for MB Adsorption capacity using teff straw biochar

Std	Run	Factor 1 A: Temperature ℃	Factor 2 B: KOH/Biomass ratio	Factor 3 C: Time hrs.	Response Adsorption Capacity (mg/g
17	1	450	2	2	55.00
4	2	600	4	1	30.59
19	3	450	2	2	55.02
13	4	450	2	1	54.6
16	5	450	2	2	54.89
15	6	450	2	2	55.06
6	7	600	0	3	32.69
11	8	450	0	2	52.2
5	9	300	0	3	51.65
10	10	600	2	2	32.62
18	11	450	2	2	55.11
12	12	450	4	2	50.44
8	13	600	4	3	29.664
2	14	600	0	1	33.41
14	15	450	2	3	54.039
7	16	300	4	3	49.846
1	17	300	0	1	51.944
9	18	300	2	2	52.5
3	19	300	4	1	50.31

4.6 ANOVA Analysis

A quadratic mathematical model was developed for optimal adsorption performance of teff straw biochar over MB. adsorption capacity (Q) as a response parameter. The adsorption capacity (Q) varied from 29.664–55.02 mg/g.

Source	Sum of square	df	Mean square	f-value	p-value	
Model	1721.12	9	191.24	408.69	< 0.0001	Significant
A-Temperature	946.26	1	946.26	2022.26	< 0.0001	
B-KOH/Biomass	12.20	1	12.20	26.07	0.0006	
C-Time	0.8791	1	0.8791	1.88	0.2037	
AB	0.7248	1	0.7248	1.55	0.2447	
AC	0.0986	1	0.0986	0.2106	0.6571	
BC	0.0177	1	0.0177	0.0378	0.8502	
A^2	349.41	1	349.41	746.71	< 0.0001	
B^2	17.74	1	17.74	37.92	0.0002	
C^2	0.5565	1	0.5565	1.19	0.3038	
Residual	4.21	9	0.4679			
Lack of Fit	4.21	5	0.8423			
Pure Error	0.0000	4	0.0000			
Cor Total	1725.33	18				

Table 4.4 analysis of variance (ANOVA) on CCD

The ANOVA test (Table) determines the statistically significant terms (P-value < 0.001) in the model at 99% confidence interval. The quadratic terms represent the interaction between temperature–KOH/Biomass (AB), temperature-Time (AC), temperature (A), and KOH/Biomass (B) have a significant effect on adsorption capacity of biochar.

The F-value (408.69) is adequately large and P-values less than 0.0500 indicate model terms are significant. In this case A, B, A^2, B^2 are significant model terms which indicates the mathematical model is in good agreement with the experimental data.

A comparison of predicted and actual experimental results for adsorption capacity is depicted in Figure 4.4. It is seen in Figure 4.4, that the actual experimental data points lie close to the diagonal line, and the developed model can be used to predict biochar yield within the limits of the experimental factors. The Predicted R^2 of 0.9895 is in reasonable agreement with the Adjusted R^2

of 0.9951; i.e., the difference is less than 0.2. Adeq. Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 51.869 indicates an adequate signal.

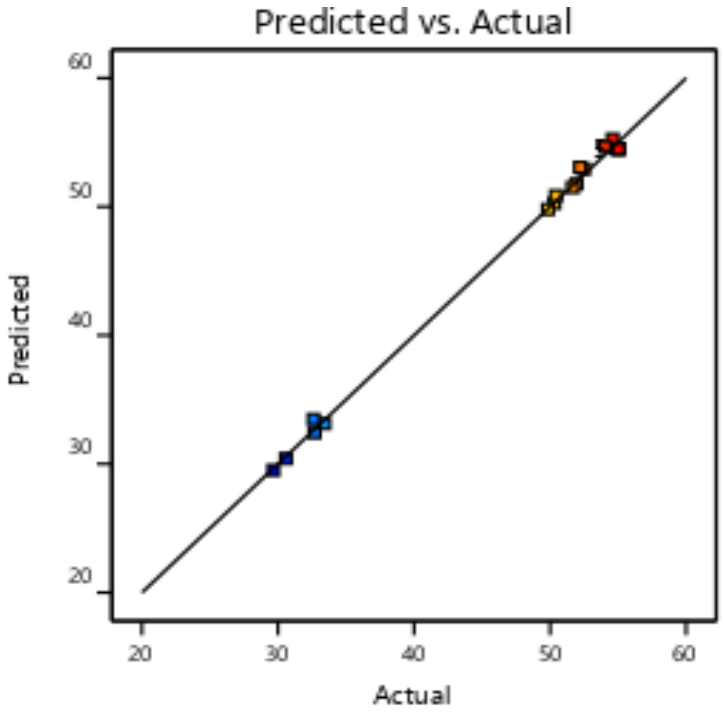

Figure 4.4 Experimental data plotted against CCD model predicted data for Adsorption Capacity

Quadratic model (QM) for teff straw biochar adsorption capacity in terms of coded factors

$$Y = 54.519.73A - 1.1B - 0.2965C - 0.301AB - 0.111AC - 0.047BC - 11.31A^2 - 2.55B^2 + 0.4513C^2$$

Where: A-Temperature, B-KOH/Biomass and C-Time

Response surface and contour plots for adsorption capacity of MB as a function of temperature (°C) and KOH/Biomass ratio are presented in Figure below. Time (C) has insignificant influence on adsorption capacity compared to other variables.

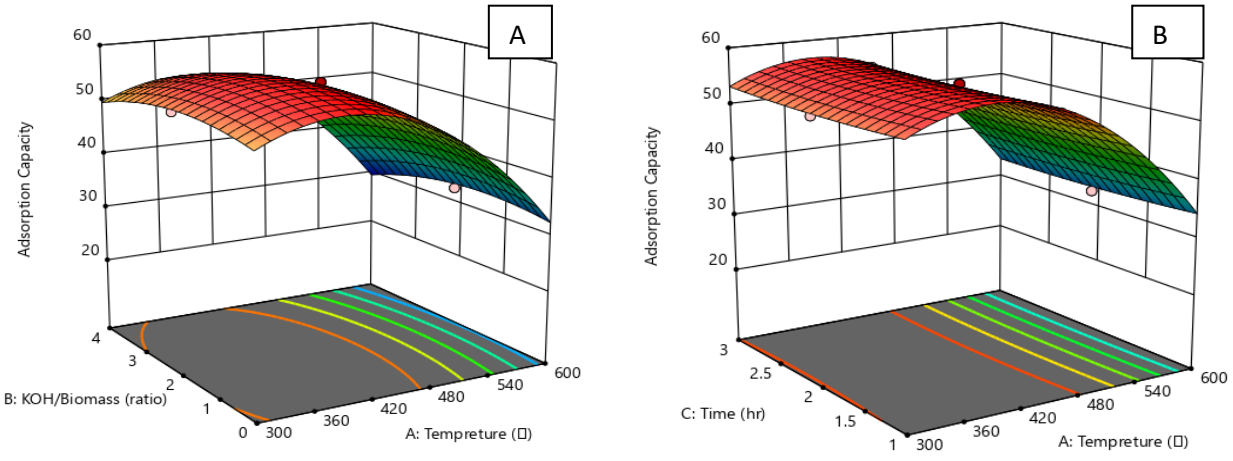

Figure 4.5 3D view showing the interaction between (A)temperature and KOH/Biomass and (B) Time and Temperature ratio on Adsorption capacity

Figure 4.5 shows the effect of two significant parameters, temperature and KOH/Biomass ratio, on adsorption capacity simultaneously. An increase in of adsorption capacity can be seen by increasing the KOH/biomass ratio from 1 to 2. At this ratio the mesoporous structure in porous biochar was formed, which resulted in an increase of the surface area and the adsorption capacity of porous activated biochar, as KOH/Biomass ratio above 3 a decrease in adsorption capacity seen. This decrease may be resulted in the KOH reaction enhanced the widening of pores and reduction of surface area.

4.7 Effect of Activation Conditions on Preparation of Activated Biochar and adsorption capacity

KOH activation, activation conditions have an important effect on the specific surface area and porous structure of porous biochar. The effect of activation conditions, such as KOH: Biomass, activation temperature, and activation time, on the adsorption capacity qe and removal percentage of methylene blue.

The adsorption capacity qe was increased from 52 $mg \cdot g^{-1}$ to 55.02 $mg \cdot g^{-1}$, and the removal percentage increased from 87.01 % to 91.7% with the increasing of ratio (KOH/biochar: w/w) from 0 to 2. However, when KOH: Biomass ratio increased from 2 to 4, q_e was found to be

decreased from 55.02 $mg \cdot g^{-1}$ to 50.44 $mg \cdot g^{-1}$, and the removal percentage were decreased from 91.7% to 84.45%. This is because the excessive amount of activating agent concentration might have accumulated on the surface of Teff straw. Two different mechanisms dominated the whole chemical activation process. In the first stage, the mesoporous structure in biochar was formed, which resulted in an increase of the surface area and the adsorption capacity of biochar, as can be seen in the impregnation ratio ranging from 0 to 2. In the second stage, the C-KOH reaction enhanced the widening of pores, which resulted in a reduction of surface area and the adsorption capacity of porous biochar. These results made it clear that KOH/teff straw ratio played an important role in the preparation of biochar.

Biochar adsorbent preparation (carbonization) temperature also have an impact on adsorption capacity and removal efficiency.as showed in the graph as temperature increase adsorption capacity also increase until 450 ℃ then after it tend to decrease. Carbonization time also found to be 2 hrs. the best after 2 hrs. the adsorption capacity decrease with time. KOH and biochar matrix may react as $6KOH+2C_2K+K_2CO_3+3H_2$ at higher temperature with enough energy, which results in the formation and widening of mesoporous structure. As for the activation tim,120 min was exactly suitable for the biochar activation and. However, with an activation time longer than 120 min, the adsorption capacity q_e and removal rate of methylene blue decreased due to the widening of aforementioned mesoporous structure.

When the KOH: Biomass ratio was set as 2:1 and the activation time was 2 hr., with the increasing of the activation temperature from 300 °C to 450 °C, q_e increased from 52 $mg \cdot g^{-1}$ to 55.01 mg/g, and the removal percentage increased from 87.5% to 91.77%.

The optimal adsorption Capacity as a function of Temperature and KOH/Biomass ratio was at 55.02mg/g adsorption capacity,450℃ and KOH/Biomass ratio of 2.

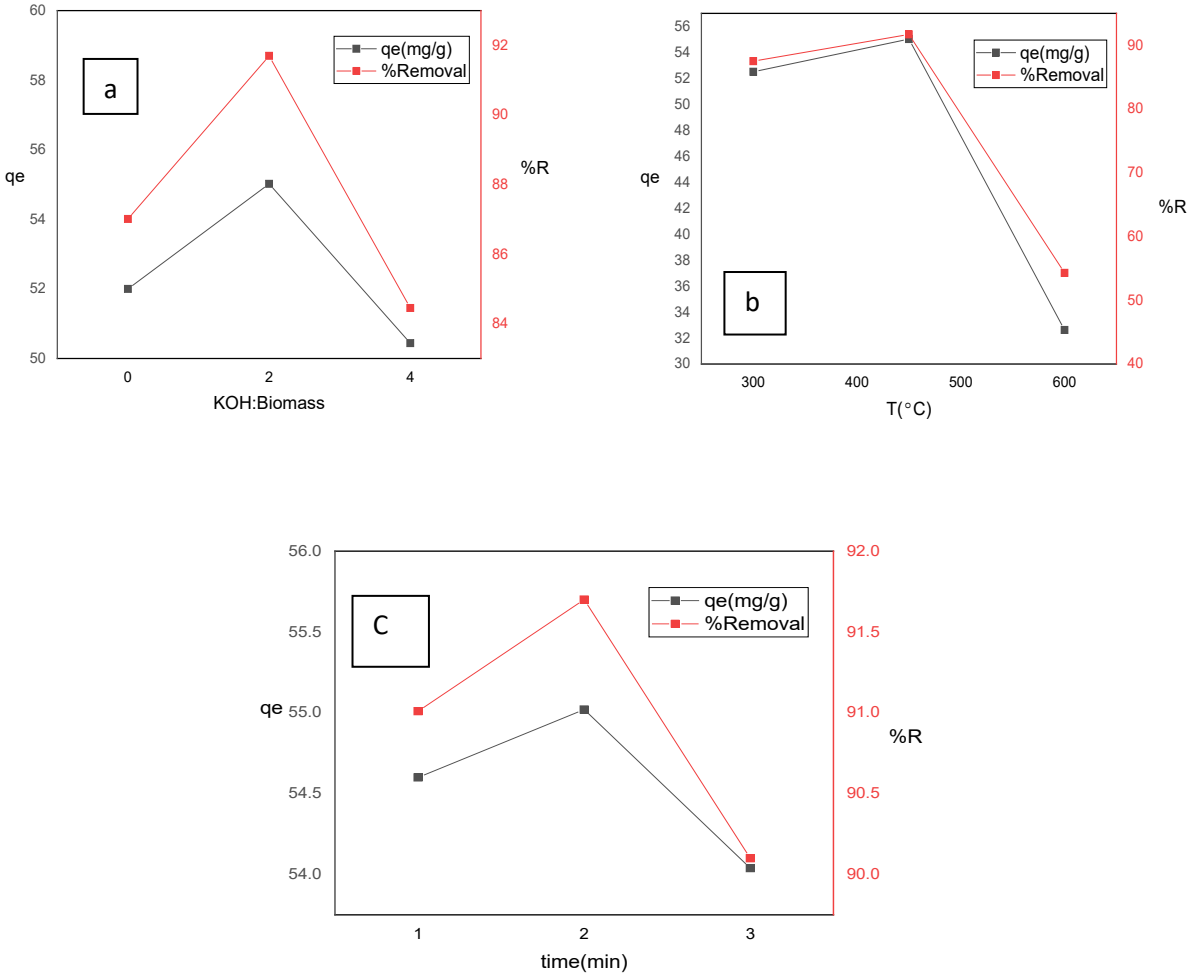

Figure 4.6 Effect of activation conditions on MB adsorption. (a) KOH: Teff straw ratio (conditions T=450 ℃ and activation time =2hrs), (b)activation temperature (conditions: KOK: ATSB=2 and time=2), and(c) activation time (conditions: T=450℃ and KOH: ATSB =2)

4.8 Effect of initial dye concentration on MB adsorption capacity of ATSB

The initial dye concentration has a significant effect on its removal from aqueous solutions. The effects of various initial MB dye concentration and contact time on the adsorptive removal of dye by activated teff char. Its effect was as shown by graph in Figure 4.7 is that maximum dye removal occurred for low initial concentration of methylene blue. It was seen that percentage removal of MB dye decreased with increase in initial dye concentration. one can observe a sharp decrease in the removal efficiency from an initial dye concentration of 50 mg/l to 100 mg/l. At

higher concentrations, all dye molecules in the solution do not interact with the binding sites of the adsorbent due to adsorbent has a limited number of active binding sites, which become saturated at a certain concentration. Hence with increase in dye concentration no further adsorption could be achieved. Therefore, adsorption rate is observed to decrease initial dye concentrations are increased.

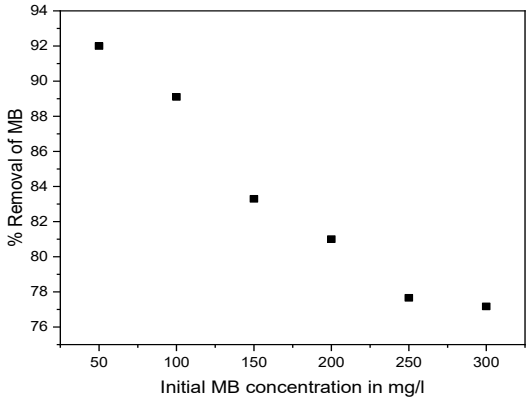

Figure 4.7 Effect of initial MB dye concentration on percentage removal of MB (Conditions: T=450℃, Time= 2hrs. and KOH: ATSB=2)

4.9 Effect on adsorbent dosage on MB adsorption capacity of ATSB

Adsorbent dosage strongly influences the adsorption process by affecting adsorption capacity of the adsorbent. The amount of adsorbent dosage was varied in the given range 0.1,0.2,0.3 and 0.4g. It was observed from Figure 4.8 that increasing the dosage increased the % removal of methylene blue. This can be simply due to the increase of adsorption sites and an increase in surface area as biomass loading is increased. A larger surface area offers more active sites.

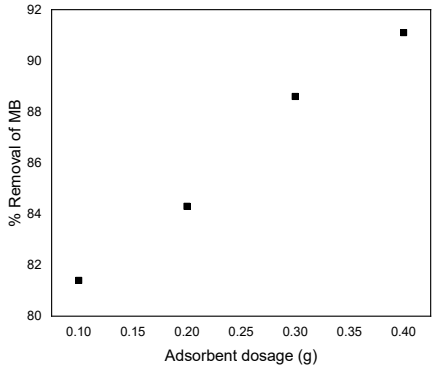

Figure 4.8 Effect of adsorbent dosage on percentage removal of MB (Conditions: T=25℃, Time=250 min dosage 0.5g/100ml and C0=300mg/l)

4.10 Effect of Contact time on MB adsorption capacity of ATSB

Experimental results showed that the contact time necessary for removal rate of MB. This Study on effect of contact time showed that methylene blue dye removal rate was rapid in 150 to 200 minutes. At higher contact time the rate of adsorption decreased due to decrease in total surface area and reached the equilibrium in 250 minutes. the large sorption rate was due to increased interactions between dye particles and the large number of active sites of bio sorbent which are occupied with an increase in time.

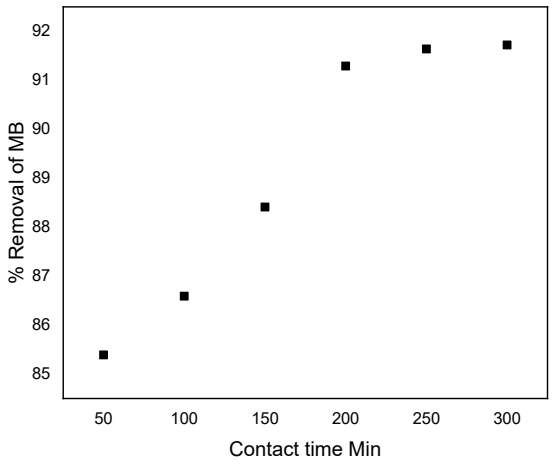

Figure 4.9 Effect of contact time on percentage removal of MB (Conditions: T=25℃, dosage 0.5g/100ml. and C0=300mg/l)

4.11 Effect of dye solution pH on MB adsorption capacity of ATSB

pH of solution is an important parameter for adsorption because it affects the surface charge and characteristics of adsorbent. As the pH increases, it is usually expected that the removal of MB which is a cationic dye increases due to decreasing the number of positively charged sites. At lower pH, the various functional groups and reactive atom of methylene blue dyes and adsorbent protonated and both get positive charge. Therefore, due to strong repulsive force between dyes and adsorbent decrease the removal percentage. In addition, the electrostatic attraction of the MB and the surface of the ATSB is weak. As the pH increased, the anions on the ATSB surface increased, with the anions neutralizing the positive charge on the surface, and eventually generating a negative charge on the surface of the adsorbent. The increased electrostatic

attraction between the ATSB and MB then favors a higher removal rate, in the experiment's Highest percentage of dye removal (91 %) was observed at pH 8.0.

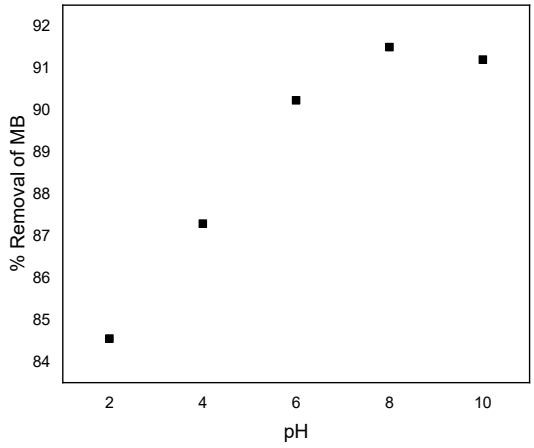

Figure 4.10 Effect of pH on the percentage removal of MB (Conditions: T=25℃, Time= 2hrs C0=300mg/l. and dosage 0.5g/100ml)

4.12 Effect of Temperature on MB adsorption capacity of ATSB

The effect of different dye solution temperatures of 25, 30, 35 and 40 °C on the adsorption kinetic was studied to determine the optimum solution temperature and the thermodynamic behavior of MB dye adsorption on KOH activated teff biochar the percentage removal of MB dye increases with increasing temperature. This may be attributed to the increase of diffusion rate of the dye molecules in the solution with temperature. Because the adsorption controlled by the diffusion process from the bulk to the surface. And also strengthening of the bonds between the dye molecules and the binding sites which are activated at higher temperatures of the sorbent might be enhanced the adsorptive interactions. This increasing trend in dye removal capacity with increasing temperature That amount of MB dye removal on Teff biochar increased from 73.78 to 81 % with increasing temperature of the solution This trend indicates that the process is endothermic. This is also supported by thermodynamic parameter ΔG° which is decreasing with the increases of temperature.

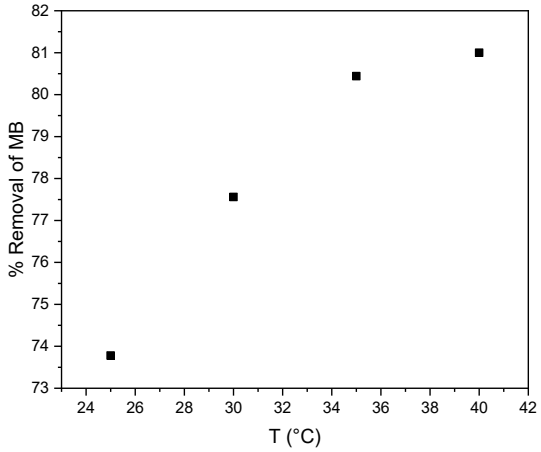

Figure 4.11 Effect of temperature on percentage removal of MB (Conditions: Time=2hrs.dossage 0.5mg/100ml and C0=300mg/l)

4.13 Equilibrium Adsorption isotherm

Adsorption isotherms are important for the description of how adsorbate will interact with an adsorbent and are critical in optimizing the use of adsorbent.(Ahmed and Dhedan 2012)(Shu et al. 2019)

4.13.1 Langmuir isotherms

For the kinetic experiment, 0.5 g of adsorbent was mixed with 100 ml of MB solution at pH 7. While the temperature was maintained at 298 K, the agitation speed was set at 150 rpm The Langmuir isotherms were plotted using table shown below and the plot of (Ce/q_e) vs. C_e. The Langmuir parameters, q and b were estimated from the slopes and intercepts of the straight lines.

Table 4.5 Tabulation for Langmuir and Freundlich isotherm model for effect of initial concentration

C_o(mg/l)	c_e(mg/l)	q_e(mg/g)	c_e/q_e(l/g)	ln C_e	ln q_e
50	5.66	44.33333	0.12782	1.734601	3.791737
100	49.33	50.66667	0.973684	3.8986	3.925268
150	97.33	52.66667	1.848101	4.578142	3.963983
200	146.6667	53.33333	2.75	4.988162	3.976562
250	198	52	3.807692	5.288267	3.951244

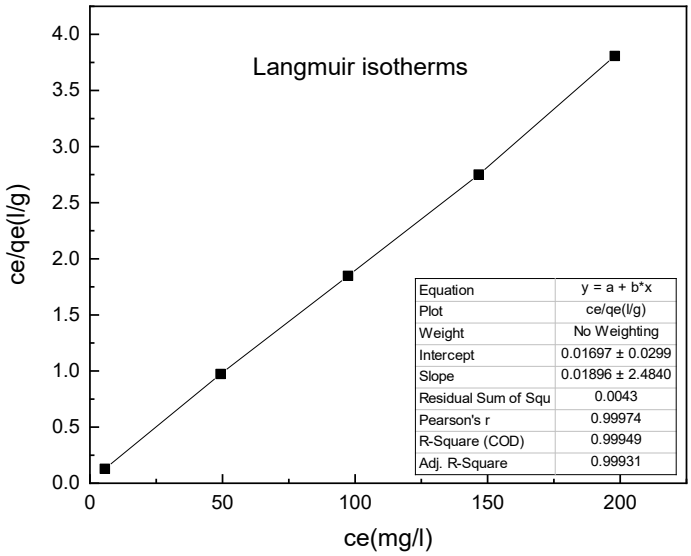

Figure 4.12 Langmuir isotherm for initial MB concentration

The linearized Langmuir isotherm equation is represented as follows:

$$\frac{c_e}{q_e} = \frac{1}{k_L q_m} + \frac{c_e}{q_m} \tag{4.1}$$

The equation from Ce/q_e vs ce graph is in the form of y = mx + b

$$y = 0.019x + 0.0169$$

where 0.019 is the slope and 0.0169 is y-intercept

The y-axis intercept gives the expression $\frac{1}{q_m} = \text{int}\,ercept$

$$q_m = \frac{1}{\text{int}\,ecept} = \frac{1}{0.0169} = 59.17\ \text{mg/g}$$

The Langmuir adsorption constant related to the free energy adsorption Kl calculated from the slope

$$slope = \frac{1}{k_l q_m} \Rightarrow k_l = \frac{1}{slope \times q_m} = \frac{1}{0.019 \times 59.17} = 0.8895\ \text{L/mg}$$

And R^2 =0.99931

4.13.2 Freundlich isotherm model

Freundlich model $$q_e = k_f c_e^{1/n} \quad (4.2)$$

The linear form can be written as: $\ln q_e = \ln k_F + \frac{1}{n_F} \ln c_e$

The Freundlich constants 1^n and K_F are determined from the gradient of and the intercept of the linear plot ln c_e vs ln q_e.

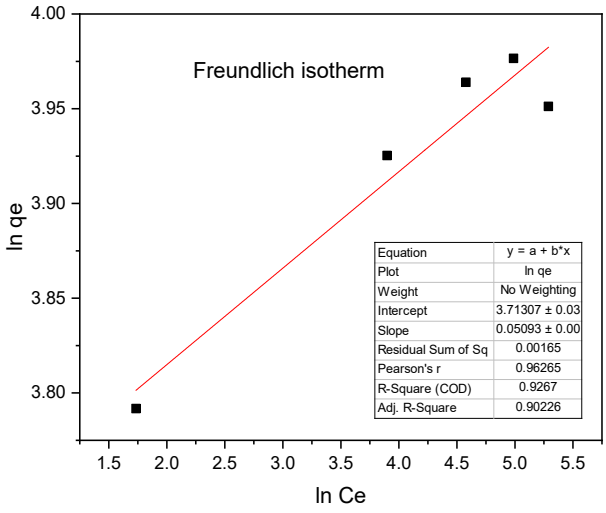

Figure 4.13 Freundlich isotherm for initial MB concentration

Freundlich isotherm for initial MB concentration

The equation from Ce/q_e vs c_e graph is in the form of y = mx + b

$$y = 0.0509x + 3.7131$$

The y-axis intercept gives the expression gives K_f value

$$k_f = \exp(\text{int}\,ercept) = \exp(3.7131) = 40.98$$

$$slop = \frac{1}{n_F} \Rightarrow n_F = \frac{1}{slop} = \frac{1}{0.0509} = 19.646$$

And R^2 value reads from the graph which is $R^2 = 0.926$

Table 4.6 Isotherm parameters for MB adsorption on teff straw biochar

Isotherms	Parameters	R^2
Langmuir	$q_m = 59.17$	$R^2 = 0.99931$
	$k_l = 0.8895$	
Freundlich	$k_f = 40.98$	$R^2 = 0.9267$
	$n_F = 19.646$	

The R^2 (0.99931) of Langmuir model is very close to 1 and much larger than Freundlich model (0.9267), indicating the good application of Langmuir model. which indicated that the adsorption of methylene blue by ATSB may be a monolayer adsorption, and the surface sites were relatively homogeneous. It suggests the adsorption of MB onto teff straw biochar follows the Langmuir isotherm.

The monolayer adsorption capacity calculated from the Langmuir isotherm was 57.19mg/g, which approximated to the experimental data (53.33mg/g) and again proved the adsorption of MB onto the ATSB were consistent with the Langmuir isotherm. Therefore, Langmuir isotherm model is fitted than Freundlich isotherm model.

4.14 Adsorption kinetics

Two different kinetic models, including

1. pseudo-first order and 2. pseudo-second order

Were studied to assess the MB adsorption rate.

The differential form of pseudo- first order can be written as below as described in(Creamer, Gao, and Zhang 2014)

Nonlinear $$q_t = q_e\left(1-\exp\left(-k_1 t\right)\right) \quad (4.3)$$

linear $$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4.4)$$

The pseudo-second order rate equation is shown as below

Nonlinear $$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$$

(4.5)

linear $$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4.6)$$

where, q_t and q_e denote the sorption capacity (mg/g) at a given time and at equilibrium, respectively, K_1 is the pseudo first order rate constant (min^{-1}), K_2 is the pseudo second order rate constant (g $mg^{-1}min^{-1}$) and t is the time (min)

Table 4.7 Tabulation for Pseudo first and second order kinetics plot for the adsorption of MB onto activated Teff straw biochar

Experiment No	Time(min)	Co(mg/l)	Ci(mg/l)	qt(mg/g)	ln(qe-qt)	t/qt (min. g/mg)
1	50	150	138.67	3.74	3.88	13.36
2	100	150	127.33	7.48	3.79	13.37
3	150	150	110	13.2	3.66	11.36
4	200	150	92.67	18.92	3.49	10.57
5	250	150	79.33	23.32	3.35	10.72
6	300	150	78.67	23.54	3.35	12.74

4.14.1. Pseudo-first order kinetic model

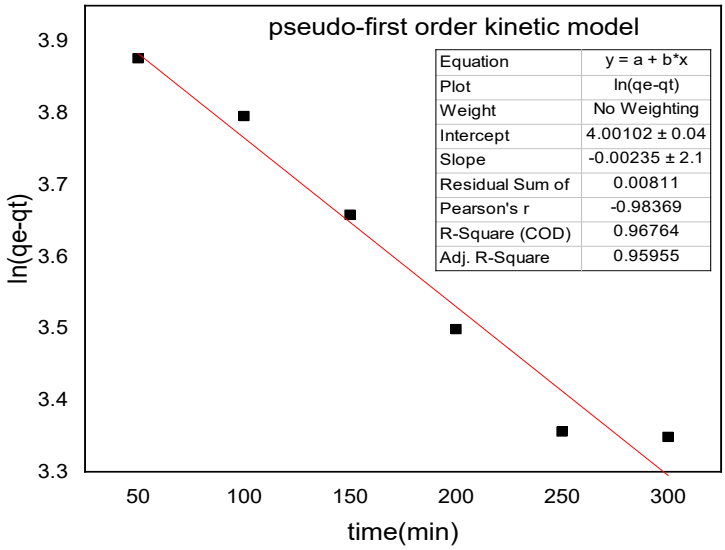

Figure 4.14 Pseudo first-order kinetics plot for the adsorption of MB onto activated Teff straw biochar

Linear form pseudo-first order kinetic model equation is

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{4.7}$$

$$slop = k_1 t \Rightarrow k_1 = \frac{slop}{t} = \frac{-0.00235}{300} = -7.83333E-06$$

$$\text{int}\, recept = \ln q_e \Rightarrow q_e = \exp(4.001) = 54.65$$

$$R^2 = 0.9676$$

4.14.2 The pseudo-second order Kinetic model

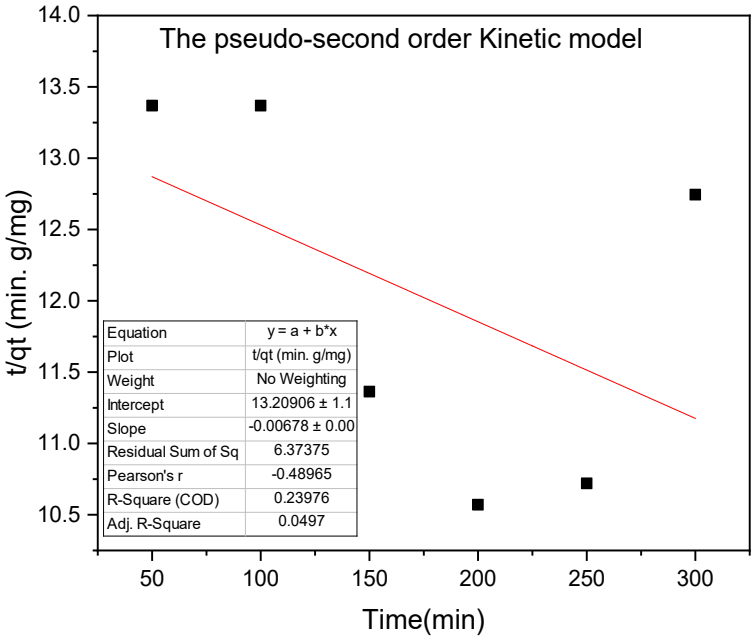

Figure 4.15 Pseudo second-order kinetics plot for the adsorption of MB onto activated Teff straw biochar.

The pseudo-second order Kinetic model linear form equation is

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4.8}$$

$$slope = \frac{1}{q_e}$$

$$q_e = \frac{1}{slope} = \frac{1}{-0.00678} = -147.493$$

$$q_e{}^2 = 21754.07$$

$$\text{int}\,ercept = \frac{1}{k_2 q_e^2}$$

$$k_2 = \frac{1}{\text{int}\,ercep \times q_e^2} = \frac{1}{13.20906 \times 21754.07} = 3.4800668^{-06}$$

R^2=0.23976

Table 4.8 Kinetic parameters for MB adsorption on activated teff biochar

Models	q_e, exp (mg/g)	q_e, Cal (mg/g)	K (1/min)	R^2
Pseudo-first order model	52	54	$K_1 = -7.83333E-06$	0.9676
Pseudo-second order model	52	147	$K_2 = 3.4800668^{-06}$	0.23976

As can be seen from Table 4.9, the R^2 values of the pseudo first order model is closer to 1.0 and much higher than that of the pseudo second order kinetics. And also, q_e, exp and q_e, Cal are very close to each other in first order than second order. These results shown that the adsorption of MB dye in aqueous solutions using activated teff biochar can be described by pseudo first order kinetic model.

4.15 Thermodynamic study

To study more in-depth through the adsorption mechanism, thermodynamics calculations are helpful. (Mallakpour and Tabesh 2019)Thermodynamic parameters such as ΔG^o, ΔH^o and ΔS^o for the adsorption system were calculated using the following equations.

$$K_d = \frac{q_e}{C_e} \times 1000 \quad (4.9)$$

$$\Delta G = -RT \ln K_d \quad (4.10)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4.11)$$

where R (8.314 J/mol K) is the universal gas constant and T (K) is the absolute solution temperature. The values of ΔH° and ΔS° were determined from the slope and intercept of the Van't Hoff plot of lnKd

versus 1/T which are shown in Figure 4.18. The calculated thermodynamics parameters are given in Table 4.10.

Table 4.9 Tabulation for Thermodynamic parameters plot for the adsorption of MB onto activated Teff straw biochar

T(K)	R (J/mol K)	Kd	ln Kd	1/T	$\Delta G°$ (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol)
298.15	8.314	562.7119	6.332768	0.003354	-15.6978	13.65	0.099
303.15	8.314	691.0891	6.538269	0.003299	-16.479		
308.15	8.314	822.7273	6.712625	0.003245	-17.1975		
313.15	8.314	709.0909	6.563984	0.003193	-17.0895		

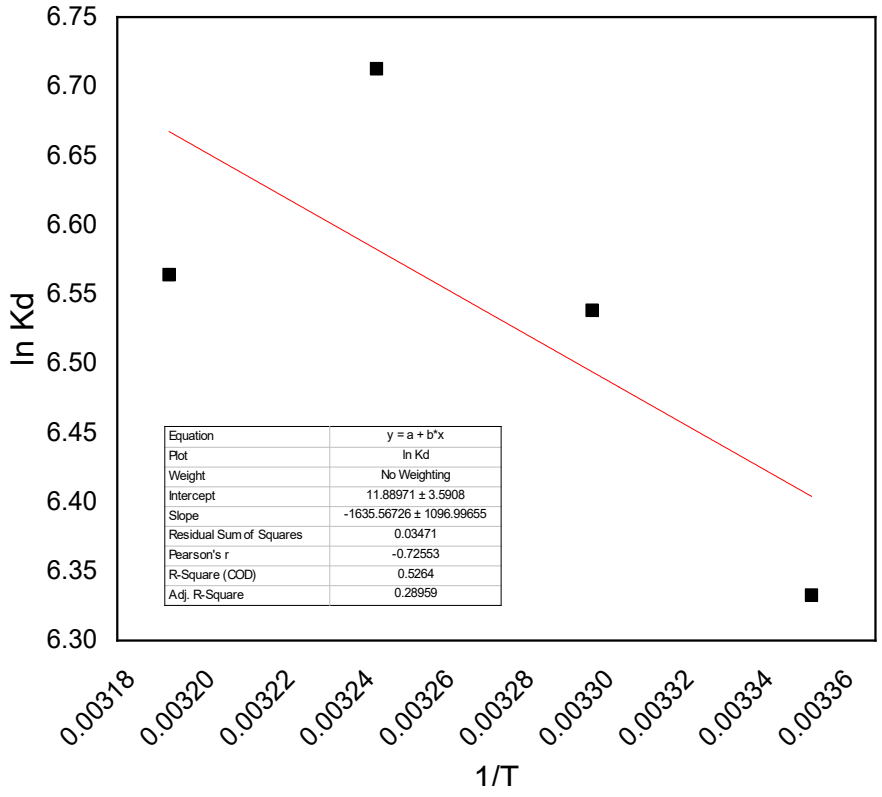

Figure 4.16 Regressions of Van's Hoff for thermodynamic parameters.

$$slope = -\frac{\Delta H^0}{R} = -1642.12269$$

$$\Delta H^0 = 1642.12269 \times 0.008314 = 13.65$$

$$\text{int}\,ercept = \frac{\Delta S^0}{R} = 11.911$$

$$\Delta S^0 = 11.911 \times 0.008314 = 0.099$$

The positive value of ΔH^0 showed that the nature of adsorption process was endothermic. The positive value of ΔS^0 indicated an increase in the randomness at the solid/solution interface during the adsorption of the MB dye on teff straw biochar. ΔG^0 has negative value and which indicate that the process is spontaneous. The increase in the absolute value of ΔG^0 as the temperature rises indicates that the affinity of MB on biochar is higher at high temperature. The lower values of ΔG^0 showed that the adsorption process may be a physical process. The enhancement of adsorption capacity of the adsorbent at higher temperatures may be attributed to an enlargement of pore size and/or activation of the adsorbent surface.

The low value of ΔH^0 shows that the effect of temperature is not significant at the range of studied temperatures, while the low value of ΔS^0 also indicates that no remarkable change on entropy occurred during the adsorption process.

4.16 Regeneration and reuse ability of adsorbent

The adsorption of methylene blue was conducted again using similar adsorbent after desorption process. The removal rate 85.86,83.88,80.3,76.08 and 69.7% of the original ATSBC removal capacity. The experimental results show that 90% of ethanol and 10% of NaOH regenerations are characterized by good recycling performances. After 4 hr. regeneration cycles, the removal rate of 300 mg /l MB with 0.5 g of ATBC is still around 79,77.17,73.9,70.65 and 64.13%.

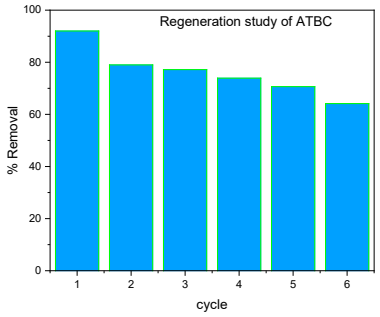

Figure 4.17 Regeneration performance of ATSB during adsorption– desorption cycles

As is shown in Figure 4.19, the dye removal efficiency decreased gradually with the increasing reuse cycles. About 64.13% removal rate can be reached after six reuse cycles, which shows a moderate regeneration performance. This indicated that the MB molecules adsorbed on ATSB were not fully removed during the regeneration process, which is mainly caused by the strong interactions between MB and ATSB.

Therefore, ATSB can be used as an efficient, economical and recyclable adsorbent for the treatment of wastewater containing MB dye.

4.17 Activation Mechanism and Possible mechanism of MB adsorption onto ATSBC adsorbent

4.17.1 Activation Mechanism

The KOH activation influence of on SBC was easily observed through BET surface area analysis and by SEM, XRD and FTIR characterization. Based on surface area measurements and SEM images, the biochar exhibited a larger surface area after KOH activation.

4.17.2 Possible mechanism of MB adsorption onto ATSBC adsorbent

The adsorption of MB on KOH activated teff straw biochar was a complicated process and various interactions co-existed during the process. The main mechanisms for MB removal by adsorbent or biochar involve physical interaction, ion exchange, electrostatic interaction, $\pi - \pi$ stacking, hydrogen bonding and pore filling.

Based on the FTIR spectrums, BET, SEM characterization and adsorption experimental results, the mechanism of ATSB adsorption of methylene blue was analyzed.

After KOH activation, the surface area of biochar significantly increased. Due to cellulose and hemicellulose in the teff straw gradually decomposed thermally Meanwhile, the carbohydrate, protein and fat compounds also gradually decomposed. Then, the specific surface area became larger and a pore structure gradually formed, both of which would play an important role in MB removal.

Based on FTIR result the intensity of the absorption peak at 3431 cm^{-1} changed to 3445 cm^{-1} after the adsorption, but no new characteristic absorption peak appeared, indicating that these functional groups contributed to the removal process, but no chemical change occurred.

The hydrogen bonding interaction was formed between the nitrogen from MB and hydrogen from activated teff straw biochar. ATBC contained abundant functional groups among which –OH and –COOH could bind with nitrogen molecules in MB through hydrogen bonding. The aromatic structure of the biochar could combine with the benzene ring in MB molecules via $\pi - \pi$ stacking. Hydrogen bonds are usually present in most adsorption systems.

According to the effect of pH, the adsorption mechanism referred to electrostatic interaction. In the lower pH the low methylene blue adsorption detected due to the possibility of development of a neutral or weakened charges at the porous biochar surface Which decrease the electrostatic motivation for the adsorption of MB on it. However, in the basic media the formation of electric double layer changes its polarity and consequently the MB adsorption capability.

Based on the results of adsorption kinetics, the adsorption process involved were physical in pseudo first order kinetics which involve adsorption of one MB onto one porous active site of the adsorbent surface. Therefore, the main MB removal mechanism of KOH-TSBC involved physical adsorption.

CHAPTER FIVE

5.Conclusion and Recommendations

5.1 Conclusion

In this study, a low-cost and high-efficiency adsorbent, ATSB, was produced from agricultural waste for MB adsorption. KOH activated Teff straw biochar is considerably efficient and effective in removal of methylene blue dye from aqueous solutions.

The adsorption removal percentage for methylene blue dye was affected by KOH: Biomass ratio, time, and temperature of activated biochar preparation process. The best activation conditions were found to be KOH/teff straw ratio 2:0, activation temperature 450 °C, and holding time 2hr.

The study on the effect of adsorption condition pH, contact time, adsorbent dosage, temperature and MB initial concentration, showed that the adsorption efficiency highly depended on contact time, initial concentration, temperature, and initial solution pH and adsorbent dosage.

A maximum MB adsorption capacity of 59.17 mg/g was obtained at operating conditions of 8 pH value, 0.5 g/100 ml adsorbent dose and 2 h contact time. Equilibrium adsorption data of MB onto ATSB were well fitted to the Langmuir model of adsorption. with R^2 value of 0.9990. The adsorption kinetic data were well described by the pseudo-first order model with K_1=7.833E-0.6 and R^2=0.9676 and the kinetics of adsorption process showed that an increase in adsorption capacity with the increasing temperature. This result confirmed the endothermic nature of the adsorption process and also the main MB removal mechanism of KOH-TSBC involved physical adsorption.

Thermodynamic parameters positive ΔH^0 indicated that the nature of adsorption process was endothermic. The positive value of ΔS^0 indicated an increase in the randomness at the solid/solution interface during the adsorption of the MB dye on teff straw biochar. ΔG^0 has negative value and which indicated that the adsorption of methylene blue by ATSB was a spontaneous, this study revealed that a potential low cost and eco-friendly KOH activated teff straw biochar adsorbent for the removal of MB from aqueous solution.

From regeneration study of using the same adsorbent for six cycles of adsorption process the removal rate of 300 mg /l MB solution with 0.5 g of ATBC the adsorption capacity is still around 79,77.17,73.9,70.65 and 64.13%.

Therefore, ATSB can be used as an efficient, economical and recyclable (reusable) adsorbent for the treatment of wastewater containing MB dye.

5.2 Recommendation

Further studies could be undertaken to improve the removal efficiency of the adsorbent by continuously optimizing additional parameters such as type of precursor, activator selection, synthesis method, post-treatment method and industries that may be the source of organic dye should be analyzed.

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Li Liu 1, Yang Li 2 and Shisuo Fan 3 Preparation of KOH and H3PO4 Modified Biochar and Its Application in Methylene Blue Removal from Aqueous Solution, 1 December 2019

APPENDICES

Appendix A: Process flow diagram

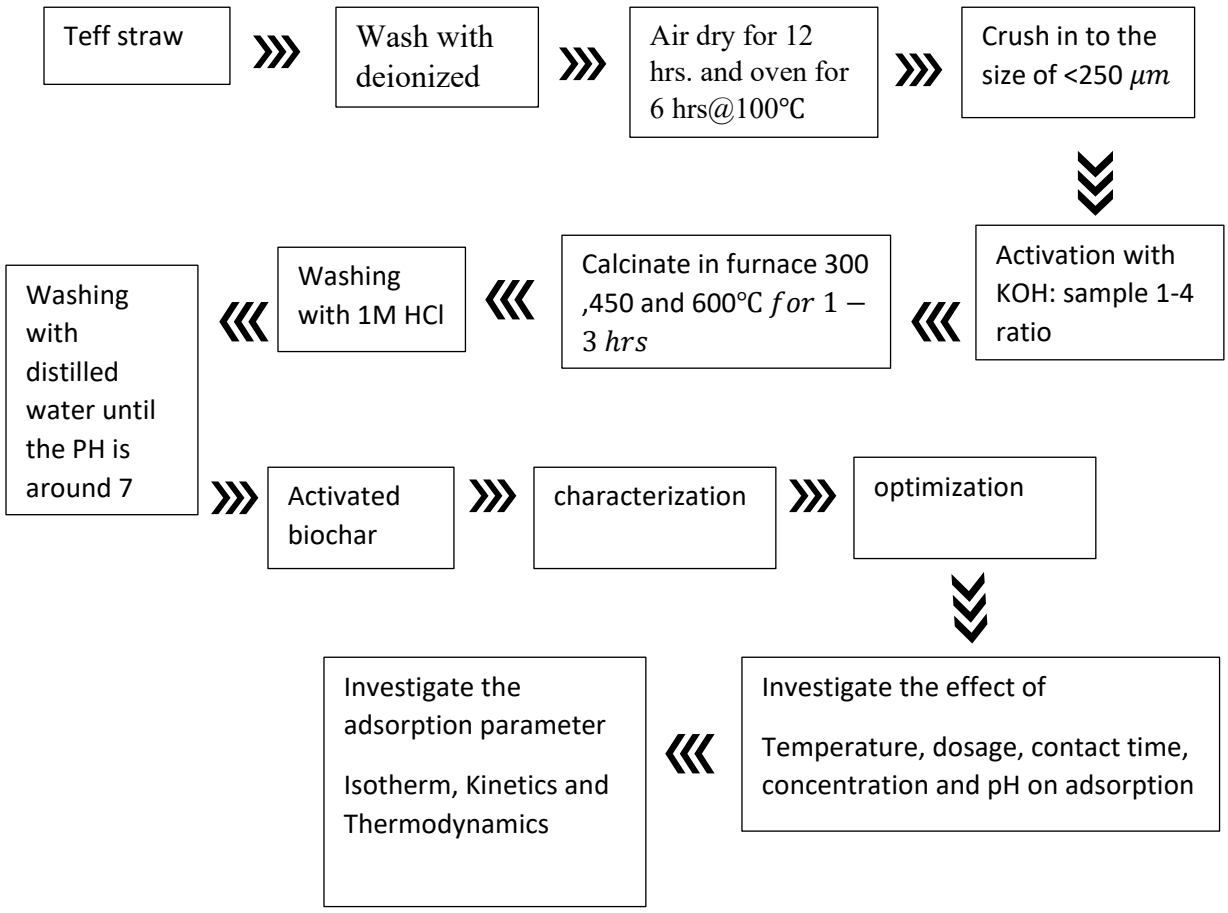


Figure A Flow chart of preparation and characterization and adsorption process

Appendix B: Tables of Effect of activation conditions on MB adsorption.

Table B.3 Effect of KOH: teff straw

KOH/B	T (℃)	q_e(mg/g)	%Removal
0	450	52	87.01
2	450	55.02	91.7
4	450	50.44	84.45

Table B.4 Effects of calcination temperature

Time(hrs.)	T (℃)	qe(mg/g)	%Removal
2	300	52.5	87.5
2	450	55.02	91.7
2	600	32.62	54.3

Table B.3 Effects of time

KOH/B	T (℃)	Time(hrs.)	qe(mg/g)	%Removal
2	450	1	54.6	91.01
2	450	2	55.02	91.7
2	450	3	54.039	90.1

Appendix C: Tables of Effect of Adsorption Process

Table C.6 Effects of teff straw biochar adsorbents on MB removal efficiency

Adsorbent dosage (g)				
	Co	Ci	A	R%
0.1	300	55.62	0.08343	81.4
0.2	300	47.61	0.07142	84.3
0.3	300	33.92	0.0508	88.6
0.4	300	26.54	0.03981	91.1

Table C.7 Effect of adsorption temperature on MB adsorption

Effects of Temperature				
T (℃)	Co	Ci	A	% Removal of MB
25	300	78.66	0.3736	73.78
30	300	67.32	0.3197	77.56
35	300	58.68	0.2787	80.44
40	300	57	0.271	81

Table C.8 Effect of contact time on MB adsorption

Effects of Contact time				
Min	Co(mg/l)	A	Ci(mg/l)	%Removal of MB
50	300	0.798	43.82	85.39
100	300	0.7258	40.23	86.59
150	300	0.627	34.76	88.41
200	300	0.528	26.123	91.29
250	300	0.452	25.07	91.64
300	300	0.4009	24.85	91.72

Table C.9 Effect of solution pH on MB adsorption

Effects of pH				
pH	Co(mg/l)	Ci	A	% Removal MB
2	300	46.348	0.22	84.55
4	300	38.13	0.181	87.29
6	300	29.28	0.139	90.23
8	300	25.49	0.121	91.5
10	300m	26.12	0.124	91.2

Table C.10 Effects of initial MB dye concentration on adsorption

Effects of Initial MB concentration			
Co(mg/l)	Ci(mg/l)	A	% Removal of MB
50	4	0.019	92
100	10.32	0.049	89.1
150	25	0.119	83.3
200	37.92	0.18	81
250	55.63	0.265	77.66
300	68.47	0.325	77.17

Appendix D Calibration curve

UV-vis spectrometer

The final concentrations of MB were attained at maximum wavelength λ_{max} of 664 nm with A°=0.0047 and correlation coefficient, $R^2 = 0.9914$.

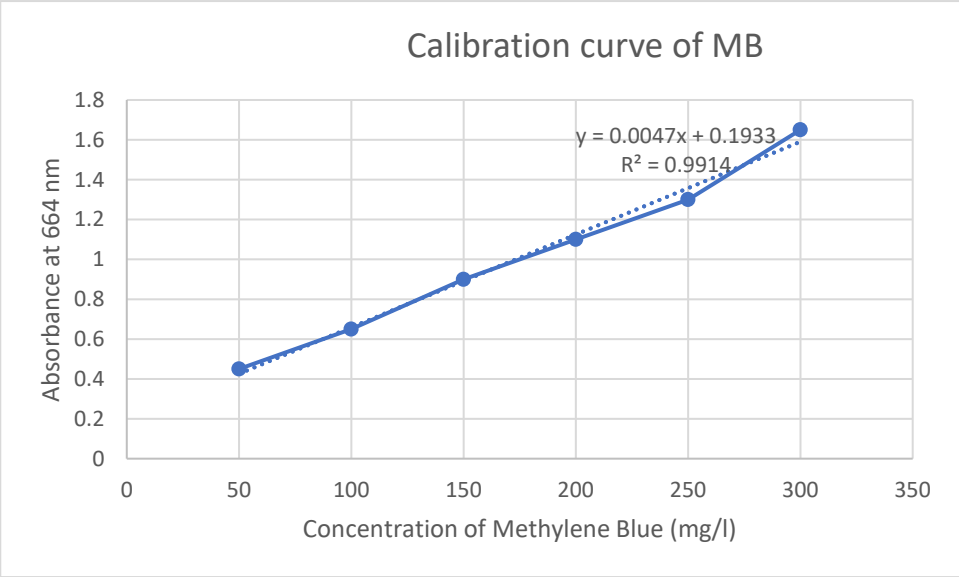
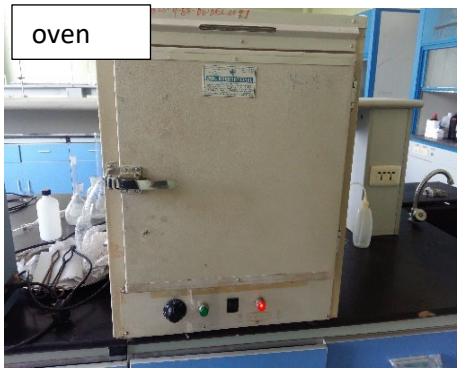


Figure D Calibration curve of Methylene blue at 664 nm

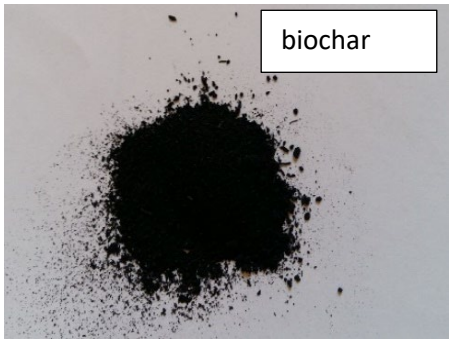
Appendix E: Laboratory Pictures

Muffle furnace

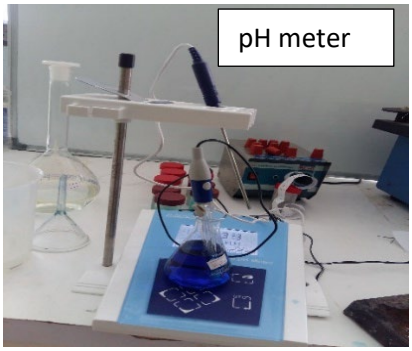
oven



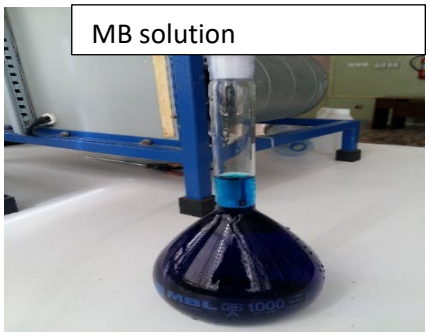
biochar



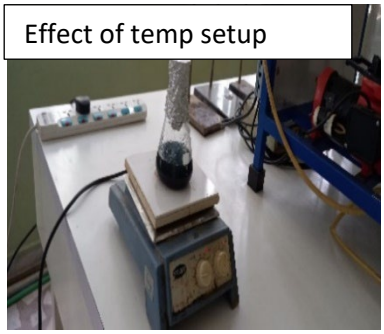
pH meter



MB solution



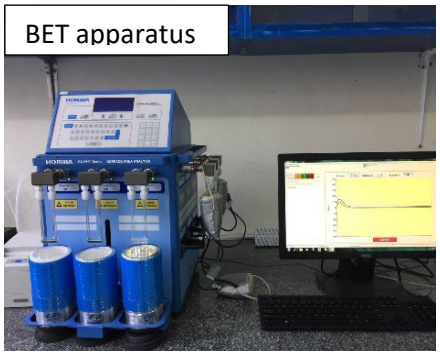
Effect of temp setup



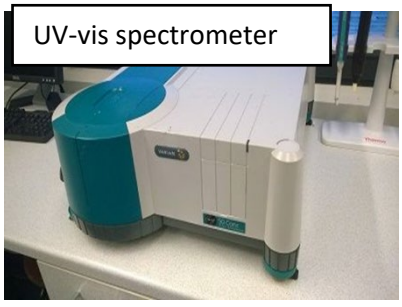
Adsorption experiment

Mechanical shaker

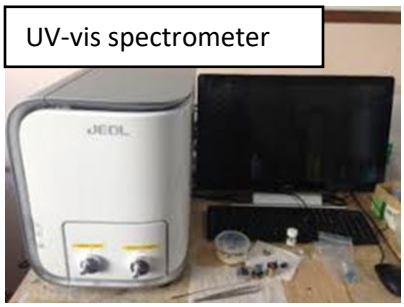
BET apparatus



UV-vis spectrometer



UV-vis spectrometer



FT-IR spectroscopy

Adsorbed MB solutions

Figure E Laboratory pictures