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DEPARTMENT OF CHEMISTRY

BROMOPHENOL BLUE DYE ADSORPTION AND KINETICS ON HYDROTHERMALLY ACTIVATED SAWDUST

BY

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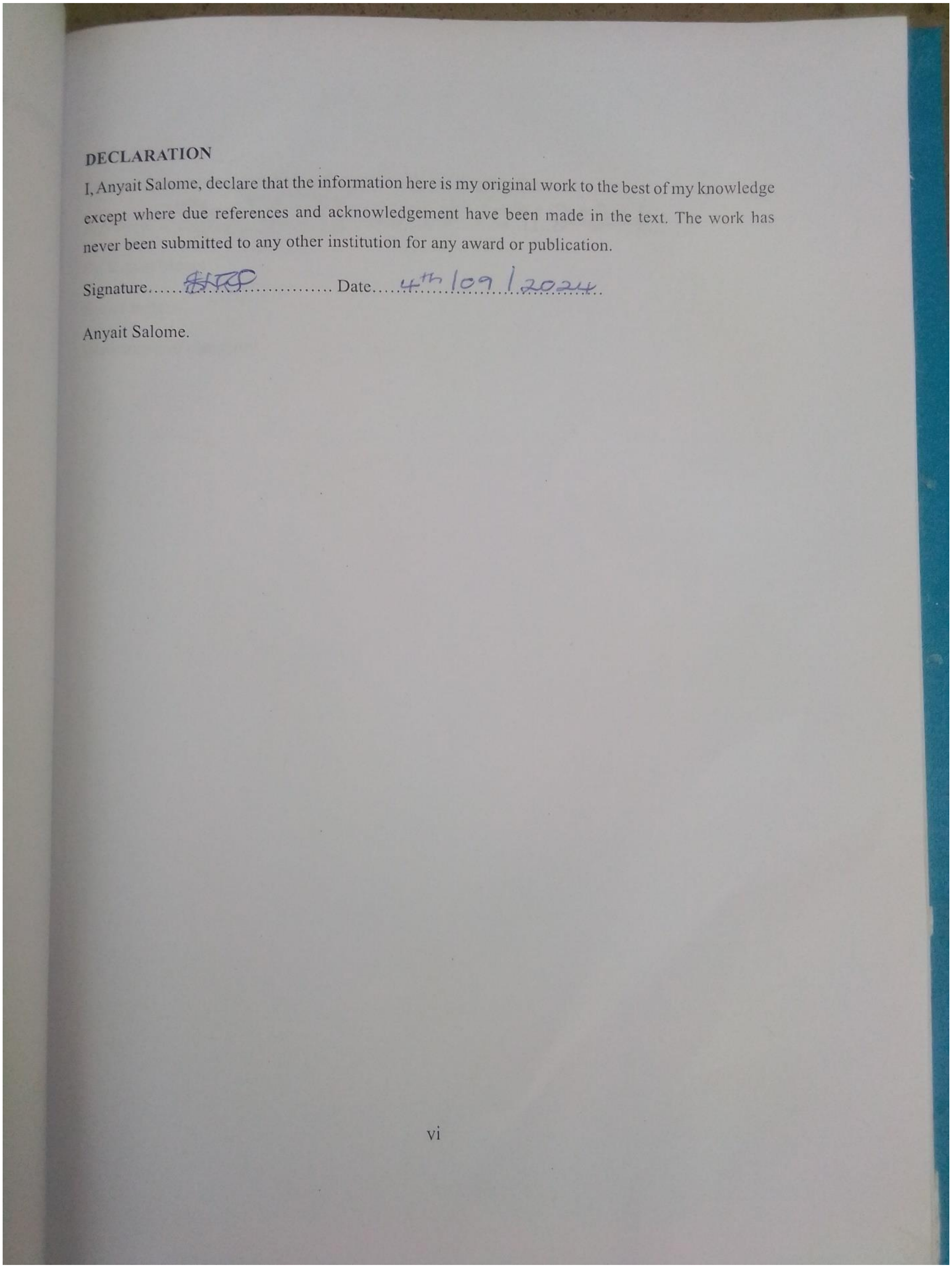

DECLARATION

I, Anyait Salome, declare that the information here is my original work to the best of my knowledge except where due references and acknowledgement have been made in the text. The work has never been submitted to any other institution for any award or publication.

Signature…………………………… Date…4th/09/2024…

Anyait Salome.

APPROVAL

This work has been supervised and approved by Dr. Kigozi Moses

Signature………………………… Date 4th/09/2024……

Dr. Kigozi Moses

Senior lecturer

Department of chemistry

DEDICATION

I dedicate this project to my parents, Mr. Asenged Gervase and Mrs. Nsimo Florence for the tireless support be it financial or otherwise, rendered during the research time to make the research possible and help me reach where I am.

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I want to thank the almighty God for the guidance and protection throughout this journey, and all the glory and honour go back to him. It gives me great pleasure to acknowledge the enormous support, sacrifices, efforts and guidance of my parents, Mr. Asenged Gervase and Mrs. Nsimo Florence in making sure that I reach where I am, my siblings Omulala Gabriel (deceased), Okello Emmanuel, Oboi benedict, Apio Angella, Otukol Cyprian, Ekaba Raphael and Oken Faustine for serving a strong pillar of encouragement and for the financial support that they rendered to me, may the good Lord surely reward the work of their hands.

Sincere appreciation goes to my supervisor, Dr. Kigozi Moses for his timely academic guidance, positive criticism that enabled me to improve my research, presentation and analytical skills am also thankful to him for his painstaking efforts in the guidance, words of wisdom that made me successfully complete this project. I truly believe that without his valuable comments and suggestions, it was impossible for me to complete this project successfully on time.

I am also thankful to the laboratory technician at the chemistry laboratory in Busitema University, Mrs. Amado Mary for the support and guidance rendered during the research process and all lecturers in the department of Chemistry. I want to thank my colleagues Abukwi Patience, Wazemba Bonifance, Nambuba Esther, Bwire Ivan and Ssemugenyi Edison for the cooperation and support during the research.

ACRONYMS USED IN THE TEXT

BPB – Bromophenol blue.

TGA – Thermogravimetric analysis.

FTIR – Fourier transform infra-red spectrophotometry.

PD – Degree of polymerization

R – Correlation coefficient

R^2 – Coefficient of determination

QFO – Pseudo first-order kinetic model

QSO – Pseudo second-order kinetic model

V_o – Initial adsorption rate (mg/gmin)

C_e – Dye concentration at equilibrium (mg/L)

q_e – Dye concentration in solid at equilibrium (mg/g)

C_o – Initial concentration of dye (mg/L)

q_m – Langmuir monolayer adsorption capacity (mg/g)

A - Absorbance

m – Mass of adsorbent in g

USEPA - United States Environmental Protection Agency

pH_{pzc} – Point of zero charge

n – Adsorption intensity

R_L – Separation factor

K_f – measure of adsorption capacity

b – Langmuir constant

CTAB – Cetyl trimethyl ammonium bromide

K_1 – Rate constant for the pseudo first-order kinetic model (L/min)

K_2 - Rate constant for the pseudo second-order kinetic model (g/mgmin)

V_1 – Volume of dye solution (µL)

C_2 – Concentration of the various dye solutions used in obtaining a calibration curve (mol/L)

q_t – Adsorption capacity at time, t

DSC - Differential Scanning calorimetry

VOCs – Volatile organic compounds

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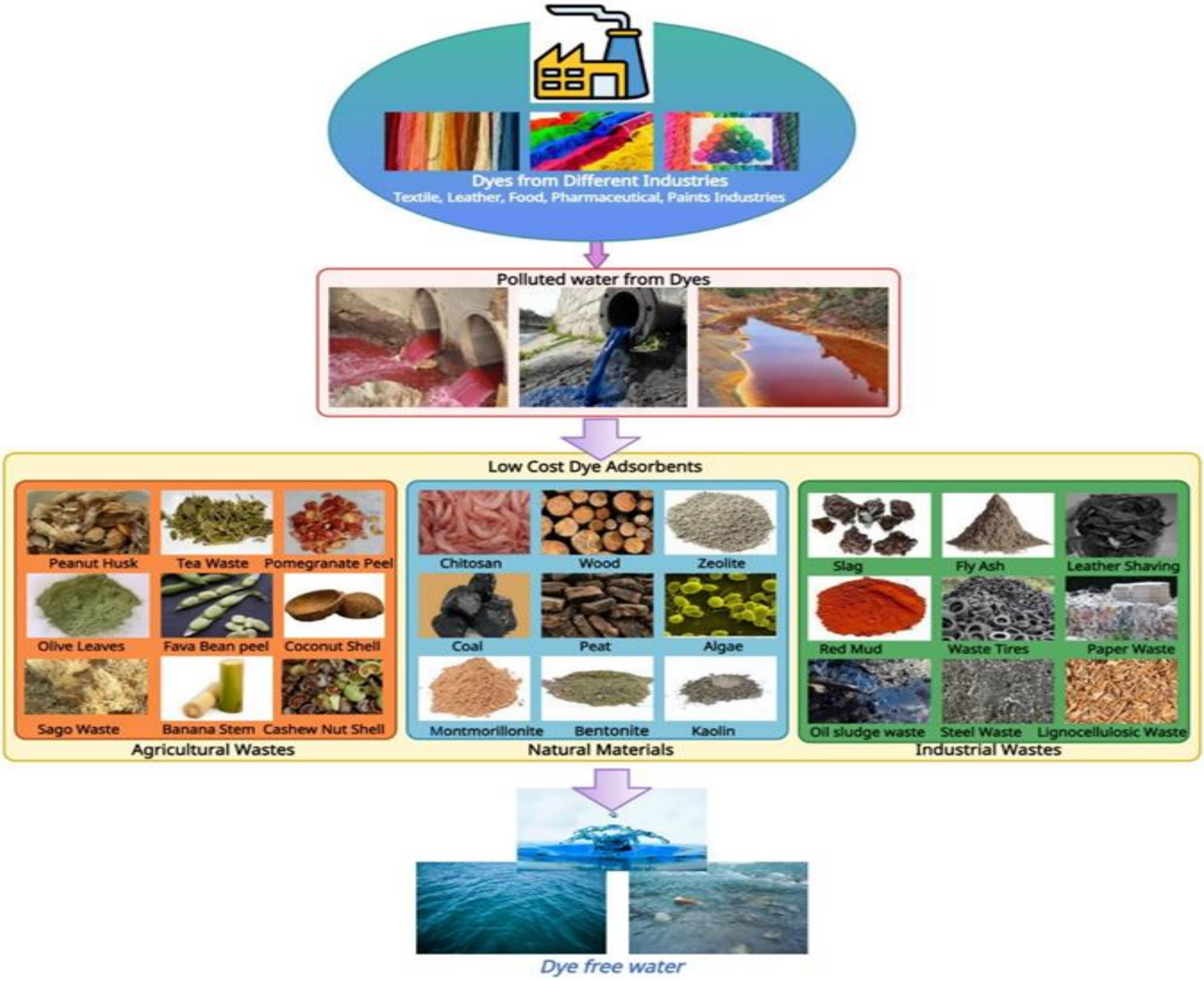
ABSTRACT

A low-cost adsorbent has been tested for its adsorption ability to remove a hazardous dye from textile wastewater. This study assesses the effectiveness and efficiency of activated sawdust in the removal of bromophenol blue dye from dye contaminated wastewater. The activated sawdust was characterized using FTIR and TGA, the results of which showed an improvement and modification in the adsorption capacity of the activated sawdust. Adsorption studies were carried out in a batch mode to examine the influence of various parameters that include; pH, contact time and adsorbent dose on the removal efficiency of the activated sawdust. The data obtained have been successfully used to equate different adsorption isotherm models, where the isothermal data were found to fit well with the Freundlich isotherm model, with a coefficient of determination of 0.9998. The adsorption interaction of BPB dye on to activated sawdust obeyed the pseudo second-order rate equation.

GRAPHICAL ABSTRACT



CHAPTER ONE: INTRODUCTION

1.1 Background to the study

Water is one of the essential resources needed for the survival of human beings on earth. About 71% of the earth's surface is covered by water. Of the total available water on earth, 96.5% is sea water and unavailable for human consumption. Only 3% is available as fresh water. Of this 3%, only a meager 0.06% can easily be accessed as the rest comprises of the frozen polar ice cap, groundwater and swamp (Rijsberman, 2006). Water pollution is one the problems that have persisted over the years and has attracted the attention of many researchers.

With the huge expansion of industrialization (such as textile, wood, rubber and dye industries), the volume of untreated wastewater that are discharged into streams and water bodies also increased. Among the waste water contaminants, particularly dyes can generate serious problems in human health due to their toxicity, mutagenicity and carcinogenicity even at low concentrations. moreover, they are highly resistant to light, aerobic digestion and oxidizing agents due to their chemical stability (Pimentel, Freire, Gómez-Díaz, & González-Álvarez, 2023). when discharged into water, they negatively affect the process of photosynthesis, disrupt the transmission of light, and disturb the biocenosis in the ecosystem (Kuśmierek, Dąbek, & Świątkowski, 2023). Dyes are natural or synthetic colorants used in various industries. Tremendous amounts of different synthetic dyes are being formulated globally which are remarkably consumed by colour industry, amongst other kinds of dyes, azo dyes account for nearly half of the total dyes consumed in the textile industries with about 10-15% of unfixed dye being lost in water and comes out as a coloured effluent from industries during the dyeing process (Khamparia & Jaspal, 2016).

Several methods are available for colour removal from waters and waste waters such as membrane separation, aerobic and anaerobic degradation using various microorganisms, chemical oxidation, coagulation and flocculation, and reverse osmosis. Some of these techniques have shown to be effective however they have some limitations such as excess amount of chemical usage, accumulation of concentrated sludge that has serious disposal problems and lack of colour reduction (Aljeboree, Alshirifi, & Alkaim, 2017). Several researchers have embraced the adsorption approach to treat the textile wastewater by means of natural and synthetic adsorbents. The present study aims to economically remove BPB dye using a low-cost natural adsorbent, sawdust, by adopting the adsorption technique. BPB dye, a member of triphenylmethane dyes family, known for its hazardous nature towards animals and humans is selected as a synthetic model dye solution for the experimentation. Ingestion of significant amount of this dye results in gastro-intestinal discomfort producing nausea and vomiting. It also has harmful effects on the skin and eyes.

Therefore, cleaning wastewater containing dyestuff becomes environmentally important to ensure a sustainable supply of water to meet the growing demands of freshwater for the growing human population and the increasing number of industries in Uganda.

1.2 Statement of the problem

Dyes are crucial in colouring fabrics and clothing to enhance their aesthetic appeal. Textile dyes are applied to fibers and clothing as a solution through various methods like dyeing and printing, creating a spectrum of vibrant colours. The choice of dyes not only influences appearance but also poses a significant environmental impact including water consumption and pollution. Synthetic dyes have an ecological impact and are harmful to human health. Following the presidential directive in Uganda on banning the importation of second-hand clothes by December 2023, the ban aimed to promote the consumption of locally produced clothing in line with the Buy Uganda Build Uganda government policy, this study sought to understand the rate at which BPB dye interacts with activated sawdust and explore its adsorption behaviour, shedding light on potential mitigation strategies for minimizing the environmental impact (water pollution) of textile dyeing processes and explore a low cost and sustainable alternative for treating the wastewater containing dyestuff.

1.3 Objectives

1.3.1 General objective

To carry out hydrothermal activation of the sawdust, Characterization, testing of the efficiency of the adsorption of BPB dye, and to understand and optimize the removal of BPB dye using activated sawdust as an adsorbent.

1.3.2 Specific objectives

i. To use the hydrothermal method to activate sawdust using the autoclave reactor.
ii. To characterize the activated sawdust using TGA and FTIR.
iii. To setup an adsorption experiment and investigate the effect of parameters (pH, contact time and adsorbent dose) on the adsorption.
iv. To determine the kinetics of adsorption of BPB dye adsorption on activated sawdust.

1.4 Justification of the study

Textile dyeing processes contribute to water pollution, and finding sustainable, cost-effective methods, such as utilizing sawdust, can offer an environmentally friendly solution. Sawdust is easily accessible, and its porous structure can effectively adsorb dyes. This research was aimed at developing an efficient water treatment strategy, reduce environmental impact, and promote a more sustainable approach to industrial processes.

CHAPTER TWO: LITERATURE REVIEW

2.1 Introduction to dye adsorption

Dyes as colourful substances have been utilized by humans since 3500 BC in various applications using natural extracts of flowers, fruits, certain insects and so on. The natural dyes constitute a very limited range of colours and are produced in low quantities. However, after the discovery of synthetic colours by William Henry Perkin in 1856, a wide range of dyes are used in various fields to colour their products such as paper, leather, rubber, textile, plastics and so on. Synthetic dyes are developed and have replaced natural dyes gradually in different industries because their molecules are stable and can resist degradation upon contact with water, detergents, or any other washing agents (Chikri, Elhadiri, Benchanaa, & Maguana, 2020).

Natural dyes cover all the dyes derived from natural sources. They are mostly non-substantive and must be applied on textiles by the help of mordants, usually a metallic salt, having an affinity for both the colouring matter and the fiber (Benkhaya, M'rabet, & El Harfi, 2020).

Commercially, more than 100,000 dyes are used and available in colour index today. Dyes are stable to light and can be classified in several ways based on their structures, application method used or even by colour. The common dyes applied in textile industries are classified as direct dyes, acid dyes, basic dyes, mordant dyes, azo dyes, reactive dyes, disperse dyes, Sulphur dyes and vat dyes. Nowadays, the classification of dyes in terms of application used in dyeing process are often in addition, dyes can also be classified by their solubility in water or else by their particle charge during dissolution such as anionic dyes (reactive, direct and acid dyes), cationic dyes (basic dyes) and also non-ionic dye (disperse dyes). In addition, anionic and cationic dye are in the category of water soluble dyes while non-ionic dye is in the category of water insoluble dyes (Razi, Hishammudin, & Hamdan, 2017).

The chemical structures of the dye and fabric molecules, and their interactions determine a dye's affinity for a given fabric. The resonance structures responsible for colour are those that cause the shifting or appearance of absorption bands in the visible spectrum of light. Three essential groups can be found in a dye molecule: the chromophore, auxochrome and matrix. Thus, dyes contain at least one unsaturated compound (chromophores) and one functional group (auxochromes). The chromophore present in the structure may be an aromatic structure containing benzene, naphthalene, or anthracene rings. The chromophore group responsible for the colour formation is represented by the following radicals: azo (-N=N-); carbonyl (=C=O); carbon (=C=C=C=); carbon-nitrogen (>C=NH or -CH=N-); nitroso (-NO or N-OH); nitro (NO or NO-OH); and Sulphur (>C=S, and other Carbon-Sulphur groups). These, in combination with a chromogen, form the basis for the chemical classification of dyes. since the chromogen-chromophore structure is often insufficient to provide adequate solubility and hence the dye cannot adhere to the fiber of the material, auxochromes are required. Auxochromes enhance the colour of the colour. Auxochromes, also known as binding affinity groups, can be amine (-NHX$_2$), hydroxyl (-OH), carbonyl groups (-COOH), aldehydes (-CHO), sulphonic acid (-SO$_3$H) or their derivatives (Rápó & Tonk, 2021).

2.2 Overview of bromophenol blue dye

Bromophenol blue dye is an orange anionic dye powder, slightly soluble in water and a member of triphenylmethane dyes family, and used for dyeing cotton fabrics coated with cationic finishing agents. bromophenol blue dye has the chemical formula $C_{19}H_{10}Br_4O_5S$, chemical name, 3,3-Bis(3,5-dibromo-4-hydroxyphenyl)-2,16-benzoxathiole-1,1(3H)-dione, molar mass of 670g with chemical structure shown below.

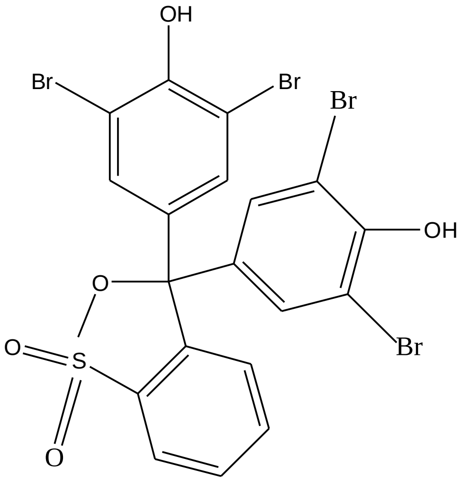


Figure 1. Chemical structure of bromophenol blue dye.

Figure 1-Chemical structure of bromophenol blue dye

2.3 Adsorption Mechanisms

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or liquid (adsorbent), forming a molecular or atomic film (the adsorbate). Generally, the adsorbent has a fixed total uptake, where a particular solute is replaced by another (Ngulube, Gumbo, Masindi, & Maity, 2018).

There are two types of adsorption: chemical adsorption (chemisorption) and physical adsorption (physisorption). The difference between the two types of adsorption is that chemical adsorption involves the formation of solid chemical associations between adsorbate and adsorbent surfaces through electron exchange. On the other hand, physical adsorption is characterized by weak Van der Waals or hydrogen bonds between adsorbate and adsorbent. Often, adsorption on most of the adsorbent is controlled by physical forces with minor exceptions of chemisorption (Chikri et al., 2020).

In the adsorption process, the adsorbent (biomass) retains dye particles (adsorbate) from dye solution, hence accumulating it on its surface. After a certain period of treatment, the saturated adsorbent will have to be regenerated/replaced depending on the feasibility of regeneration (Ngulube et al., 2018).

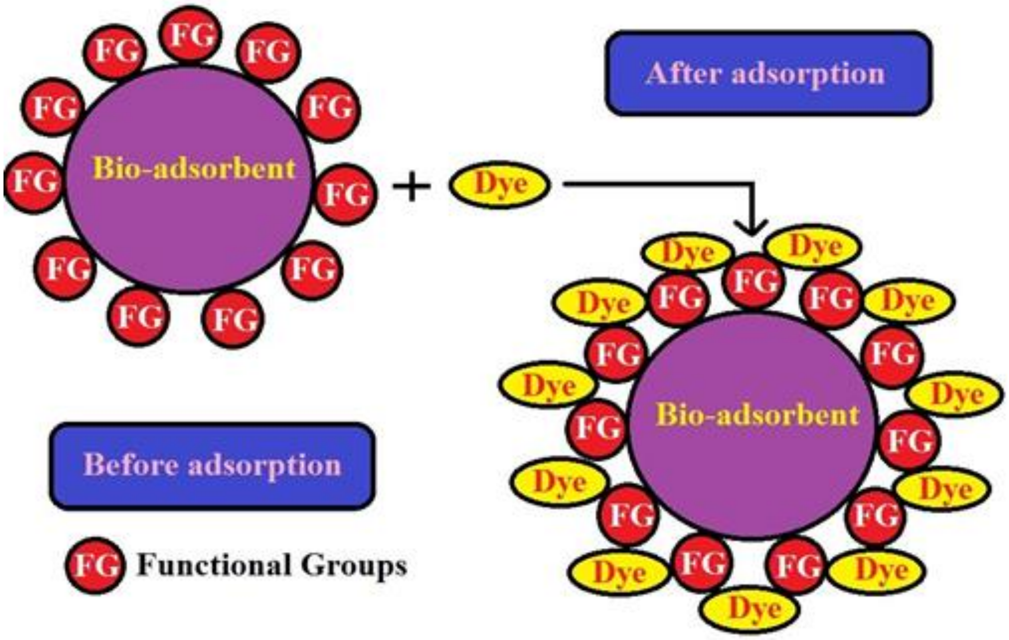


Figure 2. Shows the possible mechanism responsible for dye adsorption.

Figure 2-Possible mechanism responsible for dye adsorption.

2.4 Sawdust as an adsorbent for water treatment

In this study, saw dust is used to produce activated carbon. Saw dust is a solid by- product obtained from mechanical wood processing.

Saw dust materials are biodegradable and have an affinity for water. Wood powder does not noticeably swell in water or decompose upon prolonged contact with water (Sahmoune & Yeddou, 2016). Saw dust plays an important role in the adsorption of wastewater pollutants because it contains numerous functional groups such as carbonyl, hydroxyl, phenolic, and amide groups in its structure, which may be favorable for adsorbing a large variety of dyes (Šćiban, Radetić, Kevrešan, & Klašnja, 2007). Furthermore, sawdust can be modified by acid and alkali to increase its adsorption properties (Chikri et al., 2020). Saw dust attracts more interest from environmentalists because it is eco-friendly, abundant, accessible, cheap and easily applicable to wastewater treatment. Pine, oak, fir, and hornbeam saw dust modified with cetyl trimethyl ammonium bromide (CTAB), orange wood saw dust modified by sodium hydroxide (NaOH), sugarcane pulp modified with formaldehyde, kail (pins wallichiana) saw dust, camphor (cinnamomum camphora) saw dust, red pine saw dust, acacia saw dust, and many other types of saw dust wasted by the forest and agriculture industries that have no economic value, are found in the literature examining the potential of removing various dyes from aqueous solution (ÖZDEŞ, DURAN, OZEKEN, KALKIŞIM, & Yener, 2023).

2.4.1 composition of sawdust

For purposes of wood evaluation and its practical use, its composition is increasingly a main focus of research. The performed investigations on different wood species have showed that they are generally composed of cellulose (37-51%), hemicellulose (20-30%), lignin (20-30%) and extractives (1-5.5%). There is different bonding among cellulose, hemicellulose, and lignin, and a hydrogen bond principally couples them. In addition to this latter, a chemical bonding exists between hemicellulose and lignin. The bonding results in the lignin constantly containing a small amount of carbohydrates. Cellulose $(C_5H_8O_4)_n$ with n representing the number of glucose groups called degree of polymerization (DP) is a long homopolymer composed of glucose units as shown in figure 2 with β-(1,4) glycosidic linkage. it mainly contains carbon (44.44%), hydrogen (6.17%) and oxygen (49.39%). The DP of cellulose ranges from hundreds to tens of thousands and even higher. This component contains a large number of hydroxyl groups forming many hydrogen bonds which then build a huge network that constitutes the crystal structure (Ouafi, Rais, Taleb, Benabbou, & Asri, 2017).

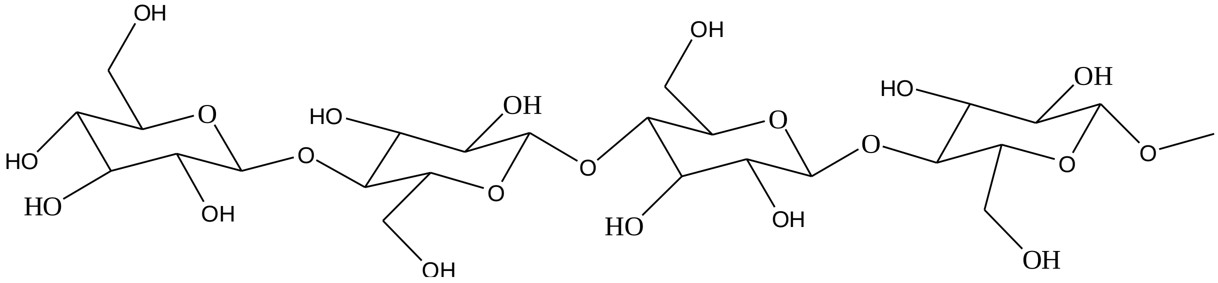
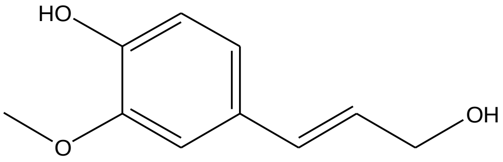


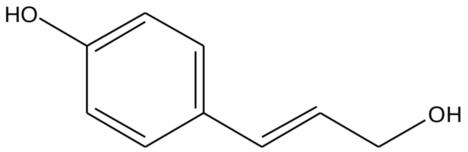
Figure 3. Molecular chain structure of cellulose.

Figure 3-Molecular chain structure of cellulose.

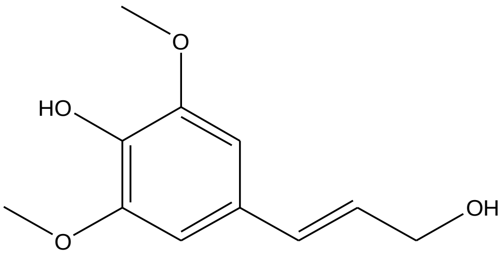
Hemicellulose is a heteropolymer that contains glucose, xylose, mannose, galactose, arabinose and other glycosyls as branched chains linked to the basic chain. Besides cellulose, lignin is the second most abundant aromatic (phenolic) polymer. It is highly branched polyphenolic polymer with a three-dimensional network. Lignin comprises phenol units that are non-linear and randomly linked, which include three main monomers namely the coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Ouafi et al., 2017).



Coniferyl alcohol



Coumaryl alcohol



Sinapyl alcohol

figure 4. The three monomers in lignin.

Figure 4-The three monomers in lignin.

Extractives can be considered as non-structural components of sawdust, which can be extracted with neutral solvents, which include resin, fats, alcohols, turpentine, tannins, fatty acids, waxes and flavonoids. Although the concentration of the extractives is low compared to those of cell wall polymers, this fraction allows the chemical Characterization of different wood species (Ouafi et al., 2017).

2.4.2. Comparison of activated sawdust with other adsorbents

Table 1-Comparison of activated sawdust with other adsorbents.

*Table 1 presents the comparison of activated sawdust with other adsorbents***.**

Adsorbent	Adsorption capacity (mg/g)	References
NaOH –modified rice husk	14.77	(Ashrafi, Kamani, & Mahvi, 2016)
Pumice	1.83	(Hossein & Behzad, 2012)
Neutral soil containing copper	41.84	(Dehghani, Ansari Shiri, Shahsavani, Shamsedini, & Nozari, 2017)
Treated bamboo sawdust	13.83	(İmran, Dahiya, & Tabrez, 2012)
Calcined magnesite	12.56	(Ngulube et al., 2018)
Balsamodendron caudatum wood waste treated with H_2SO_4	5.0354	(Sivakumar, Nithya, Karthikeyan, & Kannan, 2014)
Sugarcane bagasse treated with propionic acid	51.44	(Said et al., 2013)
Argemone Mexicana seeds	2.4	(Khamparia & Jaspal, 2016)
Powdered activated carbon	34.01	(Bhatt, Vyas, Pandit, & Sharma, 2013)
Nano-scale Zero-Valent Iron-graphene.	29.07	(Iran Manesh, Sohrabi, & Mortazavi Nik, 2022)

The porous nature of activated sawdust provides a large surface area for adsorption, facilitating the trapping of dye molecules. Besides that, it contains surface functional groups that contribute to its adsorption capacity by forming interactions with dye molecules.

2.5 Kinetics studies of adsorption of BPB

2.5.1 kinetics study

To study adsorption mechanisms like chemical reaction, mass transfer (Ngulube et al., 2018) and diffusion control (Chikri et al., 2020), there are two kinetic models commonly used and these include; the pseudo first-order kinetic model and pseudo second-order kinetic model.

2.5.1.1 The pseudo first-order kinetic model

This Lagergren kinetic model describes the adsorption of liquid-solid systems based on solid capacity (Emam, Hilal, El-Bayaa, Badawy, & Ghiat, 2017). In the pseudo first-order model, while physisorption is assumed to limit the adsorption rate of the particles onto the adsorbent, chemisorption is assumed to act as the rate limiting mechanism in the process (Tamjidi, Kamyab Moghadas, Abdollahi, Parnian, & Farhadi, 2024). The pseudo-first order equation is generally expressed as follows

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \text{..} \quad (1)$$

The integration of the above equation with initial condition, q_t=0 at t=0 leads to

$$Log(q_e - q_t) = logq_e - \frac{K_1}{2.303}t \text{..} \quad (2)$$

The values k_1 and q_e can be obtained from the intercept and slope of the line log(q_e-q_t) Vs t where, q_e and q_t are the adsorption capacity at equilibrium and time, t respectively (mg/g), k_1 is the rate constant of pseudo-first order adsorption (Lmin-1)

2.5.1.2 The pseudo-second order kinetic model

The pseudo-second order rate expression is based on the sorption capacity of solids but contrary to the previous model. It describes chemisorption's control over the whole adsorption time (Emam et al., 2017). The pseudo second-order adsorption kinetic rate equation is expressed as follows

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \text{..} \quad (3)$$

Integration of the above equation for the boundary condition q_t = 0 at t=0 and q_t = q_t at t=0 gives

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + K_2t \text{..} \quad (4)$$

Which can be rearranged to give (Qiu et al., 2009).

$$\frac{t}{q_t} = \frac{1}{V_o} + \frac{1}{q_e}t \text{..} \quad (5)$$

And $V_o = k_2q_e^2$ at t =0

Where V_o (mg/(gmin)) means initial adsorption rate, and the constants can be determined experimentally by plotting a graph of $\frac{t}{q_t}$ against t and k_2 is the rate constant of pseudo-second order adsorption (g/mgmin).

If pseudo-second order kinetics are applicable, the plot of $\frac{t}{q_t}$ against t should be linear (Bhatt et al., 2013).

2.5.2 Adsorption isotherms

In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous medium or aquatic environment to a solid phase at a constant temperature and pH. Adsorption equilibrium (the ratio between the adsorbed amount with that remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration (K. Y. Foo & B. H. Hameed, 2010). The adsorption isotherms are based on the assumption that every adsorption site is equivalent. The parameters derived from the various isotherms offer important insights into the adsorption mechanism and the surface features and attributes of the adsorbent. Two suitable isotherm models for analyzing such single state systems exist: The Freundlich and Langmuir models.

2.5.2.1 Langmuir isotherm

The Langmuir isotherm is valid for a monolayer adsorption onto a solid surface with a definite number of identical sites (İmran et al., 2012). It refers to homogeneous adsorption, in which every molecule possess constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate), with no transmigration of the adsorbate in the plane of the surface (K. Y. Foo & B. H. Hameed, 2010).

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{1}{q_m} C_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(6)}$$

Where C_e is equilibrium concentration of dye in solution, q_e is the amount of dye adsorbed at equilibrium, q_m is the Langmuir monolayer adsorption capacity (mg/g), and b is Langmuir constant related to equilibrium constant of the adsorption. A straight-line plot of $\frac{C_e}{q_e}$ Vs C_e was plotted, the slope and intercept of the plot gave the values of q_m and b, the value of the dimensionless separation factor (R_L) were calculated from Langmuir isotherm constants using the expression,

$$R_L = \frac{1}{1+bC_o} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

Where C_o is initial BPB dye concentration (mg/L) before adsorption. It is suggested that for favourable adsorption, $0 < R_L < 1$ (İmran et al., 2012).

2.5.2.2 Freundlich isotherm

Freundlich isotherm model is an exponential equation, that assumes that the concentration of adsorbate on the adsorbent surface increases as the adsorbate concentration increases. The model assumes that the adsorption could occur via multiple layers instead of a single layer. The equation has a wide application in heterogeneous systems (Lima, Adebayo, & Machado, 2015). At equilibrium conditions, the adsorbed amount, q_e can also be predicted by using the Freundlich equation (Sivakumar et al., 2014) below;

$$q_e = K_f {C_e}^{\frac{1}{n}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

where, q_e is the dye concentration in solid at equilibrium (mg/g), C_e is the dye concentration at equilibrium (mg/L), K_f is the measure of adsorption capacity and n is the adsorption intensity.

A logarithmic form of the above equation is;

$$Logq_e = logK_f + \frac{1}{n} logC_e \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

The values of n and K_f were resolute from the plot of log C_e Vs log q_e where K_f is the suggestion of the sorbent capacity and $1/n$ is a measure of the surface heterogeneity, ranging between 0 and 1, becoming more heterogeneous as its value gets closer to zero. The Freundlich equation predicts that the dye concentration on the adsorbent will rise so long as there is an enlarge in the dye concentration in the liquid. The experimental evidence indicates that an isotherm is reached at a limiting value of the solid phase concentration. If the value of the Freundlich exponent lies in the range of 1 to 10, it indicates favourable adsorption (Sivakumar et al., 2014).

2.6 Factors affecting adsorption

The efficiency of the dye adsorption process on the adsorbent is affected by several factors like solution pH, initial dye concentration, adsorbent dose, temperature and contact time.

2.6.1 Temperature

Temperature plays a very important role in determining the nature of the adsorption process because it changes the adsorption capacity of the adsorbent. If the adsorption process is endothermic, the amount of adsorption increases with increasing temperature. This may be due to increasing mobility of dye molecules, increase in the number of active sites for the adsorption with increasing temperature (Chikri et al., 2020) and also the possibility of dye molecules reaching the adsorption surface is greater at high temperatures (Abbas, Abdulrazzak, Sabbar, & Faraj, 2020). On the contrary, the amount of adsorption decreases with increasing temperature if the adsorption process is exothermic. This may be due to increasing temperature decreasing the adsorptive forces between the dye species and the active sites on the adsorbent surface as a result of decreasing the amount of adsorption (Chikri et al., 2020).

2.6.2 Initial dye concentration

A given mass of sorbent material can only adsorb a fixed amount of dye. The effect of the initial dye concentration depends on the immediate relation between the dye concentration and the available binding sites on an adsorbent surface. Generally, the percentage of dye removal decreases with an increase in initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. At low concentration, there will be unoccupied active sites on the adsorbent surface, and when initial dye concentration increases, the active sites required for adsorption of the dye molecules will disappear. However, the increase in initial dye concentration will cause an increase in the loading capacity of the adsorbent which may be due to the high driving force for mass at a high initial concentration. In other words, the residual concentration of dye molecules will be higher for high initial dye concentrations. In the case of lower concentrations, the ratio of initial number of molecules to the available adsorption sites is low and subsequently the fractional adsorption becomes independent of initial dye concentration (Albroomi, Elsayed, Baraka, & Abdelmaged, 2014).

2.6.3 pH of solution

pH of a solution is the measure of the molar concentration of hydrogen ions. A pH value > 7 indicates a basic solution whereas a pH value < 7 indicates an acidic solution. The surface charge and the degree of ionization of an adsorbent can be influenced by a variation in pH (Chikri et al., 2020). Dyes exist in ionic forms in aqueous solution so the degree of their adsorption on the adsorbent surface is influenced by the charge on the adsorbent which is in turn affected by solution, the maximum biosorption of direct red 81 on propionic acid treated pretreated bagasse was at pH=2.5 (Said et al., 2013).

pH affects the efficiency of dye adsorption through its control over the strength of electrostatic charges present in the solution or carried by the ionized dye particles present in the solution which leads to change in the rates of adsorption according to the change in pH of solution used (Abbas et al., 2020). Low pH of solution increases anionic dye removal because of the electrostatic attraction between anionic dye and the positive surface charge of the adsorbent(Mohamed Salleh, Mahmoud, Abdul Karim, & Idris, 2011). At higher pH, electrostatic repulsion is found between the negatively charged surface and dye molecules, thus decreasing the adsorption capacity and percentage removal of anionic dyes. In order to understand the adsorption mechanism, it is important to determine an essential parameter called the point of zero charge (pH_{pzc}) at which the surface charge of the adsorbent is zero. The pH_{pzc} value indicates the type of active sites and the adsorption ability of adsorbents. Anionic dye adsorption is favoured at $pH < pH_{pzc}$ where the surface becomes positively charged (Chikri et al., 2020).

2.6.4 Adsorbent dose

The adsorbent dose plays an important role in determining the ability of the adsorbent to adsorb a certain amount of adsorbent at certain laboratory conditions where the ideal weight of the adsorbent surface is determined when the maximum initial concentration of the adsorbent is adsorbed and at the time of equilibrium. Generally, as the amount of adsorbent surface increases, the amount of dye adsorbed increases due to the increase in the number of adsorption sites unoccupied on the adsorption surface and as a result, the efficiency of dye removal from the solution increases (Abbas et al., 2020). During the dye removal process, the capacity of dye adsorption may decrease because of two reasons (Rápó & Tonk, 2021):

i. Adsorption sites remain unsaturated while the number of sites available for adsorption increases.

ii. Aggregation or agglomeration of adsorbent particles may occur, reducing the available surface area and increasing the diffusion path length.

Several studies report that this increase in efficiency lasts until a saturation point is reached and then steadily decreases, sometimes slightly. This can be explained by the fact that after a certain adsorbent dose, maximum adsorption is reached and the amount of ions bound to the adsorbent and the amount of free ions remains constant, even with the further addition of adsorbent (Rápó & Tonk, 2021).

2.6.5 Contact time

The contact time between the dye and the biosorbent signifies the efficiency of the biosorbent. There is a rapid uptake of the dye which can be rationalized as a rapid attachment of the dye on the biosorbent surface or due to large number of vacant sites available at the initial stage (Said et al., 2013)

2.6.6 Adsorbent particle size

Adsorbent particle size plays an important role in manipulating the degree of surface adsorption. As particle size decreases, the surface area values increase proportionally and as a consequence, the saturation capacity per unit mass of adsorbent increases. In particular, small particles' large external surface area removes more dye in the initial stage than large particles. Meanwhile, it can be noted that with decreasing particle size, adsorption increases to some extent, beyond which decrease in particle size is negligible, which could not be due to any substantial increase in surface area. In such condition, it appears that dye molecules do not completely penetrate the adsorbent particle (large molecules of dyes are not able to penetrate into some of the interior pores of the particles when their size is large), or partly that dye molecules are preferentially adsorbed near the outer surface of the adsorbent due to steric hindrance of large dye molecules (K. Foo & B. H. Hameed, 2010).

2.7 Recent advances, research gaps and future directions

Recently, low-cost adsorbents have been used in the adsorption of BPB dye, some of which are waste products. Investigation into the use of waste materials or by-products from various industries for example Balsamodendron Caudatum wood waste (Sivakumar et al., 2014), native and citric acid modified bamboo sawdust (İmran et al., 2012), potato peels (Sharma, Tiwari, & Singh, 2014), Argemone Mexicana seeds (Khamparia & Jaspal, 2016), modified silk maze (HERAVI MOHAMMAD MOMEN, Ardalan, & Vafaie, 2014) , chamomilla plant (HERAVI M MOMEN, Kodabande, Bozorgmehr, Ardalan, & Ardalan, 2012) and others contributing to both waste management and reducing water pollution by efficient dye removal. In addition, commercial adsorbents such as commercial activated carbon (Bhatt et al., 2013) have received considerable attention due to their involvement in waste minimization. Besides, metal oxide-based adsorbents are largely preferred due to their unique properties such as highly active sites and ability to blend with other sorbents such as calcined magnesite (Ngulube et al., 2018). Furthermore, nanostructured adsorbents such as nanoparticles and Nano composites for example Nano zero-valent Iron supported on Graphene (Iran Manesh et al., 2022), enhance reactivity in dye adsorption kinetics studies. To add on the above, using various kinetic models beyond the pseudo first-order and pseudo second-order models like the intraparticle diffusion model and the Elovich model allows for a more accurate representation of complex adsorption processes. Also, environmental and green approaches focus on environmentally friendly adsorbents and green synthesis methods emphasizing sustainable and biodegradable materials for dye removal.

Future studies could target the economical and safe disposal of the spent or exhausted sawdust. Dye- loaded spent sawdust can be utilized in energy production process and also in landfilling (Dutta, Gupta, Srivastava, & Gupta, 2021). More research work has to be carried out in this sector to lower the harmful effects of this textile dye. most of the research on dye removal using low-cost methods deal with the batch adsorption process and this information must be designed for the scale up studies. The life cycle analysis of the prepared material must be evaluated to check the repeatability of the adsorbent usage and its disposal scenario (Kumar et al., 2019). Since industrial effluents are always contaminated with various additives such as inorganic salts (coexisting ions), it is important to study these ions' effects on the adsorption property of BPB dye. The adsorption of BPB dye in the presence of anions (added as sodium salts) and cations (added in the nitrate form) should be carried out. The environmental consulting industry and regulatory agencies, including the USEPA, must continue to establish reliable, accurate analytical methods for dye adsorption. Before implementing new regulations, environmental regulatory agencies must evaluate health risks posed by dye concentrations and establish background levels for aqueous solutions (accompanied by health effect studies). In addition to the above, the adsorbent should be tested with real industrial effluents to demonstrate its ability on large scale and its performance on the field so that the studies will not be limited to the laboratory alone (Bello, Adegoke, Olaniyan, & Abdulazeez, 2015).

2.8 Environmental implications of using sawdust as an adsorbent

Using sawdust as an adsorbent in environmental applications, particularly in the removal of pollutants such as dyes from wastewater presents several environmental implications that necessitate careful consideration.

2.8.1 Positive environmental impact

As a by-product of mechanical wood processing, sawdust helps to repurpose waste materials and is a sustainable adsorbent. When used in waste water treatment, sawdust does not pose a significant environmental threat because it can naturally decompose, reducing waste disposal concerns and, finally, reducing water pollution by effectively adsorbing dyes from effluents.

2.8.2 Negative environmental impact

Because of its nature and the process involved, sawdust which is often sourced from wood processing industries, may contain contaminants like heavy metals, pesticides, or preservatives used in wood treatment. As a result, using sawdust as an adsorbent for dye removal can have several detrimental environmental effects. Also, the process of preparing activated sawdust usually involves chemical treatments or thermal activation, which may release volatile organic compounds (VOCs), greenhouse gases or worsen air pollution. These contaminants have the potential to leach into wastewater during the adsorption process, causing secondary pollution if not properly treated. The disposal of spent adsorbents, which may contain adsorbed dyes and other pollutants, can also pose challenges. Improper disposal could lead to leaching of residual dyes and chemicals into soil and groundwater, affecting nearby ecosystems and possibly entering the food chain. Sawdust-based adsorption is therefore a readily available and reasonably priced solution, but in to minimize negative effects on the environment and public health, it must be carefully managed in terms of sourcing, treatment, and disposal methods.

CHAPTER THREE: MATERIALS AND METHODS

3.1 Apparatus

An oven was used to dry the sawdust, an autoclave reactor was used to activate the sawdust physically, an electric grinder used to convert the sawdust to fine material, an analytical balance used to weigh desired masses of substances, TGA and FTIR (Jasco 6600) used to monitor the thermal stability and decomposition and characterize respectively the chemically activated sawdust, Beakers(100ml) used to hold experimental solutions, Volumetric flasks (250ml and 1000ml) used for preparing standard solutions, magnetic Stirrer and an orbital shaker for mixing solutions, stir bar, Erlenmeyer conical flasks(250ml), measuring cylinders, pipettes and micropipettes, toilet paper, spatula, aluminum foil, thermometer for monitoring temperature changes, Stopwatch for monitoring time, pH meter for monitoring change in pH of solutions, centrifuge for separating mixtures, and a UV-Vis spectrophotometer for measuring absorbance.

3.2 Materials

All chemicals used were of analytical grade. They included; distilled water, bromophenol blue dye powder, ethanol, sodium hydroxide solution, hydrochloric acid and sawdust.

3.2.1 sawdust

Sawdust was obtained from a local sawmill in Nagongera town council in Tororo district and Kalupo village in Bukedea district, it was rinsed with distilled water several times and soaked for 24hours to remove dirt, lignin and impurities, dried at a temperature of 100^{o}C for 24 hours, then ground into fine powder. The powdered sawdust was then activated by an autoclave reactor using water at a temperature of 180^{o}C for 24hours.

After soaking for 24 hours **After activation**

Figure 5. State of sawdust (a) after soaking for 24hours and (b) after activation

Figure 5-State of sawdust (a) after soaking for 24hours and (b) after activation

The raw sawdust in (a) has a brown colour while the activated sawdust in (b) is dark brown in colour.

Due to their varied processing and properties, raw and activated sawdust have different characteristics. Because raw sawdust is made up of wood fibers and particles that usually have a higher moisture content, it is less porous and more densely packed. On the other hand, activated sawdust goes through a process of treatment that greatly expands both its porosity and surface area. In order to create a highly porous structure in the material, this treatment usually entails heating the sawdust to high temperatures while activating agents are present. Because of this, compared to raw sawdust, activated sawdust is lighter, more absorbent, and has a significantly higher surface area per unit mass.

3.2.2 Bromophenol blue dye

Bromophenol blue powder(1000mg) were weighed, mixed with little ethanol and dissolved in 100ml of distilled water in a 1000ml volumetric flask, the solution was stirred at a speed of 210 rpm until BPB dye powder had completely dissolved then made up to the mark with distilled water to obtain a 1000mg/L stock solution.

3.2.3 Sodium hydroxide solution

0.1M sodium hydroxide for adjusting the PH was prepared as described below;

$$\text{Molarity} = \frac{concentration(\frac{g}{L})}{Relative\ formular\ mass} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Relative formula mass of NaOH = (1*23) + (1*16) + (1*1)

= 40

Concentration (g/L) = Molarity * Relative formula mass.

= 0.1*40

= 4g/L

Therefore, $\frac{4}{4}$ = 1g was dissolved in 250ml 0f distilled water to make the 0.1M KOH

3.2.4 0.1M hydrochloric acid

$$\text{Molarity of stock solution} = \frac{Essay\ density * \%purity*1000}{RFM} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

$$= \frac{1.18*0.365*1000}{36.5}$$

C_1 = 11.8

From, $C_1V_1 = C_2V_2$ .... (12)

$11.8*V_1 = 0.1*250$

$$V_1 = \frac{0.1*250}{11.8}$$

$V_1 = 2.12$ml

Therefore, 2.12ml of HCl were added to 250ml of distilled water to make a 0.1M HCl.

The adsorption of BPB on activated sawdust was carried out in a batch system. The batch technique was selected because it is simple and reliable, the batch adsorption experiments were conducted by varying pH of solution, adsorbent dose and contact time at room temperature.

3.3 Experimental procedure

3.3.1 Preparation of activated sawdust using water

The sawdust was rinsed several times with distilled water, soaked in distilled water for 24hours, the soaked sawdust was removed from the water and placed on an aluminum foil, dried in an oven at a temperature of 100°c for 24 hours. The sawdust was removed from the oven, converted to a fine material using an electric grinder, placed on an aluminium foil, and then kept in a desiccator for future use. 20g of the ground sawdust were mixed with 100ml of distilled water, stirred, the contents transferred into an autoclave reactor and the setup was then placed in the oven set at a temperature of 180°C and left for 24 hours. The setup was removed from the oven, and the synthesized activated carbon was placed on an aluminium foil, dried in the oven for 6 hours at 80°C, and kept in the desiccator for future use.

3.3.2 Characterization of the synthesized activated sawdust

The chemical composition and functional groups of the activated sawdust were established using FTIR, the TGA was used to monitor the thermal stability and decomposition of the activated sawdust.

3.3.3 Preparation of bromophenol blue dye stock solution (1g/L)

The dye solution was prepared by dissolving 1g of bromophenol blue dye powder in little ethanol in a beaker, stirred using the magnetic stirrer until the dye had completely dissolved, was then transferred to a 1000ml volumetric flask and the solution made up to the mark with distilled water to obtain 1g/L stock solution.

The maximum absorbance of the dye solution was determined spectrophotometrically at a wavelength of 590nm.

3.3.4 The batch adsorption studies

All the experiments were carried out at room temperature (298K) and a thermometer was used to monitor any changes in temperature, concentration at 0.2mg/L, a stopwatch was used to monitor time during the experiments.

To investigate the effect of contact time of the dye; 2ml of the bromophenol blue dye stock solution were measured out using a measuring cylinder, poured in a 250ml conical flask,98ml of distilled water were added to make 100ml of solution. This solution's initial absorbance (C_o) was determined at wavelength 590nm, conical flasks 1,2,3,4,5,6 each containing 10ml of this solution, then 0.5g of the synthesized activated sawdust were added separately. The contents in each of the six flasks were stirred on an orbital shaker for 5, 25, 45,65, 85 and 105 minutes respectively at a speed of 200rpm after which the respective mixtures were separated in a centrifuge at a speed of

3000 for 10minutes, and the maximum absorbance (C_e) for the respective supernatants in each setup were determined spectrophotometrically at wavelength of 590nm. The pH was kept constant at 6.

To investigate the effect of adsorbent dose; 2ml of the bromophenol blue dye stock solution were measured out using a measuring cylinder, poured in a 250ml conical flask, 98ml of distilled water were added to make 100ml of solution. The initial absorbance (C_o) of this solution was determined at a wavelength of 590nm, conical flasks 1,2,3,4,5,6 each containing 10ml of this solution, were added 0.2g, 1g, 1.5g, 2g, 3g of activated sawdust separately then kept on an orbital shaker for 30 minutes. The mixtures were separated using a centrifuge, and the maximum absorbance (C_e) for the supernatant in each setup was determined spectrophotometrically at a wavelength of 590nm. The pH was kept constant at 6.

To investigate the effect of pH, 2ml of 1mg/L of the bromophenol blue dye solution were measured using a measuring cylinder, poured in a 250ml conical flask, 98ml of distilled water were added to make 100ml of solution, The initial absorbance (C_o) of this solution was determined at a wavelength of 590nm, conical flasks 1,2,3,4,5,6 each containing 10ml of this solution, the pH was adjusted to 2.0, 5.0, 6.0, 7.0, 9.0, 12.0 respectively using 0.1M HCl and 0.1M KOH solutions. 0.5g of the activated sawdust were added separately in each conical flask and the mixtures were shaken for 30minutes on an orbital shaker. The mixtures were separated using a centrifuge, and the maximum absorbance for the supernatant in each setup was determined spectrophotometrically at a wavelength of 590nm. A pH meter was used to determine the pH of the solutions.

The amounts of BPB dye adsorbed on activated saw dust (mg/g) and the percentage of dye removal were calculated from the following equations;

$$q_e = \frac{C_o - C_e}{m} V \quad \ldots\ldots\ldots\ldots (13)$$

$$\%\ \text{dye removal} = \left(\frac{C_o - C_e}{C_o}\right) * 100 \quad \ldots\ldots\ldots\ldots (14)$$

Where q_e is the maximum quantity of BPB dye in mg/L adsorbed, C_o is the initial BPB dye concentration in mg/L, C_e is the equilibrium concentration of BPB dye in mg/L, V is the volume of the BPB dye solution in L and m is the mass of adsorbent in g. A calibration curve was performed by measuring the solution's absorbance for each experiment. The Langmuir, Freundlich isotherms, PFO and PSO kinetic models were used to explain the adsorption kinetics.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1.1 Characterization of activated sawdust

FTIR spectroscopy of the powdered activated sawdust was done using the JASCO FTIR 6600. Figure 6 shows the FTIR spectrum of the activated sawdust used in this study.

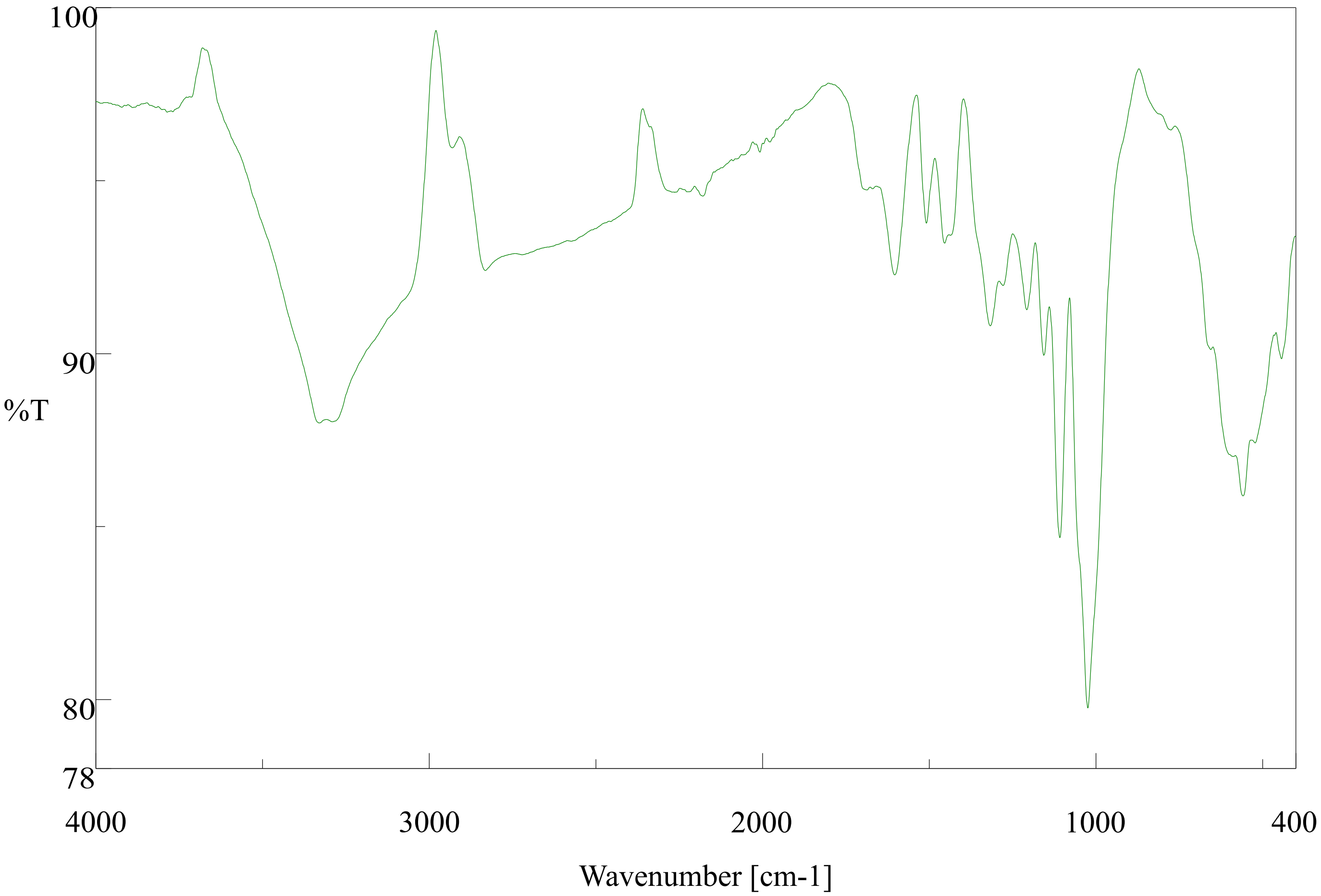


Figure 6. FTIR spectrum for activated sawdust used in this study.

Figure 6-FTIR spectrum for activated sawdust used in this study.

A peak at about 600 cm^{-1} indicates the presence of C-C stretching, Evidence of an intense peak in the range of about 600-1000cm^{-1} indicates the presence of C-C stretching bonds. The finger print region (1200-1500 cm^{-1}) reveals concentration of C-N, C-C, C-H, C-O (ethers) and nitro groups stretching in the adsorbent. A peak at 1600cm^{-1} is evidence of C=C stretching bonds. Further, the occurrence of a carbonyl group is noticed by a peak in the range of 1700-1800cm^{-1}. Aliphatic C-H stretching (CH_3-, -CH_2-, carboxylic acid) absorption bands are also evident in the range of 2800-3000cm^{-1}. A peak at about 3600cm^{-1} confirms the presence of hydroxyl groups. The presence of saturated and unsaturated carbon derivatives is indicated by a broad absorption peak between 600 and 700cm^{-1}. Therefore, by activating sawdust, its effectiveness in adsorbing BPB dye was significantly improved due to increased availability of the adsorption sites (functional groups) on its surface on which the dye molecules attach.

The thermal decomposition and stability of the activated sawdust was performed using thermogravimetric analysis at a temperature range of 25ºC to 900ºC. Figure 7 represents the mass fraction loss in percentages at different temperature ranges. There are two main stages of weight loss as shown in figure 7 below, with the first stage starting at approximately 26ºC up to 300ºC (68.9%). This was due to the desorption of water/moisture from the powder and showed an endothermic effect (Kigozi et al., 2020) in the DSC heat flow profile. The second stage was observed between 400ºC up to 600ºC (10.2%) which showed that there was decomposition of organic compounds, and groups such as carbonyl and lactonic groups present at the surface of the material. The highest mass loss at the second stage indicates that this can serve as the best carbonization temperature (Kigozi et al., 2020) for the sawdust

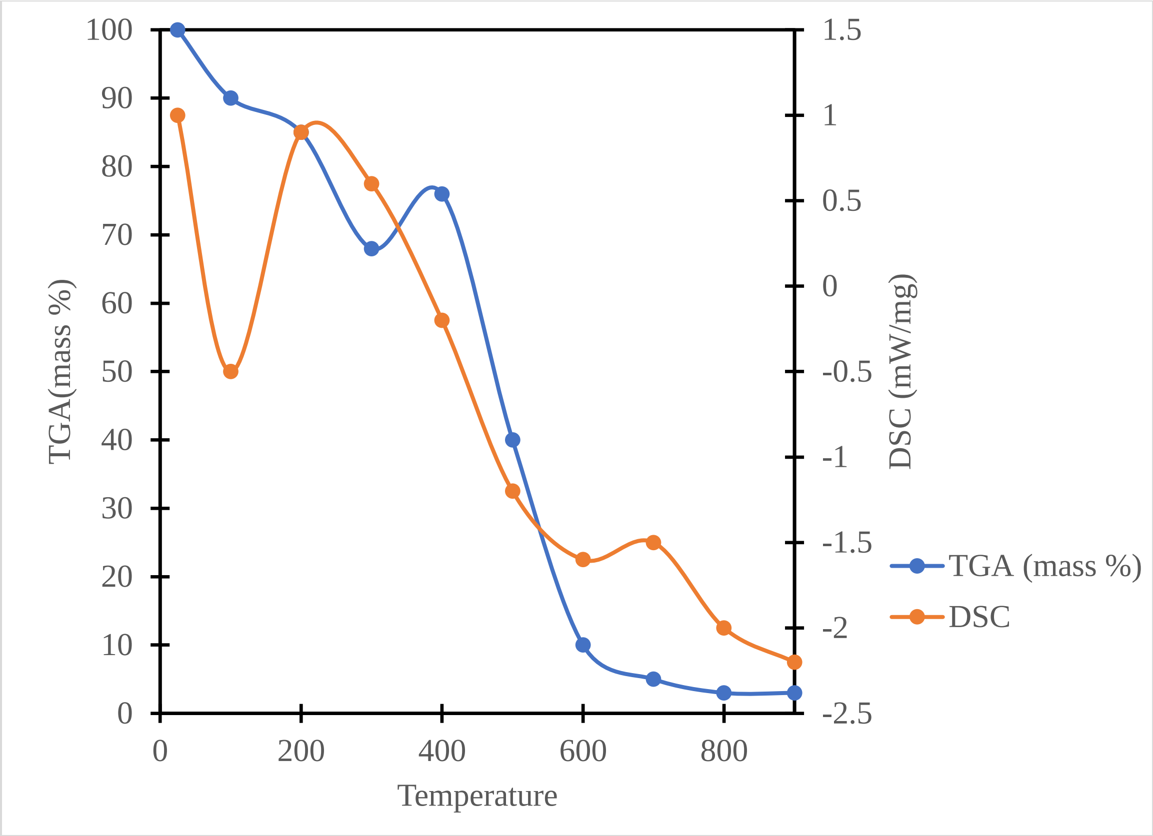


Figure 7. TGA-DSC analysis profile for activated sawdust used in this study.

Figure 7-TGA-DSC analysis profile for activated sawdust used in this study.

Table 2-Data for plotting a calibration curve.

Table 2. Data for plotting a calibration curve.

C $_1$(mole/dm^3)	V$_1$(µL) of dye solution	C$_2$(mole/dm^3)	V$_2$(ml)	A	Volume of water(ml)
0.00149	671	0.000010	100	1.104	99.33
0.00149	1007	0.000015	100	1.340	98.99
0.00149	1678	0.000025	100	1.924	98.32
0.00149	2685	0.000035	100	2.501	97.32
0.00149	3020	0.000040	100	2.799	96.98
0.00149	3355	0.000045	100	3.000	94.66

4.2.1 Calibration curve

The dye was diluted to establish various concentrations of the dye from which a calibration curve was obtained.

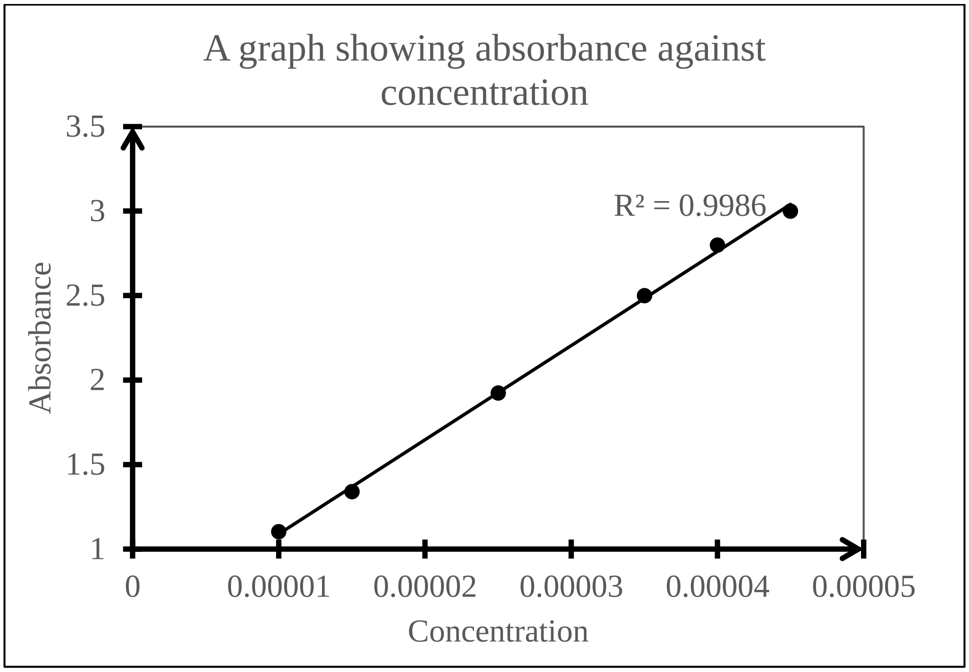


Figure 8. calibration curve of BPB dye solution used.

Figure 8-Calibration curve of bromophenol blue dye solution used.

4.2 Effect of adsorption system variables

4.2.1 Effect of contact time

The effect of contact time on the BPB adsorption at room temperature (298K) was investigated at 20mg/L concentration, pH of 6 with 0.5g of adsorbent. From the results in table 3 below, there is a clear increase in the amount of the dye adsorbed (as shown in figure 3 below) with an increase in the contact time from 5 to 105 minutes at an interval of 20 minutes with the optimum contact time being ~ 65minutes. First because there were a lot of empty active sites all over the adsorbent surface, but eventually because there were new sites for the bonding of the adsorbent and adsorbate, the situation nearly reached equilibrium (Khamparia & Jaspal, 2016).

Table 3-Data for the percentage of BPB dye removal for the effect of contact time.

Table 3. Data for the percentage of BPB dye removal for the effect of contact time.

Flask	Time(minutes)	Initial absorbance	Final absorbance	Percentage removal %
1	5	2.046	0.542	73.51
2	25	2.046	0.364	82.22
3	45	2.046	0.255	87.54
4	65	2.046	0.211	89.69
5	85	2.046	0.204	90.02
6	105	2.046	0.197	90.35

The percentage removal indicates the amount of the dye adsorbed onto the adsorbent.

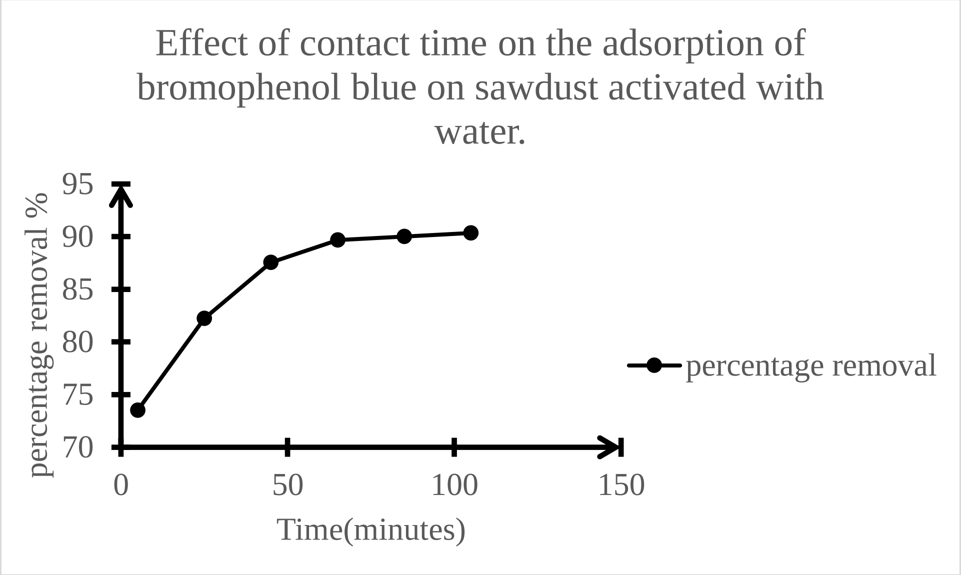


Figure 9. Effect of contact time on the adsorption of BPB dye onto activated sawdust.

Figure 9-Effect of contact time on the adsorption of BPB dye onto activated sawdust.

4.2.2 Effect of adsorbent dose.

The effect of adsorbent dose on the BPB adsorption at room temperature (298K) was investigated at 20mg/L concentration, pH of 6 with a contact time of 30minutes. Figure 4 shows the percentage of BPB dye adsorbed at different amounts of activated sawdust (0.3 to 2g). The graph trend shows an increase in the percentage of BPB adsorbed as the adsorbent dose was increased. The initial increase in the adsorbent dose increased the rate of adsorption because the number of vacant active sites (Okoye, Okey-Onyesolu, Chime, & Achike, 2018) and the surface area for adsorption on the adsorbent surface increased thereby increasing the adsorption efficiency. Higher adsorbent doses often lead to quicker attainment of equilibrium in the adsorption process. Equilibrium is reached when the rate of adsorption is equal to that of desorption, with more adsorbent present, the available adsorption sites are more quickly saturated, reducing the time required to stabilize the adsorption process. An increase in the adsorbent dose beyond 1g did not show any much difference in the adsorption capacity, because at higher doses, most of the adsorption sites may already be occupied, leading to diminishing returns in terms of increased adsorption efficiency per unit of adsorbent added and therefore, the adsorbent dose of 1g was selected as the optimum dose.

Table 4-Data for the percentage of BPB dye removal for the effect of adsorbent dose.

Table 4. Data for the percentage of BPB dye removal for the effect of adsorbent dose.

Flask	Adsorbent dose(g)	Initial absorbance	Final absorbance	Percentage removal %
1	0.3	1.791	0.372	79.23
2	0.5	1.791	0.321	82.02
3	0.8	1.791	0.255	85.76
4	1.0	1.791	0.228	87.27
5	1.5	1.791	0.224	87.52
6	2.0	1.791	0.220	87.72

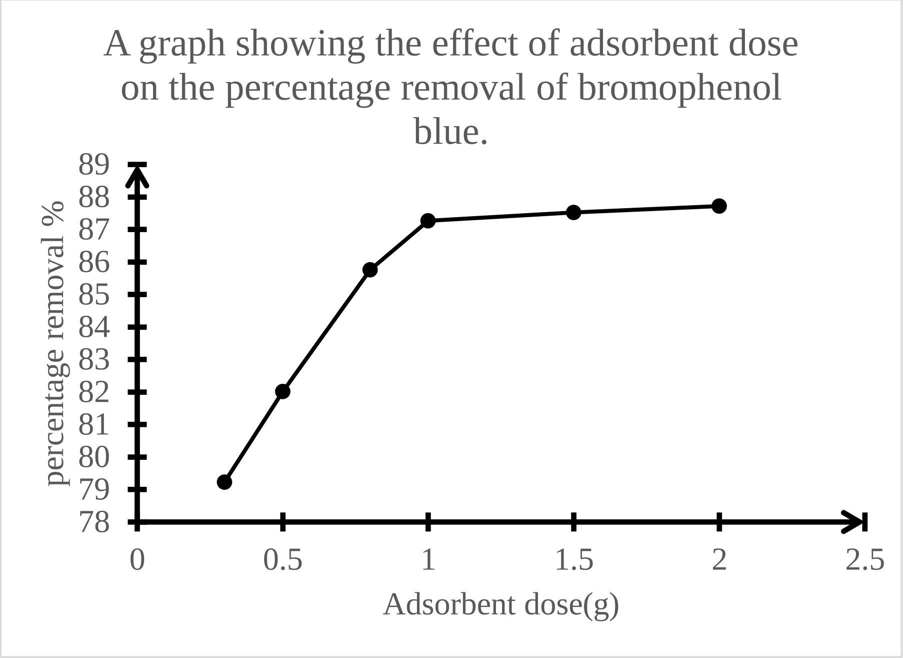


Figure 10. Effect of adsorbent dose on the adsorption of BPB dye onto activated sawdust.

Figure 10-Effect of adsorbent dose on the adsorption of BPB dye onto activated sawdust.

4.2.3 Effect of pH

The surface charge of the adsorbent and the degree of ionization of the dye present in the solution are affected by the pH of the solution; pH affects the structural stability of the dye. Therefore, pH and the surface binding sites have a great role in aqueous chemistry (Hassen, Ayfan, & Joudah, 2022). Adsorption experiments were carried out at various initial pH values (2.0 to 12.0) to determine the effect of pH on the adsorption process. It was found that as pH increased, the percentage removal of BPB dye also increased up to a pH of 6.0, which decreased as shown in figure 5 and table 5 below. Since BPB dye is an anionic dye, it produces negatively charged ions when dissolved in water, an acid pH environment facilitates the adsorption of BPB dye on the positively charged surface. At low pH, the adsorbent surface becomes positively charged resulting in significant enhancement in the adsorption of the negatively charged species the attraction of the electrostatic forces. While at high pH, the adsorption process decreases because increasing the pH of the solution will increase the tendency of the solution to acquire a negative charge, resulting in a decrease in the adsorption due to the decrease in the electrostatic force existing with the surface of the adsorbent (Hassen et al., 2022). Electrostatic repulsion exists between the dye molecules and the surface charge on activated sawdust thus the poor adsorbance recorded at high pH values (Okoye et al., 2018).

Table 5-Data for the percentage of BPB dye removal for the effect of pH.

Table 5. Data for the percentage of BPB dye removal for the effect of pH.

Flask	pH	Initial absorbance	Final absorbance	Percentage removal %
1	2.0	1.467	0.345	76.48
2	5.0	1.467	0.261	82.22
3	6.0	1.467	0.253	82.75
4	7.0	1.467	0.266	81.53
5	9.0	1.467	0.277	81.12
6	12.0	1.467	0.290	80.23

Maximum percentage removal was recorded at a pH of 6, as seen in figure 5 below therefore pH 6 was selected as the optimum pH in this study

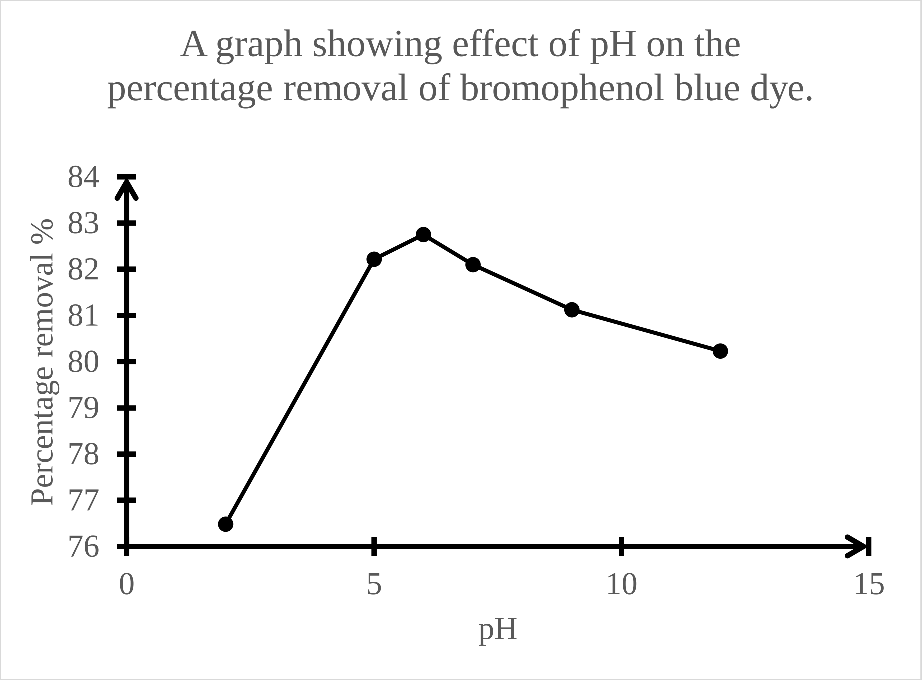


Figure 11. Effect of pH on the adsorption of BPB onto activated sawdust.

Figure 11-Effect of pH on the adsorption of BPB dye onto activated sawdust

4.3 Adsorption isotherms

Adsorption isotherms also known as equilibrium data are fundamental requirements for the design of adsorption systems. The equilibrium evaluates the capacity of the adsorbent to remove the dye under investigated conditions. Adsorption equilibrium defines a condition where the amount of solute adsorbed on the adsorbent is equal to the amount desorbed and therefore by plotting solid phase concentration against liquid phase concentration graphically, it is possible to depict the equilibrium adsorption isotherm (Okoye et al., 2018). Many theories relate to adsorption equilibrium, but this study considered the Langmuir and Freundlich isotherm models.

Table 6-Data for plotting the kinetic and isotherm models.

Table 6. Data for plotting the kinetic and isotherm models.

t(minutes)	q_t	$\frac{t}{q_t}$	C_e	q_e	$\frac{C_e}{q_e}$	$logC_e$	$logq_e$	$\log(q_e - q_t)$
5	1.504	3.32	5.30	10.6	1.69	0.724	1.025	0.959
25	1.602	15.61	3.56	7.12	2.52	0.551	0.852	0.742
45	1.791	25.13	2.50	4.99	3.59	0.398	0.698	0.505
65	1.835	35.42	2.10	4.13	4.34	0.322	0.616	0.361
85	1.842	46.15	2.00	3.99	4.5	0.301	0.601	0.332
105	1.849	56.79	1.93	3.85	4.66	0.286	0.585	0.301

4.3.1 Langmuir isotherm

This model is based on the following assumptions (Lima et al., 2015).

1. Adsorbates are chemically adsorbed at a fixed number of well-defined sites.
2. A monolayer of the adsorbate is formed over the surface of the adsorbent when it gets saturated.
3. Each site can hold only one adsorbate species.
4. All sites are energetically equivalent.

5. Interactions between the adsorbate species do not exist.

From equation 6,

The experimental data $\frac{C_e}{q_e}$ against C_e were plotted, and the values of b and q_m calculated from the intercept and slope of the plot, the R^2 value was also determined and found to be 0.9378. Further analysis of the Langmuir equation was carried out, and the dimensionless equilibrium parameter (R_L) was calculated. R_L is used as an indicator for the adsorption experiment (Dhananasekaran, Palanivel, & Pappu, 2016).

From equation 7,

Where b is the Langmuir constant and C_e is the initial concentration of the dye. If the R_L value > 1, the adsorption process is unfavourable. Whether the R_L value is equal to 1 or the value lies between 0 and 1 indicates the adsorption process is linear and favourable. If the R_L value = 0, then the adsorption process is irreversible (Dhananasekaran et al., 2016). In this study, b = -0.1444 which is very low and with a negative slope implying that the adsorption of BPB dye on to activated sawdust cannot be described using this model

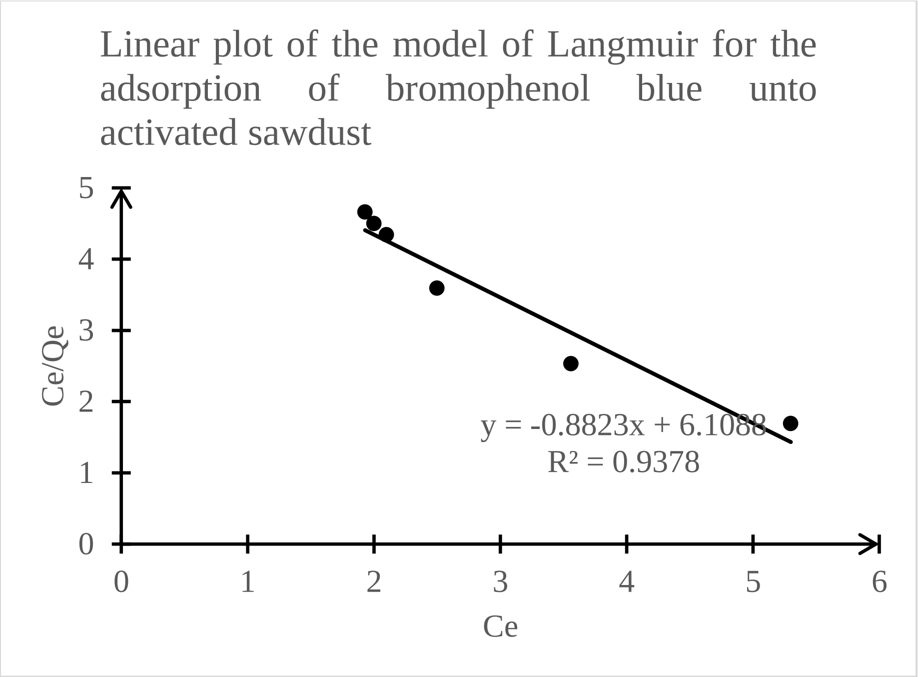


Figure 12. Plot of Langmuir isotherm for BPB dye adsorption onto activated sawdust.

Figure 12-Plot of Langmuir isotherm for BPB dye adsorption onto activated sawdust.

4.3.2 Freundlich isotherm

This model is applicable to heterogeneous systems and it involves the formation of multilayers. The equation is as shown in equation 8.

Values of $\frac{1}{n}$ and K_f were obtained from figure 7 below. The value of $\frac{1}{n}$ was obtained from the slope of the graph. The favourability of the adsorption process can be predicted from the value of n. $\frac{1}{n}$ values indicate the type of isotherm to be irreversible ($\frac{1}{n} = 0$), favourable ($0<\frac{1}{n}<1$), unfavourable ($\frac{1}{n}>1$) (Okoye et al., 2018). From the results obtained, $\frac{1}{n} = 1.008$ which is in the range of ($0<\frac{1}{n}<1$) implying that activated sawdust is a good adsorbent for adsorption, also, the R^2 value was determined and found to be 0.9998 which is higher and close to one and therefore described the adsorption process best indicating that the surface of activated sawdust is heterogeneous in nature.

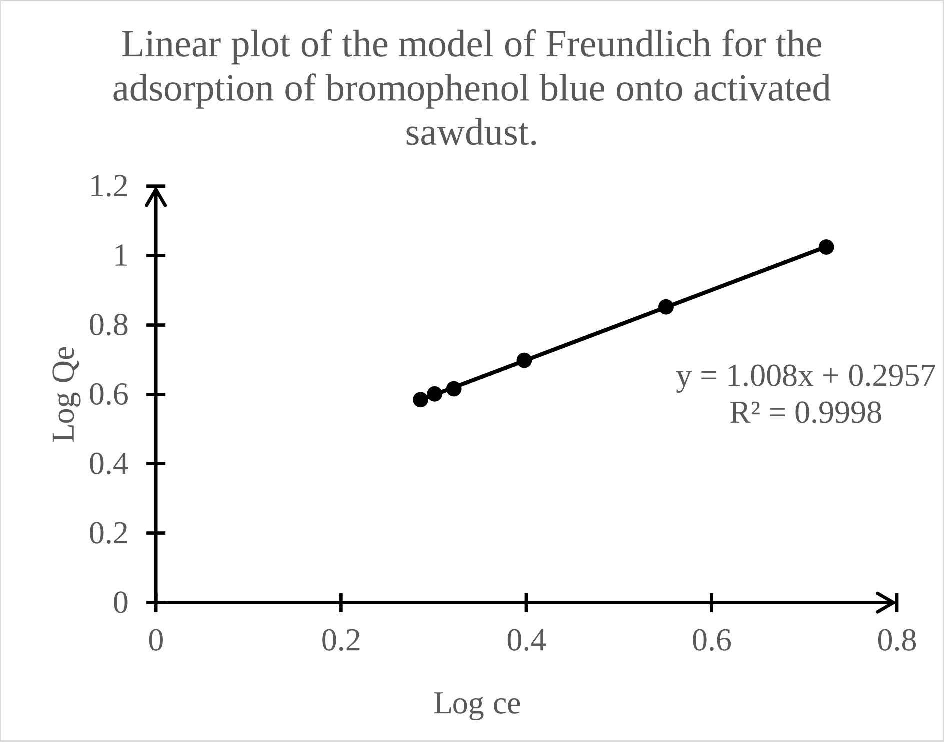


Figure 13. Plot of Freundlich isotherm for the BPB dye adsorption onto activated sawdust.

Figure 13-Plot of Freundlich isotherm for the BPB dye adsorption onto activated sawdust.

4.4 Adsorption kinetics

4.4.1 Pseudo first-order kinetic model

From equation 2 which represents the linear form of the pseudo first-order kinetic model, K_1 was obtained from the slope and q_e from the intercept of figure 14 below. The results show a low value of the coefficient of determination implying that the kinetics of adsorption of BPB dye on to activated sawdust cannot be well described by the pseudo first-order model.

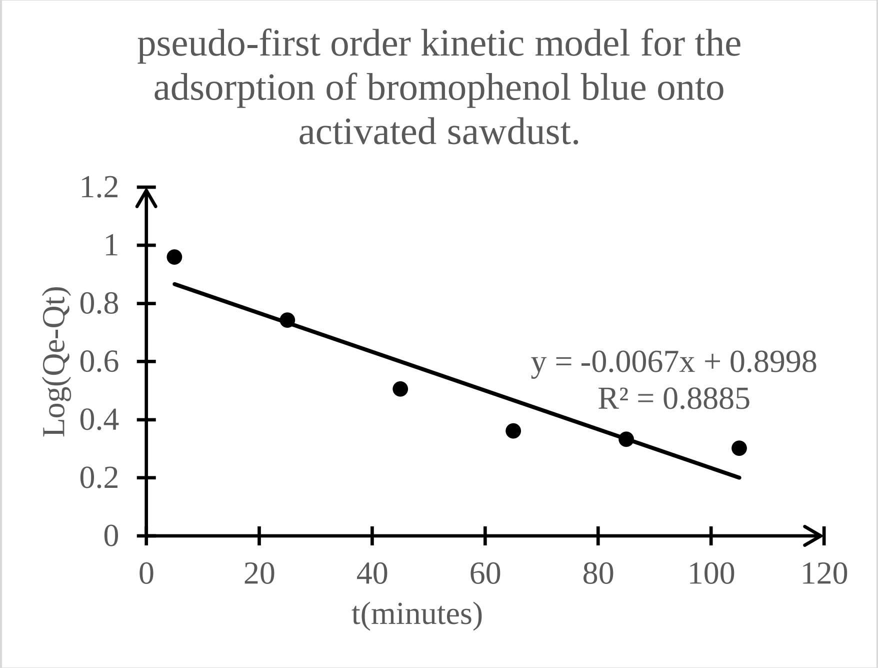


Figure 14. Plot of pseudo first-order kinetic model for the adsorption of BPB dye onto activated sawdust.

Figure 14-Plot of pseudo first-order kinetic model for the adsorption of BPB dye onto activated sawdust.

4.4.2 Pseudo second-order kinetic model

From equation 5 which shows the linear form of the pseudo second-order model, K_2 and q_e were obtained from the figure 8 below. The results show higher R^2 value for adsorption of BPB dye on to activated sawdust. The value of the coefficient of determination is close to one and therefore describes the adsorption process best.

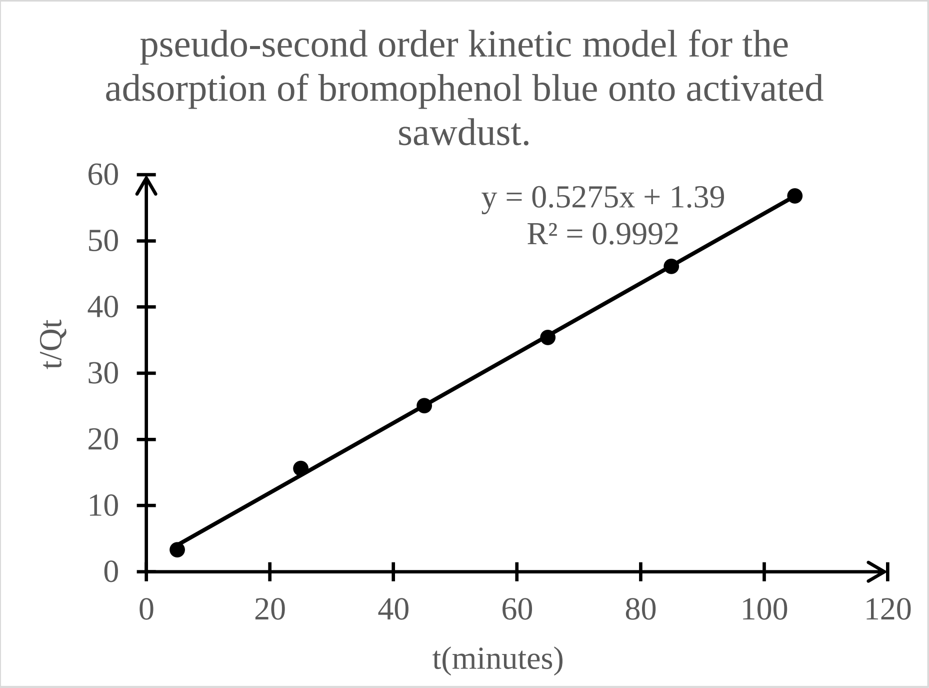


Figure 15. Plot of pseudo second-order kinetic model for the adsorption of BPB dye onto activated sawdust.

Figure 15-Plot of pseudo second-order kinetic model for adsorption of BPB dye onto activated sawdust.

CHAPTER FIVE: CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The removal of BPB from aqueous solutions by activated sawdust through the adsorption process has been experimentally investigated, with the aim of using it for cleaning textile wastewater. The percentage of BPB dye removal increased with increasing pH of the solution and attains a maximum percentage adsorption of 82.75% at pH ~ 6.0 and decreases with increase in pH above 6.0. Increase in dosage of activated sawdust and contact time increases the capacity of BPB dye removal. The increase in adsorbent dose beyond 1g did not show any much difference and therefore the adsorbent dose of 1g was selected as the optimum dose with maximum percentage adsorption of 87.27% and optimum contact time being 65minutes with maximum adsorption percentage of 89.69%. The pseudo second-order model describes the kinetic data fairly well with the R^2 value being 0.9992 compared to the pseudo first-order model with the R^2 value of 0.8885 and the Freundlich model best described the adsorption model with the R^2 value being 0.9998 as compared to the Langmuir model with the R^2 value of 0.9378. Thus, activated sawdust is a useful, cost-effective by-product of wood processing that can be recycled as a suitable BPB scavenging material from textile wastewater.

5.2 Recommendation

i. Effect of inorganic salts (coexisting ions) on the adsorption property of BPB dye should be studied since industrial effluents are always contaminated with additives like the coexisting ions.

ii. Activated sawdust should be tested with real industrial effluents to demonstrate its ability on large scale and its performance on the field.

iii. Further studies should be carried out on the economical and safe disposal of spent (used) sawdust.

iv. Most of the research on dye removal using low-cost methods deal with the batch adsorption process and this information must be designed for the scale up studies.

v. Since batch adsorption studies were employed in this study, further adsorption studies should focus on the column adsorption studies.

REFERENCES

Abbas, A. M., Abdulrazzak, F. H., Sabbar, W. J., & Faraj, R. A. S. (2020). Adsorption of dyes by activated carbon surfaces were prepared from plant residues, A Review. *J. Mater. Environ. Sci, 11*, 2007-2015.

Albroomi, H., Elsayed, M., Baraka, A., & Abdelmaged, M. (2014). *Removal Of A Basic And Azo Dye From Aqueous Solution By Adsorption Using Activated Carbon.* Paper presented at the The International Conference on Chemical and Environmental Engineering.

Aljeboree, A. M., Alshirifi, A. N., & Alkaim, A. F. (2017). Kinetics and equilibrium study for the adsorption of textile dyes on coconut shell activated carbon. *Arabian journal of chemistry, 10*, S3381-S3393.

Ashrafi, S., Kamani, H., & Mahvi, A. (2016). The optimization study of direct red 81 and methylene blue adsorption on NaOH-modified rice husk. *Desalination and Water Treatment, 57*(2), 738-746.

Bello, O. S., Adegoke, K. A., Olaniyan, A. A., & Abdulazeez, H. (2015). Dye adsorption using biomass wastes and natural adsorbents: overview and future prospects. *Desalination and Water Treatment, 53*(5), 1292-1315.

Benkhaya, S., M'rabet, S., & El Harfi, A. (2020). Classifications, properties, recent synthesis and applications of azo dyes. *Heliyon, 6*(1).

Bhatt, P., Vyas, R. K., Pandit, P., & Sharma, M. (2013). Adsorption of reactive blue and direct red dyes on Powdered Activated Carbon (PAC)-Equilibrium, kinetics and thermodynamic studies. *Nature Environment and Pollution Technology, 12*(3), 397.

Chikri, R., Elhadiri, N., Benchanaa, M., & Maguana, Y. (2020). Efficiency of sawdust as low-cost adsorbent for dyes removal. *Journal of Chemistry, 2020*, 1-17.

Dehghani, M., Ansari Shiri, M., Shahsavani, S., Shamsedini, N., & Nozari, M. (2017). Removal of Direct Red 81 dye from aqueous solution using neutral soil containing copper. *Desalination and Water Treatment, 86*, 213-220.

Dhananasekaran, S., Palanivel, R., & Pappu, S. (2016). Adsorption of methylene blue, bromophenol blue, and coomassie brilliant blue by α-chitin nanoparticles. *Journal of advanced research, 7*(1), 113-124.

Dutta, S., Gupta, B., Srivastava, S. K., & Gupta, A. K. (2021). Recent advances on the removal of dyes from wastewater using various adsorbents: A critical review. *Materials Advances, 2*(14), 4497-4531.

Emam, A., Hilal, N. M., El-Bayaa, A., Badawy, N., & Ghiat, U. (2017). Application of modified Maple Wood Saw Dust with Polyaniline for the Removal of Anionic Dyes From Waste water: Kinetics and IsothermStudies. *Journal of Scientific Research in Science, 34*(part1), 575-591.

Foo, K., & Hameed, B. H. (2010). An overview of dye removal via activated carbon adsorption process. *Desalination and Water Treatment, 19*(1-3), 255-274.

Foo, K. Y., & Hameed, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical engineering journal, 156*(1), 2-10.

Hassen, J., Ayfan, A. H., & Joudah, M. T. (2022). Determination of the optimal adsorbent for bromophenol blue dye: adsorption from aqueous solution. *Egyptian Journal of Chemistry, 65*(131), 645-651.

Hossein, M. A., & Behzad, H. (2012). Removal of reactive red 120 and direct red 81 dyes from aqueous solutions by pumice. *Research Journal of Chemistry and Environment, 16*(1), 62-68.

İmran, A., Dahiya, S., & Tabrez, K. (2012). Removal of direct red 81 dye from aqueous solution by native and citric acid modified bamboo sawdust-kinetic study and equilibrium isotherm analyses. *Gazi University Journal of Science, 25*(1), 59-87.

Iran Manesh, M., Sohrabi, M. R., & Mortazavi Nik, S. (2022). Nanoscale Zero-Valent Iron Supported on Graphene Novel Adsorbent for the Removal of Diazo Direct Red 81 from Aqueous Solution: Isotherm, Kinetics, and Thermodynamic Studies. *Iranian Journal of Chemistry and Chemical Engineering, 41*(6), 1844-1855.

Khamparia, S., & Jaspal, D. (2016). Adsorptive removal of Direct Red 81 dye from aqueous solution onto Argemone mexicana. *Sustainable Environment Research, 26*(3), 117-123.

Kigozi, M., Kali, R., Bello, A., Padya, B., Kalu-Uka, G. M., Wasswa, J., . . . Dzade, N. Y. (2020). Modified activation process for supercapacitor electrode materials from african maize cob. *Materials, 13*(23), 5412.

Kumar, P. S., Joshiba, G. J., Femina, C. C., Varshini, P., Priyadharshini, S., Karthick, M., & Jothirani, R. (2019). A critical review on recent developments in the low-cost adsorption of dyes from wastewater. *Desalin. Water Treat, 172*, 395-416.

Kuśmierek, K., Dąbek, L., & Świątkowski, A. (2023). Removal of Direct Orange 26 azo dye from water using natural carbonaceous materials. *Archives of Environmental Protection*, 47-56-47-56.

Lima, É. C., Adebayo, M. A., & Machado, F. M. (2015). Kinetic and equilibrium models of adsorption. *Carbon nanomaterials as adsorbents for environmental and biological applications*, 33-69.

Mohamed Salleh, M., Mahmoud, D., Abdul Karim, W., & Idris, A. (2011). Cationic and Anionic dye adsorption by Agricultural Solid Wastes. *A comprehensive review, Desalination, 280*, 1-13.

MOMEN, H. M., Ardalan, P., & Vafaie, A. (2014). EQUILIBRIUM AND KINETIC STUDIES OF DIRECT RED BIOSORPTION ONTO MODIFIED SILK MAZE AS AN ECONOMICAL BIOSORBENT.

MOMEN, H. M., Kodabande, A., Bozorgmehr, M., Ardalan, T., & Ardalan, P. (2012). Kinetic and thermodynamic studies on biosorption of Direct Red 81 from aqueous solutions by Chamomilla plant.

Ngulube, T., Gumbo, J., Masindi, V., & Maity, A. (2018). Calcined magnesite as an adsorbent for cationic and anionic dyes: Characterization, adsorption parameters, isotherms and kinetics study. *Heliyon, 4*(10).

Okoye, C., Okey-Onyesolu, C., Chime, D., & Achike, C. (2018). Adsorptive removal of bromophenol blue dye from aqueous solution using acid activated clay. *Int J Sci Research Mgt, 6*(3), 1-15.

Ouafi, R., Rais, Z., Taleb, M., Benabbou, M., & Asri, M. (2017). SAWDUST IN THE TREATMENT OF HEAVY METALS-CONTAMINATED WASTEWATE. *Environmental Research Journal, 11*(1).

ÖZDEŞ, D., DURAN, C., OZEKEN, S. T., KALKIŞIM, Ö., & Yener, T. (2023). Natural and H2SO4 modified plane sawdust as a low-cost adsorbent: Removal of anionic and cationic dyes from aqueous solutions. *Turkish Journal of Analytical Chemistry, 5*(1), 32-42.

Pimentel, C. H., Freire, M. S., Gómez-Díaz, D., & González-Álvarez, J. (2023). Preparation of activated carbon from pine (Pinus radiata) sawdust by chemical activation with zinc chloride for wood dye adsorption. *Biomass Conversion and Biorefinery*, 1-19.

Qiu, H., Lv, L., Pan, B.-c., Zhang, Q.-j., Zhang, W.-m., & Zhang, Q.-x. (2009). Critical review in adsorption kinetic models. *Journal of Zhejiang University-Science A, 10*(5), 716-724.

Rápó, E., & Tonk, S. (2021). Factors affecting synthetic dye adsorption; desorption studies: a review of results from the last five years (2017–2021). *Molecules, 26*(17), 5419.

Razi, M. A. M., Hishammudin, M. N. A. M., & Hamdan, R. (2017). *Factor affecting textile dye removal using adsorbent from activated carbon: A review.* Paper presented at the MATEC Web of Conferences.

Rijsberman, F. R. (2006). Water scarcity: fact or fiction? *Agricultural water management, 80*(1-3), 5-22.

Sahmoune, M. N., & Yeddou, A. R. (2016). Potential of sawdust materials for the removal of dyes and heavy metals: examination of isotherms and kinetics. *Desalination and Water Treatment, 57*(50), 24019-24034.

Said, A. A., Aly, A. A. M., Abd El-Wahab, M. M., Soliman, S., Abd El-Hafez, A., Helmey, V., & Goda, M. N. (2013). An efficient biosorption of direct dyes from industrial wastewaters using pretreated sugarcane bagasse. *Energy and Environmental Engineering, 1*(1), 10-16.

Šćiban, M., Radetić, B., Kevrešan, Ž., & Klašnja, M. (2007). Adsorption of heavy metals from electroplating wastewater by wood sawdust. *Bioresource technology, 98*(2), 402-409.

Sharma, N., Tiwari, D., & Singh, S. (2014). Efficiency of chemically treated potato peel and Neem bark for sorption of Direct Red-81 dye from aqueous solution. *Rasayan J. Chem, 7*(4), 399-409.

Sivakumar, B., Nithya, P., Karthikeyan, S., & Kannan, C. (2014). Kinetics, equilibrium and isotherms of direct red 81 removal from aqueous solution using balsamodendron caudatum wood waste activated nanoporous carbon. *Rasayan J. Chem, 7*(2), 161-169.

Tamjidi, S., Kamyab Moghadas, B., Abdollahi, P., Parnian, N., & Farhadi, A. (2024). Industrial By-Products as Potentially Economic and Promising Adsorbents for Removing Dyes from Effluents: A Review Study. *Physical Chemistry Research, 12*(2), 361-382.