ADSORPTIVE REMOVAL OF METHYLENE BLUE FROM WASTEWATER BY NaOH CHEMICALLY MODIFIED SUGARCANE BAGASSE BIOCHAR

SELAMAWIT SEID HASSEN

A Thesis Submitted to the Department of Applied Chemistry

School of Applied Natural Science

In Partial Fulfillment of the Requirements for the Degree of

Master of Science in Applied Chemistry (Industrial Chemistry)

Office of Graduate Studies

Adama Science and Technology University

December, 2021

Adama, Ethiopia

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DECLARATION

I hereby declare that this Master thesis entitled “Adsorptive removal of methylene blue from wastewater by NaOH chemically modified sugarcane bagasse biochar” is my original work. It has not been submitted to any other institutions for the award of any academic degree. All sources of materials that are used for this thesis have been duly acknowledged through citation.

_____	_____	_____
Name of the student	Signature	Date

RECOMMENDATION

We, the advisor of this thesis, hereby certify that we have read the revised version of the thesis entitled **"Adsorptive removal of methylene blue from wastewater by NaOH chemically modified sugarcane bagasse biochar"** prepared under our guidance by Selamawit Seid submitted in partial fulfillment of the requirements for the degree of Mater's of Science in Applied chemistry. Therefore, we recommend the submission of revised Version of the thesis to the department following the applicable procedures.

_____	_____	_____
Advisor Name	Signature	Date
_____	_____	_____
Co Advisor	Signature	Date

APPROVAL SHEET

We, the advisor of the thesis entitled "**Adsorptive removal of Methylene Blue Dye from wastewater by NaOH chemically modified sugarcane bagasse biochar**" and developed by **Selamawit Seid Hassen**; hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

Advisor	Signature	Date
Co Advisor	Signature	Date

We, the undersigned, members of the Board of Examiners of the thesis by **Selamawit Seid Hassen** have read and evaluated the thesis entitled '**Adsorptive removal of Methylene Blue Dye from wastewater by NaOH chemically modified sugarcane bagasse biochar**" and examined the candidate during the open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Applied Chemistry (Specialization in Industrial Chemistry).

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Finally, approval and acceptance of the thesis are contingent upon submission of its final copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

Department Head	Signature	Date
School Dean	Signature	Date
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List of abbreviation and acronyms

AC	Activated Carbon
BET	Brunauer-Emmett Teller method
BSCB	Modified in sodium hydroxide sugarcane bagasse
FTIR	Fourier Transform Infrared spectroscopy
MB	Methylene Blue
NSCB	Unmodified sugarcane bagasse
SCB	Sugarcane Bagasse
SEM	Scanning Electron Microscope
XRD	X-ray diffraction
TGA	Thermogravimetric analysis
TA	Thermal analysis
MSCB	Methylene blue treated with sugarcane bagasse

ABSTRACT

During the past years different methods were studied for the removal of dyes from industrial effluents as their disposal have toxic effects to humans, animals, plants and the aquatic organisms. Very recently biochar based adsorbents have been extensively used as efficient and cost effective materials to remove Methylene Blue (MB) dye from wastewater. Therefore, in this research work, NaOH modified sugarcane bagasse (SCB) biochar was used as a low-cost bio- sorbent for removal of MB dye present in textile wastewater. The chemical and physical characteristic of biochar's were characterized by Fourier transformed infrared spectroscopy (FTIR), X-ray diffraction spectroscopy (XRD), Scanning electron microscopy (SEM), TGA, and BET. During adsorption: effects of the contact time, mass of the adsorbent, pH, and initial dye concentration on the adsorption capacity were studied. SCB biochar at BSCB500 ^{o}C provided the highest surface area of 732.6 m^2/g. The optimal results in effect of process parameters of the analysis were for optimum adsorption of MB on selected porous SCB biochar 86.55 %, pH 8, adsorbent dose 0.8 g, and concentration of MB 5.49 g/ml and contact time 80 min. The result for the present study shows the pseudo-first-order model with correlation coefficient 0.81 and (0.76) was not fit the experimental data therefore this data was not suitable for this model while the pseudo second-order model fitted very well with R^2 was equal to a unit (R^2 = 0.99) so this data was suitable for this work. Generally, the MB adsorption on SCB biochar can be described as the pseudo-second-order model, which indicated that the adsorption of MB on SCB biochar can be described as chemical adsorption. Therefore, an adsorption test of wastewater was conducted with BSCB500 ^{o}C as adsorbent. The results obtained in this study indicated that SCB biochar will be an attractive for removing cationic dyes from the dye wastewater.

Keyword adsorption, sugarcane bagasse, pyrolysis, biochar, methylene blue.

CHAPTER ONE

1. INTRODUCTION

1.1 Back ground of the study

Organic dyes are widely used in various fields and seriously induce water pollution. Most of the industrial dyes are toxic, carcinogenic, and teratogenic and unfortunately most of them are stable and resistance to photo degradation, biodegradation, and chemical oxidation. Dye removal from water sources has become a serious environmental problem but also a difficulty in recent years. Techniques for recovering and recycling dye wastewater have recently gotten a lot of attention because clean water sources are fast depleting and, no reliable solution has been developed. The environment would significantly benefit from the development of a permanent solution to remove dye particles from textile effluents (Katheresan, Kansedo, & Lau, 2018).

From the different forms of dyes methylene blue (MB) is one kind of common industrial dyes, it is usually used for dying wood, silk, and cotton. It is harmful to human beings, animals, and plants. So, the treatment of wastewater containing such dye is very important. Figure 1 shows a commonly used synthetic dye of Methylene Blue (MB), which has an empirical formula of $C_{16}H_{18}ClN_3S$. Due to their complex chemical structure; synthetic dyes are harder to biodegrade and thus more resistant to conventional biological treatment (Bakre, 2018).

Conventional methods used for the removal of MB from wastewater system involves physical and chemical processes, photocatalytic degradation, ion exchange, electrochemical, coagulation, physicochemical treatment and adsorption. This method can be used to treat industrial effluent or treat drinking water. Those methods are also expensive and ineffective in the treatment of various dyes in wastewater. Conventional methods cannot be utilized to remove synthetic dyes from dye effluent and wastewater due to their inexpensive and efficient solid supports was considered as a simple and economical method for the removal from wastewater (Zhou, Lu, Zhou, & Liu, 2019). As a result, adsorption is one of the most effective techniques to remove the dyes. The treated water quality was higher when dye effluents were

treated using the adsorption method than other removal methods. The only drawback of this method was the high cost of adsorbents, but with the development of low-cost equally effective adsorbents, it has become a cost-effective way of dye removal all over the world (Katheresan et al., 2018). In various processing technologies, adsorption is widely considered to be superior to other technologies in terms of cost, flexibility, design simplicity, ease of operation, and sensitivity to toxic pollutants (Sardar, Manna, Maharana, & Sen, 2021).

The adsorption process is effective on both an industrial and laboratory scale. The rate of adsorption is affected by factors such as the adsorbent dose, the contact time between the adsorbate and the adsorbent, the dye concentration, the pH of the solution, and the temperature of the solution. The rate of adsorption is affected by changes in any of the five factors. When doing lab-scaled tests, optimal adsorption conditions should be specified to confirm that the appropriate rate of removal is achieved. This can aid in the development and improvement of industrial-scaled dye removal methods (Q. Zhao et al., 2018). Furthermore, research has shown that agricultural by-products can be easily modified to increase their adsorption capacity to form activated carbon inexpensive and commonly available suitable adsorbent materials are found in a wide range.

Biochar is a cost-effective carbonaceous material. It has abundance in feedstock, high surface area, micro-porosity and ion exchange capacity material recently some studies focused on the preparation of activated biochar from different agro by-products like livestock manure, sludge, sugarcane bagasse, industrial waste, etc. it identified as economic sources for the preparation of activated biochar with the improvement of modifying environmental pollutions (Hiloidhari *et al.*, 2020), etc. Adsorption capabilities and mechanisms differ depending on the physicochemical qualities of the adsorbent.

Biochar production is a complex physicochemical process that is influenced by organic substances, pyrolysis mechanisms, and interactions of biomass's primary components such as cellulose, hemicellulose, and lignin. Many factors determine the characteristics of biochar, including the biomass feedstock, the pyrolysis temperature, and the residence duration at the pyrolysis temperature, and the pyrolysis environment. Two major factors affecting the properties of biochar are the temperature of preparation and the parent material (raw material, precursor, and feedstock). Researchers examined the potential of agricultural

wastes as a feedstock for biochar production by slow pyrolysis (Yuan, Wang, Pan, Shen, & Wu, 2019).

Although activated carbon has a large specific surface area and high adsorption capacity, it has a very high production cost compared to other adsorbents such as silica gel, alumina, adsorption resin, and so on. In developing countries, the technique for producing high-quality activated carbon is not yet fully established; thus, there is a need to produce activated carbon from less expensive and readily available materials that can be employed on a wide scale economically. Providing a cost-effective and ecologically friendly adsorbent for the removal of dyes from aqueous solutions appears to be critical, based on what has been said (El-Sayed, Yehia, & Asaad, 2014). As a result, finding low-cost, high-efficiency, and ecologically acceptable adsorbents to remove MB is critical. Some research studies described chemical activation with an alkali hydroxide or acid solution, followed by heat treatment. The activated carbon has good adsorption ability, according to the results. The chemicals used for activation, on the other hand, are not environmentally friendly. After activation, liquid waste has a higher environmental impact and requires treatment. The effort has been performed to synthesize activated carbon with steam activation as part of the effectiveness of bagasse waste from the sugar industry.

The biochar has a large surface area, a porous structure, and functional groups, indicating that it could be a suitable alternative for removing various contaminants from wastewater. Furthermore, earlier biochar adsorption studies have reported that the degree of MB adsorption capability changes with temperature. The reason is that biochar's adsorb ability is greatly influenced by its physical and chemical characteristics. For 1h, carbonized bagasse activated by steam obtained an optimal temperature of 800°C (Xia, Noda, Kagawa, & Wakao, 1998). The carbonized residual biomass sources were treated with steam at 110°C, which is required for activation (Jaguaribe, Medeiros, Barreto, & Araujo, 2005). Activated carbon extracted from olive bagasse was created at 900°C for 45 minutes under a steam atmosphere, and the surface area rise to 1106 m^2/g (Demiral, Demiral, Karabacakoğlu, & Tümsek, 2011), similar to N_2 activation and activation under various chemical atmospheres (Rahmawati et al., 2021). The optimum surface area obtained by bagasse fly ash at 700°C for 1h steam activation was only 656 m^2/g, whereas activation using KOH as the chemical agent at 700°C raised the

surface area to 2571 m^2/g (Purnomo, Salim, & Hinode, 2012). An increase in surface area, followed by an increase in aromatic surface groups and a decrease in polar/nonpolar surface groups, was recently reported by rising the steam activation time (Muthmann *et al*., 2020), even though the interaction mechanism was not developed.

The above studies were discussed chemical activation with activated-carbon treated by alkali hydroxide or acid solution, followed by a heat treatment has good adsorption ability, according to the results. The chemicals used for activation, on the other hand, are not environmentally friendly. After activation, liquid waste has a greater environmental impact and requires treatment (Muthmann *et al.*, 2020).

Therefore, the present study was to prepare low-cost adsorbent from agricultural by product SCB biochar at different temperature, to examine the potential of sugarcane bagasse biochar, as a non-conventional adsorbent in the removal of a MB dye from wastewater and the effectiveness of alkaline modified biochar. The adsorbent was characterized using Brunauer–Emmett–Teller (BET) method, Fourier transform infrared spectroscopy (FTIR), TGA and scanning electron microscopy (SEM) techniques. The effect of operating parameters like, initial pH, contact time, adsorbent dose and initial contaminant concentration studies were investigated in batch adsorption techniques and the equilibrium effective conditions for these parameters were evaluated. Study of adsorption isotherms and kinetics were carried out and best fitting models for the adsorption process were suggested.

1.2 Statement of the problem

SCB is one possible low-cost agricultural waste it is easily available from sugar factory in Ethiopia as a solid waste. The study forwards the problem for underutilization of SCB from three different perspectives. These are the environmental, economic and health impacts.

Despite of the conversion of the agricultural solid waste in to valuable products such as adsorbent, the economic emphasis for foreign exchanges is one of the issues in sourcing the products. Furthermore the dye effluent in textile factory are considered to be highly toxic to the aquatic species and affect symbiotic process by disturbing the natural equilibrium by reducing photosynthetic activity and primary production due to the colorization of water. Major problems associated with colored effluent are lowering light penetration, photosynthesis

and damages the aesthetic nature of the water surface. Moreover, their degradation products may be teratogenic, mutagenic and carcinogenic. Many dyes may cause allergic dermatitis, skin irritation, and dysfunction of kidney, liver, and brain, reproductive and central nervous system. The management system of SCB is to maximize the economic benefit from the waste resource and maintain acceptable environmental standards. Hence, proper use SCB byproduct could help to mitigate the problem of industries wastewater treatment by adding value of byproduct and produced SCB based activated carbon. Moreover, the uses of biochar prepared from locally available resources in Ethiopia as adsorbent is not well investigated. Therefore in this study was to prepare a biochar locally available agricultural by product adsorbent from sugarcane bagasse and to investigate the removal efficiency of methylene blue from wastewater by using sugarcane bagasse biochar modified by sodium hydroxide chemical activation as a cheap and easily available adsorbent.

1.3 Objective of the study

1.3.1 General objective

The general objective of the study is to investigate the efficiency of Alkali modified biochar from sugarcane bagasse for the removal of methylene blue from wastewater.

1.3.2 Specific objectives

- To prepare, chemically modify biochar and characterize biochar from sugarcane bagasse by SEM, XRD, TGA, BET and FTIR.
- To optimize the dye removal efficiency of biochar and alkaline modified biochar prepared at a pyrolysis temperature of 400^{o}C, 500^{o}C, and 600^{o}C, by varying adsorbent dosage, contact time, pH and initial dye concentration of the aqueous solution.
- Investigate the removal efficiency of selected sugarcane bagasse biochar and biochar modified with NaOH at optimized condition as a sorbent for MB from wastewater.

1.4 Scope of the study

- To achieve the above mentioned objectives, the following scopes drawn;
- Adsorbents were prepared from low cost agricultural waste materials. This includes activated carbon prepared from SCB the carbonization condition was at the

temperature of 400^{o}C, 500^{o}C and 600^{o}C carbonization time 2h. The carbonized sugarcane bagasse was prepared by the treatment of alkaline in order to develop surface area to increase its adsorption capacity.

- The major emphasis of this study was on the utilization of the prepared biochar for the activation of bagasse which was applied for the removal of dyes specifically MB from wastewater.
- The characterization of the adsorbents was limited by the techniques of surface chemistry (FTIR, and proximate analysis), surface morphology and texture (surface area SEM and BET) XRD and TGA.
- Adsorptive capacities of the prepared adsorbents were investigated by Batch mode using central composite design to determine optimal removal conditions and model equation.

1.5 Significance of the study

The study signifies to protect the environment, to make solution regarding health and to intervene in minimizing the economic loss. SCB is one possible low-cost material that can be obtain in large quantities as a solid waste easily available negligible price and deliver locally for the production of activated carbon.

One of the major challenges associated with adsorption using activated carbon is its cost-effectiveness. In the last few years, great attention has been placed utilizing waste, as precursor for producing low cost activated carbon.

Ethiopia most of industries uses activated carbon for treatment of utility water that obtained from ground and surface water, use to remove odor, color, taste however, this activated carbon are imported from external countries because of not produced in Ethiopia. In recent years, the need for safe and economical methods for the elimination of dye from wastewater has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon.

Provide an economical feasible option to produce SCB biochar which will play a major role substituted imported biochar that confirm to be profitable and create job opportunity for

unemployed people in Ethiopia. From the economic point of view, it decreases foreign currency. In general, Due to lack of awareness of its properties and applications, SCB not being utilize effective and application of SCB domestic, industrial processing and alternative solution to disposal problem of SCB. Ethiopia and so that it is substitute product for activated carbon to use for and wastewater treatment.

CHAPTER TWO

2. Literature review

2.1 Wastewater

Large amounts of water and energy exist used during the production processes of textile. When environmental conventions are not required this can have enormous impacts on freshwater biodiversity and freshwater resources. In Ethiopian textile industry will not concern the removal of wastewater. In Ethiopia, several textile and garment factories are not well found with any effluent treatment plants and discharge their effluent directly to surrounding soil and river bodies (Jingyi Li, Liu, & Chen, 2018). From the textile industry, wastewater generated consists of various types of dyes, synthetic chemicals used in industrial processes, and these dyes have high molecular weight and complex structure. As industrialization develops, wastewater treatment requires suitable concern in recent years but wastewater is not only the main cause of environmental imbalance but also to decrease the source of fresh water on the earth. nowadays, there is a demand for new and environmentally friendly wastewater treatment technology as the freshwater is polluting (B. Yadav, Pandey, Kumar, & Tyagi, 2020).

The most important sources of wastewater between many process stages are pretreatment, dyeing, printing, and finishing of textile products the textile industry consumes more than 107 kg/year, and about 90% of dye ends up on fabrics. Dye manufacturers and customers are involved in the strength and fastness of dyes and subsequently are producing dyestuffs that are more challenging to degrade after being used. It evaluated that 10-15% are lost during the dyeing process and released with the sewage among, those dyes methylene blue is the most common (Jose, Samant, Bahuguna, & Pandit, 2020)

METHYLENE BLUE DYE STRUCTURE AND PROPERTY

Methylene blue is known as methylthioninium chloride it is a basic cationic dye with the molecular formula of $C1_6H_{18}N_3SCl$ with a molecular mass of 319.87 g/mol. It is one of the cationic dyes when introduced with aqueous solutions; it gives a net positive charge because

of the presence of chemical groups like amine or sulfur. At room temperature, methylene blue is solid, odorless, dark green powder and gives a blue solution if dissolved in water (Laysandra *et al*., 2017). It is used to several applications like the coating and coloring of paper, hair, cotton, and wool; it is also used as an indicator of oxidation-reduction and as a disinfectant, besides its many other medical usages in medicine, in pharmaceutical formulations, in pesticide production, varnish, and lacquer manufacturing, among others (Zaghbani, Hafiane, & Dhahbi, 2007). The IUPAC name of MB is 3,7-bis (Dimethylamino)-phenazathionium chloride, or Tetra methylene blue, the chemical structure is present in Figure 2.1.

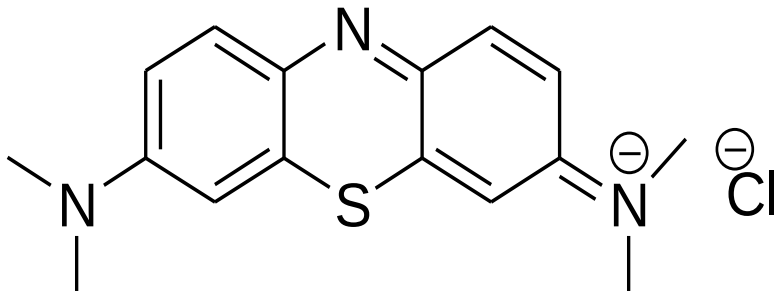

Figure 2.1. Chemical structure of methylene blue

Table 2. 1 Physical and chemical properties of methylene blue

Chemical and physical properties	Values
Melting Temperature	180^{o}C
Boiling Temperature	No data
Solubility in water	35.5 g/L
PH	3(10 g/L H_2O)
Molecular weight	319.09 g/mole
Color Dark	blue-green in oxidized form, colorless in reduced form (leucomethylene blue)
Chemical formula	$C_{16}H_{18}ClN_3S$

2.1.1 Industrial and medicinal uses of methylene blue

MB dye is used in dye, paint production and wool dying. Various dyes are widely used in different industries, such as textile, paper, rubber, plastic, leather, food and pharmaceutical Medicinal use of MB includes therapeutically in the treatment of methemoglobinemia and cyanide poisoning (Tronsmo *et al*., 2016). Other medicinal uses of methylene blue include the management of chronic urolithiasis and treatment of cutaneous viral infections as well as the treatment of manic-depressive psychosis. MB is also used to increase vascular tone myocardial function in a patient with septic shock. Generally, MB is used safe drugs with dose-related hemolytic effect (Hosseinian, Weiner, Levin, & Fischer, 2016)

2.1.2 Toxicological effect of methylene blue in human and animal

Methylene blue has been acute exposure found to cause increased heart rate, cyanosis, vomiting, shock, jaundice, quadriplegia, and tissue necrosis in humans. Furthermore, corneal and conjunctival injury has been reported following acute exposure to this compound. (Gupta, Kushwaha, & Chattopadhyaya, 2016). Methylene blue has been acute exposure found to cause increased heart rate, cyanosis, vomiting, shock, jaundice, quadriplegia, and tissue necrosis in humans. Furthermore, corneal and conjunctival injuries have been reported following acute exposure to this compound (Gupta, Kushwaha, & Chattopadhyaya, 2016). It is an Intravenous administration that causes bluish discoloration of the urine and stool. Several data reports found in the literature relating the effects of methylene blue on the baby, following the injection of this compound into the amniotic fluid before delivery, following the injection of this compound into the amniotic fluid before delivery (Amarah, 2015). Methylene blue-containing Chronic application of eye drops has been found to result in staining of the bulbar and palpebral conjunctiva, the lid margins, and slight staining of the corneal epithelium (N. Kumar, Singh, Sharma, & Kishore, 2019). Methylene blue has been found to cause an elevation in follicle-stimulating hormone and estradiol in fallopian tube secretions, and uterine and peritoneal fluids in vitro. In addition, methylene blue was found to significantly prevent sperm motility in vitro in samples prepared from human semen (Nazem, Aharon, & Copperman, 2020).

In different literature describe various reports were found the association in animals. In cats, methylene blue was observed to cause bluish-stained skin, anemia, discolored urine, dyspnea, depression, respiratory stimulation, and increased blood pressure. In addition, methylene blue causes corneal and conjunctival injury in rabbits. No data were available on the pre chronic, effects of methylene blue in animals (Rosique *et al.*, 2017). Administration of this compound at a concentration of 4% in the diet for 2years was not found to induce tumor formation. Methylene blue inhibits the ability of mouse embryos to grow and cleave in vitro. This compound also caused an increase in implantations and resorptions in litters born to rats fed a diet containing methylene blue. MB toxicity has followed at a wide range of doses. Dose related toxicity of MB is summarized in table 2.2 (Rosique *et al.*, 2017)

Table 2.2. Dose relate toxicity of MB dye

Animal studies	Toxic doses (mg/Kg)	Manifestation
Rat	5-50	Neuronal apoptosis, reduced MAC isoflurane
Dog	10-20	Hypotension, decreased SVR, renal blood flow, pulmonary hypertension
Human studies	Toxic doses (mg/Kg)	Toxic Manifestation
	2-4	Hemolytic anemia, skin desquamation in infants
	7	Nausea, vomiting, abdominal pain, chest pain, fever, hemolysis
	7.5	Hyperpyrexia, confusion
	80	Bluish discoloration of skin (similar to cyanosis)

2.1.3 Methylene blue dye in industrial effluents

About 70,000 tons of approximately 10,000 of dye and pigments produced worldwide industries can affect our atmosphere 20%-30% are wasting in industrial effluents through the textile dyeing and finishing process. Dyes are usually used in textiles, printing, pharmaceuticals, food, toys, paper, plastic, and cosmetics and also use chemicals like dyes, acids, alkalis, starch, and surfactants these industries can affect our atmosphere (Amarah, 2015). The waste released from these industries can affect our atmosphere causing pollutions. The textile industry is a large factory in terms of raw materials, processes, products,

equipment, and complicated industrial chain (Behera, Nayak, Banerjee, Chakrabortty, & Tripathy, 2021). In the textile industry, different methods of color impregnation in fibers use detergents, dye, microfiber, and inorganic salts. These processes produce a large amount of wastewater having toxic pollutants leading to the contamination of natural water bodies. Most of the dye used in the textile industry consumes large amounts of water during the manufacturing process also discharges a large number of effluents with synthetic dyes into the environment causing public concern (Eyupoglu & Merdan, 2018). MB dyes applied in textile industries are considered health-risk factors. Several physicochemical and biological methods for dye removal from wastewater investigated in the last decades (Kausar *et al*., 2018). Synthetic dyes are commonly used in most textile industries. Over 7 lakh tones of about 10,000 different types of dyes and pigments are produced worldwide (Kiran *et al*., 2019).

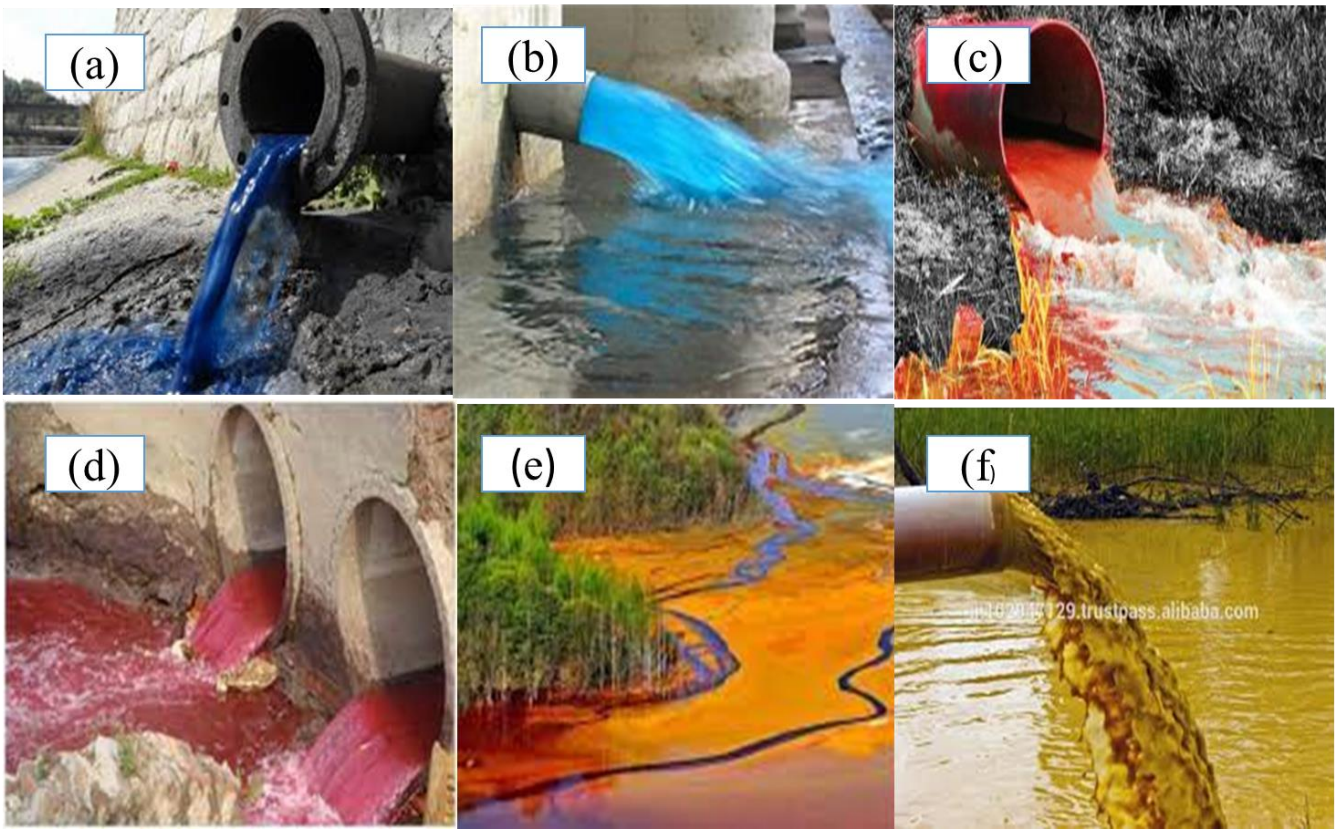

Figure 2.2. Dye-containing wastewater from textile industries

2.2 Methods of treatment for removing dyes

The manufacture of liquid effluent pollutants due to the high quantities of water used in dyeing processes is the textile industry. Conventional biological, physical, and chemical techniques like sedimentation, flocculation, aerobic, and anaerobic treatment were used to remove dyes that require higher initial costs for the treatment (Mani, Chowdhary, & Bharagava, 2019). The most popular methods for the decolorization of the effluents are precipitation, ion exchange, reverse osmosis, and biosorption. Biosorption is the most versatile and commonly used technique out of these methods (V. Yadav, Ali, & Garg, 2021). These processes are expensive and cannot efficiently be used to treat the wide range. One of the current processes in treating dyes wastewater is adsorption (Katheresan et al., 2018). It is an effective method for the removal of dyes from wastewater it's important to the sludge-free clean operation and is completely removed even from the diluted solution. The removal of MB by using activated carbon in the adsorption process has able to established by effectively treatment cost using the adsorbent is considered expensive due to its high energy cost (Natarajan, Bajaj, & Tayade, 2018). Lignocellulosic is composed of dry matter plant Lignocellulosic biomass 25–30% hemicellulose, 40–50% cellulose, 15–20% lignin, and traces of pectin, nitrogen compounds, and inorganic components this is the most promising source of renewable raw material. Lignocellulosic for various biotechnological processes useful bio-based chemicals and fuels due to low economic value and high availability (Arevalo-Gallegos, Ahmad, Asgher, Parra-Saldivar, & Iqbal, 2017). Therefore, in this study, sugarcane bagasse SCB is use as a low-cost bio- sorbent for removal of MB dye present in textile wastewater. Sugarcane bagasse contains approximately 30% - 50% of cellulose and 20% - 24% of lignin. It is many different functional groups that act as adsorptive sites, including –OH, –COOH, –NH_2, –$CONH_2$, –SH_2, and –OCH_3 groups (Andrade Siqueira et al., 2020). These sites enable the bio adsorbents to attract and bind pollutant ions, either by replacing them with hydrogen ions (ion exchange), adsorption, or by the donation of electron pairs (complexation) this unique binding sites are effective to remove pollutants (Sarker, Azam, Abd El-Gawad, Gaglione, & Bonanomi, 2017). Therefore sugarcane bagasse is one of the lignocellulosic material in this paper use these materials to remove MB from wastewater (Khan, 2017). Sugarcane bagasse is a solid industrial waste remaining after crushing the sugarcane to obtain

its juice. This leaves a large amount of excess bagasse available for possible utilization for purposes outside the milling process (Varshney, Mandade, & Shastri, 2019). Also, excess biomass obtained from the cane harvesting process is available. It amounts to approximately 25 -30 % of the sugarcane mass. The sugarcane bagasse is currently used as the main source of energy required by the sugar and ethanol mills for generating electricity to be sold (Hanaki & Portugal-Pereira, 2018). It is sure that with the necessary technological improvements of the boilers and the processes. It is possible to supply the energy needs of the plants with only half of the produced bagasse. The sugarcane bagasse excess could be more than forty different applications, such as the production of biofuel, pulp and paper, boards, animal feed, and furfural (Chandel *et al*., 2019). For this sugarcane bagasse and its derivatives can efficiently remove a wide range of target adsorbates from aqueous solutions, including toxic heavy metals, dyes, petroleum, phenolic compounds, and organic nutrients.

Moreover, sugarcane bagasse is easily treated and modifiable and it amalgamates well with other agro-industrial residues, including tea waste, corncobs, sawdust, apple peel, and grape stalks (Sarker *et al*., 2017). Sugarcane bagasse has a higher MB removal capability than commercial activated carbon, depending on the pH of the water medium and the type of sugarcane bagasse (Ejaz, Muhammad, Ali, Hashmi, & Sohail, 2019). Sugarcane bagasse shows that much better performance adsorbing MB in an alkaline environment than in an acidic environment. Because of this alkaline or sodium hydroxide modified sugarcane bagasse is extremely higher removal capacity of unmodified sugarcane bagasse (Sarker *et al*., 2017).

Therefore this paper is to prepare biochar from sugarcane bagasse and treaties with alkaline to remove MB from wastewater this work is not done by the previous researchers. Treatment using alkali solution (mercerization) has been proven to be effective for removal of lignin in the fibers therefore enhanced fiber surface adhesion which allowed an effective stress transfer from matrix to fiber. Relatively fewer studies have investigated the surface modification on lignocellulosic fibers obtained from sugarcane bagasse (Zuccarello & Zingales, 2017). The goal of this current work is to investigate the effect of different treatment time on the structural and morphological modification on sugarcane bagasse fibers treat with sodium hydroxide (NaOH).

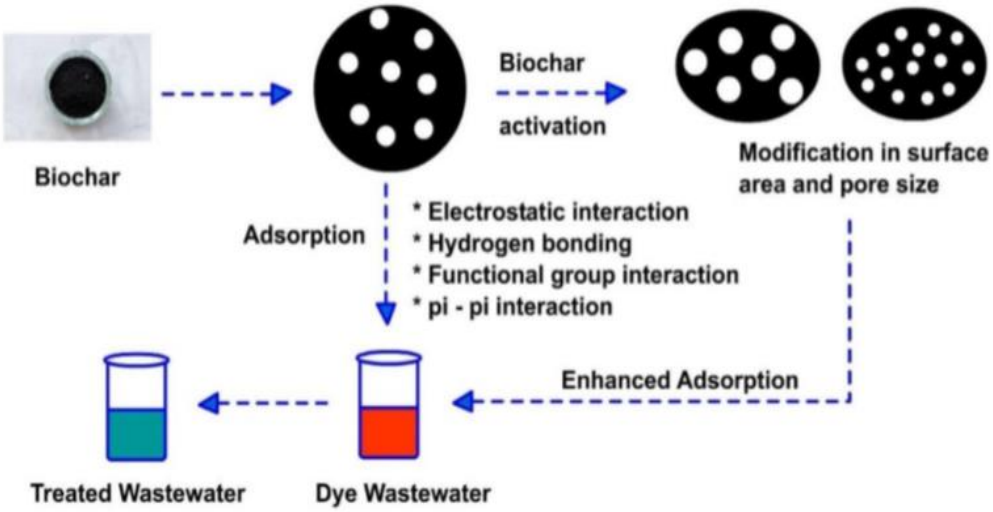

Figure 2 dye adsorption mechanism using biochar

Figure 2.3. Dye adsorption mechanism using biochar (Qiu, Zheng, Zhou, & Sheng, 2009)

2.3 Biochar production process

Biochar is a porous carbon-rich solid material derived from the thermochemical conversion of biomass under a limited/no oxygen environment. Biochar production includes pyrolysis and minor extent from gasification and imperfect combustion processes (Akhtar, Krepl, & Ivanova, 2018). Biochar has been used as an efficient and cost-effective environmentally sorbent for the removals of MB effectively. The biochar production process is environmentally caring as it decreases the formation of dangerous products reduces the emission of contaminants unlike the direct burning of biomass (Shaheen et al., 2019). The biochar produced varies with composition, porosity, surface area and, total pore volume variation in biochar properties depends on the biomass type, preparation conditions such as heating temperature, reaction time, and activation methods. There are various methods to modify biochar to improve its properties for the environmental application, particularly as adsorbents for the removal of MB includes physical (steam or gas purging), chemical oxidation, steam activation, microwave, and impregnation with nanoscale materials activation methods. (Tomczyk, Sokołowska, & Boguta, 2020).

PYROLYSIS

Pyrolysis is the most common method used as biochar production of splitting a substance into new compounds by using heat in a low oxygen environment. It comes from Greek words for fire and splitting. Pyrolysis is a thermal process mainly used for converting solid materials to gas, liquid, and new solid formations. It is the first stage of the thermal breakdown processes before the gasification stage and the full combustion stage (Pecha & Garcia-Perez, 2020). Based on the reaction temperature, heating rate and residence time pyrolysis process can divide into two. Slow pyrolysis can be divided into traditional charcoal making and more modern processes. It is characterized by slower heating rates, relatively long solid and vapors residence times, and usually a lower temperature than fast pyrolysis, typically 400℃ (Ronsse, Nachenius, & Prins, 2015) . The solid char target product is often, but this always to be accompanied by liquid and gas products although always recovered. Among productions methods, slow pyrolysis appears to be the optimal process for maximizing Biochar output. Any reactor that utilizes particles larger than 2mm in diameter is considered a slow pyrolysis reactor. Modified slow pyrolysis is shown as follows (Campbell, Anderson, Daugaard, & Naughton, 2018). Fast pyrolysis is described as a pyrolysis regime in which vapor production is enhanced and char minimized by rapid heating. Fast pyrolysis is characterized by high heating rates and short vapor residence times. This generally requires feedstock prepared as small particle sizes and a design that removes the vapors quickly from the presence of the hot solids. There are many different reactor configurations that can achieve this including ablative systems, fluidized beds, stirred or moving beds, and vacuum pyrolysis systems (Venderbosch, 2019).

GASIFICATION

Gasification is thermochemical process to transform biomass into a combustible gas mixture by partial oxidation at a high temperature above 800^0c. Gasification can be conducted by various gasification agents such as air steam or oxygen. The product is mainly a mixture of gases CO, H_2, CH_4, and CO_2 often referred to as producer gas. Syngas is the upgraded producer gas to mixture of H_2 and, CO. Syngas allows the production of methanol and hydrogen, which can be used as a potential fuel for transportation (Sridhar, 2016).

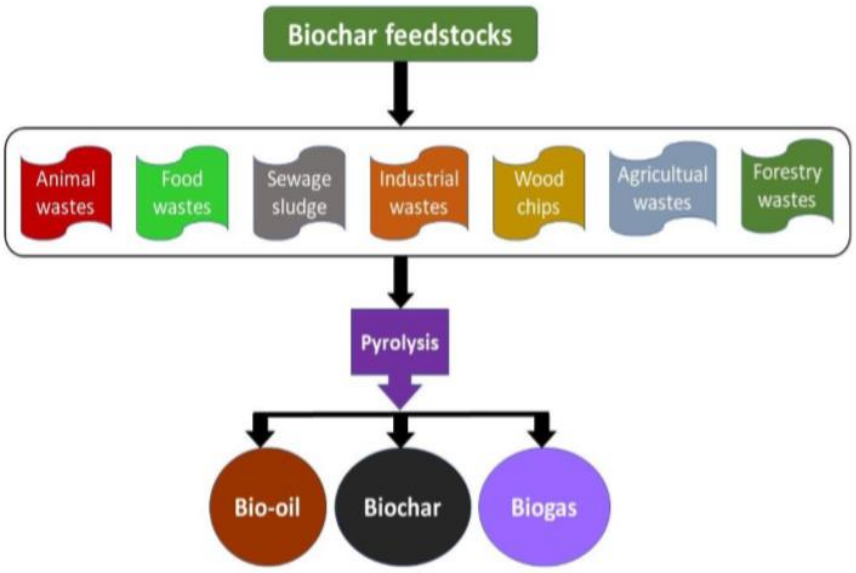

Figure 2.4. Conversion route of biomass (Panwar, Kothari, & Tyagi, 2012)

2.4 Factors affecting biochar production

Depend on the various types of feedstock uses the moisture content of the feedstock and, the operating temperature and pressure point the performance of biochar production technologies broadly. Biomass mainly consists of cellulose, hemicellulose, and lignin, with small amounts of minerals that varied in composition according to biomass type (Weber & Quicker, 2018) The moisture content of biochar may be due to the natural water content in the raw biomass species. The moisture content affects the char reaction and is extensively used to produce activated carbon. In the fast pyrolysis processes around 10% moisture content is fairly desirable during the charcoal-making process, with feedstock having 15–20% moisture that can be carbonized (Nanda, Dalai, Berruti, & Kozinski, 2016). In the production of biochar thermochemical process and temperature plays a major role in the properties of biochar and its suitability for soil health. Biochar can be produce in laboratory scale to the ability of pyrolysis from pin, mixed larch and spruce chips and from softwood pellets with various temperatures between 350 and 550^0c. The stability of biochar increases as the temperature increases, and the yield of biochar are independent of temperature (Panwar, Pawar, & Salvi, 2019). The chemical and surface properties of biochar are affected by pyrolysis temperature. The volatile matter, hydrogen and oxygen contents of the biochar were decreased the pyrolysis temperature

is increased from 400 to 700 °C, but the value of fixed carbon was increased. At low pyrolysis temperature (300^0c) biomass cannot be converted into biochar because at this temperature the desired carbon frame structure has not developed (S.-X. Zhao, Ta, & Wang, 2017). The reactor operating temperature plays a vital role in deciding the fixed carbon and oxygen content of biochar. It has been found that higher operating temperatures have higher fixed carbon contents and lower oxygen contents. Operating pressure also affects the biochar yield. The two phase properties of olive mill wastes absolute effect of pressure (0.1 – 1.5 MPa) and peak temperature. Both absolute pressure and peak temperature results in a decrease in biochar yield through the fixed carbon yield increase (Manyà, Azuara, & Manso, 2018).

The effect of particle size along with pressure and peak temperature on stability of vine shoot derived biochar. The pyrolysis process carried out at high temperature (750°C) electrical conductivity significantly increased, but there is scope vitalization of heavy metal (Zn) with the low melting point. Pyrolysis operating reactor under high pressure and high temperature maximizes pyrolysis gas production, but reduces the char yield (Panwar *et al*., 2019).

2.5 Modification of biochar surface properties

In order to enhance the affinity of biochar for pollutants (to improve the adsorption capacity of biochar) and increase the removal efficiency of pollutants, various methods are used to modify the physical/chemical properties of biochar such as varying the specific surface area, pore structures, and content of the functional group(Y. Li, Xing, Ding, Han, & Wang, 2020b). The activation methods are either one-step activation, where pyrolysis and modification step are achieved simultaneously two steps activation, where direct pyrolysis of biomass is followed by modification methods (Dai, Zhang, Xing, Cui, & Sun, 2019). The common methods of biochar modification include chemical modifications, physical modifications, impregnation with nanoscale materials, and microwave-assisted modifications. Chemical modification is the most widely used method of surface oxidation modification by adding acids, alkaline, oxidizing agents, metal salts, or carbonaceous materials(Godwin, Pan, Xiao, & Afzal, 2019).

Acidic treatment (e.g., HCl, or HNO_3, weak acids such as oxalic acid and citric acid) usually increases the surface area of biochar has a slightly lower average surface area than other types of modifications due to the breakup of pore structures. Increasing concentration of acids

increased the number of acidic functional groups (such as hydroxyl, carboxylic, ketonic, and other oxygen-containing moieties) on biochar surface studied biochar's modified with 0.1M − 1.0M CH_3COOH and H_2SO_4 revealing an increase in the amount of acidic functional groups from 13 to 17% and from 9 to 15%, respectively (Panwar & Pawar, 2020). A significant increase of acidic functional groups for biochar's, modified with HCl and HNO_3 occurred only at the highest concentrations of these acids. Acid treatment increases in O/C and H/C ratios of biochar indicated that a decrease in hydrophobicity and increase in polarity hence it promotes the chemisorption of hydrophilic pollutants (e.g., inorganic contaminants from wastewater.) (Y. Li, Xing, Ding, Han, & Wang, 2020a).

The physical modification mainly includes steam and gas purging methods. The steaming activation method increases the porosity and introduces more oxygen-containing functional groups to the biochar. It increases the aromaticity and hydrophobicity of biochars (Vijayaraghavan, 2019). In the steam activation process, firstly biomass is heated at the temperature of (300–700 °C) in the limited amount of oxygen followed by conveying it to a reactor and further heating at higher temperature (800–900 °C) with the agents such as CO_2, N_2, and steam. The steam activation of biochar made from sugar cane bagasse has shown that at 700 ºC, 800ºC, and 900ºC produce biochar with a large surface area of 441 $m^2\ g^{-1}$, 570 $m^2\ g^{-1}$, and 561 m^2g^{-1} respectively. (Ravenni, Elhami, Ahrenfeldt, Henriksen, & Neubauer, 2019). Under steam gasification, the surface areas increase with increasing temperatures hence can improve the adsorption capacity of the biochar. They also determined the surface area for N_2 gas purging activation of the biochar. The surface areas of the biochar at 800 ºC and 900 ºC were 349 m^2g^{-1} and 452 m^2g^{-1} respectively. The result indicates the efficiency of N_2 gas purging activation is lower than the steam activation method at a given temperature (Dobbs, 2017).

Biochar activation by using nanoscale materials such as nanometals, nonmetal oxides, and nanometal composites (alloy) provides advantages higher number of pore volume, surface area, well-distributed active sites, fast electronic transfer, and magnetic properties of biochar because of the smaller particle size of nanoscale materials. Iron metal oxides such as magnetic Fe_3O_4 nanocomposite and nano zero-valent iron (nZVI) activation increase the magnetic properties of biochar hence the affinity of biochar for toxic heavy metal pollutants increase.

However, the leakage of metal ions from the biochar materials is a problem after activation (Ndirangu, Liu, Xu, & Song, 2019).

Recently microwave-assisted pyrolysis was applied as a better activation method of biochar than the conventional heating methods. Microwave-assisted activated biochar possesses improved porosity, specific surface area, and total pore volume than the biochar obtained by traditional pyrolysis methods (X.-f. Tan *et al*., 2017). Microwave heating offers many advantages over conventional pyrolysis such as rapid heating rate, excellent heat transfer, energy savings at lower processing temperatures, easily controllable, higher heating efficiency, energy transfer rather than heat transfer, less feedstock pre-treatment needed, and decreased production costs. The microwave steam activation of biochar derived from waste palm shell for the adsorption of methylene blue was studied (Jing Li et al., 2016). The result provided the highest activated biochar yield of 80 wt% with the highest adsorption efficiency 38.5 mg of methylene blue dye/ g of activated biochar (94% removal efficiency) were obtained at 550 °C of activation temperature, 10 min of activation time, and 70 g of biochar used. The activated biochar produced was detected with a high micropore area and surface area of 763.1 m^2/g and 570.8 m^2/g, respectively (Sajjadi, Chen, & Egiebor, 2019).

Alkaline treatment of biochar (using alkaline chemicals such as KOH, NaOH, NH_3, K_2CO_3 and $ZnCl_2$) produces a larger surface area with a higher ratio of surface aromaticity (H/C) and higher N/C ratio with lower value of O/C compared to acid modified biochar. Modification of biochar with oxidizing agents such as H_2O_2 and $KMnO_4$ increases the oxygen containing functional groups by introducing mainly the carboxylic groups and increase the surface area of biochar (Takaya, 2016). This project use this modification of biochar due to the complexity of the high surface site after chemical treatment, high surface modification, SCB with low lignin residue content is the most favorable adsorbent for MB adsorption and the cellulose rich BSCB could better remove organic dyes in neutral alkaline water environment.

2.6 Application of biochar based adsorbents for the removal of organic pollutants

In recent reports, high efficiency removal of organic pollutants from industrial effluents was observed for biochar; however, the physicochemical properties of biochar may play as limiting factors the disposal of organics and inorganics has become a serious environmental problem, and due to this, there have been stringent regulations for such wastes (Ambaye, Vaccari, van Hullebusch, Amrane, & Rtimi, 2020). Recent research articles showed that technology-based on biochar adsorption is effective in removing heavy metals from wastewater. This material has good adsorption capacity for typical industrial wastewater pollutants such as potentially toxic metals, organic pollutants, phosphorus and nitrogen compounds (Gunatilake, 2015). Biochar can be used as a release controlling agent in fertilizers thanks to its good adsorption capacity for phosphorus and nitrogen as previously reported. Because biochar is an environmentally friendly absorbent, the knowledge of its physicochemical properties and a systematic understanding of the adsorption mechanisms is a matter of topical interest (Ambaye *et al*., 2020). The adsorption mechanism of biochar to remove organic and inorganic pollutants can be based on electrostatic interaction, ion exchange, pore filling and precipitation. This depends upon the physiochemical characteristics of biochar such as dosage, pyrolysis temperature, pH of the medium/ effluent However, due to rapidly growing urbanization and industrialization in developing countries, a large volume of wastewater is generated, which contains chemicals generating high environmental risks which could affect health and socio- economic activities (Abbas *et al*., 2018).

Consequently, the application of biochar in wastewater treatment and water purification gets increasing attention even if there is a lack of data dealing with adsorbents for industrial wastewater treatment. In this paper, we review various forms of biochar sorbing materials for the abatement of pollutants from industrial wastewater. The biochar characterizations involved during pollutant adsorption are discussed, as well as biochar regeneration (Shaheen *et al*., 2019). Its economic and environmental benefit is also analyzed, especially regarding its application on a large scale. The review also highlights the future research directions, especially regarding environmental applications of biochar. Biochar itself has the advantages of large pores, high surface area, and rich surface functional groups. Rich surface functional

groups are considerably more important than high porosity in the adsorption process (Ambaye *et al*., 2020)

Application of biochar prepared from different biomasses for textile effluent treatment has been reported by some researchers. Table 3 shows a comparison of adsorption capacity of different biochar's for methylene blue (Y. Wang & Liu, 2017).

Table 2. 3. Comparisons of biochar are used in the adsorption of methylene blue

Biochar adsorbent type	Maximum adsorption capacity (mg·g-1)	References
Water Hyacinth based biochar	44.13	(Mathew, Desmond, & Caxton, 2016)
Palm oil Empty Fruit Bunch biochar	55.25 at 30°C	(Mathew et al., 2016)
Sawdust-derived biochar	333.33	(Ghani *et al*., 2013)
Biochar from co-pyrolysis of dewatered sludge and pine sawdust	16.75	(CHENG, SUN, JIAO, & XIAO, 2013)
Wheat straw biochar	12.04 ± 0.41 at 293 K	(Liu, Zhao, Li, Ma, & Han, 2012)

2.7. Mechanism of MB removal by biochar based adsorbents

The adsorption mechanism removal of dyes from wastewater using various biochar includes different complex interactions both chemically (chemisorption) and physically (physisorption) between the adsorbate (dye) and adsorbent (biochar). In adsorption technique the adsorbents and adsorbate are interact physically (Physisorption) or chemically (Chemisorption) mechanisms these are various interaction mechanisms. Physical adsorption is an important surface phenomenon caused by intermolecular force of attraction is called van der Waals forces. In addition the adsorbate can form a multilayer in physical adsorption mechanisms to provide high adsorption capacity. Whereas chemical adsorption is irreversible in nature and it is referred to as activated adsorption. It is mainly involve in catalysis so the energy of chemical adsorption is considered similar with chemical reaction and the process may be

exothermic or endothermic. This adsorption process is requires activation energy. In chemical adsorption the adsorbate is forming a monolayer adsorption process that provides high adsorption capacity. Chemical adsorption is occurring by ion-exchange, electrostatic interaction, surface complexation, π-π interactions; cation-π interactions could play important roles in the adsorption process (Sun *et al*., 2012).

2.8. Factors affecting the dye removal efficiency in the adsorption process

Effect of Contact time

Some researchers state that the removal efficiency of dye increases rapidly with time up to 60 min and then the adsorption rate decreases gradually. This shows that the contact time is high between dye and adsorbent, the removal efficiency is higher until the equilibrium time is reached (Subramaniam & Ponnusamy, 2015). Effect of time in adsorption system is necessary to develop the cost-effective procedure. Removal time significantly depends on AC surface properties such as pore size, pore-volume, and surface. In wastewater treatment procedures, decreasing the removal time is necessary. The adsorption of MB onto AC was studied in various contact times to control the suitable adsorption equilibrium time (M Ghaedi, Nasab, Khodadoust, Rajabi, & Azizian, 2014). The initial adsorption rate is increase because of the high available surface area and vacant site of prepared AC and then gradually increases with rising time and reaches equilibrium contact time (M Ghaedi, Nasab, et al., 2014).

Effect of adsorbent dose

The amount, size, and pore volume of adsorbent significantly influence the capacity of adsorption toward various molecules. The vacant site and pore size of the adsorbent limit the rate and amount of migration of dye molecules to the adsorbent surface. AC reaction sites depend on the number of adsorbents (M Ghaedi, Ansari, Habibi, & Asghari, 2014). The removal efficiency increased sharply with an increasing amount of activated carbon up to a fixed amount of activated carbon then removal efficiency decreased beyond the fixed carbon dosage. Then removal efficiencies did not change significantly with an increasing amount of adsorbent (Menya, Olupot, Storz, Lubwama, & Kiros, 2018). Removal of methylene blue from wastewater using activated carbon prepared from rice husk. This adsorption efficiency

increased due to the increased number of adsorption sites. Therefore, removal efficiency reached equilibrium with a fixed amount of activated carbon (Subramaniam & Ponnusamy, 2015)

Effect of pH

The surface and the type of surface-active centers are indicating the adsorption ability of the significant factor that is the point of zero charge (pHpzc). The point of zero charges (pHpzc) and typically used to quantify the electro kinetic properties of a surface is pH at which the surface charge is zero. The impact of pH is relating pHpzc only for systems in which H^+/OH^- are the potential determining ions (Dinga, *et al*., 2014). The point of zero charge (pHpzc) of many adsorbents prepared from agricultural by product to understand the adsorption mechanism. Due to the presence of various functional group such as OH^- group, cationic dye adsorption is preferred at pH > pHpzc, while, anionic dye adsorption is preferred at pH < pHpzc where the surface becomes positively charged (Yagub *et.al*., 2014). They observed that, the effect of pH on the removal of methylene blue in the presence of activated carbon. When initial pH of the dye solution is increase from 4 to 11 values, the percentage removal also increased from lower to higher. The increasing trend of removal of the methylene blue with increasing pH is dependent on the nature of the adsorbent. At lower pH, the percentage of the removal of methylene blue decrease and interestingly, at higher pH, the trend of the removal was increased. As the electrostatic attraction between the cationic dye and activated carbon is strengthen along with PH increasing, the highest adsorption amount obtained around PH ~10 under testing conditions conversely (Rahman, Amin, & Alam, 2012). Similar result obtained by (Yun, *et al*., 2013; Djilani *et al*., 2015)

Effect of Initial concentration

Removal efficiency is significantly dependent on the initial concentration of a solution of the adsorbate. The removal efficiency is decreased with an increase of initial concentrations while the amount of total methylene blue increases. The total addition of methylene blue increased with increasing initial concentration is possibly due to more contact adsorbent sites with methylene blue. At low concentration, most of the methylene blue in the sample, a solution might contact with active sites of adsorbent and when the concentration is increased all

methylene blue species will not be available to contact with the active surface due to active sites already filled up (Rahman *et al*., 2012).

2.9. Characterization methods of biochar

Biochar characterizations are mainly useful to understand the physicochemical and morphological properties of biochar, to evaluate its applicability in anticipated field and to assess contaminants associated with biochar (Campos *et al*., 2020). In this study, first, representative samples are taken randomly for certain analyses after pyrolysis. Through the entire process of sampling, the biochar is crushing or grinding to reduce the heterogeneity of the sample. After drying and homogenization, the sample is divided into portions and is dried at 40°C flushed with inert gas and will be stored in airtight plastic containers under vacuum below 0°C. The prepared biochar will be characterized for properties including proximate analysis, physicochemical analysis, surface analysis, and structural analysis. The methods used for biochar characterization are based on the standard guidelines suggested by the International Biochar Initiative (IBI, 2015).

CHAPTER THREE

3. Materials and methods

3.1. Apparatus and equipment's

The apparatus and equipment's used during this work are: XRD (Japan, XRD-7000S South Korea,) UV Vis-spectrophotometer ((JASCO T 80+ UV-Vis spectrophotometer) SEM (Inspect F50 made in Japan), Digital electronic balance(FA2104, made in China),Muffle Furnace(Ambassador F-07,Made in India), shaker (IKA KS 4000 I control) pH/conductivity meter(AD8000,Made in Romania),Oven, glass-filters, beakers, Magnetic stirrer(JHMS-6293), filter paper(What man 125 mm), mortar and pestle, glass rod, Pipettes, spatulas, Erlenmeyer flask, volumetric flask, different types of beakers, and sample collection materials(buckets, glass bottles and plastic bottles).

3.2. Chemicals and reagents

The chemicals and reagents used in this study were: Hydrochloric acid (HCl) (Sigma Aldrich), distilled water, Sodium hydroxide (NaOH) (CENTRAL DRUG HOUSE(P) LTD), Sodium chloride (NaCl), Methylene blue ($C_{16}H_{18}N_3ClS$, Mw = 319.87 g/mol) (SAMIR TECH-CHEM, PVT, LTD). All chemicals and reagents used for the study were analytical grades and purchased from the fine Chemical industry and trading (Addis Ababa). All aqueous solutions were prepared using distilled water.

3.3. Methods

3.3.1. Pyrolysis of Sugar cane bagasse (SCB)

SCB was collected from Wonji shoa sugar factory which is located in East shoa zone of Oromiya National regional state at 8.38^{o}N 39.30^{o}E,10 Km from Adama 110 Km East of Addis Ababa, Ethiopia ,lies between 1223 and 1553 m above sea level. The area has a semi-arid climate with a 70 mm ten year mean monthly rainfall temperature of 27^{o}C mean monthly maximum temperature, and 12^{o}C mean monthly minimum temperature. The soil was predominantly Andsols, Fluvisols, Laptosols and Phaezemes, according to the FAO soil classification. 2 kg bagasse sample was collected and washed to remove different impurities,

especially salt and organic compound and dried in an oven at 60^{o}C for 72h. The dry sugarcane bagasse were ground into fine powder using a grinder, sieve with 75μm mesh size. The bagasse powders were washed in distilled water then carbonize by pyrolysis kiln. This process was slow pyrolysis so the temperatures were under the condition of 400^{o}C, 500^{o}C and 600^{o}C for 2h to get biochar.

3.3.2. Production and surface modification of biochar

First the biochar was labeled as nonmodified sugarcane bagasse (NSCB) and modified sugarcane bagasse biochar in sodium hydroxide (BSCB). The BSCB was prepared by mixing 20 g of NSCB with concentrated 1 M of NaOH in 500 mL beaker glass to delignify SCB (Mulinari, 2010). The mixture was left overnight and the SCB were filtered and dried in the oven the next day for approximately 4 h. The SCB was stored as BSCB in a Labeled container.

3.3.3. Characterization of SCB biochar

i). XRD analysis

The mineralogical composition of SCB biochar were conducted by taking a small amount of powder samples packed with standard sample holder and analyzed by using Cu-Kα radiation source at (λ = 1.54 nm), operating at 40 kV and 30 mA. X-ray diffracts grams of SCB biochar powders were obtained for the 2θ angles ranging from 0˚ to 80˚with scans step 0.02˚. All the experiments were performed at room temperature, with a scans speed of 3˚/min, an angular step of 0.02˚, and a counting time of 0.40 sec. Generally, XRD analysis was used Scherer's equation (Equation 3.1) to calculate the average crystallite size of SCB biochar. Generally from XRD analysis Scherer's equation was applied to calculate the average crystallite size of SCB biochar.

$$D = \frac{k\lambda}{\beta\cos\theta}$$

where k:- is Scherer's constant, which is 0.9, λ is the wavelength of the X-ray radiation which is 0.15406 nm, β is peak width at half maximum (radians), and θ is Bragg's angle. This XRD analysis was performed in Jimma Institutions of Technology, at the Department of Material Science and Engineering.

ii). FT-IR analysis

Structural analyses of the SCB biochar before and after adsorption and after desorption were done by FT-IR transmission spectra using the KBr pellets disc technique. This analysis was carried out on Spectrum 65 FT-IR (PerkinElmer) in the wavenumber range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1}, with several scans. The FT-IR analysis was carried out in Jimma Institutions of Technology, at the Department of Material Science and Engineering.

iii). Scanning electron microscope (SEM) analysis

The superficial morphology of the SCB was characterized by scanning electron microscopy (SEM) before and after adsorption of MB was analyzed by JCM-6000Plus Bench Top SEM, JEOL, and Japan. The NSCB biochar, BSCB biochar and MSCB at 400^{o}C, 500^{o}C and 600^{o}C SEM images were taken. The analysis was carried out in ASTU, at the Department of Applied Biology.

iv). Thermal gravimetric analysis (TGA)

Thermogravimetric analyses were carried out using a Perkin Elmer Pyris 6 TGA equipped with a closed perforated pan at a heating rate of 10^{o}C.min^{-1}. Approximately 2 mg of each sample was heated from 30 - 900^{o}C under N_2 gas flow rate of 10 $ml.min^{-1}$. This analysis was carried out in Bahirdar University at the department of chemistry.

v). BET surface area, pore volume, and pore size distribution

Multi point BET method was used in this project to determine surface area of the biochar, and modified biochar as recommended by IBI. The International Biochar Initiative standardized product definition and product testing guidelines of biochar (IBI, 2015) recommend, the Brunauer-Emmett-Teller (BET) involving N_2 adsorption measurements for estimating surface area for biochar, which was originally adopted for the standard test method for black carbon was carried by model nova 4000e, USA. This analysis was done in Bahirdar University at the department of chemistry.

The BET method of N_2 adsorption measurements involves the physical adsorption of N_2 gas at low temperature (77 K) and across a range of pressures. The N_2 isotherm, or volume of N_2 adsorbed versus relative pressure data, is then analyzed to obtain a surface area value generally with pores between 2 and 50 nm in diameter. Surface area analysis is reported in

square meters per gram (m^2/g). Using N_2 sorption isotherms, the specific surface area based on BET (Bru- nauer, Emmett, and Teller) equation can be calculated (Ngan et al., 2019). The specific surface area determined by BET relates to the total surface area (reactive surface) as all porous structures adsorb the small gas molecules.

3.3.3.1. Proximate and ultimate analysis

i) The moisture content

The moisture content was found by oven-drying test method. A sample of biochar weighed accurately 2 g, put into crucible and placed oven at a temperature 105^oC for 24 h. The sample was dried until it reaches to constant weight. Then Sample removed from the oven and cooled in to desiccator at room temperature and after cooled weighed again accurately. The percentage difference of weight is express as the moisture content of the sample (Aller, Bakshi, & Laird, 2017).

The proximate analysis calculations is as follows

Moisture (%) = $(w_1 - w_2)/w_1 \times 100$----------I

ii) Volatile matter

The percentage of volatile matter of the biochar samples was determined by sample of 2 g was taken in crucible with cover. The covered crucible was placed in furnace regulated at 950 ^oC for 5min. Then the covered crucible was cooled to room temperature in a desiccator and recorded the weight. The percentage weight loss was regarded as the percentage of volatile matter.

Volatile matter (%) = $(w_2 - w_3)/w_2 \times 100$----------II

iii) Ash content

Ash content Sample of biochar weighed 0.1g was taken into the crucible of known weight. The crucible was placed in the furnace at a temperature of $700°C$ and ashing was considered to be completed when constant weight is achieved. The crucible is cooled to room temperature in

a desiccator and the percentage weight of the sample remained was considered as ash content ASTM D2866 – 11(2018).

Ash (%) = (w_4 /w_2) x 100----------III

iv) Fixed carbon content

Fixed carbon is a calculated value and it is the resultant of summation of percentage moisture, ash, and volatile matter subtracted from 100.

Fixed carbon (%) = 100 – (moisture, % + ash, % + volatile matter, %)

% Fc = 100 - Mc –Vm –Ac----------IV

The yield of biochar was calculated on a chemical-free basis and can be regarded as an indicator of the process efficiency for the chemical activation process. It calculated as the percentage weight of the resultant biochar divided by weight of dried SCB biochar.

3.3.3.2. Point of zero charge (PH $_{ZPC}$)

The pH at which the Charge of the solid surface adsorbent is zero referred to as the point of zero charge (pHpzc). The point of zero charge of SCB biochar was determined by the solid addition method (Ponnusami, V., & Srivastava, S. N. 2009). 50 mL, 0.1 N of NaCl standard solutions transferred 100ml of Erlenmeyer flasks. The initial pH of solution (pHi) were approximately adjusted from (2, 4, 6, 8 and 10) by adding either 0.1M HCl or NaOH and The total volume of the solution in each flask was made exactly to 50 mL by adding the 0.1N NaCl solution of the same strength (Singh, Bharose, & Verma, 2019). The initial pH of solution accurately noted and added 0.5 g of adsorbent to each flask and cover immediately. The suspensions were shaken and allowed to equilibrate for 24h. Finally; the final pH values of the supernatant liquid (pH_f) were noted. The final pH value in y-axis was plotted against the initial pHi (x-axis). The point of intersection of the resulting curve with the x-axis gave the pHpzc (Miyah *et al*., 2017).

3.4. Batch adsorption experiment procedures

Batch mode adsorption studies for individual parameters were carried out using a 250 mL Erlenmeyer flask and the parameters such as adsorbate concentration, adsorbent dose, contact time, and pH were studied (Raposo, De La Rubia, & Borja, 2009). The Erlenmeyer flask was treated with the adsorbate for 24 h to avoid adsorption of adsorbate on the container wall. Standard solutions of the MB dye were mixed with the modified sugarcane bagasse adsorbent and agitated at different agitation rates on a mechanical shaker (Wen, 2017). These procedures were used to determine the optimum adsorption time, effect of adsorbent dose, effect of pH and effect of SCB concentration on the removal rate of MB (Buthiyappan, Gopalan, & Raman, 2019). Finally, the resulting suspension of each of the dyes was filtered using a Whitman filter paper then the filtrate was analyzed for the corresponding MB dye concentration. Removal efficiency will calculate by using the relationship.

The adsorption capacity of the modified sugarcane bagasse biochar was the concentration of the MB dye on the adsorbent mass and calculated based on the mass balance principle.

$$q_e = \frac{Co - Ce}{m} \times V \quad \text{.....(I)}$$

Where qe = adsorption capacity of modified sugarcane bagasse (mg/g)

V = the volume of reaction mixture (L).

m = the mass of the biochar (g)

Co = the initial concentration (mg/L) of the MB dye and

Ce= final concentration (mg/L) of the MB dye.

3.4.1. Calibration curve methylene blue solution

The preparation of 1 g/L stock solution of MB dye was performed by dissolving 1g of commercial-grade MB dye in a1L volumetric flask by filling distilled water up to mark at room temperature. Then, the storage bottle was wrapped with aluminum foil to prevent de colorization of the solution as MB was naturally very sensitive to light. The λ max (665 nm) absorbance observed on UV-Vis spectrum obtained for 10 mg/L solution indicated in Figure

5, confirmed the stock solution was MB dye. Thus, the wavelength of 665 nm was selected for determining the remaining concentration of MB after batch adsorption experiment (Utomo, Phoon, Shen, Ng, & Lim, 2015; Vijwani, Nadagouda, Namboodiri, & Mukhopadhyay, 2015).

3.4.2. Effect of contact time:

Contact time is one of the most important parameters for the assessment of practical application of adsorption process. 50 mL of the working solution which was 50 mg/L concentration was put in each different conical flask. An adsorbent dose of 0.2 g/50 mL and an initial pH of 8 were used. All the flasks were put in the shaker at 150 rpm and 25^{o}C for a predetermined time period ranging from 20 to 100 min, on a 20 min interval. For the case of contact time was carried out until the % adsorption become constant or starts to decrease (Jacob, M. M., Ponnuchamy,2020). Other parameters were kept constant. Then, flasks were withdrawn from the shaker, solution was filtered and absorbance of the solutions was measured. A graph is plotted with % qe *vs*. contact time (Mulugeta & Lelisa, 2014).

3.4.3. Effect of adsorbent dose:

50 mL of 50 mg/L of the working solution was put in each different conical flask. Then, different adsorbent dose from (0.2, 0.4, 0.6, 0.8 and 1 g) was added in each flask other parameters are constant. And all the flasks were kept inside the shaker at 150 rpm and 25^{o}C for the optimized time, 80 min (Mulugeta & Lelisa, 2014)..

After 80 minutes, the flasks were withdrawn from the shaker and the dye solutions separate from adsorbents by using filtration. The absorbance of all the solutions was measured. A graph were plots with percent removal (%qe) *vs*. adsorbent dose.

3.4.4. Effect of pH:

50 mL of 50 mg/L methylene blue dye solution was put in each different conical flask. The optimum adsorbent dose as obtained from the above study (0.8 g) was put in each flask. The pHs of each flask adjust in the range of 2-10 in the interval of 2 with dilute HCl (0.1 M) and NaOH (0.1 M) solution by the use of pH meter. Then, all the flasks were kept inside the shaker at 150 rpm and 25^{o}C for 80 min. After that, flasks will withdraw, solutions were filter

and absorbance of the solutions was measured. Graphs were plotted with % qe *vs*. initial pH (Mulugeta & Lelisa, 2014).

3.4.5. Effect of adsorbate concentration:

50 mL of methylene blue dye solution with varies concentration 10 mg/L, 50 mg/L, 100 mg/L, 200 mg/L, 400 mg/L was put in each different conical flask this concentration were selected MB concentration values in wastewater (Zhu et al., 2018). The optimum contact time, adsorbent dose and pH as obtained from the above studies were put in each flask. Then, all the flasks were kept inside the shaker at 150 rpm and 25^{o}C. After that, flasks were withdrawn, solution was filtered and absorbance of the solutions was measured. Graphs were plot with % qe *vs*. adsorbate concentration.

3.5. Adsorption isotherm

Adsorption Isotherms Model In a liquid-solid system, adsorption isotherm is important in describing the interaction of adsorbates and adsorbents. Langmuir models and Freundlich models are the two most commonly used isotherm models.

The relationship between the amount of a substance adsorbed at constant temperature and its concentration in the equilibrium solution is called the adsorption isotherm. Adsorption isotherm is important from both a theoretical and a practical point of view. In order to optimize the design of an adsorption system to remove the contaminant, it is important to establish the most appropriate correlations of the equilibrium data of each system. Equilibrium isotherm equations are used to describe the experimental adsorption data. These data provide information about the capacity of the adsorbent or the amount required for removing a unit mass of pollutant under the system concentrations(Uddin, Rahman, Rukanuzzaman, & Islam, 2017)

The most widely accepted surface adsorption models for single-solute systems are the Langmuir and Freundlich isotherm (Seeds and Sepehr., 2011). These two most common isotherm equations have been tested in the present study to analyze equilibrium data of solute between adsorbent and adsorbate. The parameters obtained from these different models provide important information on the adsorption mechanisms and the surface properties and

affinities of the adsorbent. Linear regression is frequently used to determine the best-fitting isotherm, and the applicability of isotherm equations is compared by judging the correlation coefficients (I. Tan, Ahmad, & Hameed, 2008).

The Langmuir isotherm is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface (Langmuir *et al*, 1916). The experimental data were analyzed according to the linear form of the Langmuir isotherm. The linear plots of Ce/qe versus Ce suggest that Langmuir isotherms for the removal of MB. The values of qm and kL of linear expression of Langmuir adsorption isotherm was calculated from the slopes and intercept of the linear plot of Ce/qe *v.s* Ce (Khaled, El Nemr, El-Sikaily, & Abdelwahab, 2009)

Freundlich isotherm model

While Langmuir isotherm assumes that enthalpy of adsorption is independent of the amount adsorbed, the empirical Freundlich equation, based on adsorption on heterogeneous surface, can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites (Freundlich *et al*, 1906).

The Freundlich equation is purely empirical based on adsorption on heterogeneous surface and is commonly given by non-linear equation. K_f and 1/n can be obtained from the intercept and slope of the linear plot of ln qe versus ln Ce.

The Freundlich model provides a means of fitting data related to adsorption on heterogeneous surfaces. Langmuir model is given by Eq. I (Piccin, Cadaval, de Pinto, & Dotto, 2017).

$$\frac{\mathrm{Ce}}{\mathrm{qe}} = \frac{\mathrm{Ce}}{\mathrm{qm}} + \frac{1}{\mathrm{qmKL}} \quad \text{..... (I)}$$

The Freundlich model is given by Eq. (II):

$$\mathrm{lnqe} = \mathrm{lnKF} + \frac{1}{\mathrm{n}}\mathrm{lnCe} \quad \text{..... (II)}$$

In equations I and II, Ce is the equilibrium concentration of methylene blue (mg/L), qe is the equilibrium adsorption capacity (mg/g), q_m is the maximum adsorption capacity (mg/g), K_L is the Langmuir constant related to the free energy of adsorption (mg/L), K_F is Freundlich parameters related to adsorption capacity, and n is the adsorption intensity.

3.6. Adsorption kinetics model

Kinetic models were used to investigate the controlling mechanism of sorption process such as chemical reaction, diffusion control and mass transfer It is very important to know the rate at which the process takes place and the factors that control the rate of the process, for this purpose kinetics of the process was evaluated (Wakkel, Khiari, & Zagrouba, 2019).

Kinetics is a critical parameter in the design of the sorption process and in evaluating the suitability of a sorbent because it controls the size of the sorption units, which is helpful for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes (Santhi and Smitha., 2010). Thus, the kinetics of MB adsorption onto BSCB biochar was analyzed using pseudo-first-order and pseudo-second-order kinetic models. In the present study, the kinetics study of methylene blue removal was carried out to understand the behavior of prepared low-cost adsorbent activated BSCB biochar.

3.6.1. Pseudo-first-order and pseudo-second-order kinetic models

The pseudo-first-order kinetic model assumes that the speed of occupation of adsorption sites is proportional to the number of unoccupied sites. The values of ln(qe – qt) were linearly correlated with t. The values of K_1 and qe were calculated from the slopes and intercepts of ln(qe – qt) against the t plots using equations and the different parameters of pseudo-first-order kinetics. The pseudo-first-order kinetic model, which is commonly used to determine the adsorption rate based on the adsorption capacity (Somasekhara *et al*., 2012), can be expressed as follows.

$$\text{In } (qe - qt) = \text{In} qe - k_1 t \quad \text{(III)}$$

Where qt (mg/L) is the amount of adsorbed MB at time t (min), qe (mg/L) is the amount of the adsorbed MB on the adsorbent at time under equilibrium conditions, and k1 is the pseudo-first-order rate constant (min^{-1}).

In adsorption kinetics, the pseudo-first-order and the pseudo-second-order models are commonly employed to fit the data. The linear form of pseudo-first-order model is given by Eq. (IV)**:**

$\ln (qe - qt) = \ln qe - k_1 t$ …….. (IV)

The linear form of pseudo-second-order is given by Eq. (V) (Ho and McKay 1998).

$\frac{t}{qt} = \frac{1}{k2qe\ 2} + \frac{1}{qe} t$ …… (V)

In these equations qe and qt are the adsorption capacities corresponding to the equilibrium and time t (mg/g), k_1 is the pseudo-first-order constant (h^{-1}), k_2 is the pseudo-second-order constant (mg/gh), and t is the contact time (min).

These experiments were conducted for the optimum contact time by setting MB concentration of (10, 50, 100, 200, and 400) mg/L pH of 8, adsorbent dosage of 0.8 g/L and constant agitation speed 150rpm. Then samples were withdrawn in every 20 min interval in the time frame of 20 to 100 min for determination of residual MB concentration in the solution. Then data from the experiment was introduced into pseudo-first order models and pseudo-second order models.

3.6.2. Textile wastewater sampling

The wastewater collected from Kanoria Afica textile Plc, which is the a subsidiary of India's Kanoria Chemicals and Industries, is setting up a denim fabric manufacturing plant that will be a first for Ethiopia and East Africa. It located in Deberazet (Bishoftu) town, 62 km from Adama. 2 L Samples were collected; from the inlet of the dying process by Plastic containers were used for sample collection after cleaned sample collection and preserved in a refrigerator at 4^oC in order to minimize the chance of their characteristics changes until used for experiment.

3.7. Data analysis

The data generated were analyzed by using Min tap to compute the mean, standard deviation and linear regression values. All data was subjected to; analysis of variance (ANOVA) and correlation analysis which were carried out with SPSS software package.

CHAPTER FOUR

4. RESULTS AND DISCUSSIONS

4.1 Biochar yield at different pyrolysis temperature

As shown in Table 4.1, the yield values of carbonized SCB biochar's were 30.78%, 25.7% and 23.63% for the carbonization temperature 400^{o}C, 500^{o}C and 600^{o}C, respectively. Biochar formed at high temperatures has a greater surface area and carbon content due to the rising micro-pore volume caused large amount of volatile organic molecules removed (J. Wang & Wang, 2019). Finally conclude that the prepared biochar at high temperature were effective in the sorption of dye contaminate at high surface area, micro porosity and hydrophobicity (Yuan *et al*., 2019).

Table 4.1.Sugarcane Bagasse Biochar yield at different temperature and a residence time of 2h and heating rate of 10-20^{o}C/min.

Pyrolysis condition	**Initial mass**	**Heating rate(^{o}C/min)**	**Residence time**	**Biochar yield**
400^{o}C	450 g	10-20^{o}/min	2h	30.78%
500^{o}C	500 g	10-20^{o}/min	2h	25.7%
600^{o}C	500 g	10-20^{o}/min	2h	23.63%

4.1.1. Proximate analysis

Moisture content, ash content, volatile matter content and fixed carbon content analysis were done for biochar and the calculations are shown in Table 4.2 for each adsorbent. It is known that the higher the pyrolysis temperature, the higher would be the ash content. From this studies the moisture content decrease at pyrolysis temperature increase while the amount of volatile content released due to the value of unstable volatile content on the carbon sample increase (Bachrun, AyuRizka, Annisa, & Arif, 2016). Also the amount of ash content increase at the temperature increase finally the fixed carbon content was 63.27%, 61.58% and 54.12% at the temperature of 400^{o}C, 500^{o}C and 600^{o}C respectively.

Table 4.2 .Proximate analysis of SCB biochar at different temperature

Sample	Moisture (%)	Volatile matter (%)	Ash (%)	Fixed Carbon (%)
SCB 400^{o}C	3	65.98	10.20	63.27
SCB 500^{o}C	2.4	71.82	10.25	61.58
SCB 600^{o}C	2	73.47	11.86	54.12

4.1.2. Point of zero charge (PZC)

pH_{pzc} is the pH value at which the charge on the surface of the adsorbent is zero. From the present study, the result of pH $_{pzc}$ for local SCB biochar was presented at 400^{o}C 8.7, 500^{o}C 8.2 and 600^{o}C 7.6 respectively. This indicates the SCB biochar works well for adsorption at this value of pH 8.2 pzc. The pH of SCB biochar adsorbent generally falls in the basic and slightly neutral region as depicted in figure 6. The values of pH_{pzc} < 8.7 show the dominancy of acidic groups over basic groups and values of pH_{pzc}> 8.7 show dominance of basic groups over-acidic groups. The net surface charge of the adsorbents under pH_{pzc} is positive, while it is negative above pH_{pzc} (Akinola, Ibrahim, & Mohammed, 2019). The negative charge density on the surface of the biochar increases due to the presence functional group such as OH^{-} group, which favors the sorption of basic (cationic) dyes. Many researchers studied the point of zero charge (pH $_{pzc}$) of various adsorbents prepared from agricultural solid wastes; in order to understand the adsorption mechanism. Due to the presence functional group, cationic dye adsorption is favored at pH > pH_{pzc} (Afroze & Sen, 2018). Removal of methylene blue found that Delonix Regia Seed Pods (5.3) and Vigna Subterranea Fruit Hulls (4.8), rice husk (6.3), cow dung (7.8) and sludge biochar (6). This obtained PZc results for SCB were found to be greater/smaller than those reported values in literature. Therefore, knowledge of pH $_{pzc}$ value helps in deciding which pH value which works efficiently during adsorption removal of pollutants (Albalasmeh *et al*., 2020).

In this study, the pHpzc of SCB NaOH biochar found to be 8.7, 8.2 and 7.6 respectively and Optimum pH value of adsorption found at 10. Methylene blue is cationic (basic) dye adsorption enhanced at pH of greater than pH_{PZC}, 10. In water, it produces cation (C^{+}) and reduced ions (CH^{+}). In order to study optimum adsorption process of SCB treated NaOH biochar adjust solution pH is above the zero point of charge at 8.69 in this case, the negative

charge density on the surface of the activated carbon increases due to the presence functional group such as OH^- group, which favors the sorption of basic (cationic) dyes. From the above result observed that, determinations of point of zero charge of BSCB biochar positively influence pH optimum value because optimum values above point of zero charge.

Table 4.3. Point of zero charge of all adsorbent at 400^{o}C, 500^{o}C, 600^{o}C

Initial (pH)	**Final (f)400^{o}C**	**Final (f)600^{o}C**	**Final (f)500^{o}C**	**ΔpH 500^{o}C**	**ΔpH 600^{o}C**	**ΔpH 400^{o}C**
2	5.2	5.6	5.3	-3.3	-2.9	-3.2
4	6.8	6.1	6.4	-2.4	-1.4	-2.8
6	7.9	7.2	7.6	-1.6	-1.2	-1.9
8	8.5	8.1	8.4	-0.4	0.4	-0.5
10	8.9	7.9	8.1	1.9	1.8	1.1
11	9.4	8.3	9.3	1.7	2.4	1.6
12	9.2	8.7	9.4	2.6	3.6	2.8

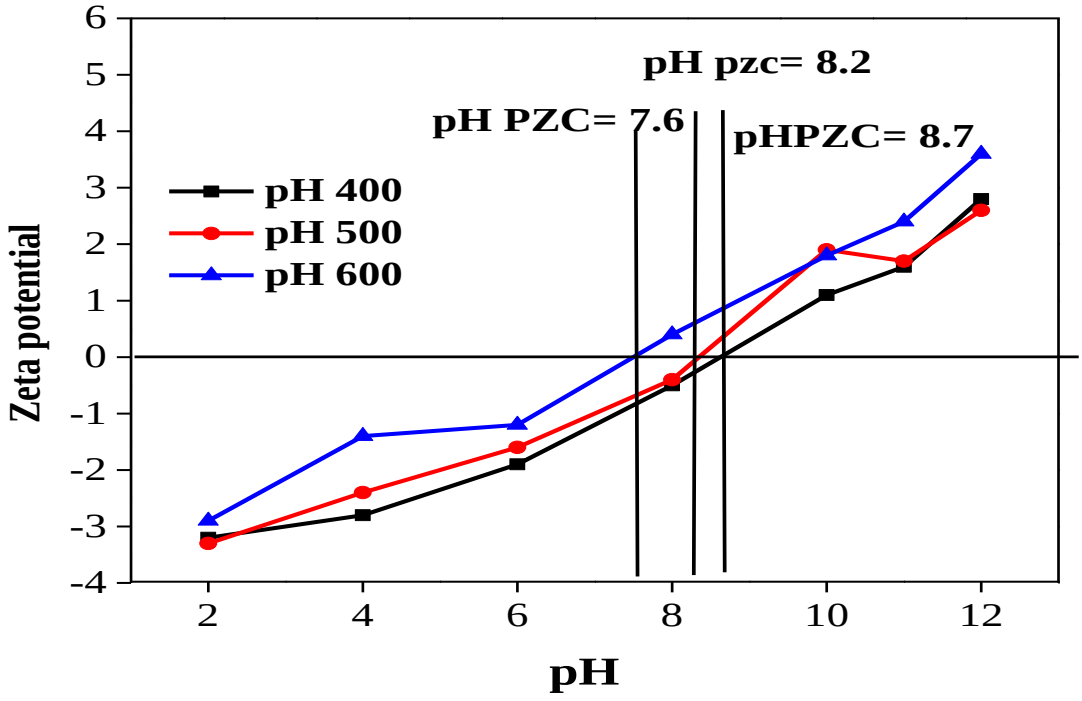

Figure 4.1. Point of zero charge of all adsorbent

4.2. Characterization

4.2.1 XRD characterization of SCB biochar

Figure 4.2 shows the XRD results of adsorbents prepared. The X-ray diffraction spectrum at 22.8˚ and 16.4˚ - 19.8˚ showed the existence of cellulose at the sample on MSCB at 500^{o}C (Utomo *et al.*, 2015). BSCB at 500^{o}C showed the highest intensity at 25.9˚ and 16.42^{o} respectively at the intensity of 002 among the prepared adsorbent. The lowest crystalline size was found with adsorbents NSCB and MSCB prepared at 500^{o}C. The crystalline sizes of NSCB and MSCB was small due to its highest amount of amorphous content (Utomo *et al.*, 2015) was reported that crystalline size of the adsorbent prepared from Chemically Modified Sugarcane Bagasse for BSGB, CSGB and NSGB are 3.245, 3.327 and 3.196 nm, respectively with the details of 002 peaks (Utomo *et al.*, 2015). Therefore in this studies have the smallest crystallite size among the prepared adsorbents, all adsorbents have very similar crystallite size.

Table 4.4. Crystallite size for all SCB biochar from the XRD data.

No of Sample	2θ	θ	D	FWHS	Crystallinity
NSCB 500	21.51087	10.75544	0.412770034	31.53255	0.256444349
BSCB 500	16.42884	8.21442	0.539131164	14.89026	0.539053039
MSCB500	26.03529	13.01765	0.341973892	28.12744	0.289889039

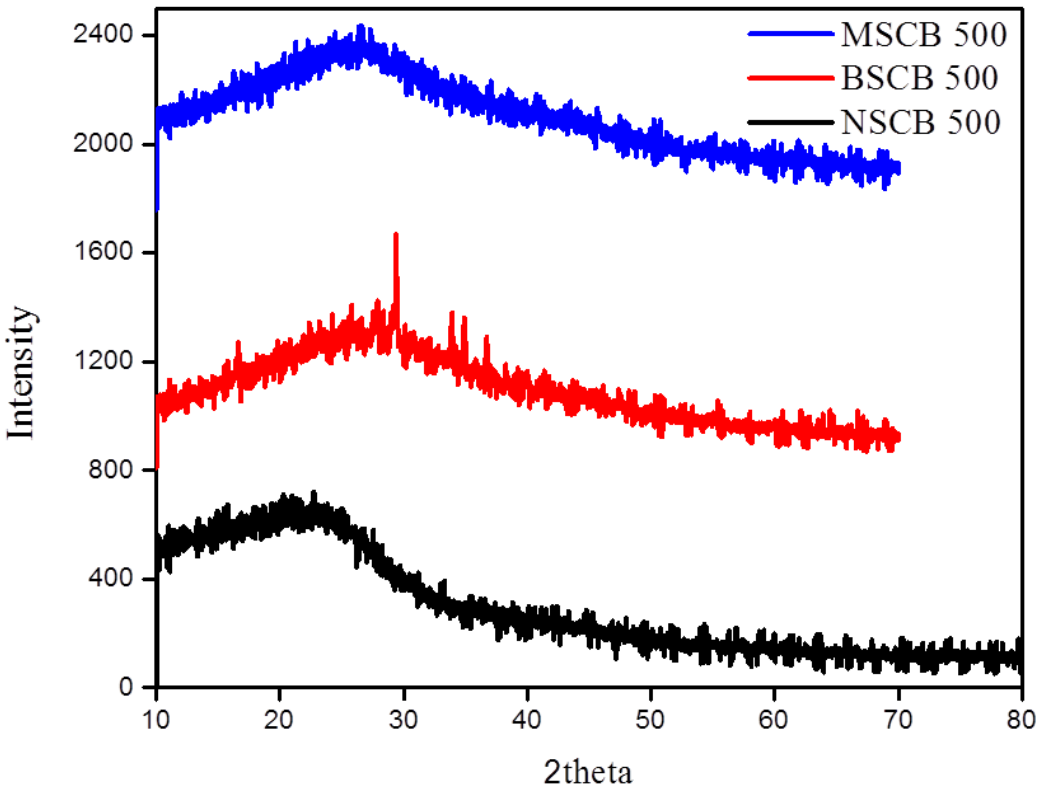

Figure 4.2. X-ray diffraction patterns for SCB biochar at 400 ^{o}C, 500 ^{o}C, 600^{o}C

4.2.2. FT-IR characterization of the adsorbent

The FT-IR spectra show unmodified SCB biochar and modified BSCB biochar. The SCB biochar presented different peaks located in figure 4.3.

The band between at 3442 cm^{-1} and 3497 cm^{-1} was corresponding to (O–H) vibrations in hydroxyl groups. The position and shape of this band suggest that the hydroxyl groups were involved in hydrogen bonding. According to the four types of hydrogen-bonded structures, the predominant one in SCB was self-associated OH groups. The band at 3415 cm^{-1} is somewhat broader towards lower wavenumbers suggests that SCB also contains OH^-ether hydrogen bonds (Edreis, Luo, & Yao, 2014). The band between 2808cm^{-1} and 2821cm^{-1} indicate the presence of (C–H) vibrations. The form of(C–H) adsorption bands shows the presence of methyl and methylene groups in SCB. However, the peak at 1459 cm^{-1} was attributed to (CH_3) stretching vibration. The characteristic absorption of a methyl group at 1380 cm^{-1} and 1343 cm^{-1} was valuable for methyl group estimation. Hence the band at 1459 cm−1 was slightly weaker than the band at 1380 cm^{-1}, proving the presence of acetoxy groups (–O–$COCH_3$) in SCB (Babaei *et al*., 2016). The olefinic (C=C) and aromatic (C=C) vibrations were detected at 1604–1459 cm^{-1} region, respectively. The absorbance bands of 1000–1100 cm^{-1} were attributed to (C–O) vibrations in primary C–OH, secondary O–H, and the presence of silica, Si–O–Si in all samples except MSCB at 600^oC, NSCB 400^oC, and 500^oC (Edreis *et al*., 2014). These functional groups may produce surface compounds with MB dye, increasing MB adsorption intensity by biochar. A comparison of SCB biochar FTIR spectra before and after MB dye adsorption reveals that MB adsorption results in changes in absorption frequencies at 2025 and 1455 cm^{-1}, which are visible in the adsorbent's surface. The MB adsorption on the SCB appears to be influenced by the functional groups indicated (Chen, Yan, Xu, & Li, 2018).

Table 4.5. Functional groups of SCB biochar prepared under different conditions

NSCB 400°C	**BSCB 400°C**	**MSCB 400°C**	**NSCB 500°C**	**BSCB 500°C**	**MSCB 500°C**	**NSCB 600°C**	**BSCB 600°C**	**MSCB 600°C**	**Functional group**
3497	3493	3442	3490	3484	3462	3453.5	3479	3493	–OH
2815	2811	2821	2819	2812	2814	2814.75	2808	2820	C-H
-	2026	2025	2025	2501-2195	2026	2024	2025	2026	C=O
1604	1576	1611	1611	1620	1607	1607	1579	1612	Aromatic hydrocarbon
1455	-	-	1457	1485	-	1459	-	-	(–O–$COCH_3$
1380	1345	1357	1356	1343	1346	1356	1346	1346	C – H (methyl)
	1126	1005		1107	1004	1105	1000		C - O

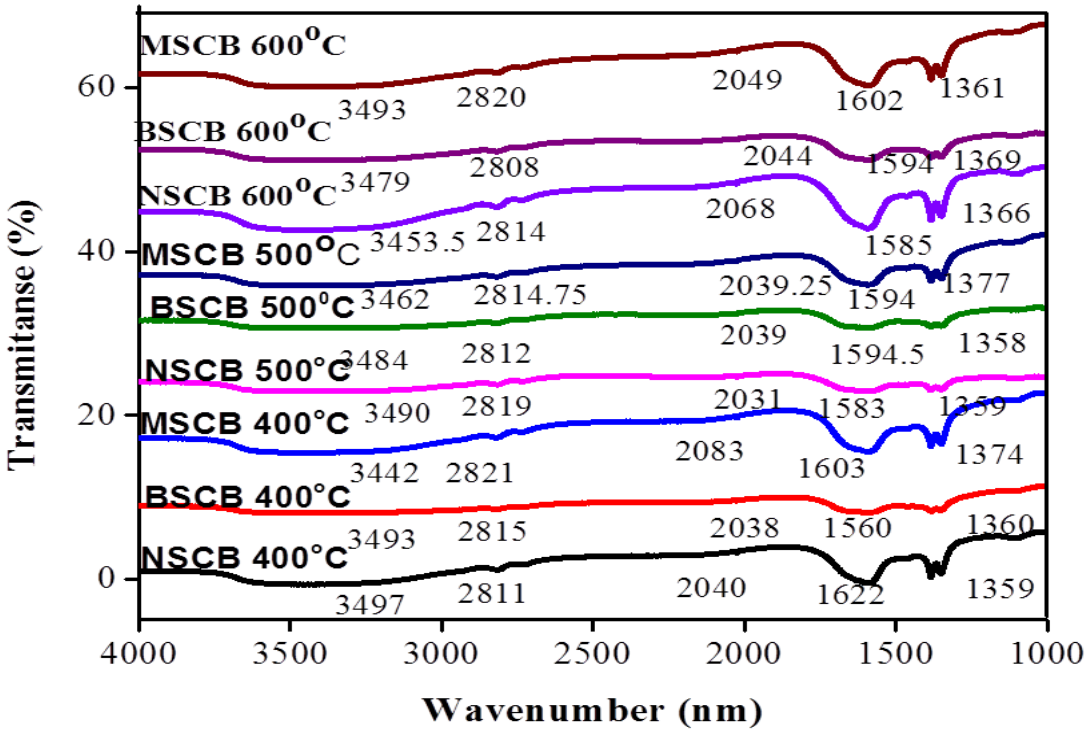

Figure 4.3. FTIR of SCB biochar prepared under different conditions.

4.2.3. Scanning Electron Microscope (SEM) Analysis

The SEM results of unmodified SCB biochar adsorbent showed very small pores while on surface medication with NaOH at different temperatures showed surface pore enhancements and surface characteristics changes as shown in figure 4.4.

The less availability of pores and the internal surface as displayed in the SEM image of the SCB biochar before adsorption. Meanwhile the pores of surface modified adsorbents resulted different sized and different shaped pores were obtained irrespective of temperature treatment. As shown in Figure 4.4, modified SCB has irregular structure and larger pores, which can favor the bio sorption of MB on different parts of the bio sorbent. The images confirm the previous results obtained by the analysis of the porosity of SCB similar data was observed by (Andrade Siqueira *et al*., 2020).

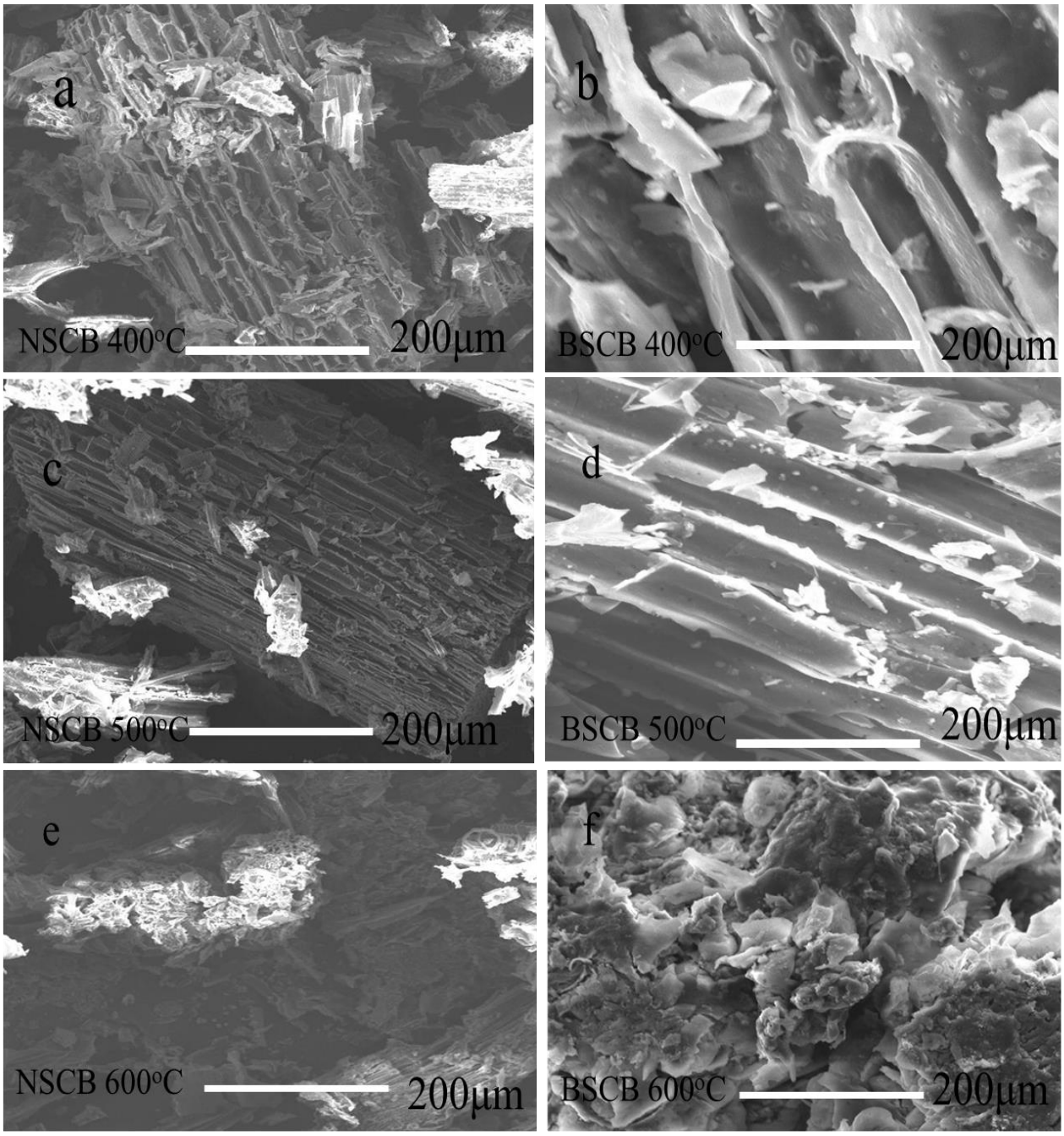

Figure 4.4. SEM images of SCB biochar at 400^0C, 500^0C and 600^0Cview of the sample of sugarcane bagasse (SCB) biochar, showing fibers and residues with 200µm magnification.

4.2.4 Thermal Gravimetric Analysis (TGA)

The plots of the percent weight loss versus temperature are shown in Figure 4.5 Thermogravimetric Processes (TG) experiments were performed at a temperature range starting from 25^{o}C to 900^{o}C with 10^{o}C/min as heating rate. The TG pyrolysis plots show in all adsorbents the characteristic reverse s-shaped curves distinctive of the thermal degradation of lignocellulosic biomass under an inert atmosphere (Nyakuma *et al*., 2016). Also, the TG curves show that the thermal degradation of sugarcane bagasse biochar occurred in two stages in all sample of NSCB 400^{o}C, NSCB 500^{o}C and NSCB 600^{o}C. In this stage the highest % weight loss was observed at 54.61%, 47.5% and 37.23% observed respectively which followed at 340^{o}C, 388.11^{o}C and 353.63^{o}C which may be recognized to the release of moisture. The second stage 9.61%, 2.18% and 10.63% respectively. In this stages comprised the thermal degradation of the lignocellulosic components, being much more evident in the SCB sample. Continuous mass loss was observed with the rising of temperature at 655^{o}C, 631^{o}C and 776.5^{o}C respectively (Miyah *et al.*, 2017). The temperatures at which these components degraded were found to be 200–350^{o}C for hemicellulose, 250–400^{o}C for cellulose, and 150–1000^{o}C for lignin (Díez, Urueña, Piñero, Barrio, & Tamminen, 2020). At the end of this stage, it was observed that sugarcane bagasse biochar were completely pyrolysis, followed by a gradual drop in weight loss.

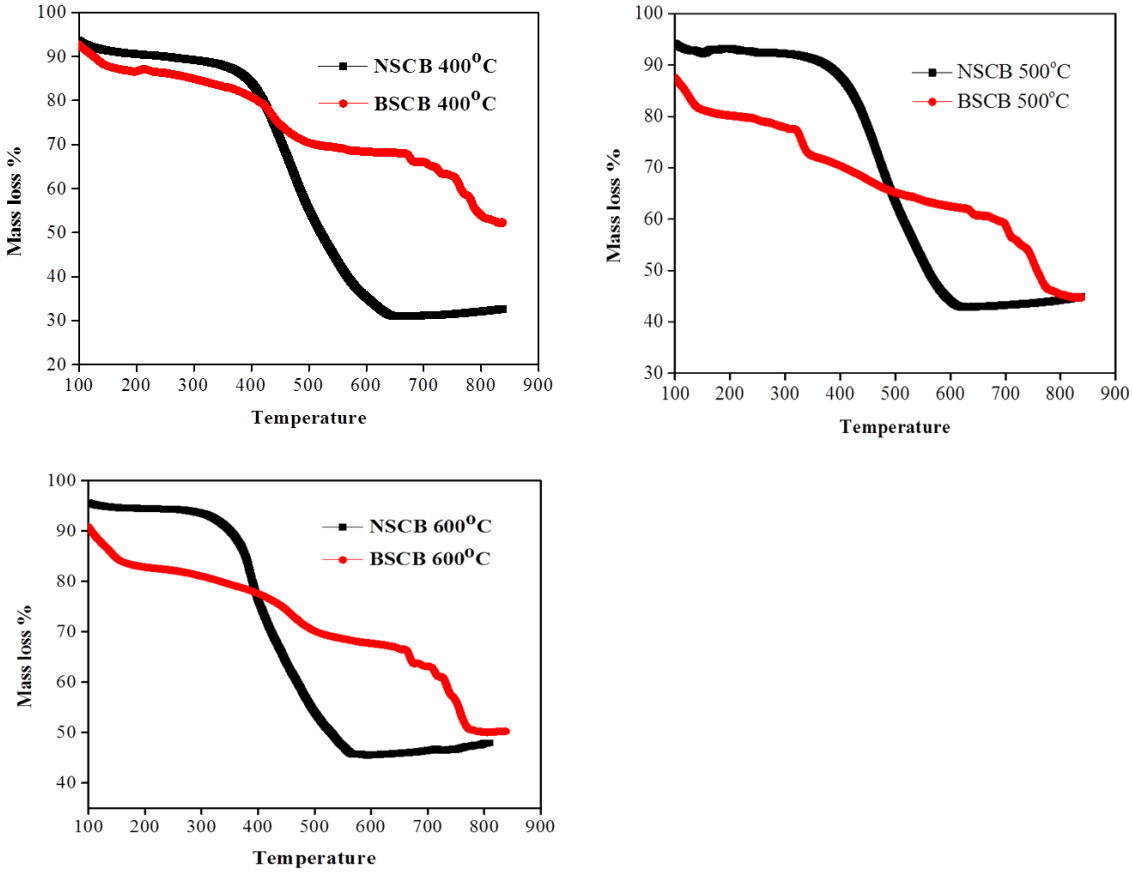

Figure 4.5. TGA curve of sugarcane bagasse biochar at 400°c, 500°C and 600°C.

4.2.5 BET Analysis

Table 4.6 shows the BET surface area and total pore volume of all the biochar adsorbent. The results shown that the porous characteristics were basically dependent on the pyrolysis temperature the total pore volume increased at the carbonization temperature increase, which resulted in a higher surface area, was observed at BSCB 500°C of 732.6m^2/g. Even though the SCB biochar had the highest pore size observed at BSCB 500^0C 1.93 nm. similarly, (El-Sayed et al., 2014) was reported activated carbon prepared from corncob by chemical activation with concentrated H_3PO_4 acid followed by pyrolysis at 400, 500, and 600°C have surface area of 700, 633, and 600 m^2/g, respectively. The significant growth in surface area with increased pyrolysis temperature is due to the release of volatiles. The amount of volatile organic chemicals produced and the number of pores generated increased when the pyrolysis temperature was raised, resulting in a larger surface area. Higher surface area is preferred

because it assists in soil structure improvement, enhances overall water retention in the soil, and provides ecological niches for soil microorganisms (J. Zhang et al., 2018). However, the activation with steam was preferable with regard to environmental issues. The MB adsorption on SCB500 indicates the high contribution of the large pore size due to its highest surface area and mesoporous available within the SCB500. Therefore for adsorption tests with such macromolecule as methylene blue (MB), SCB500 was chosen. Another previous adsorption study was conducted for water vapor (Rahmawati *et al*., 2021).

Table 4.6. Characteristics of porosity in SCB biochar prepared with different carbonization temperatures.

Biochar bagasse	**Surface Area Multi Point BET (m^2 /g)**	**Total Pore Volume ($\times 10^{-1}$ cc/g)**	**Average Pore Size (nm)**
NSCB 400	522.3	3.747	1.7211
BSCB 400	652.5	2.212	1.658
NSCB 500	678.4	3.67	1.7501
BSCB 500	732.6	4.498	1.938

4.2.6. Adsorption mechanism of SCB biochar

The following is a potential carboxyl mechanism of action: Carboxyl groups emit protons in neutral and alkaline environments, becoming negatively charged and attracting MB cations. SCB oxygen-containing functional groups (–OH) attract MB electrostatically, causing it to be removed. SCB biochar oxygen-containing functional groups (–COOH, –OH) hydrogen bind with MB as well electrostatic bond. One of the reasons why MB adsorption decreases as pyrolysis temperature rises is that the CMB surface becomes more hydrophobic, reducing the adsorption capability of polar molecules likes MB (Zhu et al., 2018).

Figure 4.6 depicts the interaction of MB molecules with the SCB biochar surface, taking into account the high electron density within the orbital, the electrostatic potential force of N^+, and the potential creation of hydrogen bonds. Other recent research (Ghaffar & Younis, 2015) predicted those relevant interactions as well. Because the - coupling contact would be difficult

to form due to the steric effect generated by the surface functional groups of C=N chromophores, the presence of Cl as a counter ion would limit the interaction between the MB–MB molecules leaving only hydrogen bonding as a viable option. Vander Waals forces are the interactions between organic compounds Electron-donor acceptor, hydrophobic interaction, hydrogen bonding, electrostatic and covalent contact, and carbon. They can work separately or simultaneously (Yang & Xing, 2010). MB molecules interact through - electron coupling on the hydrophobic side of carbon, which produces a high electron of sp2 carbons. Furthermore, the acidity of the SCB biochar surface increases the likelihood of electrostatic interactions and hydrogen bonding formation between the AC surface and the MB molecules (Rahmawati *et al*., 2021).

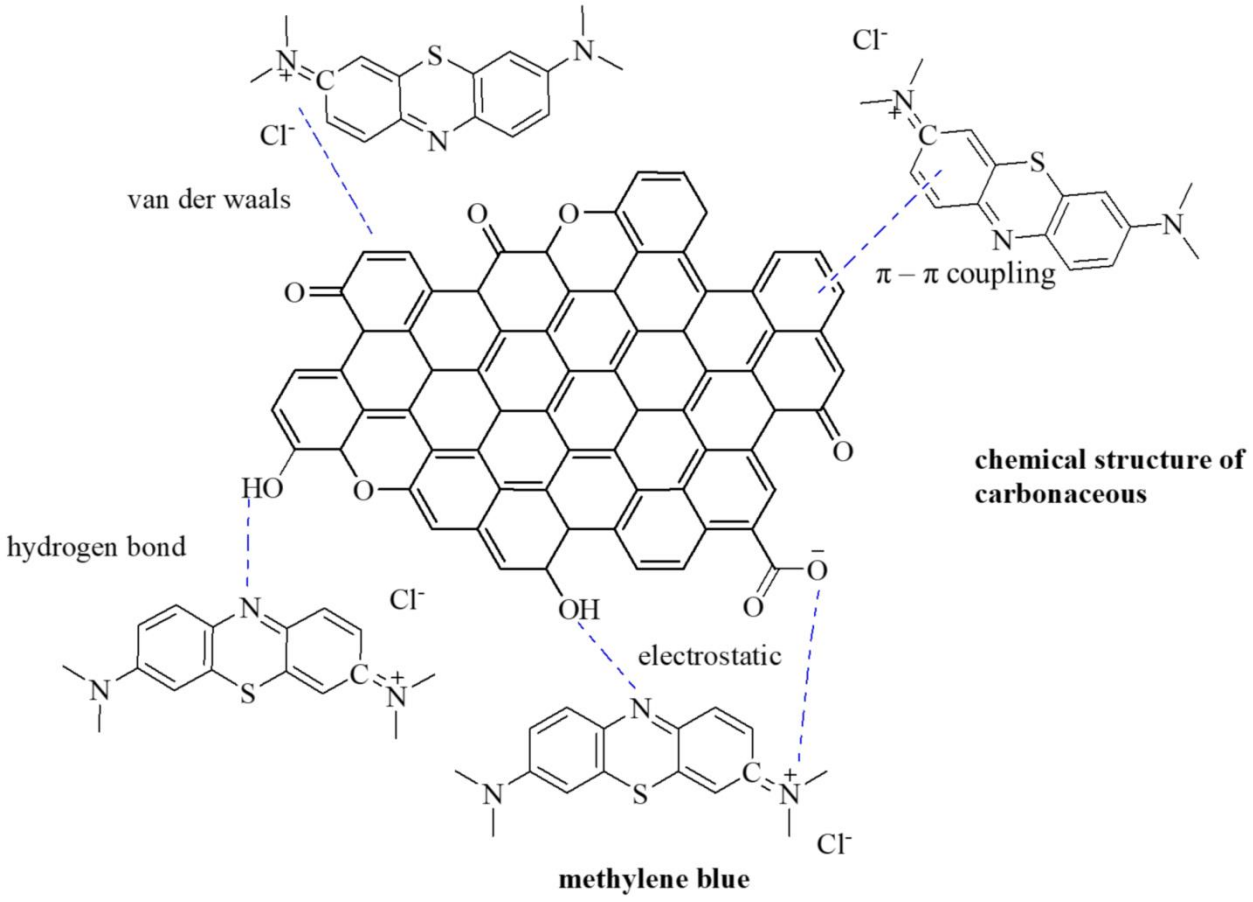

Figure 4.6. Scheme of the proposed-interaction between carbonaceous surface and methylene blue (Rahmawati et al., 2021).

4.3. Batch adsorption experiment result

4.3.1. Standard Curve of MB stock solution

The measurement of methylene blue concentration in final solution was initiated with searching the maximum wavelength. From UV-VIS spectrophotometer result, it was observed that maximum peak was acquired at 665 nm. Subsequently, methylene blue solutions at various concentrations were prepared and analyzed at 665 nm. The standard curve was obtained by plotting the recorded absorbance from spectrophotometer versus the prepared concentration of solution. The accuracy was excellent with coefficient correlation (R^2) of 0.943 (Fig 4.7).

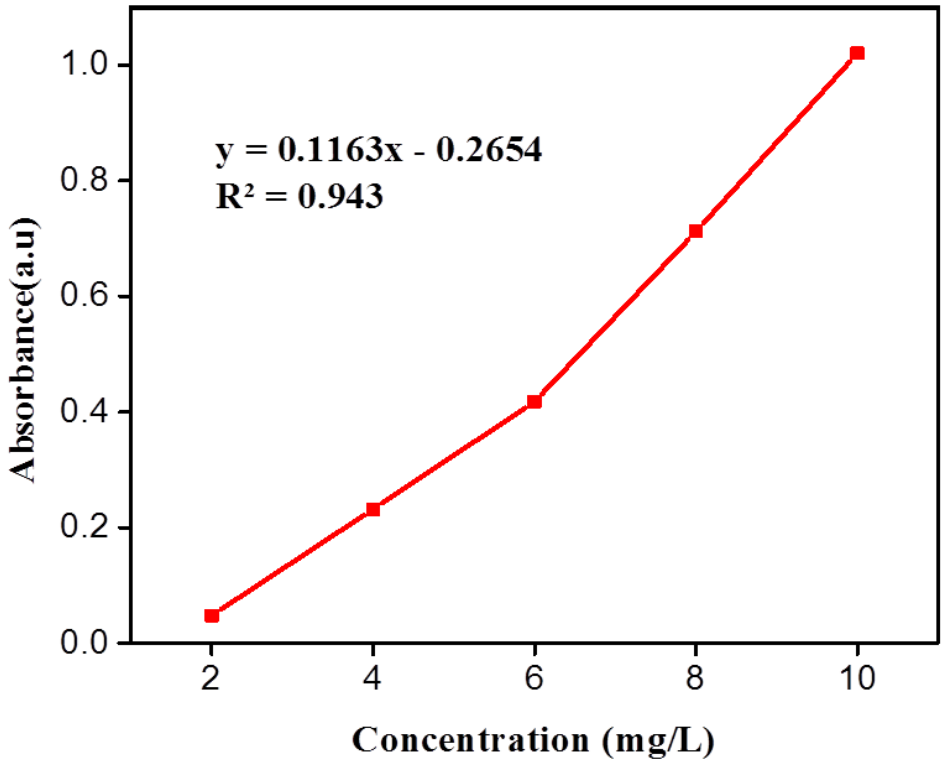

Figure 4.7. Calibration plot absorbance vs. Concentration in mg/L

4.3.2. Effects of contact time

The influence of contact time on removal efficiency of MB dye from aqueous solution was carried out at constant parameters like pH = 8, initial concentration of MB dye = 10 mg/L,

SCB dosage = 0.2 g, mixing speed =150rpm, and temperature = 25˚C, for different contact time from 20min - 100min. The maximum amount of adsorbed MB was observed at the temperature of 400^{o}C and 500^{o}C nearly constant, and the average removal efficiency of MB reached approximately 77.2% (1.93 mg/g adsorption capacity), 77.1% (1.92 mg/g adsorption capacity), but at 600^{o}C 77% (1.91 mg/g adsorption capacity) at 25^{o}C and pH 8 at initial MB concentrations of 10 mg/L, respectively. The result of this study indicates the effect of contact time on the removal of MB dye from an aqueous solution was increase as the contact time increase, similar data was reported (Husseien, Amer, El-Maghraby, & Taha, 2007; P. S. Kumar, Ramalingam, & Sathishkumar, 2011). As depicted in Figure 4.8 the removal efficiency increase in the first 40 min. After the first 40 min, a small increase in adsorption of MB dye and reached nearly equilibrium. But, during the first 20 min, the adsorption of dye was very fast. This is due to strong forces of attraction between the positive sites of cationic dyes and the anionic sites of activated carbon can explain this (Mehrorang Ghaedi, Tashkhourian, Pebdani, Sadeghian, & Ana, 2011).

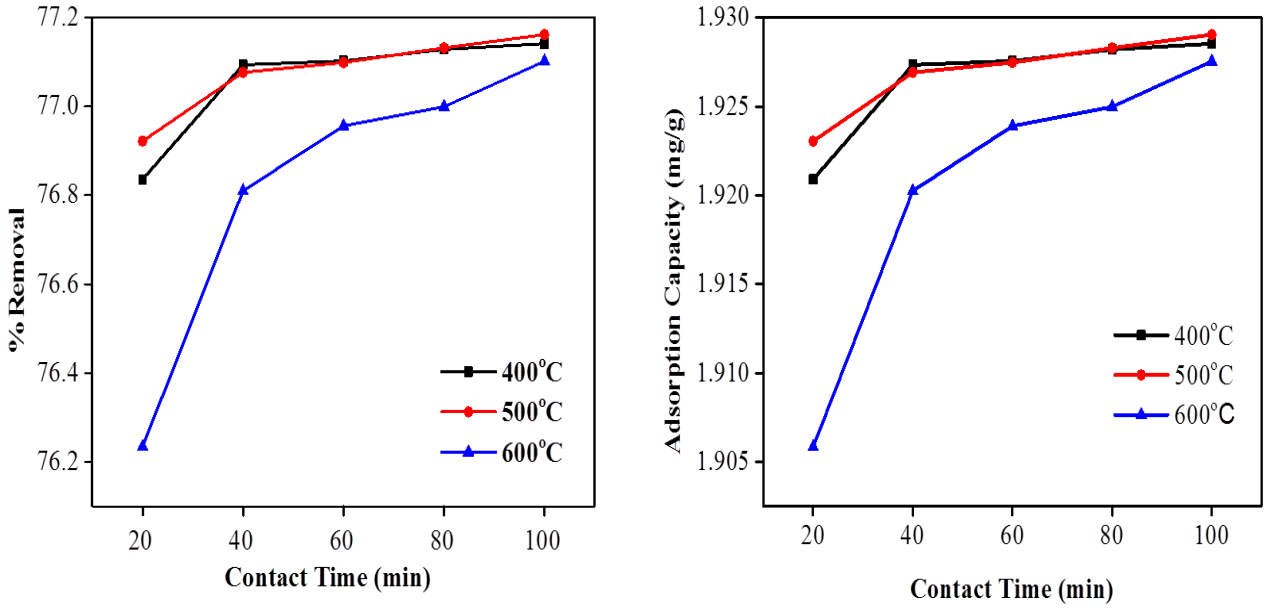

Figure 4.8. Effect of the contact time on MB adsorption by the BSCB biochar (a) Removal efficiency (%) and (b) Adsorbent capacity (mg/g) (initial pH=8, amount of sorbent 0.2 g/50 mL, 25^{o}C).

4.3.3. Adsorbent dose

The effect of adsorbent dosage was carried out by keeping all parameters constant like pH= 8, initial dye concentration of MB dye = 10 mg/L, contact time = 80min, temperature = 25°C, mixing speed = 150rpm and volume = 50ml. The present study was obtained the adsorption process indicates that the removal efficiency of MB dye at the temperature of 400^{o}C and 600^{o}C BSCB biochar was similar removal efficiency but in 500^{o}C BSCB biochar the maximum removal efficiency starts at 0.6 g adsorbent dose. This might be due to the presence of more adsorption sites present at 500^{o}C surface as adsorbent dosage increases. As shown in Figure 4.9 both temperature 400^{o}C and 600^{o}C BSCB biochar there is a slow increase of adsorption efficiency above 0.2 g and a sharp increase above 0.6 g to 1 g at 500^{o}C the adsorption efficiency (Garg, Gupta, Yadav, & Kumar, 2003). However, no significant changes in removal efficiency were observed beyond 0.6 g/50 ml adsorbent dose. Because of the higher surface area and the availability of various adsorption sites on the surface, the removal ratio of MB increased as the adsorbent dosage increased. Similar results were reported previously in the adsorption of MB (Hu, Gao, Liu, & Yuan, 2018) by red mud, indicating that the removal of dyes increased with increasing dosage, but that any additional SCB dosage beyond a critical quantity had little contribution to the adsorption process. Increased adsorption with adsorbent dosage can be related to higher adsorbent surface area and the availability of good adsorption sites. This can be explained by increasing the amount of biochar in a solution increases the number of exchangeable sites for ions, which enhances SCB biochar adsorption from solution to solid (Georgin, Dotto, Mazutti, & Foletto, 2016).

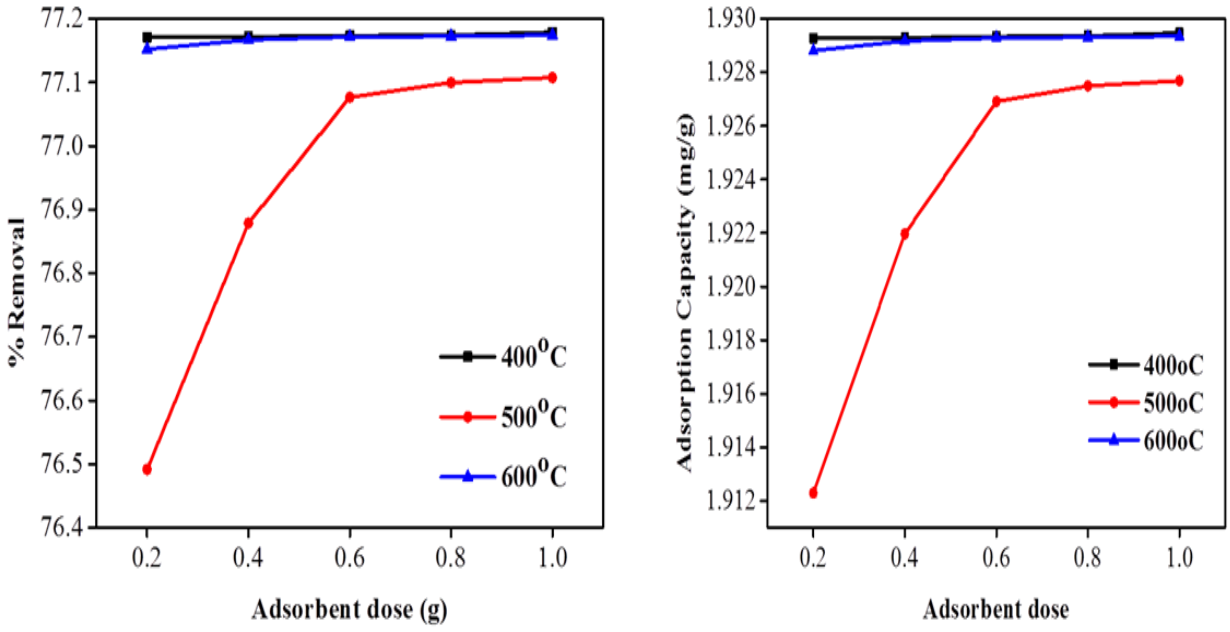

Figure 4.9. Effects of adsorbent dose on MB adsorption Removal efficiency (%) (b) Adsorbent capacity (mg/g) (At pH 8 initial conc.10mg/L and contact time 80 min 25^{o}C).

4.3.4 Effect of PH

The pH of the solution was varied from 2, 4, 6, 8 and 10 the optimum pH of MB dye solution which had the best removal efficiency of MB dye. The maximum adsorption capacity was obtained at 10. SCB biochar have showed a similar MB adsorptive property at a higher pH, it could be decided that MB adsorption is more favorable in the alkaline water environment than acidic environment. This might be due to the excess H^+ ions competing with the MB cations for the adsorption sites in acidic water medium. With an increasing pH of the MB solution, the surface containing carboxyl groups was deprotonated, resulting in an increase of negatively charged sites that favor the adsorption of MB due to electrostatic attraction effect becomes more pronounced. The biochar surface is negatively charged due to the deprotonation of carboxyl and phenol hydroxyl groups (Qiu, Cheng, Xu, & Sheng, 2008). As a result, the functional groups on the surface of the biochar and the positively charged MB ions in the alkaline solution form an electrostatic interaction. On the other hand, the surface of biochar has a positive charge and the electrostatically repelled by the positive MB ions (Qiu et al., 2008; Zhu et al., 2018). There is competition for adsorption between H^+ and MB cations in an

acidic environment, and the MB adsorption efficiency decreases. From the graph the pH has a small effect on adsorption capacity, with an increase in pH decreasing adsorption capacity (Fathy, El-Shafey, & Khalil, 2013). The adsorbent is positively charged (from the point of zero charge value) for pH less than 8.2, indicating an affinity for MB solutions with a more acidic pH. The adsorbent is negatively charged (from the point of zero charge value) for pH greater than 8.2, indicating an affinity for MB solutions with a more basic pH (Eduah, Nartey, Abekoe, Henriksen, & Andersen, 2020).

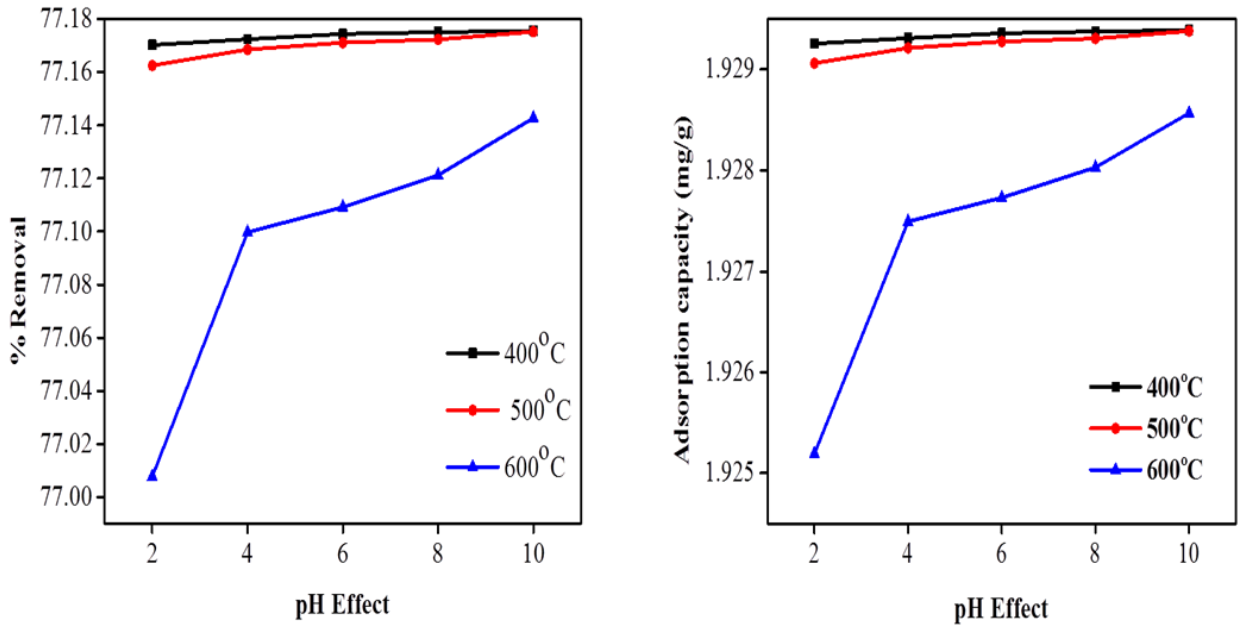

Figure 4.10. Effects of pH on MB adsorption Removal efficiency (%) (a), Adsorbent capacity (mg/g) (b) (initial conc.10 mg/L, adsorbent dose 0.8 g and contact time 80 min 25^{o}C).

4.3.5. Effect of initial concentration of MB dye

From the present study, the results indicates, as the initial concentration of MB dye increases from 10 mg/L to 400 mg/L the removal efficiency of MB dye increase as shown in Figure 4.11. A rapid adsorption took place in the first concentration in both temperature 400^{o}C and 600^{o}C but at 500^{o}C after 100 mg/g the removal efficiency starts. The adsorption equilibrium was reached at 200 mg/g at all temperature. This is due to increase in SCB biochar concentration, surface area, and active sites of the adsorbent were saturated and hence percentage removal decreases (Park et al., 2019; Y. P. Zhang, Adi, Huang, Lin, & Huang,

2019). The adsorption occurs more at lower concentration indicates the presence of more vacant adsorption site on the adsorbent to adsorb the dye molecules. At lower concentrations, all dye molecules present in the solution could interact with binding sites and thus be higher than those at higher concentrations (Bharathi & Ramesh, 2013).

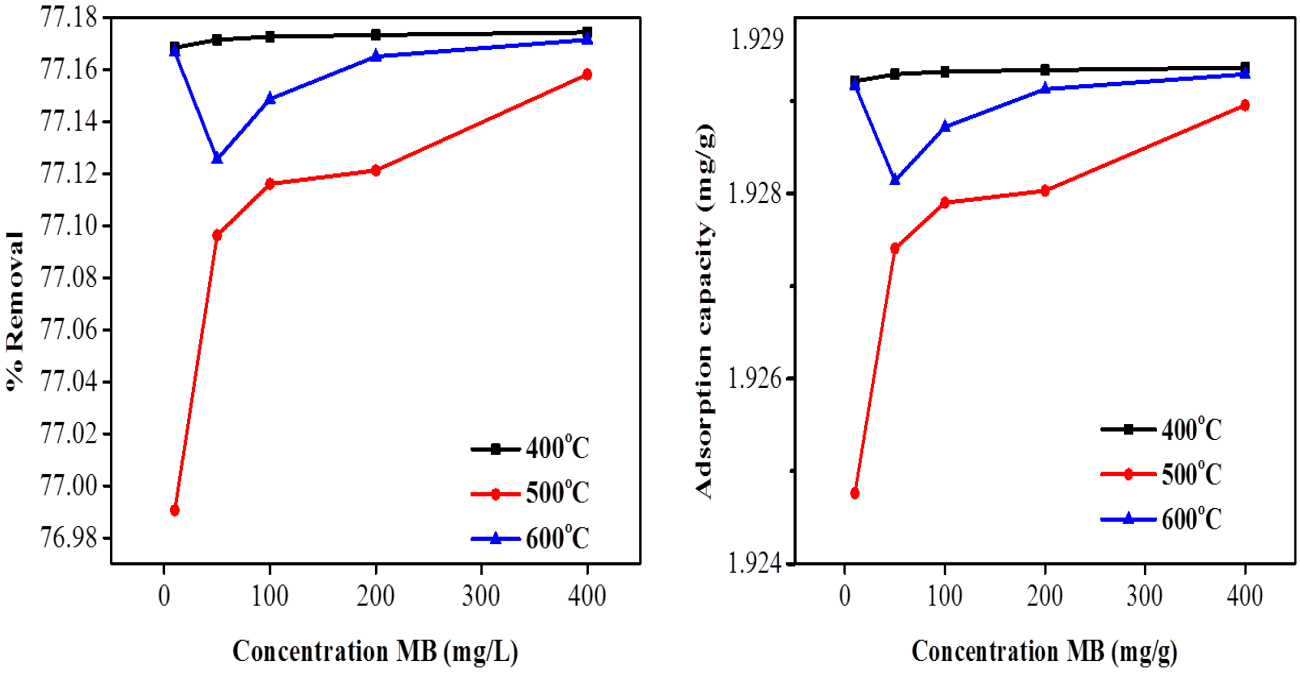

Figure 4.11. Effect of initial concentration of MB adsorption Removal efficiency (%) (a), Adsorbent capacity (mg/g) (b) (At pH 10 adsorbent dose 0.8 g and contact time 80 min 25°C).

4.5. Adsorption equilibrium isotherms

Langmuir Isotherm and Freundlich isotherm model

Langmuir and Freundlich isotherm models are based on the adsorption occurs specific homogeneous (single-layer) site and successfully on different monolayer adsorption whereas heterogeneous of the surface and assumes that the adsorption occurs at sites with different energy levels of adsorption (multi-layer) adsorption of the adsorbate onto the adsorbent surfaces, respectively (Freundlich, 1907; Langmuir, 1918). The favorability of MB adsorption onto the SCB biochar was examined using a dimensionless parameter, R_L (Azari et al., 2015).

The dimensionless equilibrium parameter (R_L) can be used to express the important attributes of the Langmuir isotherm. The type of isotherm is determined by the value of R_L, which might be unfavorable ($R_L>1$), linear ($R_L=1$), favorable ($0<R_L<1$), or irreversible ($R_L=0$) (Geçgel, Özcan, & Gürpınar, 2013). The values of R_L in the current study ranged from 0 to 1. The Langmuir isotherm was shown to be favorable for MB adsorption on SCB biochar once more. Furthermore, it is clear from Table 4.7 and 4.8 that the value of the Freundlich constant 1/n found for the current systems shows unfavorable adsorption because it is less than 0, which is owing to the negative slope of the graph therefore in the present study which indicated that the adsorption of methylene blue by SCB biochar may be a monolayer adsorption, and the surface sites were relatively homogeneous.

Table 4.7. Line fit graph of Langmuir Isotherm model for all adsorbent.

Adsorbent	Intercept	Slope	q_{max}(mg/g)	K_L	R_L	R^2
400	-0.35003	0.6717	1.48884852	1.488848525	0.00334706	0.99
500	-0.3542	0.6735	1.48484713	1.484847135	0.003356049	0.989
600	-0.35095	0.6721	1.48796238	1.487962384	0.003349046	0.987

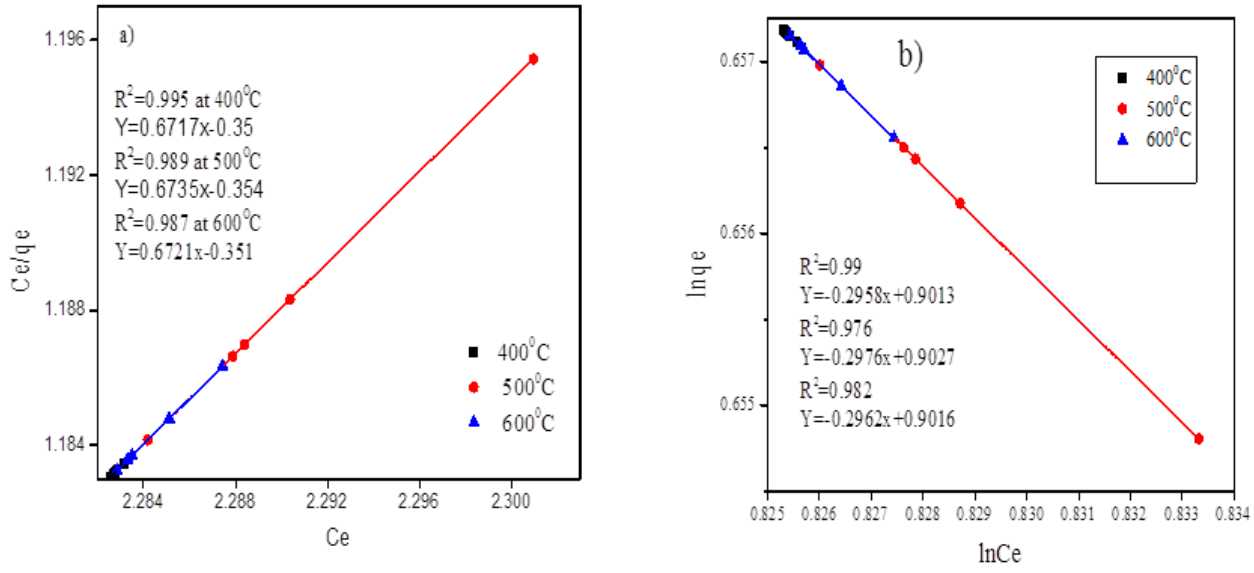

Figure 4.12. Langmuir and Freundlich isotherm model for MB adsorption on BSCB biochar

at constant adsorbent dose (0.8 g/L), pH optimum (8), contact time (80 min)) shaker speed 150 rpm, at 25^{o}C and concentration (10, 50, 100, 200, and 400) mg/L

Table 4.8. Summary table for the line fit graph of Freundlich Isotherm model

Adsorbent	Intercept	Slope	1/n	K_f	R^2
400^{o}C	0.90133	-0.296	-0.296	7.96765	0.99
500^{o}C	0.90277	-0.298	-0.298	7.99411	0.976
600^{o}C	0.90165	-0.296	-0.296	7.97352	0.982

4.6 Adsorption kinetics result

The pseudo-second order model ($R^2 > 0.99$) fits the adsorption kinetics better than the pseudo-first order model at 25 °C. The pseudo-second order model is valid for external liquid membrane diffusion, surface adsorption, and intra-particle diffusion, implying that the adsorption process is influenced by chemical adsorption, which involves electron exchange or sharing between the MB cations and functional groups on the biomass surface (Mitrogiannis, Markou, Çelekli, & Bozkurt, 2015).

Generally, the MB adsorption on SCB biochar can be described as the pseudo-second-order model, which indicated that the adsorption of MB on SCB biochar can be described as chemical adsorption. The pseudo-first-order kinetic model and results pseudo-second-order kinetic model are summarized in table 4.10. The mechanisms of adsorption and rate control were investigated using the intra-particle diffusion model. Because $C \neq 0$, different adsorption mechanisms may be involved in the adsorption process (El Achaby, Fayoud, Figueroa-Espinoza, & Aboulkas, 2018). The surface adsorption is represented by the first linear section of the curve, while the gradual diffusion of the adsorbate from the surface to the inner holes is represented by the second linear portion (Guo, Li, Liu, & Lv, 2014). Surface adsorption and intra-particle diffusion become more essential in the mechanism of SCB adsorption as the concentration of the solution increases. Surface adsorption is shown to be quick and is the major step in low concentrations of MB solution (Zhu *et al*., 2018).

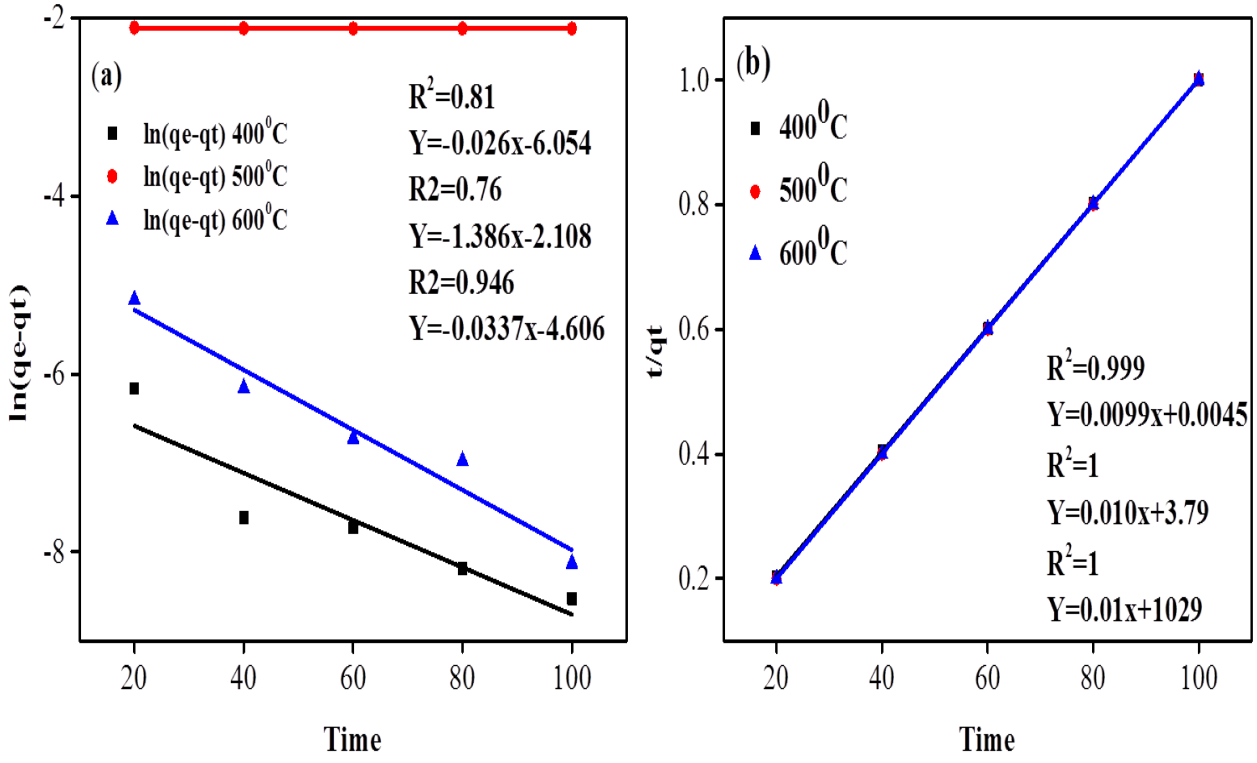

Figure 4.13: (a) Pseudo first order kinetic model and (b) Pseudo second --order kinetic curve

Table 4.9. Parameters of pseudo-first-order and pseudo-second-order kinetics models for MB adsorption

Time(min)	**The initial concentration of MB 100 mg/L**					
	qt 400^{0}C	qt 500^{0}C	qt 600^{0}C	ln(qe-qt)	ln(qe-qt)	ln(qe-qt)
20	98.62129945	99.85576	99.85146174	-6.16293	-2.66278	-5.16414
40	98.62679824	99.85673	99.85506234	-7.61323	-2.67674	-6.15758
60	99.85737317	99.85687	99.85597592	-7.72843	-2.67877	-6.72229
80	99.85737317	99.85707	99.85624463	-8.18461	-2.68175	-6.97488
100	99.85737317	99.85726	99.85688414	-8.52572	-2.6845	-8.1266

Table 4.10. Parameters of pseudo-first-order and pseudo-second-order kinetics models for MB adsorption

	Adsorption kinetics parameters					
Pseudo-first-order kinetics	Intercept	K_1(1/min)		qe (mg/g)	R^2	
400^0C	-6.05389	-0.00026		0.002348708	0.81	
500^0C	-2.10829	-1.39E-06		0.121445461	0.76	
600^0C	-4.60643	-0.00034		0.00998741	0.946	
Pseudo-second-order kinetics	Intercept	Slope	qe(mg/g)	qe^2	K_2	R^2
400^0C	0.00451	0.00996	100.4016	10080.48	0.021996	0.999
500^0C	3.79E-06	0.01001	99.9001	9980.03	26.40883	1
600^0C	1.29E-05	0.01001	99.9001	9980.03	7.746312	1

4.7. Treatment of contaminated water sample

Table 4.11 shows the removal efficiency BSCB at 500^oC for contaminated real water samples that were collected from Kanoria Africa Textile plc (methylene blue dye contaminated water). The adsorbent removed methylene blue from the methylene blue dye contaminated water with an efficiency of 86.55%.

The contaminated water samples were first determined for their initial concentration of Methylene blue dye content 5.494 mg/L. Then, the samples were treated at room temperature and shaker speed of 150 rpm with BSCB at 500^oC using the optimized values of other parameters (adsorbent dose 0.8 g/L, pH 8, contact time 80 min,)

BSCB at 500^oC effectively removed the contaminants as it can be seen on Table 4.11. The percentage removal of real water samples were high compared to standard solutions (used for optimization process) this means the adsorbent was better performance removal in real sample.

Table 4.11. Real contaminant water samples data

Contaminated water samples	**Contaminant concentration Before Adsorption (mg/L)**	**Adsorbent (BSCB 500^{o}C) Dose (g/L)**	**pH**	**Contact time(min)**	**Concentration after adsorption (mg/L)**	**%Removal efficiency**
Wastewater affected by methylene blue	5.493967353	0.8	8	80	0.738822	86.55213

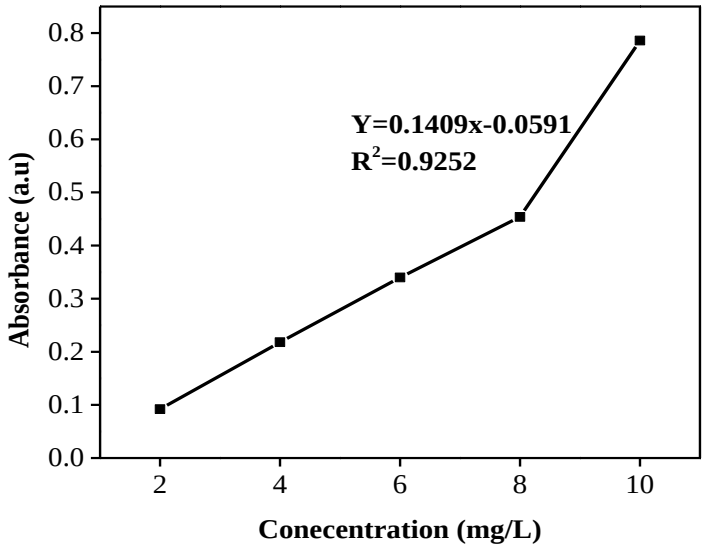

Figure 4.14. Calibration curve of MB in Wastewater

CHAPTER FIVE

5.1 CONCLUSION

The study examined the removal of methylene blue from methylene attacked wastewater by using low-cost, environmentally friendly, and locally available prepared adsorbent sugarcane bagasse from agricultural by-products. To enhance the adsorption ability of the raw SCB, thermal treatment (at 400 ^{o}C, 500 ^{o}C, and 600^{o}C) and was modified using sodium hydroxide.

Using chemical activation of sodium hydroxide and surface area development of SCB biochar to remove methylene blue from wastewater, SCB biochar was more successful in producing a large surface area. As a result, SCB indicated a higher surface area.

The optimum removal efficiency of alkaline modified sugarcane bagasse biochar (86.55%) confirmed that BSCB prepared at pyrolysis temperature of 500^{o}C were found to exhibit high removal capacity of MB dye which could be attributed to the higher surface area and oxygen-containing functional group in their biochar.

Alkaline treatment of SCB improved the surface area, increase the removal efficiency as it was depicted by BET analysis at a higher temperature the BET specific surface and total pore volume were higher due to enhancement of the pore development. The result of SCB biochar was reached 522.3 to 732.6 it was a better performance to remove MB. From the XRD characterizations were present all the adsorbents are very similar amorphous structure and it indicate only one phase. The FTIR figure illustrates the chemical structure and functional group of SCB and its chars generated at different carbonization temperatures using FTIR spectroscopy. After the carbonization procedure, the intensity of all bands observed in the raw SCB reduced more or less. SCB has a number of atomic groups and structures, according to typical infrared band designations. SEM was image depicted the SCB biochar before adsorption there are less holes and internal surfaces available. Meanwhile, regardless of temperature treatment, the pores of surface modified adsorbents resulted in different sizes and shaped pores and how it is associated to the removal efficiency of the adsorbent. Finally all this characteristics are to get a high performance to remove MB from wastewater in this study.

The study also confirmed that the dye removal efficiency of SCB depends on pH, adsorbent dose, and residence time and adsorbate concentration and there should be optimized for maximum efficiency.

The result of adsorption kinetics was in good agreement with pseudo 2nd order kinetic equation and the adsorption isotherm showed good fitting to Langmuir equation.

Further studies may be carried out to evaluate the removal efficiency of differently activated SCB prepared from different feedstock materials for methyl blue dye removal from wastewater. And,

Mechanism of methylene blue removal by using activated SCB

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6. REFERANCE

Abbas, Z., Ali, S., Rizwan, M., Zaheer, I. E., Malik, A., Riaz, M. A., . . . Al-Wabel, M. I. (2018). A critical review of mechanisms involved in the adsorption of organic and inorganic contaminants through biochar. *Arabian Journal of Geosciences, 11*(16), 1-23.

Afroze, S., & Sen, T. K. (2018). A review on heavy metal ions and dye adsorption from water by agricultural solid waste adsorbents. *Water, Air, & Soil Pollution, 229*(7), 1-50.

Akhtar, A., Krepl, V., & Ivanova, T. (2018). A combined overview of combustion, pyrolysis, and gasification of biomass. *Energy & Fuels, 32*(7), 7294-7318.

Akinola, L., Ibrahim, A., & Mohammed, M. (2019). Adsorption of methylene blue on adsorbents derived from Delonix Regia seed pods and Vigna Subterranea fruit hulls: a kinetic study. *Science World Journal, 14*(1), 23-27.

Albalasmeh, A., Gharaibeh, M. A., Mohawesh, O., Alajlouni, M., Quzaih, M., Masad, M., & El Hanandeh, A. (2020). Characterization and Artificial Neural Networks Modelling of methylene blue adsorption of biochar derived from agricultural residues: Effect of biomass type, pyrolysis temperature, particle size. *Journal of Saudi Chemical Society, 24*(11), 811-823.

Aller, D., Bakshi, S., & Laird, D. A. (2017). Modified method for proximate analysis of biochars. *Journal of Analytical and Applied Pyrolysis, 124*, 335-342.

Amarah, J. O. M. (2015). *Removal of Methylene Blue from Industrial Wastewater in Palestine Using Polysiloxane Surface Modified with Bipyrazolic Tripodal Receptor.*

Ambaye, T., Vaccari, M., van Hullebusch, E. D., Amrane, A., & Rtimi, S. (2020). Mechanisms and adsorption capacities of biochar for the removal of organic and inorganic pollutants from industrial wastewater. *International Journal of Environmental Science and Technology*, 1-22.

Andrade Siqueira, T. C., Zanette da Silva, I., Rubio, A. J., Bergamasco, R., Gasparotto, F., Aparecida de Souza Paccola, E., & Ueda Yamaguchi, N. (2020). Sugarcane bagasse as an efficient biosorbent for methylene blue removal: kinetics, isotherms and thermodynamics. *International journal of environmental research and public health, 17*(2), 526.

Arevalo-Gallegos, A., Ahmad, Z., Asgher, M., Parra-Saldivar, R., & Iqbal, H. M. (2017). Lignocellulose: a sustainable material to produce value-added products with a zero waste approach—a review. *International journal of biological macromolecules, 99*, 308-318.

Azari, A., Kakavandi, B., Kalantary, R. R., Ahmadi, E., Gholami, M., Torkshavand, Z., & Azizi, M. (2015). Rapid and efficient magnetically removal of heavy metals by magnetite-activated carbon composite: a statistical design approach. *Journal of Porous Materials, 22*(4), 1083-1096.

Babaei, A. A., Alavi, S. N., Akbarifar, M., Ahmadi, K., Ramazanpour Esfahani, A., & Kakavandi, B. (2016). Experimental and modeling study on adsorption of cationic methylene blue dye onto mesoporous biochars prepared from agrowaste. *Desalination and Water Treatment, 57*(56), 27199-27212.

Bachrun, S., AyuRizka, N., Annisa, S., & Arif, H. (2016). *Preparation and characterization of activated carbon from sugarcane bagasse by physical activation with CO2 gas.* Paper presented at the IOP Conference Series: Materials Science and Engineering.

Bakre, P. V. (2018). *Synthesis, Properties and Applications of Nano Metal Oxides and Nano Composites.* Goa University.

Behera, M., Nayak, J., Banerjee, S., Chakrabortty, S., & Tripathy, S. K. (2021). A review on the treatment of textile industry waste effluents towards the development of efficient mitigation strategy: An integrated system design approach. *Journal of environmental chemical engineering*, 105277.

Bharathi, K., & Ramesh, S. (2013). Removal of dyes using agricultural waste as low-cost adsorbents: a review. *Applied Water Science, 3*(4), 773-790.

Buthiyappan, A., Gopalan, J., & Raman, A. A. A. (2019). Synthesis of iron oxides impregnated green adsorbent from sugarcane bagasse: Characterization and evaluation of adsorption efficiency. *Journal of environmental management, 249*, 109323.

Campbell, R. M., Anderson, N. M., Daugaard, D. E., & Naughton, H. T. (2018). Financial viability of biofuel and biochar production from forest biomass in the face of market price volatility and uncertainty. *Applied energy, 230*, 330-343.

Campos, P., Miller, A. Z., Knicker, H., Costa-Pereira, M. F., Merino, A., & De la Rosa, J. M. (2020). Chemical, physical and morphological properties of biochars produced from

agricultural residues: Implications for their use as soil amendment. *Waste Management, 105*, 256-267.

Chandel, A. K., Albarelli, J. Q., Santos, D. T., Chundawat, S. P., Puri, M., & Meireles, M. A. A. (2019). Comparative analysis of key technologies for cellulosic ethanol production from Brazilian sugarcane bagasse at a commercial scale. *Biofuels, Bioproducts and Biorefining, 13*(4), 994-1014.

Chen, T., Yan, B., Xu, D.-M., & Li, L.-l. (2018). Enhanced adsorption performance of methylene blue from aqueous solutions onto modified adsorbents prepared from sewage sludge. *Water Science and Technology, 78*(4), 803-813.

CHENG, G., SUN, L., JIAO, L., & XIAO, B. (2013). Preparation of biochar from co-pyrolysis of dewatered sewage sludge-pine sawdust and its adsorption capability. *Industrial Water & Wastewater, 44*(3), 55-59.

Dai, Y., Zhang, N., Xing, C., Cui, Q., & Sun, Q. (2019). The adsorption, regeneration and engineering applications of biochar for removal organic pollutants: a review. *Chemosphere, 223*, 12-27.

Demiral, H., Demiral, İ., Karabacakoğlu, B., & Tümsek, F. (2011). Production of activated carbon from olive bagasse by physical activation. *Chemical Engineering Research and Design, 89*(2), 206-213.

Díez, D., Urueña, A., Piñero, R., Barrio, A., & Tamminen, T. (2020). Determination of hemicellulose, cellulose, and lignin content in different types of biomasses by thermogravimetric analysis and pseudocomponent kinetic model (TGA-PKM method). *Processes, 8*(9), 1048.

Dobbs, J. (2017). *The potential use of PEI modified biochar for different environmental applications*: Mississippi State University.

Edreis, E. M., Luo, G., & Yao, H. (2014). Investigations of the structure and thermal kinetic analysis of sugarcane bagasse char during non-isothermal CO2 gasification. *Journal of Analytical and Applied Pyrolysis, 107*, 107-115.

Eduah, J. O., Nartey, E. K., Abekoe, M. K., Henriksen, S. W., & Andersen, M. N. (2020). Mechanism of orthophosphate (PO4-P) adsorption onto different biochars. *Environmental Technology & Innovation, 17*, 100572.

Ejaz, U., Muhammad, S., Ali, F. I., Hashmi, I. A., & Sohail, M. (2019). Methyltrioctylammonium chloride mediated removal of lignin from sugarcane bagasse for themostable cellulase production. *International journal of biological macromolecules, 140*, 1064-1072.

El-Sayed, G. O., Yehia, M. M., & Asaad, A. A. (2014). Assessment of activated carbon prepared from corncob by chemical activation with phosphoric acid. *Water Resources and Industry, 7*, 66-75.

El Achaby, M., Fayoud, N., Figueroa-Espinoza, M.-C., & Aboulkas, A. (2018). New highly hydrated cellulose microfibrils with a tendril helical morphology extracted from agro-waste material: application to removal of dyes from waste water. *RSC advances, 8*(10), 5212-5224.

Eyupoglu, S., & Merdan, N. (2018). Eco-friendly production methods in textile wet processes *Sustainable Innovations in Textile Chemical Processes* (pp. 31-65): Springer.

Fathy, N. A., El-Shafey, O. I., & Khalil, L. B. (2013). Effectiveness of alkali-acid treatment in enhancement the adsorption capacity for rice straw: the removal of methylene blue dye. *International Scholarly Research Notices, 2013*.

Freundlich, H. (1907). Über die adsorption in lösungen. *Zeitschrift für physikalische Chemie, 57*(1), 385-470.

Garg, V., Gupta, R., Yadav, A. B., & Kumar, R. (2003). Dye removal from aqueous solution by adsorption on treated sawdust. *Bioresource technology, 89*(2), 121-124.

Geçgel, Ü., Özcan, G., & Gürpınar, G. Ç. (2013). Removal of methylene blue from aqueous solution by activated carbon prepared from pea shells (Pisum sativum). *Journal of Chemistry, 2013*.

Georgin, J., Dotto, G. L., Mazutti, M. A., & Foletto, E. L. (2016). Preparation of activated carbon from peanut shell by conventional pyrolysis and microwave irradiation-pyrolysis to remove organic dyes from aqueous solutions. *Journal of environmental chemical engineering, 4*(1), 266-275.

Ghaedi, M., Ansari, A., Habibi, M., & Asghari, A. (2014). Removal of malachite green from aqueous solution by zinc oxide nanoparticle loaded on activated carbon: kinetics and isotherm study. *Journal of Industrial and Engineering Chemistry, 20*(1), 17-28.

Ghaedi, M., Nasab, A. G., Khodadoust, S., Rajabi, M., & Azizian, S. (2014). Application of activated carbon as adsorbents for efficient removal of methylene blue: kinetics and equilibrium study. *Journal of Industrial and Engineering Chemistry, 20*(4), 2317-2324.

Ghaedi, M., Tashkhourian, J., Pebdani, A. A., Sadeghian, B., & Ana, F. N. (2011). Equilibrium, kinetic and thermodynamic study of removal of reactive orange 12 on platinum nanoparticle loaded on activated carbon as novel adsorbent. *Korean Journal of Chemical Engineering, 28*(12), 2255-2261.

Ghaffar, A., & Younis, M. N. (2015). Interaction and thermodynamics of methylene blue adsorption on oxidized multi-walled carbon nanotubes. *Green Processing and Synthesis, 4*(3), 209-217.

Ghani, W., Mohd, A., Mahmoud, D. K., Rebitanim, N., Sanyang, L., & Zainudin, R. (2013). Adsorption of methylene blue on sawdust-derived biochar and its adsorption isotherms. *J. Purity Util. Reac. Environ, 2*(2), 34-50.

Godwin, P. M., Pan, Y., Xiao, H., & Afzal, M. T. (2019). Progress in preparation and application of modified biochar for improving heavy metal ion removal from wastewater. *Journal of Bioresources and Bioproducts, 4*(1), 31-42.

Gunatilake, S. (2015). Methods of removing heavy metals from industrial wastewater. *Methods, 1*(1), 14.

Guo, J.-Z., Li, B., Liu, L., & Lv, K. (2014). Removal of methylene blue from aqueous solutions by chemically modified bamboo. *Chemosphere, 111*, 225-231.

Gupta, N., Kushwaha, A. K., & Chattopadhyaya, M. (2016). Application of potato (Solanum tuberosum) plant wastes for the removal of methylene blue and malachite green dye from aqueous solution. *Arabian Journal of Chemistry, 9*, S707-S716.

Hanaki, K., & Portugal-Pereira, J. (2018). The effect of biofuel production on greenhouse gas emission reductions *Biofuels and sustainability* (pp. 53-71): Springer, Tokyo.

Hiloidhari, M., Bhuyan, N., Gogoi, N., Seth, D., Garg, A., Singh, A., . . . Kataki, R. (2020). Agroindustry wastes: biofuels and biomaterials feedstocks for sustainable rural development *Refining Biomass Residues for Sustainable Energy and Bioproducts* (pp. 357-388): Elsevier.

Hosseinian, L., Weiner, M., Levin, M. A., & Fischer, G. W. (2016). Methylene blue: magic bullet for vasoplegia? *Anesthesia & Analgesia, 122*(1), 194-201.

Hu, Z.-P., Gao, Z.-M., Liu, X., & Yuan, Z.-Y. (2018). High-surface-area activated red mud for efficient removal of methylene blue from wastewater. *Adsorption Science & Technology, 36*(1-2), 62-79.

Husseien, M., Amer, A., El-Maghraby, A., & Taha, N. A. (2007). Utilization of barley straw as a source of a activated carbon for removal of methylene blue from aqueous solution. *Journal of Applied Sciences Research, 3*(11), 1352-1358.

Jaguaribe, E. F., Medeiros, L. d. L., Barreto, M. d. C. S., & Araujo, L. P. d. (2005). The performance of activated carbons from sugarcane bagasse, babassu, and coconut shells in removing residual chlorine. *Brazilian Journal of Chemical Engineering, 22*(1), 41-47.

Jose, S., Samant, L., Bahuguna, A., & Pandit, P. (2020). Opportunities of Agro and Biowaste in the Fashion Industry. *Recycling from Waste in Fashion and Textiles: A Sustainable and Circular Economic Approach*, 73-100.

Katheresan, V., Kansedo, J., & Lau, S. Y. (2018). Efficiency of various recent wastewater dye removal methods: A review. *Journal of environmental chemical engineering, 6*(4), 4676-4697.

Kausar, A., Iqbal, M., Javed, A., Aftab, K., Bhatti, H. N., & Nouren, S. (2018). Dyes adsorption using clay and modified clay: a review. *Journal of Molecular Liquids, 256*, 395-407.

Khaled, A., El Nemr, A., El-Sikaily, A., & Abdelwahab, O. (2009). Removal of Direct N Blue-106 from artificial textile dye effluent using activated carbon from orange peel: adsorption isotherm and kinetic studies. *Journal of hazardous materials, 165*(1-3), 100-110.

Khan, M. Q. (2017). *Preparation, Characterization and Applications of Ion-Exchange Membranes.* Aligarh Muslim University.

Kiran, S., Nosheen, S., Abrar, S., Anjum, F., Gulzar, T., & Naz, S. (2019). Advanced approaches for remediation of textile wastewater: A comparative study. *Advanced Functional Textiles and Polymers: Fabrication, Processing and Applications*, 201-264.

Kumar, N., Singh, A., Sharma, D. K., & Kishore, K. (2019). Toxicity of food additives *Food safety and human health* (pp. 67-98): Elsevier.

Kumar, P. S., Ramalingam, S., & Sathishkumar, K. (2011). Removal of methylene blue dye from aqueous solution by activated carbon prepared from cashew nut shell as a new low-cost adsorbent. *Korean Journal of Chemical Engineering, 28*(1), 149-155.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American Chemical society, 40*(9), 1361-1403.

Li, J., Dai, J., Liu, G., Zhang, H., Gao, Z., Fu, J., . . . Huang, Y. (2016). Biochar from microwave pyrolysis of biomass: A review. *Biomass and Bioenergy, 94*, 228-244.

Li, J., Liu, H., & Chen, J. P. (2018). Microplastics in freshwater systems: A review on occurrence, environmental effects, and methods for microplastics detection. *Water research, 137*, 362-374.

Li, Y., Xing, B., Ding, Y., Han, X., & Wang, S. (2020a). A critical review of the production and advanced utilization of biochar via selective pyrolysis of lignocellulosic biomass. *Bioresource technology*, 123614.

Li, Y., Xing, B., Ding, Y., Han, X., & Wang, S. (2020b). A critical review of the production and advanced utilization of biochar via selective pyrolysis of lignocellulosic biomass. *Bioresource technology, 312*, 123614.

Liu, Y., Zhao, X., Li, J., Ma, D., & Han, R. (2012). Characterization of bio-char from pyrolysis of wheat straw and its evaluation on methylene blue adsorption. *Desalination and Water Treatment, 46*(1-3), 115-123.

Mani, S., Chowdhary, P., & Bharagava, R. N. (2019). Textile wastewater dyes: toxicity profile and treatment approaches *Emerging and eco-friendly approaches for waste management* (pp. 219-244): Springer.

Manyà, J. J., Azuara, M., & Manso, J. A. (2018). Biochar production through slow pyrolysis of different biomass materials: Seeking the best operating conditions. *Biomass and Bioenergy, 117*, 115-123.

Mathew, M., Desmond, R. D., & Caxton, M. (2016). Removal of methylene blue from aqueous solutions using biochar prepared from Eichhorrnia crassipes (Water Hyacinth)-molasses composite: Kinetic and equilibrium studies. *African Journal of Pure and Applied Chemistry, 10*(6), 63-72.

Menya, E., Olupot, P., Storz, H., Lubwama, M., & Kiros, Y. (2018). Production and performance of activated carbon from rice husks for removal of natural organic matter from water: a review. *Chemical Engineering Research and Design, 129*, 271-296.

Mitrogiannis, D., Markou, G., Çelekli, A., & Bozkurt, H. (2015). Biosorption of methylene blue onto Arthrospira platensis biomass: kinetic, equilibrium and thermodynamic studies. *Journal of environmental chemical engineering, 3*(2), 670-680.

Miyah, Y., Lahrichi, A., Idrissi, M., Boujraf, S., Taouda, H., & Zerrouq, F. (2017). Assessment of adsorption kinetics for removal potential of Crystal Violet dye from aqueous solutions using Moroccan pyrophyllite. *Journal of the Association of Arab Universities for Basic and Applied Sciences, 23*, 20-28.

Mulugeta, M., & Lelisa, B. (2014). Removal of methylene blue (Mb) dye from aqueous solution by bioadsorption onto untreated Parthenium hystrophorous weed. *Mod. Chem. Appl, 2*(4), 146.

Muthmann, J., Bläker, C., Pasel, C., Luckas, M., Schledorn, C., & Bathen, D. (2020). Characterization of structural and chemical modifications during the steam activation of activated carbons. *Microporous and Mesoporous Materials, 309*, 110549.

Nanda, S., Dalai, A. K., Berruti, F., & Kozinski, J. A. (2016). Biochar as an exceptional bioresource for energy, agronomy, carbon sequestration, activated carbon and specialty materials. *Waste and Biomass Valorization, 7*(2), 201-235.

Natarajan, S., Bajaj, H. C., & Tayade, R. J. (2018). Recent advances based on the synergetic effect of adsorption for removal of dyes from waste water using photocatalytic process. *Journal of Environmental Sciences, 65*, 201-222.

Nazem, T. G., Aharon, D., & Copperman, A. B. (2020). Evaluation of the Infertile Couple. *Obstetrics and Gynecology*, 263-273.

Ndirangu, S. M., Liu, Y., Xu, K., & Song, S. (2019). Risk evaluation of pyrolyzed biochar from multiple wastes. *Journal of Chemistry, 2019*.

Nyakuma, B., Oladokun, O., Dodo, Y., Wong, S., Uthman, H., & Halim, M. (2016). Fuel characterization and thermogravimetric analysis of melon (Citrullus Colocynthis L.) seed husk. *Chemistry & Chemical Technology*(10,№ 4), 493-498.

Panwar, N., Kothari, R., & Tyagi, V. (2012). Thermo chemical conversion of biomass–Eco friendly energy routes. *Renewable and Sustainable Energy Reviews, 16*(4), 1801-1816.

Panwar, N., & Pawar, A. (2020). Influence of activation conditions on the physicochemical properties of activated biochar: a review. *Biomass Conversion and Biorefinery*, 1-23.

Panwar, N., Pawar, A., & Salvi, B. (2019). Comprehensive review on production and utilization of biochar. *SN Applied Sciences, 1*(2), 168.

Park, J.-H., Wang, J. J., Kim, S.-H., Kang, S.-W., Jeong, C. Y., Jeon, J.-R., . . . Seo, D.-C. (2019). Cadmium adsorption characteristics of biochars derived using various pine tree residues and pyrolysis temperatures. *Journal of colloid and interface science, 553*, 298-307.

Pecha, M. B., & Garcia-Perez, M. (2020). *Pyrolysis of lignocellulosic biomass: oil, char, and gas.* Paper presented at the Bioenergy.

Piccin, J. S., Cadaval, T. R. S. A., de Pinto, L. A. A., & Dotto, G. L. (2017). Adsorption isotherms in liquid phase: experimental, modeling, and interpretations *Adsorption processes for water treatment and purification* (pp. 19-51): Springer.

Purnomo, C. W., Salim, C., & Hinode, H. (2012). Effect of the activation method on the properties and adsorption behavior of bagasse fly ash-based activated carbon. *Fuel Processing Technology, 102*, 132-139.

Qiu, Y., Cheng, H., Xu, C., & Sheng, G. D. (2008). Surface characteristics of crop-residue-derived black carbon and lead (II) adsorption. *Water research, 42*(3), 567-574.

Qiu, Y., Zheng, Z., Zhou, Z., & Sheng, G. D. (2009). Effectiveness and mechanisms of dye adsorption on a straw-based biochar. *Bioresource technology, 100*(21), 5348-5351.

Rahman, M. A., Amin, S. R., & Alam, A. S. (2012). Removal of methylene blue from waste water using activated carbon prepared from rice husk. *Dhaka University Journal of Science, 60*(2), 185-189.

Rahmawati, F., Ridassepri, A. F., Wijayanta, A. T., Nakabayashi, K., Miyawaki, J., & Miyazaki, T. (2021). Carbon from Bagasse Activated with Water Vapor and Its Adsorption Performance for Methylene Blue. *Applied Sciences, 11*(2), 678.

Raposo, F., De La Rubia, M., & Borja, R. (2009). Methylene blue number as useful indicator to evaluate the adsorptive capacity of granular activated carbon in batch mode: Influence of adsorbate/adsorbent mass ratio and particle size. *Journal of hazardous materials, 165*(1-3), 291-299.

Ravenni, G., Elhami, O., Ahrenfeldt, J., Henriksen, U., & Neubauer, Y. (2019). Adsorption and decomposition of tar model compounds over the surface of gasification char and active carbon within the temperature range 250–800° C. *Applied energy*, *241*, 139-151.

Ronsse, F., Nachenius, R. W., & Prins, W. (2015). Carbonization of biomass *Recent advances in thermo-chemical conversion of biomass* (pp. 293-324): Elsevier.

Rosique, M. J., Rosique, R. G., Faria, F. M., Oliveira, C. C., Farina Jr, J. A., & Évora, P. R. (2017). Methylene blue reduces progression of burn and increases skin survival in an experimental rat model. *Burns*, *43*(8), 1702-1708.

Sajjadi, B., Chen, W.-Y., & Egiebor, N. O. (2019). A comprehensive review on physical activation of biochar for energy and environmental applications. *Reviews in Chemical Engineering*, *35*(6), 735-776.

Sardar, M., Manna, M., Maharana, M., & Sen, S. (2021). Remediation of dyes from industrial wastewater using low-cost adsorbents *Green Adsorbents to Remove Metals, Dyes and Boron from Polluted Water* (pp. 377-403): Springer.

Sarker, T. C., Azam, S. M. G. G., Abd El-Gawad, A. M., Gaglione, S. A., & Bonanomi, G. (2017). Sugarcane bagasse: a potential low-cost biosorbent for the removal of hazardous materials. *Clean Technologies and Environmental Policy*, *19*(10), 2343-2362.

Shaheen, S. M., Niazi, N. K., Hassan, N. E., Bibi, I., Wang, H., Tsang, D. C., . . . Rinklebe, J. (2019). Wood-based biochar for the removal of potentially toxic elements in water and wastewater: a critical review. *International Materials Reviews*, *64*(4), 216-247.

Singh, K., Bharose, R., & Verma, S. K. (2019). *Effective Removal of Cane-Phenolics onto Activated Rice Husk Ash (ARHA).* Paper presented at the PROCEEDING OF INTERNATIONAL SYMPOSIUM ON ADVANCES IN FUNCTIONAL AND BIOLOGICAL MATERIALS (ISAFBM-2019).

Sridhar, R. (2016). *Chemistry models for major gas species estimation and tar prediction in fluidized bed biomass gasification.* Massachusetts Institute of Technology.

Subramaniam, R., & Ponnusamy, S. K. (2015). Novel adsorbent from agricultural waste (cashew NUT shell) for methylene blue dye removal: optimization by response surface methodology. *Water Resources and Industry*, *11*, 64-70.

Sun, Y., Yue, Q., Gao, B., Li, Q., Huang, L., Yao, F., & Xu, X. (2012). Preparation of activated carbon derived from cotton linter fibers by fused NaOH activation and its application for oxytetracycline (OTC) adsorption. *Journal of colloid and interface science, 368*(1), 521-527.

Takaya, C. A. (2016). *Nutrient sorption potential of treated and untreated hydrochars and biochars derived from various waste feedstocks.* University of Leeds.

Tan, I., Ahmad, A., & Hameed, B. (2008). Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies. *Desalination, 225*(1-3), 13-28.

Tan, X.-f., Liu, S.-b., Liu, Y.-g., Gu, Y.-l., Zeng, G.-m., Hu, X.-j., . . . Jiang, L.-h. (2017). Biochar as potential sustainable precursors for activated carbon production: multiple applications in environmental protection and energy storage. *Bioresource technology, 227*, 359-372.

Tomczyk, A., Sokołowska, Z., & Boguta, P. (2020). Biochar physicochemical properties: pyrolysis temperature and feedstock kind effects. *Reviews in Environmental Science and Bio/Technology, 19*(1), 191-215.

Tronsmo, A., Gjøen, T., Sørum, H., Godfroid, J., Yazdankhah, S. P., Jelmert, A., . . . Skaar, I. (2016). Antimicrobial resistance due to the use of biocides and heavy metals: a literature review.

Uddin, M. T., Rahman, M. A., Rukanuzzaman, M., & Islam, M. A. (2017). A potential low cost adsorbent for the removal of cationic dyes from aqueous solutions. *Applied Water Science, 7*(6), 2831-2842.

Utomo, H. D., Phoon, R. Y. N., Shen, Z., Ng, L. H., & Lim, Z. B. (2015). Removal of methylene blue using chemically modified sugarcane bagasse. *Natural resources, 6*(04), 209.

Varshney, D., Mandade, P., & Shastri, Y. (2019). Multi-objective optimization of sugarcane bagasse utilization in an Indian sugar mill. *Sustainable Production and Consumption, 18*, 96-114.

Venderbosch, R. H. (2019). Fast pyrolysis. *Thermochemical processing of biomass: conversion into fuels, chemicals and power*, 175-206.

Vijwani, H., Nadagouda, M. N., Namboodiri, V., & Mukhopadhyay, S. M. (2015). Hierarchical hybrid carbon nano-structures as robust and reusable adsorbents: Kinetic studies with model dye compound. *Chemical Engineering Journal*, *268*, 197-207.

Wakkel, M., Khiari, B., & Zagrouba, F. (2019). Textile wastewater treatment by agro-industrial waste: equilibrium modelling, thermodynamics and mass transfer mechanisms of cationic dyes adsorption onto low-cost lignocellulosic adsorbent. *Journal of the Taiwan Institute of Chemical Engineers*, *96*, 439-452.

Wang, J., & Wang, S. (2019). Preparation, modification and environmental application of biochar: a review. *Journal of Cleaner Production*, *227*, 1002-1022.

Wang, Y., & Liu, R. (2017). Comparison of characteristics of twenty-one types of biochar and their ability to remove multi-heavy metals and methylene blue in solution. *Fuel Processing Technology*, *160*, 55-63.

Weber, K., & Quicker, P. (2018). Properties of biochar. *Fuel*, *217*, 240-261.

Wen, C. Q. (2017). *Removal of dye from wastewater of textile industry using banana stem-derived biochar/Wen Chang Qi*. University of Malaya.

Xia, J., Noda, K., Kagawa, S., & Wakao, N. (1998). Production of activated carbon from bagasse (waste) of sugarcane grown in Brazil. *Journal of chemical engineering of Japan*, *31*(6), 987-990.

Yadav, B., Pandey, A., Kumar, L. R., & Tyagi, R. D. (2020). Bioconversion of waste (water)/residues to bioplastics-A circular bioeconomy approach. *Bioresource technology*, *298*, 122584.

Yadav, V., Ali, J., & Garg, M. C. (2021). Biosorption of methylene blue dye from textile-industry wastewater onto sugarcane bagasse: response surface modeling, isotherms, kinetic and thermodynamic modeling. *Journal of Hazardous, Toxic, and Radioactive Waste*, *25*(1), 04020067.

Yang, K., & Xing, B. (2010). Adsorption of organic compounds by carbon nanomaterials in aqueous phase: Polanyi theory and its application. *Chemical reviews*, *110*(10), 5989-6008.

Yuan, P., Wang, J., Pan, Y., Shen, B., & Wu, C. (2019). Review of biochar for the management of contaminated soil: Preparation, application and prospect. *Science of the Total Environment*, *659*, 473-490.

Zaghbani, N., Hafiane, A., & Dhahbi, M. (2007). Separation of methylene blue from aqueous solution by micellar enhanced ultrafiltration. *Separation and Purification Technology, 55*(1), 117-124.

Zhang, J., Huang, B., Chen, L., Li, Y., Li, W., & Luo, Z. (2018). Characteristics of biochar produced from yak manure at different pyrolysis temperatures and its effects on the yield and growth of highland barley. *Chemical Speciation & Bioavailability, 30*(1), 57-67.

Zhang, Y. P., Adi, V. S. K., Huang, H.-L., Lin, H.-P., & Huang, Z.-H. (2019). Adsorption of metal ions with biochars derived from biomass wastes in a fixed column: adsorption isotherm and process simulation. *Journal of Industrial and Engineering Chemistry, 76*, 240-244.

Zhao, Q., Wu, F., Xie, K., Singh, R., Zhao, J., Xiao, P., & Webley, P. A. (2018). Synthesis of a novel hybrid adsorbent which combines activated carbon and zeolite NaUSY for CO2 capture by electric swing adsorption (ESA). *Chemical Engineering Journal, 336*, 659-668.

Zhao, S.-X., Ta, N., & Wang, X.-D. (2017). Effect of temperature on the structural and physicochemical properties of biochar with apple tree branches as feedstock material. *Energies, 10*(9), 1293.

Zhou, Y., Lu, J., Zhou, Y., & Liu, Y. (2019). Recent advances for dyes removal using novel adsorbents: a review. *Environmental pollution, 252*, 352-365.

Zhu, Y., Yi, B., Yuan, Q., Wu, Y., Wang, M., & Yan, S. (2018). Removal of methylene blue from aqueous solution by cattle manure-derived low temperature biochar. *RSC advances, 8*(36), 19917-19929.

Zuccarello, B., & Zingales, M. (2017). Toward high performance renewable agave reinforced biocomposites: Optimization of fiber performance and fiber-matrix adhesion analysis. *Composites Part B: Engineering, 122*, 109-120.

APPENDIX

EXPERIMENTAL DATA

1) Moisture content determination.

A) Moisture content At 400^{o}C

$$\%Mc = \frac{W_1 - W_2}{W_1 - w3} * 100$$

Where: - %Mc: percentage of moisture in SCB biochar

W_1: weight of the wet SCB biochar plus crucible = 23.24g

W_2: weight of the dry SCB biochar plus crucible 23.18g

W_3: Mass of empty crucible =21.24 g

$$\%Mc = \frac{23.24 - 23.18}{23.24 - 21.24} * 100$$

$$\underline{\%\text{Mc} = 3\%}$$

B) Volatile content determination 400^{o}C

Where: - %Mc: percentage of moisture in SCB biochar

W_1: weight of the wet SCB biochar plus crucible =23.24g

W_2: weight of the dry SCB biochar plus crucible 23.18g

W_3: Mass of empty crucible =21.24 g

W_4: weight of the volatile SCB biochar plus crucible 21.9g

W_5: weight of the ash content plus crucible 21.67g

$$\%Vc = \frac{W_2 - W_4}{W_2 - w3} * 100$$

$$\%Vc = \frac{23.18 - 21.9}{23.18 - 21.24} * 100$$

$$\underline{\%Vc = 65.98\%}$$

C) Calculation of ash content determination 400^{o}C

$$\%Ac = \frac{W_4 - W_5}{W_2 - w3} * 100$$

$$\%Ac = \frac{12.43 - 12.33}{13.15 - 12.17} * 100$$

$$\underline{\%Ac = 10.2\%}$$

2) Moisture content determination At 500^{o}C

A) Moisture content 500^{o}C

$$\%Mc = \frac{W_1 - W_2}{W_1 - w3} * 100$$

Where: - %Mc: percentage of moisture in SCB biochar

W_1: weight of the wet SCB biochar plus crucible = 23.51g

W_2: weight of the dry SCB biochar plus crucible 23.462g

W_3: Mass of empty crucible = 21.51g

$$\%Mc = \frac{23.51 - 23.462}{23.51 - 21.51} * 100$$

$$\underline{\%Mc = 2.4\%}$$

B) Volatile content determination 500^{o}C

Where: - %Mc: percentage of moisture in SCB biochar

W_1: weight of the wet SCB biochar plus crucible = 23.51g

W_2: weight of the dry SCB biochar plus crucible 23.462g

W_3: Mass of empty crucible =21.51g

W_4: weight of the volatile SCB biochar plus crucible 22.06g

W_5: weight of the ash content plus crucible 21.86g

$$\%Vc = \frac{W_2 - W_4}{W_2 - w3} * 100$$

$$\%Vc = \frac{23.462 - 22.06}{23.462 - 21.51} * 100$$

$$\underline{\%\text{Vc} = 71.82\%}$$

C) Calculation of ash content determination 500^{o}C

$$\%Ac = \frac{W_4 - W_5}{W_2 - w3} * 100$$

$$\%Ac = \frac{22.06 - 21.86}{23.462 - 21.51} * 100$$

$$\underline{\%\text{Ac} = 10.25\%}$$

3) Moisture content calculation for SCB biochar

A) MC At 600^{o}C

$$\%Mc = \frac{W_1 - W_2}{W_1 - w3} * 100$$

Where: - %Mc: percentage of moisture in SCB biochar

W_1: weight of the wet SCB biochar plus crucible = 13.17g

W_2: weight of the dry SCB biochar plus crucible 13.15g

W_3: Mass of empty crucible =12.17 g

$$\%Mc = \frac{13.17 - 13.15}{13.17 - 12.17} * 100$$

$$\underline{\%\text{Mc} = 2\%}$$

B) Volatile content determination 600^{o}C

Where: - %Mc: percentage of moisture in SCB biochar

W_1: weight of the wet SCB biochar plus crucible = 13.17g

W_2: weight of the dry SCB biochar plus crucible 13.15g

W_3: Mass of empty crucible =12.17 g

W_4: weight of the volatile SCB biochar plus crucible 12.43g

W_5: weight of the ash content plus crucible 12.33g

$$\%Vc = \frac{W_2 - W_4}{W_2 - w3} * 100$$

$$\%Vc = \frac{13.15 - 12.43}{13.15 - 12.17} * 100$$

$$\underline{\%\text{Vc} = 73.47\%}$$

C) Calculation of ash content determination

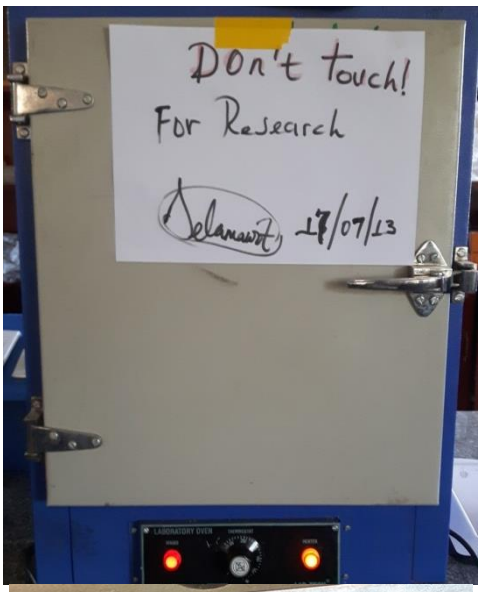
$$\%Ac = \frac{W_4 - W_5}{W_2 - w3} * 100$$

$$\%Vc = \frac{21.9 - 21.67}{23.18 - 21.24} * 100$$

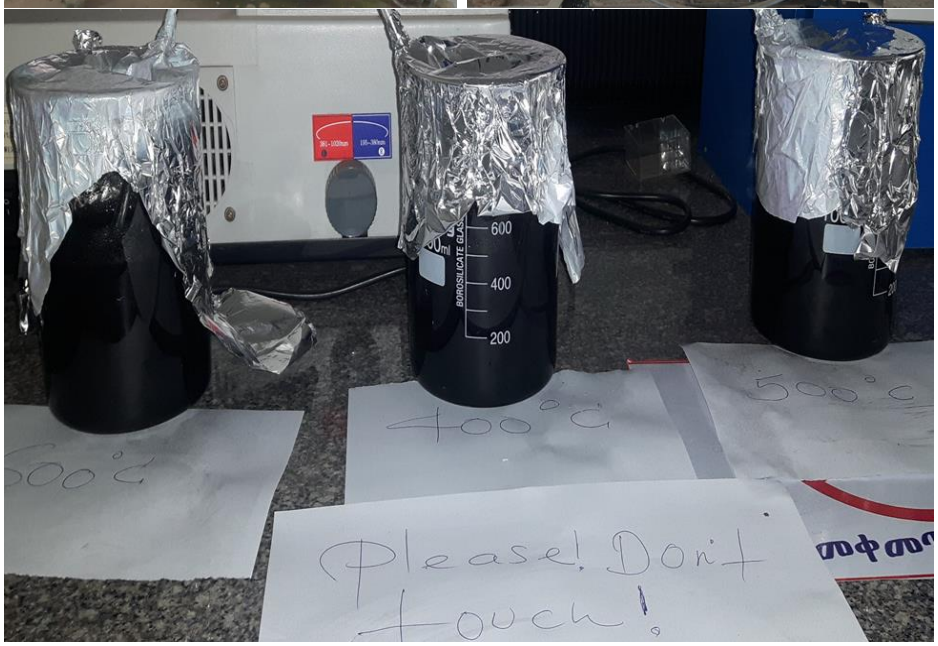
$$\underline{\%\text{Vc} = 11.86\%}$$

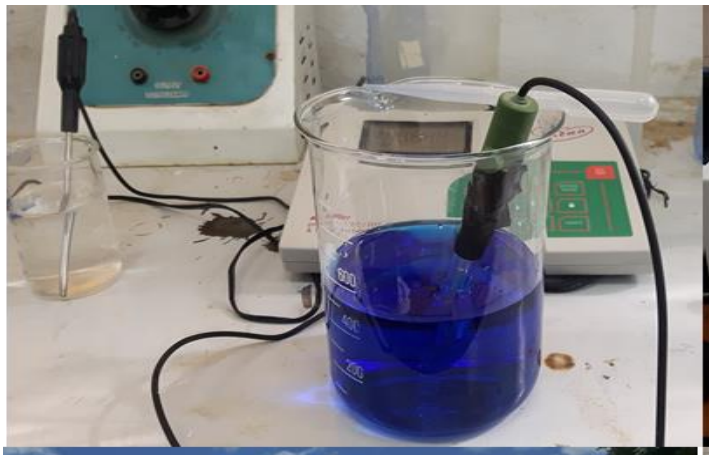
APPENDIX B: EXPERIMENTAL PICTURES

Sample preparation washes the sample to remove impurity**.**


DOn't touch!
For Research
17/07/13


UP


600
400
200
400°C
500°C
Please! DOn't touch!




DOUBLE BEAM
UV/VIS SPECTROPHOTOMETE


Kenoria
Africa
TEXTILES PLC


78-1 MAGNETIC STIRRER HOTPLATE