Hydrothermal Activation of Pineapple Peelings for the Adsorption and Kinetics of Methylene Blue Dye

Tibenda Christine

BU/UP/2021/1759

A Research Project Proposal Submitted to the Department of Chemistry in Partial Fulfilment of the Requirement for the Award of the Degree of Bachelor of Science Education of Busitema University

August 2024

Declaration

I, Tibenda Christine, declare that this research work is my original work and has not been submitted for any award in any University or other institution of higher learning. The information derived from the literature has been fully acknowledged in the text by citation and a list of references provided.

Signature……………………………… Date 27/08/2024……………

Approval

This research project report has been submitted for examination with the approval of my supervisor.

Dr Kigozi Moses

Signature……………………………………………………Date 27/08/201……

Dedication

I dedicate this project to my mother, Ms. Babireba Teopista and my father Mr. Kibodhe George William for the support given to me throughout my life since my childhood; in terms of monetary support, emotional guidance, everlasting care and encouragement. I am eternally grateful for your contributions towards my life and pledge to forever have you at heart for the kindness, sacrifice, commitment and sincere support towards the better version of me.

Acknowledgements

I take this opportunity to express my deepest gratitude to my project supervisor Dr Kigozi Moses for giving me this opportunity to work under his guidance, mentorship and valuable support from the start of this study up to the end. He has always been available and sacrificed his time to me for consultations and encouragements and I am greatly indebted to him for his valuable advice and support.

I also thank the entire Chemistry Department staff members of Busitema University, Nagongera campus for the endless mentorships, guidance and parenting me; pointing out in particular the laboratory technician, for guiding me with laboratory works. Special appreciation goes to my family members for their financial support during this study. I also wish to extend my sincere gratitude to my fellow colleagues; Mr. Ssekitto Nathan, Madam Abokwe Patience and Madam Namalike Mariam for their collaborations, positive contributions and criticisms plus all-round help given to me during times of need. May the Almighty God bless you all abundantly and gives you what your heart's desires.

I take this opportunity to thank the Almighty God for the gift of life, knowledge, wisdom, basic needs, sound health, guidance and protection since I was born.

List of Acronyms and abbreviations

ALLPC – Hydrothermally Activated Pineapple Peelings Carbon
PP – Pineapple Peelings
pH – potential of hydrogen
MB – Methylene Blue
UV – Vis – Ultra Violet – Visible light
EC – Electro-Coagulation
ESI-MS – Electrospray Ionisation Mass Spectroscopy
FESEM – Field Emission Scanning Electron Microscopy
IQ – Intelligence Quotient
NEERI – National Environmental Engineering Research Institute
NF – Nano Filtration
PXRD – Power X-ray diffraction
TISAB – Total Ionic Strength Adjustment Buffer
UNBS – Uganda National Bureau of Standards
WHO – World Health Organisation
XPS – X-ray Photoelectron Spectroscopy

Table of Contents

List of Figures

List of Tables

Abstract

The unavailability of clean drinking water is one of the significant health issues in modern times. Industrial dyes are one of the dominant chemicals that make water unfit for drinking. Among these dyes, methylene blue (MB) is toxic, carcinogenic, and non-biodegradable and can cause a severe threat to human health and environmental safety. It is usually released in natural water sources from effluents of mainly textile industries, hospitals and others which becomes a health threat to human beings and living organisms hence, there is a need to develop an environmentally friendly, efficient technology for removing MB from wastewater. This study was aimed at developing an inexpensive and effective adsorbent for removing MB from waste water to the safety limit of at most 5 mk/kg where the toxicity of methylene blue dye can induce fatal serotonin toxicity in humans. Pineapple peelings obtained from Nagongera market, Tororo district were hydrothermally activated in an autoclave reactor using potassium hydroxide as the modifier to form the hydrochar (HAPPC) and effectiveness in adsorbing MB was confirmed by batch adsorption studies. The adsorption data were analyzed by Freundlich and Langmuir isotherms and kinetic models. The adsorption on the HAPPC obeyed the pseudo second order kinetic model. The adsorption capacity HAPPC was studied with variation in size of adsorbent dose, size particles, pH, adsorbent dose and initial MB concentration. The extent of adsorption of MB by HAPPC adsorbent increased with increase in adsorbent dose, contact time and pH until an optimum value but decreased with the increase in particle size and initial MB concentration. In future, the potential HAPPC adsorbent can be used to design both industrial and household units for effective and economical MB removal.

Chapter 1: Introduction

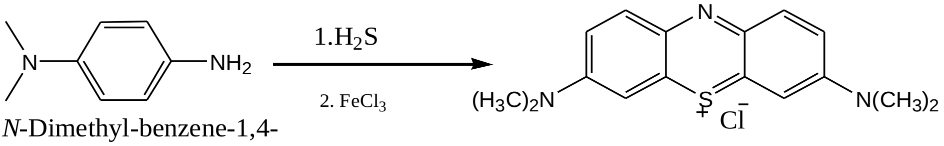
1.1 Background

Dyes are hydro or oil-soluble, colored organic chemical compounds that are usually dissolved in water and bound to surfaces or fabrics to impart color to textiles. The majority of dyes are complex organic molecules that are designed to bind strongly to the polymer molecules that make up the textile fiber, and must be able to withstand a wide range of external effects (Benkhaya, M'rabet, & El Harfi, 2020a; Rápó & Tonk, 2021). According to (Chatwal, 2009) dyes are colored organic compounds or mixtures used to color paper, cloth, plastics and leather. The dye substrate must be resistant to washing and stable to light. It is important to note that not all colored materials are dyes, as a dye must be fixed to the material to give it a permanent color. A dye is generally a substance that bears an affinity to the substrate to which it is being applied. It is often applied in aqueous solution. It requires a mordant to improve its binding with the fabrics (Dash, 2010), (Mahmoud, Salleh, Karim, Idris, & Abidin, 2012). It appears to be colored because they absorb some wavelengths of light in particular than other.

Various industries discharge wastewaters like chemical, refineries, textile, plastic and food processing plants (Lokman, 2006; Mahmoud et al., 2012), pharmaceutical, leather, paint and varnishing industry effluents. Other sources are households, and moreover the untreated or partially treated effluents from wastewater treatment plants. These wastewaters include dyes as residues which cause many hazards. Such residual dyes are non-biodegradable due to their complex molecular structures making them more stable and harder to biodegrade (Dash, 2010; Lokman, 2006). They cause water pollution and also pose a serious threat to environment. These colored stuffs along with being aesthetically displeasing also inhibit sunlight penetration into water bodies and thus affect aquatic ecosystem (Lokman, 2006; Mahmoud et al., 2012). Many of them are also toxic in nature and can cause direct destruction or can affect catalytic capabilities of various microorganisms (Dash, 2010; Lokman, 2006). Moreover, their degradation products may be mutagenic and carcinogenic (Liu et al., 2012; Saha & Das Mishra, 2012). Many dyes may cause allergic dermatitis, skin irritation, dysfunction of kidney, liver, brain, reproductive and central nervous system (Tabrez, Sangeeta, & Imran, 2011). Organic dyes are harmful to human beings, the need to remove color from wastewater effluents to become environmentally important.

Among the dyes include; Methylene Blue, Congo Red, Malachite Green, Crystal Violet and others. Dyes are usually large aromatic molecules, often with many rings linked together. An aromatic ring structure linked to a side chain in the dye molecule structure is necessary for resonance and hence for the transfer of color (Trakoli, 2012). The resonance structures responsible for color are those that cause the shifting or appearance of absorption bands in the visible spectrum of light. In the synthesis of a dye, the correlation of chemical structure and color is achieved by a chromogen-chromophore-auxochrome combination. Three essential groups can be found in a dye molecule: the chromophore, auxochrome and matrix (Benkhaya, M'rabet, & El Harfi, 2020b). Thus, dyes are organic colorants that 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 color 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); sulfur and other carbon-sulfur groups (>C=S). 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 thus the dye cannot adhere to the fiber of the material, auxochromes are required. Auxochromes enhance the color of the dye. Auxochromes, also known as binding affinity groups, can be amine ($-NHX_2$), hydroxyl (-OH), carboxyl groups (-COOH), aldehydes (-CHO), sulfonic acid (-SO3H) or their derivatives (El-Sikaily, 2012; Gurses, 2016). The dyes are classified according to the method of application as reactive, direct and acid (anionic dyes), basic (cationic dyes), or disperse and vat (non-ionic dyes) (Gurses, 2016; Yagub, Sen, Afroze, & Ang, 2014).

Methylene blue (MB) is a methylthionine chloride salt used as a dye and as a medication. It is a thiazine dye which is applied in various industries including dyeing, printing, chemical indicators, and biological applications (Jain et al., 2018). Methylene blue (MB) containing wastewaters pose serious risks to both microorganisms in the environment and human health due to large organic loads, reduced biodegradability, and high chromaticity (Benadjemia, Millière, Reinert, Benderdouche, & Duclaux, 2011). Methylene blue can be prepared by the oxidation of dimethyl-4-phenylenediamine in the presence of sodium thiosulfate or by N, N-dimethyl-p-phenylenediamine and N, N, -dimethylaniline hydrochlorides with iron (III) chloride or another suitable oxidizing agent or by oxidation of p- amino dimethyl aniline with ferric chloride in the presence of hydrogen sulphide.



N,*N*-Dimethyl-benzene-1,4-diamine

3,7-Bis-dimethylamino-phenothiazin-5-ylium; chloride

Many modern technologies such as photo degradation (Sun & Xu, 1997), Coagulation, flocculation, chemical oxidation, electro-chemical oxidation, Biological process (Han et al., 2006) are all available for the removal of dye from the waste water. (Adak, Bandyopadhyay, & Pal, 2006) Adsorption, which has been extensively used in industrial process for a variety of separation and purification purposes, is rapidly becoming a prominent method of treating aqueous effluents. Adsorption is the phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid resulting in to higher concentration of the molecules on the surface. The color removal from textile waste water is considered as an important application of the adsorption process using low-cost adsorbents mainly agricultural wastes such as shale oil ash, chitosan, sunflower stalk (Sun & Xu, 1997), natural clay (Nassar, El-Geundi, & Al-Wahbi, 2012) and others against expensive ones.

Hydrothermally Activated Pineapple Peelings Carbon has a high adsorption capacity due to the high surface areas of active sites and increased pore size, polar functional groups making it possible to adsorb cationic dyes like methylene blue dye on particle external site and in interlayer positions. Adsorption and desorption of cationic dyes by the Hydrothermally Activated Pineapple Peelings Carbon are primarily controlled by surface properties of the adsorbent and the chemical properties of the adsorbate. Pineapple peelings exhibit negative charges and very many polar functional groups like hydroxyl groups(-OH), amine functional group ($-NH_2$), carboxylic group (-COOH) which allows it to adsorb cationic dyes and upon activation by hydrothermal process using potassium hydroxide as the modifier not only leads to a higher surface area but also increases the activation yield and total pore volume due to the increased oxygen-containing functional groups and charges on the surface of the adsorbent (Kohzadi, Marzban, Godini, Amini, & Maleki, 2023) though induces a low adsorption capacity for anionic dyes (Negi, Satpathy, Tyagi, & Gupta, 2012; Xu, Shen, & Guo, 2014). Owing to the multifunctional characteristics of Hydrothermally Activated Pineapple Peelings Carbon, adsorption of methylene blue is facilitated by a combination of processes, involving diffusion, complexation and electrostatic interactions (Xu et al., 2014). Thus, this report is on cationic dye adsorption by Hydrothermally Activated Pineapple Peelings Carbons and to evaluate its efficiency as an adsorbent for the removal of MB dye from aqueous solutions. Adsorption of methylene blue by natural adsorbents is affected by the surface area of the adsorbents (powdered), initial dye concentration, temperature, pH, adsorbent dose, contact time has been studied (Noroozi & Sorial, 2013).

1.2 Problem Statement

Dyes are non-biodegradable, toxic in nature, can affect catalytic capabilities of various microorganisms, their degradation products may be mutagenic and carcinogenic, may cause allergic dermatitis, skin irritation, dysfunction of kidney, liver, brain, reproductive and central nervous system. Since the president of Uganda banned the import of second-hand clothes, the use of dyes in textile industries is very profound hence there is a pressing need to develop sustainable and eco-friendly alternatives for the removal of dyes from wastewater effluents before discharge. Many modern technologies available are expensive, less environmentally friendly, difficulty in regeneration and have low efficiency under high dyes concentration. Upon modification, bio-sorbents (pineapple hydrochar) offer satisfactory results in terms of dye removal from waste water.

1.3 Objectives

1.3.1 General Objective

The general objective of this study is to develop an effective, low cost and environmentally friendly modified natural adsorbent from pineapple peels to remove methylene blue dye from waste water.

1.3.2 Specific Objectives

i) To synthesize an effective and efficient adsorbent from Pineapple peels biomass and carry out hydrothermal activation of Pineapple peelings for the removal of methylene blue dye from wastewater
ii) To set up adsorption experiments.
iii) To carry out adsorption kinetic and isotherm studies of removal of methylene blue dye from wastewater using Pineapple peelings activated biomass as modified natural adsorbents.

1.4 Justification

One of the main reasons why pollution of dyes is still remaining as a problem is the expensive and environmentally hazardous (unfriendly) industrial methods used. There is therefore need to develop effective locally available and low-cost methods for the removal of dyes from waste water to replace the expensive ones. The major sources of these natural adsorbents are agricultural wastes whose efficacy and effectiveness can be increased by activation using different cheap methods. Several researches have been made on action of natural adsorbents on removal of dyes from waste water but the use of hydrothermally activated locally available pineapple peelings has been left out hence this study is to determine the effectiveness of hydrothermally activated Pineapple peels adsorbent in removal of methylene blue dye and make awareness of its potential adsorption powers for the dye.

1.5 Scope

This experimental research is aimed at qualitatively developing a higher adsorption capacity adsorbent using Pineapple peelings (obtained from Nagongera market, Tororo Uganda) activated by hydrothermal carbonization method using potassium hydroxide as the modifier; carried out in Busitema University Nagongera campus laboratory from February, 2024 up to March, 2024. This research involved the study of effects of various experimental parameters on adsorption like effect of pH, effect of contact time, effect of adsorbent dose and adsorption kinetic study.

Chapter 2: Literature Review

2.1 Sites and Effects of Methylene Blue Waste Water in Uganda

Methylene blue waste water can obtained from hospitals like Mulago National Referral Hospital, Mengo Hospital and others due to its application in medical researches, sulphide indicator in titration experiments and analytical methods, as medicine, in microscopy (Gendrot et al., 2021), microbiology and pharmacology (Tardivo et al., 2005). The methylene blue dye waste water is widely obtained from dyeing, textile, papermaking, cosmetics, food and leather industries (Mulushewa, Dinbore, & Ayele, 2021) which may include Fine Spinners Uganda Limited, Phenix Logistics (U) Ltd, Sigma Knitting Industries Ltd, Chrisams Designs, Leather Industries (U) Ltd, Nytil Picfare Ltd, Simba Blankets, Solaire Fashions, Summer Enterprises, A To Z Textile Mills Ltd, Blankets & Textiles Manufacturer Ltd, Calico Textile Industries Ltd, Garments Manufacturer Ltd, Kiliimanjaro Textile Mills Ltd, Latif Art & Design, Runa Fashioner and others.

The usage of methylene blue dye beyond permissible levels leads to several adverse side effects serious which may include fatal serotonergic syndrome (serotonin toxicity) in humans when used in combination with serotonergic drugs or at concentrations of MB beyond 5 mk/kg, apart from being a threat to fauna in aquatic ecosystem (Oladoye, Ajiboye, Omotola, & Oyewola, 2022). Symptoms of serotonin toxicity can range from mild to severe and may include agitation, confusion, rapid heart rate, high blood pressure, dilated pupils, loss of muscle coordination, muscle rigidity, heavy sweating, diarrhea, headache, shivering, goosebumps, tremor, seizures, irregular heartbeat, unconsciousness and may eventually cause death (Foong, Grindrod, Patel, & Kellar, 2018).

2.2 Some of the Methods for Removal of Methylene Blue Dye from Waste Water.

Some of the methods of removal of methylene blue dye from waste water include ; coagulation and flocculation, membrane filtration, ion exchange and adsorption (Malatji et al., 2021).

2.2.1 Coagulation-Flocculation Technique

The coagulation-flocculation technique is a technique which involves mainly three steps: coagulation, flocculation and decantation. Coagulation is achieved by adding a coagulant that aims at destabilizing the colloidal suspensions through neutralizing their charges. Flocculation is achieved by adding a flocculant leading to formation of flocs in the second step, also called the slow step. In this step, the small particles already destabilized during the first step are grouped to form flocs which sediment and separate easily from the water during the third and final stage called decantation (sedimentation) (Ihaddaden, Aberkane, Boukerroui, & Robert, 2022). The present work focusses on the use of a bentonite-based coagulant and cactus-based flocculant (Opuntia Ficus indica (OFIP)) in the elimination of methylene blue dye from waste water (Ihaddaden et al., 2022). Bentonite clay is known for its high specific surface area, negative surface charge density as well as its high cation exchange capacity and these properties show that it can contribute in the coagulation process. Opuntia Ficus indica act as a bio-flocculant and the molecules involved in the flocculation mechanism are macromolecular quercetin (a flavonoid with polyphenol groups) and water-soluble polysaccharides (starch).

The coagulation-flocculation technique is a simple and easy way to treat effluents from textile industries; however, the method has some drawbacks like excessive usage of chemical coagulants in highly colored wastewater result in the creation of a large amount of harmful chemical sludge (Bushra, Mohamad, Alias, Jin, & Ahmad, 2021).

2.2.2 Membrane Separation Techniques

The membrane separation is one of the effective methods for removal of methylene blue dye from the wastewater. The techniques of membrane separation include; Reverse osmosis (RO), electrodialysis, Ultrafiltration (UF) and Nanofiltration. Reverse osmosis involves the movement of water molecules from a region of higher concentration of the solute to a region of lower concentration of the solute (or pure water) through a semi-permeable membrane and application of hydrostatic pressure greater than the osmotic pressure (Ssekitto, 2023). Electro-dialysis is the removal of ionic components from aqueous solutions through ion exchange membranes under the driving force of an electric current. Electro-dialysis is like reverse osmosis except for it, current rather than pressure is used to separate ionic contaminants from water in which different ionic selective exchange membranes are used that allow only a specific type of ions to go through them (Korngold, Kock, & Strathmann, 1977). Ultrafiltration (UF) is a type of membrane filtration that separates particles based on their size using a semipermeable membrane that has a pore size that is fine enough to retain colloidal particles, viruses or large molecules. Suspended solids and solutes of high molecular weight are retained in the so-called retentate, while water and low molecular weight solutes pass through the membrane in the permeate (Bielska & Szymanowski, 2006). Nanofiltration (NF) is a membrane separation technique that uses nanometer-sized pores of pore sizes 1-10 nm to separate molecules based on size. It is a later invention among all the membrane processes that operates in the realm between reverse osmosis and ultrafiltration (Zhang et al., 2022). Nanofiltration membranes have smaller pore size than those used in microfiltration and ultrafiltration, but slightly bigger than those in reverse osmosis. The membranes are predominantly made of polymer thin films such as polyethylene terephthalate or metals such as aluminum. The pore dimensions are controlled by pH, temperature, and time during development with pore densities ranging from 1 to 106 pores per cm^2.

However, in these processes dense ceramic or polymeric membranes have been used, resulting in low permeability, thus to get the desired throughput (permeate flux), high operating pressure is required and even the commercially available polymeric membranes are very expensive and regeneration and reuse is a difficult task (Doke & Yadav, 2014).

2.2.3 Ion-Exchange Process

Ion-Exchange process is the process involves exchanging the dye ions with other ions that are bound to the resin which is usually made of a polymer matrix that contains functional groups that can attract and hold onto specific ions and in this case, the resin would be designed to attract and hold onto the methylene blue dye ions and are always cation-exchange resin. ammonium phosphomolybdate (APM) particles synthesized under ambient conditions can be used as cation-exchange resin for removal of methylene blue dye from waste water as long as the pH range permitted the dye to retain its cationic behaviour. This is attributed to ion-exchange between ammonium ions in APM with cationic dye moieties and removal efficiency of 94.6% could be retained up to 16th cycle (Joseph, Radhakrishnan, Johnson, Joy, & Thomas, 2020).

$$\mathbf{(NH_4)_3PMo_{12}O_{40}(aq) \quad + \quad 3\ MB \longrightarrow (MB)_3PMo_{12}O_{40}\ (aq) \quad + \quad 3\ \overset{+}{NH_4}(aq)}$$

The efficiency of the ion-exchange process depends on several factors, including the type of resin used, the concentration of the methylene blue dye in the wastewater, and the flow rate of the wastewater through the column. This method is effective though expensive, introduces other impurities like cations in the water, the ion exchange resin itself can sometimes become the source of organic contamination and other draw backs may be experienced (Hubicki & Kołodyńska, 2012).

2.2.4 Electro-coagulation Method

Electro-coagulation is a technique that involves applying direct current to sacrificial electrodes that are submerged in an aqueous solution. It is a straightforward and efficient technique in removing the flocculating agent produced by electro-oxidation of a sacrificial anode and generally made of iron or aluminum in simple terms an electrocoagulation reactor is made up of an electrolytic cell with one anode and one cathode. When connected to an external power source, the anode material will electrochemically corrode due to oxidation, while the cathode will be subjected to passivation. During electrolysis, the positive side undergoes anodic reactions, while on the negative side, cathodic reactions occur. Consumable metal plates, such as iron or aluminum, are commonly used as sacrificial electrodes to continuously produce ions in the water. The released ions neutralize the charges of the particles and thereby initiate coagulation. The released ions take away undesirable contaminants either by chemical reaction and precipitation, or by causing the colloidal materials to coalesce, which can then be removed by flotation (Aoudj, Khelifa, Drouiche, & Hecini, 2015). The removal of MB by electrocoagulation (EC) process was investigated in the presence of sodium chloride as electrolyte, Stainless steel electrodes used as cathode and anode in the electrochemical cell and the results showed that the removal percent of 20 mg/L MB is 100%, using stainless steel electrodes with an interspace of 1.5 cm and 20 mA/cm² for 6 min in the presence of 0.1 M sodium chloride at natural pH (Titchou, Afanga, Zazou, Akbour, & Hamdani, 2020).

In this process, the treatment is done without including any chemical coagulant or flocculants hence lessening the amount of sludge which may be disposed but still there are challenges like the ‘sacrificial electrodes’ are dissolved into wastewater streams as an after effect of oxidation, and should be regularly replaced, the utilization of electricity may be expensive in numerous spots, an impermeable oxide film may be surrounded on the cathode prompting loss of productivity of the EC unit, high conductivity of the wastewater suspension is needed, gelatinous hydroxide may tend to solubilize occasionally and many others (Aoudj et al., 2015).

2.2.5 Adsorption

Adsorption is the phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid resulting in to higher concentration of the molecules on the surface (Bahl, Bahl, & Tuli, 2008). As contrast with different methods of MB removal from waste water, adsorption method is prominent because of its straightforwardness and also accessibility of extensive variety of cheap adsorbents which may be from industrial wastes or agricultural wastes (natural adsorbents) like activated alumina, activated carbon, activated alumina coated silica gel, calcite, activated saw dust, activated coconut shell powder, activated fly ash, groundnut shell, coffee husk, rice husk and others (Rafatullah, Sulaiman, Hashim, & Ahmad, 2010). Bio-chars are the efficient adsorbents in the removal of contaminants from aqueous solution, have a low energy cost, and can be obtained from renewable and abundant precursors in comparison with industrial wastes and others. Pineapple peelings can be toxic if left to accumulate in the environment and the alternative to this environmental pollution is to make the waste product into a valuable product; in this case, the peelings can be used as a precursor material for making hydrochars when modified using modifiers like potassium hydroxide, zinc chloride and others enhancing the adsorption efficiency and effectiveness.

2.3 UV-Vis Spectrophotometry in Determination of Methylene Blue Concentrations

UV –Vis spectroscopy is an analytical technique that measures the amount of discrete wavelengths of UV or Visible light that are absorbed or transmitted through a sample in comparison to a reference or blank sample.

The method uses light described by the different wavelengths to analyze and identify different substances by locating the specific wavelengths corresponding to the maximum absorbance. The machine employed in this technique is the UV/Vis spectrometer which may be a single beam or double beam spectrometer. The spectrometer consists of five major components which include; the light source, wave length selector, sample, detector and computer to process output.

The most commonly used light sources in the technique is the tungsten lamps for visible light and deuterium lamp for UV light. The choice of wave length selector will always depend on the sample type and analyte. The most commonly used wave length selectors are the monochromators which are usually fitted with filters to narrow their wavelength selection and also improve on the signal to noise ratio.

Methylene blue dye has a strong absorption band centered at 660nm. The peak absorption of methylene blue is at 668nm and 609nm (Cwalinski et al., 2020).

An appropriate light source and wave length selector is chosen and the light passes to the sample placed in a cuvette. For this case distilled water will be used as a blank sample and then methylene blue dye is the analyte of interest. It is advisable to use quartz cuvettes because quartz is transparent to most of the UV light. Plastics are discouraged for examination because plastic generally absorbs UV light. Light having passed through the sample; the detector converts the light into a readable signal.

The UV – Vi’s spectroscopy information may be represented as a graph of absorbance, optical density or transmittance as a function of wave length. The wave length is always on the x – axis and the former on the y – axis. The graph is typically referred to as a spectrum. The absorbance (A) is equal to the logarithm of the fraction of light intensity before passing through the sample (IO) divided by light after passing through the sample (I). The fraction I divided by IO is called transmittance (T), which expresses how much light passed in the sample.

The concentration of an analyte in solution can be determined by measuring the absorbance at some wavelength and applying the Lambert– Beer Law (Delgado, 2022).

$$A = \varepsilon\, lc = \log\left(\frac{I_o}{I}\right) = log\left(\frac{I}{T}\right) = -log(T)$$

2.4 Mechanism of Adsorption of Methylene blue Dye on Hydrochar

The adsorption of methylene blue dye onto hydrochar is based on physical or chemical process. In the physical adsorption mechanism, the forces of attraction existing between adsorbate and adsorbent are weak van der Waals forces and the dye molecules attach onto the adsorbent surface under the influence of van der Waals forces. The hydrochar provide a porous surface with functional groups that can attract and bind methylene blue dye molecules through interactions such as electrostatic forces, hydrogen bonding and Van der Waals forces. Methylene blue dye molecules carry a positive charge and the hydrochar surface has regions with opposite charge which lead to electrostatic interactions. In chemical adsorption mechanism the forces of attraction existing between adsorbate particles and adsorbent are almost of the same strength as chemical bonds, the functional groups on the hydrochar surface such as hydroxyl, carboxyl, and other oxygen-containing groups form bonds with the dye molecules (Li et al., 2021).

2.5 Adsorption Isotherms

2.5.1 Langmuir Adsorption Isotherm

The Langmuir adsorption isotherm is used to describe the equilibrium between adsorbate and adsorbent system. The adsorbate adsorption is limited to one molecular layer at or before a relative pressure of unity is reached. It is assumed that the adsorption sites have equal affinities for molecules of adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site. The Langmuir isotherms are useful for determining the efficiency of adsorbent at higher temperature (Azizian & Eris, 2021). It explains quantitatively the formation of monolayer adsorbate on outer surface of the adsorbent, and after that no further adsorption takes place. The theoretical Langmuir isotherm is valid for adsorption of solute from a liquid solution as monolayer adsorption on a surface containing a large number of identical sites (Hammond & Conner, 2013). The linear form of Langmuir equation is as follows;

$$\frac{C_t}{q_t} = \frac{1}{K_L q_m} + \frac{C_t}{q_m}$$

Where; q_t is the amount of adsorbate absorbed per unit, q_m is the maximum adsorption capacity for monolayer adsorption, c_t is the equilibrium adsorbate concentration in solution and K_L is Langmuir constant.

The graph of $\frac{1}{q_t}$ against $\frac{1}{C_t}$ gives a straight line where the vertical intercept = $\frac{1}{q_m}$ and slope = $\frac{1}{K_L q_m}$ from which constants; K_L and q_m can be calculated.

2.5.2 Freundlich Adsorption Isotherm

The Freundlich isotherms are applicable only at lower temperatures to get an idea about the adsorption phenomena and monolayer coverage of the adsorbent. It is basically empirical but is often useful as a mean for data description. The equation generally agrees with the Langmuir equation and experimental data over moderate ranges of concentration. It is also commonly used to describe the adsorption characteristics for the heterogeneous surface. Freundlich isotherm assumes unlimited sorption sites which is correlated with better heterogeneous surface of the adsorbent media (Wang & Guo, 2020). The linear form of Freundlich equation is as follows;

$$\log q_t = \log \mathrm{K}_f + \frac{1}{\mathrm{n}}(\log C_t)$$

Where; K_f is the Freundlich adsorption capacity and n is the adsorption intensity, q_e is the amount of adsorbate adsorbed per unit weight of adsorbent and C_e is the equilibrium adsorbate concentration in solution.

A plot of log q_e versus log C_e gives a linear graph with slope = $\frac{1}{n}$ and vertical =logK_f.

2.6 Kinetic Models

Kinetic models are used to test experimental data so as to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction. There are several kinetic models proposed for the mechanism by which methylene blue dye is adsorbed on the surface of adsorbents. To analyze the adsorption kinetics of methylene blue dye onto the hydrothermally activated pineapple peelings, the pseudo-first-order and pseudo-second-order kinetic models are used to process the data (Revellame, Fortela, Sharp, Hernandez, & Zappi, 2020).

2.6.1 Pseudo First Order Model

The pseudo-first order rate model is used as a rate equation for assigning the rate of adsorption of an adsorbate into adsorbent. The linear form of the pseudo-first-order kinetic model is represented by the equation;

$$\frac{dqt}{dt} = K_1(q_o - q_t)$$

And the integrated pseudo first order rate equation is;

$$log(q_o - q_t) = \log q_e - \frac{K_1}{2.303}t$$

A linear graph of log $(q_e - q_t)$ against time, t must be obtained for the data to fit the pseudo-first order rate mode(Revellame et al., 2020) .

2.6.2 Pseudo Second Order Model

The kinetic rate equation for the pseudo-second order adsorption reaction is expressed as;

$$\frac{dqt}{dt} = K_2(q_o - q_t)^2$$

And the integrated pseudo second order rate equation is;

$$\frac{1}{q_o - q_t} = \frac{1}{q_o} + K_2 t$$

Pseudo-second order kinetic expression for describing the adsorption of some ions onto the adsorbent is also useful for determining q_o and K_2 values from the graph of $\frac{t}{qt}$ against t after rearrangement of the above equation as;

$$\frac{t}{qt} = \frac{1}{K_2 {q_o}^2} + \frac{t}{q_o}$$

A linear graph of $\frac{t}{qt}$ against time, t must be obtained for the data to fit the pseudo-second order rate model. The slope of the graph = $\frac{1}{q_o}$ and the vertical intercept = $\frac{1}{K_2 {q_o}^2}$ hence q_o and K_2 values can be determined from the graph Where q_O and q_t in mg/g are the amount of adsorbed methylene blue dye at equilibrium and at any time t respectively, K_1 and K_2 are equilibrium rate constants of pseudo first and second order reactions.

Chapter 3: Materials and Methods

3.1 Materials

pH meter, thermally isolated magnetic stirrer, polytetrafluoroethylene (PTFE)-coated stir bar, orbital shaker, 250 mL Erlenmeyer conical flasks, centrifuge, beakers, measuring cylinders, pipettes, stopwatch, dry soft lint-free tissue (toilet paper), vortex mixer, magnetic stirrer MS7-H550-S, Oven and Autoclave reactor.

Weighing balance of precision 0.1 mg and capacity of 210 g.

UV-Vis spectrophotometer Jenway 7305 with a wavelength range of 190 – 1100 nm and bandwidth 0.4 – 4.0 nm controlled using a computer software. Fourier Transform Infrared Spectroscopy (FTIR).

1M Potassium hydroxide solution was made by dissolving 56 g in sufficient deionized water to make 1L of solution and will be stored in a tightly sealed polyethylene bottle.

Deionized water, Methylene blue and other necessary chemicals were obtained from Abbott laboratory store-smc ltd (Kampala, Uganda).

Raw pineapple peelings were collected from the market in Nagongera Town Council, Tororo district, Uganda.

3.1.1 Preparation of Hydrothermally Activated Pineapple Peelings Carbon (HAPPC)

Raw pineapple peelings (PP) were placed in deionized water for 24 hours to remove organic pollutants, dried at 100ºC for 24 hours prior to hydrothermal activation process and then milled into small particles of diameters 2 mm and below. 20 g of milled PP were mixed with 240 ml of 1M Potassium hydroxide solution in an autoclave reactor, tightened well and then reactor were put in the oven at 180ºC for 24hours. The reactor after 24 hours, were cooled, its content filtered and hydrochars were washed with deionized water several times until when the pH was 7, then dried at 60ºC for 24 hours. HAPPC powder was stored in a cleaned and dried container and ready for use for batch experiments.

3.1.2 Preparation of Stock and Calibration Standards of Methylene Blue (MB) Dye

The stock solution of MB was prepared by dissolving 1mg of dye (measured using a weighing balance of precision 0.1 mg and capacity of 210 g) in deionized water, then stirred with magnetic stirrer (MS7-H550-S) for 10 minutes and then diluted to a mark of 1000 mL volumetric flask to give the concentration of 1mg/L stock solution which was stored in a cleaned and dried bottle. Series of calibration standards were prepared by measuring 5.0, 10.0, 25.0, 37.5 and 50.0 mL of the 1 mg/L standard solution and then diluted to 50.0 mL with distilled water to make 0.10, 0.20, 0.50, 0.75 and 1.00 mg/L of MB calibration standards respectively using the technique of $M_1V_1 = M_2V_2$ where M_i is the corresponding concentration in a volume V_i.

3.1.3 Calibration of UV-Vis Spectrophotometer and Measurement of MB Concentrations

A blank solution (deionized water) was placed in a cuvette (10 mm long), then inserted into the spectrophotometer and a maximum absorption wavelength for MB, $\Lambda_{\max}$ = 668nm was set to record the baseline absorbance so as to ensure accurate baseline readings. The corresponding absorbances of freshly prepared MB calibration standards of 0.10, 0.20, 0.50, 0.75 and 1.00 mg/L were then measured by the UV-Vis spectrophotometer at wavelength of 668nm so as to generate a calibration curve, starting with that of a low concentration to the highest as recorded in Table 1. The concentrations of the MB samples were obtained by referencing the absorbance values of the samples to the calibration curve obtained at 668nm. In each measurement, the cuvettes and spectrophotometer components were thoroughly cleaned and dried using a dry soft lint-free tissue (toilet paper) to avoid contamination.

3.2 Batch Adsorption Experiments

3.2.1 Effect of Adsorbent Dose on MB Removal

To different Erlenmeyer flasks containing 20 mL of 10 mg/L MB solution were added 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 g of the HAPPC in powder form. The setup was left to stand for 20 minutes while shaking constantly at 200 rpm using an orbital shaker. After 20 minutes, each dye sample was separated from the HAPPC by centrifugation process at 2000 rpm for 5 minutes and then the supernatant was analyzed by UV-Vis spectrophotometer at the wavelength for maximum absorbance of MB, 668nm to determine the concentration of MB dye adsorbed and the results recorded in Table 5.

3.2.2 Effect of Contact Time on MB Removal

8 samples of 20 mL of 10 mg/L MB concentration were made and then placed in different Erlenmeyer flasks. To each flask, 4 g of HAPPC were added and then the mixtures shaken using the orbital shaker at 200 rpm. The samples from the different flasks were picked after 3, 5, 10, 15, 20, 30, 40 and 60 minutes. After the specific time, each dye sample was separated from the HAPPC by centrifugation process at 2000 rpm for 5 minutes and then the supernatant was analyzed by UV-Vis spectrophotometer at the wavelength for maximum absorbance of MB, $\Lambda_{\max}$ = 668nm to determine the concentration of MB dye adsorbed and the results recorded in Table 3.

3.2.3 Effect of pH on MB Removal

8 samples of 20 mL of 10 mg/L MB concentration were prepared and placed in different Erlenmeyer flasks. The samples in the flasks were adjusted to pH values of range 4-12 using 0.1 M hydrochloric acid and 0.1 M sodium hydroxide solution. 1.4 g of HAPPC in powder form was separately added in the flasks containing the samples and then the different mixtures shaken at 200 rpm in the orbital shaker for 20 minutes. After 20 minutes, each dye sample was separated from the HAPPC by centrifugation process at 2000 rpm for 5 minutes and then the supernatant was analyzed by UV-Vis spectrophotometer at the wavelength for maximum absorbance of MB, 668nm to determine the concentration of MB dye adsorbed and the results recorded in Table 4.

3.2.4 Effect of Initial MB concentration on MB Removal

5 samples of 20 mL of 1.0, 3.0, 5.0, 10.0, 15.0mg/L of MB were prepared and placed in different Erlenmeyer flasks. To each flask, 1.0 g of HAPPC was added and then the setup was left to stand for 20 minutes while shaking constantly at 200 rpm using an orbital shaker. After 20 minutes, each dye sample was separated from the HAPPC by centrifugation process at 2000 rpm for 5 minutes and then the supernatant was analyzed by UV-Vis spectrophotometer at the wavelength for maximum absorbance of MB, $\Lambda_{\max}$ = 668nm to determine the concentration of MB dye adsorbed and the results recorded in table 6.

Chapter 4: Results and Discussion

4.1 Effect of Adsorbent Dose on Percentage Removal

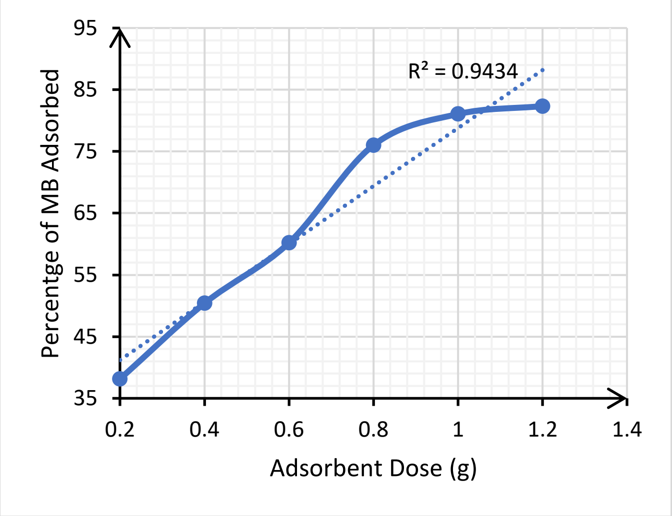


Figure 1: Effect of Adsorbent Dose on MB Removal

Percentage adsorption increased from 38.13% to 82.34% as the adsorbent dose increased from 0.2 to 1.2 g per 20 ml of adsorbate. The percentage removal increased with an increase in adsorbent dosage which was due to an increase in the adsorption sites available for adsorption. Having a closer looking at Figure __, it can be seen that at adsorbent dose higher than 1 g, no significant changes in the removal efficiency may be observed. This may be due to the overlapping of active sites at high adsorbent dose, thus bringing about in a reduced active surface area for adsorption.

4.2 Effect of Contact Time on MB Removal

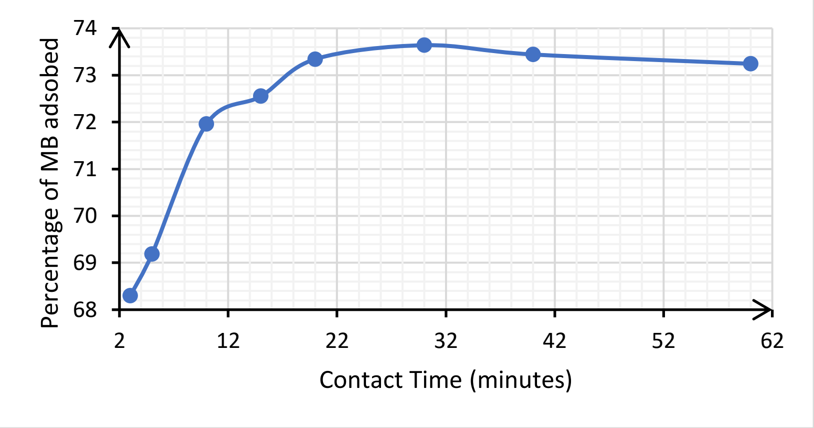


Figure 2: Effect of Contact Time on MB Removal

The percentage adsorbed increased sharply from 3 to 20 minutes contact time and remained almost constant beyond 20 minutes. The initial rapid increase in the adsorption rate for the range of 3 - 20 minutes is due to the presence of completely free active sites for adsorption and this made the MB to effortlessly move onto the HAPPC adsorbent to occupy the vacant sites. The removal rate remained almost constant beyond 20 minutes because many sites were occupied by most of the MB and there were few vacant sites left and even some MB begun to undergo desorption from the sites they already occupied. Maximum adsorption was observed at contact time of 30 minutes.

4.3 Effect of pH on MB Adsorption

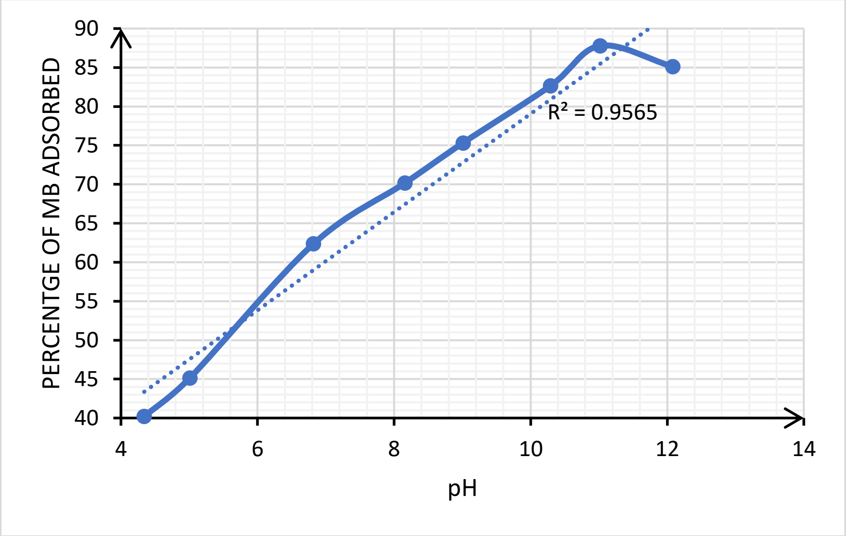


Figure 3: Effect of pH on MB removal

From the graph above the percentage adsorption of MB increased with increase in pH between pH range of 4.34 – 11.02 and the percentage of MB removal was most effective in the pH range of 10 to 11.02. The percentage adsorption of MB decreased gently in the pH range above 11.02 and the maximum percentage adsorption was 87.78%. At low pH, the concentration of MB in the solution is high which disturbs the bonding between the dye and adsorbent since hydrogen ions compete with MB to occupy the active site on the adsorbent surface hence increase in pH decreases the competition for adsorption sites between MB and hydrogen ions.

4.4 Effect of Initial MB Concentration on Adsorption

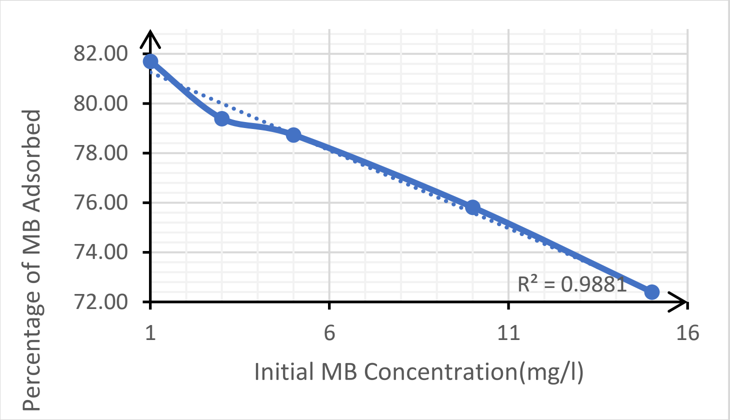


Figure 4: Effect of Initial MB Concentration on Adsorption

It was observed from the graph above that the percentage adsorption of MB decreased with increase in the initial MB concentration. This is because at low initial concentrations, there were more available vacant adsorption sites but at higher initial concentrations, very few available vacant adsorption sites were present and most of the MB particles were left desorbed due to saturation of the adsorption sites.

4.5 Adsorption Isotherm

To study the adsorption Isotherm, table 6 was used.

$$\text{Adsorption Capacity}, q_t = \left(\frac{\mathrm{C_o} - \mathrm{C_t}}{\mathrm{m}}\right)\mathrm{V}$$

Where, Co is the initial Fluoride concentration, Ct is the final fluoride concentration present at time t, m is the Mass of adsorbent and V is the Volume of the solution used in the batch.

$\mathrm{C_o}$ (mg/l)	$\mathrm{A_o}$ (nm)	$\mathrm{A_t}$ (nm)	$\mathrm{C_t}$ (mg/l)	$\mathrm{C_o} - \mathrm{C_t}$ (mg/l)	q_t	$\frac{\mathrm{C_t}}{q_t}$	$\log q_t$	$\log C_t$
1	0.101	0.018	0.183	0.81701286	16.3403	0.0112	1.21326	-0.7376
3	0.303	0.062	0.6182	2.3818002	47.636	0.01298	1.67794	-0.2089
5	0.505	0.107	1.0633	3.93669634	78.7339	0.01351	1.89616	0.02666
10	1.01	0.244	2.4184	7.58160237	151.632	0.01595	2.18079	0.38353
15	1.516	0.418	4.1395	10.8605341	217.211	0.01906	2.33688	0.61694

Table 1: Data for Adsorption Isotherm

4.5.1 Freundlich Adsorption Isotherm

The linear form of Freundlich equation is as follows;

$$\log q_t = \log \mathrm{K}_f + \frac{1}{\mathrm{n}}(\log C_t)$$

Where; K_f is the Freundlich adsorption capacity and n is the adsorption intensity, q_t is the amount of adsorbate adsorbed per unit weight of adsorbent and C_t is the final MB concentration.

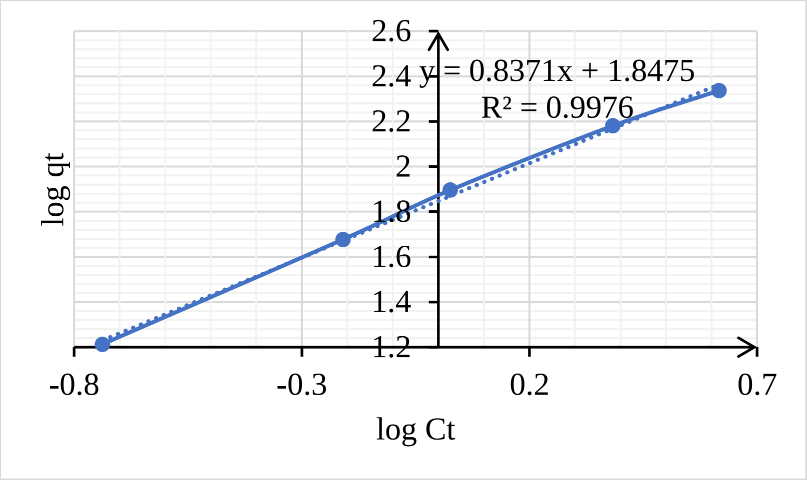


Figure 5: Freundlich Adsorption Isotherm

Since the plot of log q_t against log Ct gives a linear graph with slope = 1/n and vertical intercept = logK_f, the data for the adsorption of MB by HAPPC adsorbent fit the Freundlich Adsorption Isotherm. From the graph above n ≈ 1.195, logK_f = 1.8475 hence K_f ≈ 70.39 Therefore, there is a limit to the adsorption by a given mass of adsorbent and hence possibly adsorption takes place unless a unimolecular layer is formed with adsorption capacity, K_f ≈ 70.39 and intensity of adsorption, n ≈ 1.195.

4.5.2 Langmuir adsorption isotherm

The linear form of Langmuir equation is as follows;

$$\frac{C_t}{q_t} = \frac{1}{K_L q_m} + \frac{C_t}{q_m}$$

Where; q_t is the amount of MB absorbed per unit, q_m is the maximum adsorption capacity for monolayer adsorption, c_t is the final MB concentration and K_L is Langmuir constant.

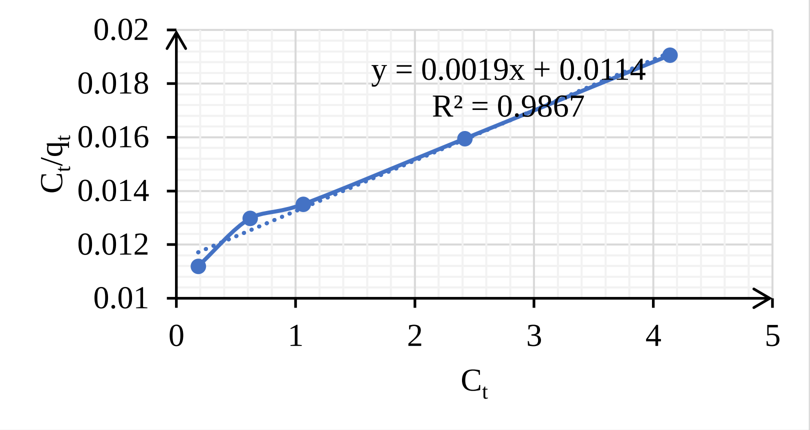


Figure 6: Langmuir adsorption isotherm

The data for the adsorption of MB by HAPPC adsorbent fit the Langmuir Adsorption Isotherm since it is a linear graph. From the graph, $q_m \approx 526.3\times10^{-6}$ and $K_L \approx 0.1667$.

4.6 Kinetic Models

Adsorption kinetics is vivid in finding the mechanism of adsorption. In this study two kinetic models were studied using the results from effect of contact time on the MB removal. The pseudo first order model postulates that adsorption proceeds by diffusion while pseudo second order model postulates that adsorption proceeds by chemisorption (formation of chemical bonds).

t (mins)	A_t (nm)	Ct (mg/l)	C_o - C_t (mg/l)	q_t	q_o -q_t	log(q_o -q_t)	t/q_t
3	0.32	3.1701	6.8299	34.1494	15.8506	1.2000	0.0878
5	0.311	3.0811	6.9189	34.5945	15.4055	1.1877	0.1445
10	0.283	2.8042	7.1958	35.9792	14.0208	1.1468	0.2779
15	0.277	2.7448	7.2552	36.2760	13.7240	1.1375	0.4135
20	0.269	2.6657	7.3343	36.6716	13.3284	1.1248	0.5454
30	0.266	2.6360	7.3640	36.8200	13.1800	1.1199	0.8148
40	0.268	2.6558	7.3442	36.7211	13.2789	1.1232	1.0893
60	0.27	2.6756	7.3244	36.6222	13.3778	1.1264	1.6384

Table 2: Data for Adsorption kinetics

4.6.1 Pseudo First Order Kinetic Model

The linear integrated form of the pseudo-first-order kinetic model is represented by the equation;

$$log(q_o - q_t) = \log q_e - \frac{K_1}{2.303}t$$

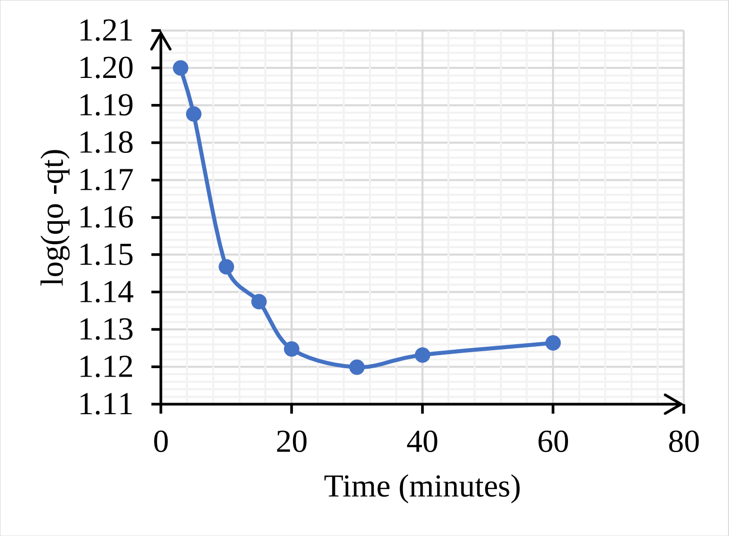


Figure 7: Pseudo First Order Kinetic Model

The graph does not give a straight line hence adsorption of MB by HAPPC adsorbent does not follow a pseudo first order kinetic model and therefore it does not proceed by diffusion through a boundary.

4.6.1 Pseudo Second Order Kinetic Model

The integrated linear modified pseudo second order rate equation is;

$$\frac{t}{qt} = \frac{1}{K_2{q_o}^2} + \frac{t}{q_o}$$

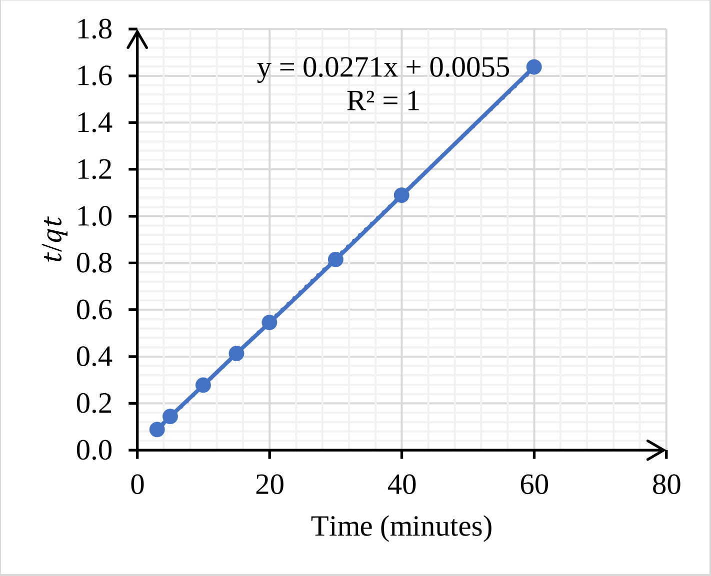


Figure 8: Pseudo Second Order Kinetic Model

The data best fit the pseudo second order kinetic model because the correlation coefficient (R^2) is 1 and the line of best fit passes through all the points hence the adsorption of MB by HAPPC adsorbent follows a pseudo second order model and the adsorption proceeds by chemisorption (formation of chemical bonds).

Chapter 5: Conclusion and Recommendations

5.1 Conclusion

In this study, hydrothermally activated pineapple peelings carbon was successfully prepared from waste pineapple peelings and the feasibility of using this waste product for an environmentally valuable application was tested and hypothesis of the study was true. The adsorbent HAPPC was used for adsorption studies, the contact time for maximum removal of MB was determined to be 30 minutes and pH range for maximum removal of MB was determined to be 10 – 11. The data best fitted both isotherm models though it best fits in the Freundlich adsorption model ($R^2 = 0.9976$) compared to that of Langmuir ($R^2 = 0.9867$). In the adsorption kinetics modeling studies, pseudo second order kinetics best fit the experimental data for HAPPC adsorption of MB. This study helped in inventing a very useful economical and effective household MB adsorbent that can be used to put MB concentration on permissible levels according to the WHO.

5.2 Recommendations

The HAPPC adsorbent developed in this study is strongly recommend to be used as an adsorbent material for MB removal from waste water. When using this adsorbent for adsorption, the optimal contact time should be 30 minutes, adsorbent dosage should be greater than 1.0g per 20ml, the particle size should be powder form of HAPPC and optimal pH range of 10 - 11 for maximizing the removal of MB from waste water up to the permissible limits.

Further studies need to be conducted to investigate the structure of the pores on the made adsorbent using the PXRD, XPS, FESEM and Nitrogen gas adsorption analysis and also investigate the effect of concentration of potassium hydroxide modifier on the HAPPC adsorption capacity.

References

Adak, A., Bandyopadhyay, M., & Pal, A. (2006). Fixed bed column study for the removal of crystal violet (CI Basic Violet 3) dye from aquatic environment by surfactant-modified alumina. *Dyes and Pigments, 69*(3), 245-251. doi:https://doi.org/10.1016/j.dyepig.2005.03.009

Aoudj, S., Khelifa, A., Drouiche, N., & Hecini, M. (2015). Development of an integrated electro-coagulation–flotation for semiconductor wastewater treatment. *Desalination and Water Treatment, 55*(6), 1422-1432.

Azizian, S., & Eris, S. (2021). Chapter 6 - Adsorption isotherms and kinetics. In M. Ghaedi (Ed.), *Interface Science and Technology* (Vol. 33, pp. 445-509): Elsevier.

Bahl, A., Bahl, B. S., & Tuli, G. D. (2008). *Essentials of Physical Chemistry* (1st ed.). India: S. Chand Publishing.

Benadjemia, M., Millière, L., Reinert, L., Benderdouche, N., & Duclaux, L. (2011). Preparation, characterization and Methylene Blue adsorption of phosphoric acid activated carbons from globe artichoke leaves. *Fuel Processing Technology, 92*(6), 1203-1212. doi:https://doi.org/10.1016/j.fuproc.2011.01.014

Benkhaya, S., M'rabet, S., & El Harfi, A. (2020a). A review on classifications, recent synthesis and applications of textile dyes. *Inorganic Chemistry Communications, 115*, 107891. doi:https://doi.org/10.1016/j.inoche.2020.107891

Benkhaya, S., M'rabet, S., & El Harfi, A. (2020b). A review on classifications, recent synthesis and applications of textile dyes. *Inorganic Chemistry Communications, 115*, 107-891.

Bielska, M., & Szymanowski, J. (2006). Removal of methylene blue from waste water using micellar enhanced ultrafiltration. *Water research, 40*(5), 1027-1033.

Bushra, R., Mohamad, S., Alias, Y., Jin, Y., & Ahmad, M. (2021). Current approaches and methodologies to explore the perceptive adsorption mechanism of dyes on low-cost agricultural waste: A review. *Microporous and Mesoporous Materials, 319*, 111040.

Chatwal, G. R. (2009). *synthetic dyes*. Mumbai, India: Himalaya Publishing House.

Cwalinski, T., Polom, W., Marano, L., Roviello, G., D'Angelo, A., Cwalina, N., . . . Polom, K. (2020). Methylene Blue-Current Knowledge, Fluorescent Properties, and Its Future Use. *J Clin Med, 9*(11). doi:10.3390/jcm9113538

Dash, B. (2010). *Competitive Adsorption of dyes (congo red, methylene blue, malachite green) on Activated Carbon.* (Doctoral dessertation), Retrieved from www.ethesis.nitrkl.ac.in

Delgado, R. (2022). Misuse of Beer-Lambert Law and other calibration curves. *R Soc Open Sci, 9*(2), 211103. doi:10.1098/rsos.211103

Doke, S. M., & Yadav, G. D. (2014). Novelties of combustion synthesized titania ultrafiltration membrane in efficient removal of methylene blue dye from aqueous effluent. *Chemosphere, 117*, 760-765.

El-Sikaily, A. K., A.; El Nemr, A. (2012). *Textile Dyes Xenobiotic and Their Harmful Effect. In Non-Conventional Textile Waste Water*
Treatment (1st Ed.). New York, NY, USA: Nova Science Publishers.

Foong, A.-L., Grindrod, K. A., Patel, T., & Kellar, J. (2018). Demystifying serotonin syndrome (or serotonin toxicity). *Canadian Family Physician, 64*(10), 720-727.

Gendrot, M., Delandre, O., Robert, M. G., Foguim, F. T., Benoit, N., Amalvict, R., . . . Pradines, B. (2021). Absence of association between methylene blue reduced susceptibility and polymorphisms in 12 genes involved in antimalarial drug resistance in African Plasmodium falciparum. *Pharmaceuticals, 14*(4), 351.

Gurses, A., Acikyildiz, M., Gunes, K. and Gurses, M.S. (2016). *Dyes and Pigments.Their Structure and Properties.* (1st ed.). Cham, Switzerland: Springer Briefs in Green Chemistry Sustainability. Springer International Publishing.

Hammond, K. D., & Conner, W. C. (2013). Chapter One - Analysis of Catalyst Surface Structure by Physical Sorption. In B. C. Gates & F. C. Jentoft (Eds.), *Advances in Catalysis* (Vol. 56, pp. 1-101): Academic Press.

Han, R., Wang, Y., Han, P., Shi, J., Yang, J., & Lu, Y. (2006). Removal of methylene blue from aqueous solution by chaff in batch mode. *Journal of Hazardous Materials, 137*(1), 550-557. doi:https://doi.org/10.1016/j.jhazmat.2006.02.029

Hubicki, Z., & Kołodyńska, D. (2012). Selective removal of heavy metal ions from waters and waste waters using ion exchange methods. *Ion exchange technologies, 7*, 193-240.

Ihaddaden, S., Aberkane, D., Boukerroui, A., & Robert, D. (2022). Removal of methylene blue (basic dye) by coagulation-flocculation with biomaterials (bentonite and Opuntia ficus indica). *Journal of Water Process Engineering, 49*, 102952.

Jain, M., Yadav, M., Kohout, T., Lahtinen, M., Garg, V. K., & Sillanpää, M. (2018). Development of iron oxide/activated carbon nanoparticle composite for the removal of Cr (VI), Cu (II) and Cd (II) ions from aqueous solution. *Water Resources and Industry, 20*, 54-74.

Joseph, J., Radhakrishnan, R. C., Johnson, J. K., Joy, S. P., & Thomas, J. (2020). Ion-exchange mediated removal of cationic dye-stuffs from water using ammonium phosphomolybdate. *Materials Chemistry and Physics, 242*, 122488.

Kohzadi, S., Marzban, N., Godini, K., Amini, N., & Maleki, A. (2023). Effect of Hydrochar Modification on the Adsorption of Methylene Blue from Aqueous Solution: An Experimental Study Followed by Intelligent Modeling. *Water, 15*(18), 3220.

Korngold, E., Kock, K., & Strathmann, H. (1977). Electrodialysis in advanced waste water treatment. *Desalination, 24*(1-3), 129-139.

Li, H.-Z., Zhang, Y.-N., Guo, J.-Z., Lv, J.-Q., Huan, W.-W., & Li, B. (2021). Preparation of hydrochar with high adsorption performance for methylene blue by co-hydrothermal carbonization of polyvinyl chloride and bamboo. *Bioresource Technology, 337*, 125442. doi:https://doi.org/10.1016/j.biortech.2021.125442

Liu, T., Li, Y., Du, Q., Sun, J., Jiao, Y., Yang, G., . . . Wang, K. (2012). Adsorption of methylene blue from aqueous solution by graphene. *Colloids and Surfaces B: Biointerfaces, 90*, 197-203. doi:https://doi.org/10.1016/j.colsurfb.2011.10.019

Lokman, F. (2006). *Dye removal from simulated wastewater by using empty fruit bunch as an adsorption agent.* KUKTEM, Retrieved from http://umpir.ump.edu.my/55/1/DYE_REMOVAL_FROM_SIMULATED_WASTEWASTER_BY_USING_EMPTY_FRUIT_.pdf

Mahmoud, D. K., Salleh, M. A. M., Karim, W. A. W. A., Idris, A., & Abidin, Z. Z. (2012). Batch adsorption of basic dye using acid treated kenaf fibre char: Equilibrium, kinetic and thermodynamic studies. *Chemical Engineering Journal, 181*, 449-457. doi:https://doi.org/10.1016/j.cej.2011.11.116

Malatji, N., Makhado, E., Modibane, K. D., Ramohlola, K. E., Maponya, T. C., Monama, G. R., & Hato, M. J. (2021). Removal of methylene blue from wastewater using hydrogel nanocomposites: A review. *Nanomaterials and Nanotechnology, 11*, 18479804211039425. doi:10.1177/18479804211039425

Mulushewa, Z., Dinbore, W. T., & Ayele, Y. (2021). Removal of methylene blue from textile waste water using kaolin and zeolite-x synthesized from Ethiopian kaolin. *Environmental Analysis, Health and Toxicology, 36*(1).

Nassar, M. M., El-Geundi, M. S., & Al-Wahbi, A. A. (2012). Equilibrium modeling and thermodynamic parameters for adsorption of cationic dyes onto Yemen natural clay. *Desalination and Water Treatment, 44*(1-3), 340-349. doi:https://doi.org/10.1080/19443994.2012.691701

Negi, R., Satpathy, G., Tyagi, Y. K., & Gupta, R. K. (2012). Biosorption of heavy metals by utilising onion and garlic wastes. *International Journal of Environment and Pollution, 49*(3-4), 179-196. doi:https://doi.org/10.1504/IJEP.2012.050898

Noroozi, B., & Sorial, G. A. (2013). Applicable models for multi-component adsorption of dyes: A review. *Journal of Environmental Sciences, 25*(3), 419-429. doi:https://doi.org/10.1016/S1001-0742(12)60194-6

Oladoye, P. O., Ajiboye, T. O., Omotola, E. O., & Oyewola, O. J. (2022). Methylene blue dye: Toxicity and potential technologies for elimination from (waste) water. *Results in Engineering*, 100678.

Rafatullah, M., Sulaiman, O., Hashim, R., & Ahmad, A. (2010). Adsorption of methylene blue on low-cost adsorbents: a review. *Journal of hazardous materials, 177*(1-3), 70-80.

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. doi:https://doi.org/10.3390/molecules26175419

Revellame, E. D., Fortela, D. L., Sharp, W., Hernandez, R., & Zappi, M. E. (2020). Adsorption kinetic modeling using pseudo-first order and pseudo-second order rate laws: A review. *Cleaner Engineering and Technology, 1*, 100032. doi:https://doi.org/10.1016/j.clet.2020.100032

Saha, P., & Das Mishra, R. (2012). Adsorption of safranin onto chemically modified rice husk in a upward flow packed bed reactor: artificial neural network modeling. *Biotechnol. Adv, 44*(1), 7579-7583.

Ssekitto, N. (2023). Defluorination of water using aluminium–loaded lemon peelings carbon as modified natural adsorbents.

Sun, G., & Xu, X. (1997). Sunflower stalks as adsorbents for color removal from textile wastewater. *Industrial & engineering chemistry research, 36*(3), 808-812. doi:https://doi.org/10.1021/ie9603833

Tabrez, A. K., Sangeeta, S., & Imran, A. (2011). Adsorption of Rhodamine B dye from aqueous solution onto acid activated mango (Magnifera indica) leaf powder: equilibrium, kinetic and thermodynamic studies. *Journal of Toxicology and Environmental Health Sciences, 3*(10), 286-297.

Tardivo, J. P., Del Giglio, A., De Oliveira, C. S., Gabrielli, D. S., Junqueira, H. C., Tada, D. B., . . . Baptista, M. S. (2005). Methylene blue in photodynamic therapy: From basic mechanisms to clinical applications. *Photodiagnosis and photodynamic therapy, 2*(3), 175-191.

Titchou, F. E., Afanga, H., Zazou, H., Akbour, R. A., & Hamdani, M. (2020). Batch elimination of cationic dye from aqueous solution by electrocoagulation process. *Mediterranean Journal of Chemistry, 10*(1), 1-12.

Trakoli, A. (2012). IARC monographs on the evaluation of carcinogenic risks to humans. Volume 99: Some aromatic amines, organic dyes, and related exposures. International Agency for Research on Cancer. In (pp. 232): Oxford University Press.

Wang, J., & Guo, X. (2020). Adsorption isotherm models: Classification, physical meaning, application and solving method. *Chemosphere, 258*, 127279. doi:https://doi.org/10.1016/j.chemosphere.2020.127279

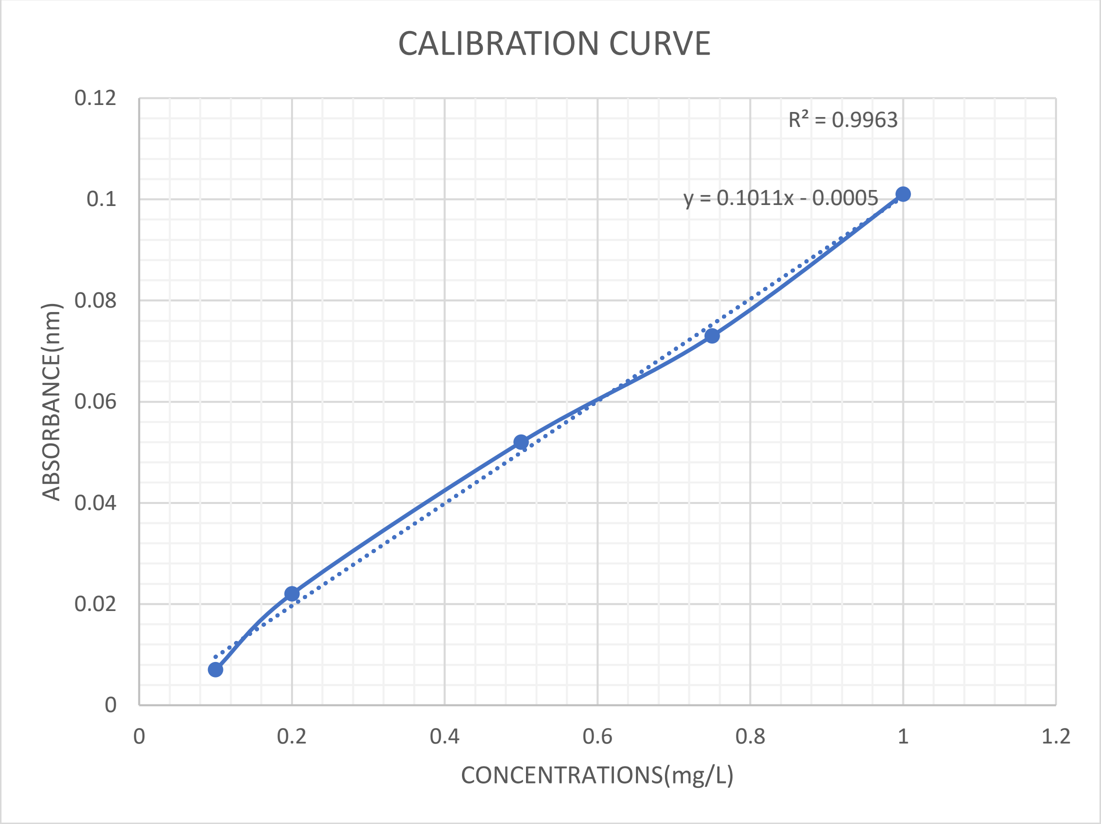
Xu, G. F., Shen, Z. X., & Guo, R. X. (2014). *The kinetics studies for the adsorption of furadan from aqueous solution by orange peel.* Paper presented at the Advanced Materials Research.

Yagub, M. T., Sen, T. K., Afroze, S., & Ang, H. M. (2014). Dye and its removal from aqueous solution by adsorption: a review. *Advances in colloid and interface science, 209*, 172-184. doi:https://doi.org/10.1016/j.cis.2014.04.002

Zhang, L., Xu, L., Yu, H., Yao, P., Zhang, M., Guo, F., & Yu, L. (2022). Capsaicin mimic-polyethyleneimine crosslinked antifouling loose nanofiltration membrane for effective dye/salt wastewater treatment. *Journal of Membrane Science, 641*, 119923.

Appendix

Calibration curve



Tables of Results

Table 3: Effect of Contact Time on MB removal

TIME (mins)	ABSORBANCE MEASURED (nm)	CONCENTRATION OF MB PRESENT (mg/l)	ADSORBED CONCENTRATION OF MB (mg/l)	PERCENTGE OF MB ADSORBED (mg/l)
0	1.01	9.995054402	0.004945598	0.049455984
3	0.32	3.170128586	6.829871414	68.29871414
5	0.311	3.081107814	6.918892186	69.18892186
10	0.283	2.804154303	7.195845697	71.95845697
15	0.277	2.744807122	7.255192878	72.55192878
20	0.269	2.665677547	7.334322453	73.34322453
30	0.266	2.636003956	7.363996044	73.63996044
40	0.268	2.65578635	7.34421365	73.4421365
60	0.27	2.675568744	7.324431256	73.24431256

Table 4: Effect of pH on MB removal

pH	ABSORBANCE MEASURED (nm)	CONCENTRATION PRESENT (mg/g)	ADSORBED CONCENTRATION (mg/l)	PERCENTGE OF MB ADSOBED (%)
4.34	0.604	5.979228487	4.020771513	40.20771513
5.01	0.554	5.484668645	4.515331355	45.15331355
6.82	0.38	3.763600396	6.236399604	62.36399604
8.16	0.301	2.982195846	7.017804154	70.17804154
9.01	0.249	2.46785361	7.53214639	75.3214639
10.29	0.175	1.735905045	8.264094955	82.64094955
11.02	0.123	1.221562809	8.778437191	87.78437191
12.08	0.15	1.488625124	8.511374876	85.11374876

Table 5: Effect of Adsorbent Dose on MB removal

ADSORBENT DOSE(g)	ABSORBANCE (nm)	CONCENTRATION OF MB PRESENT (mg/L)	ADSORBED CONCENTRATION (mg/L)	PERCENTAGE OF MB ADS0RBED (%)
0.2	0.625	6.18694362	3.81305638	38.1305638
0.4	0.501	4.960435213	5.039564787	50.39564787
0.6	0.402	3.981206726	6.018793274	60.18793274
0.8	0.242	2.398615232	7.601384768	76.01384768
1	0.191	1.894164194	8.105835806	81.05835806
1.2	0.178	1.765578635	8.234421365	82.34421365

Table 6: Effect of Initial MB concentration on MB Removal

INITIAL MB CONCENTRATION (mg/l)	INITIAL ABSORBANCE (nm)	ABSORBANCE AFTER ADSORPTION (nm)	FINAL MB CONCENTRATION (mg/l)	MB CONCENTRATION ADSORBED (mg/l)	PERCENTAGE ADSORBED (%)
1	0.101	0.018	0.182987141	0.817012859	81.70
3	0.303	0.062	0.618199802	2.381800198	79.39
5	0.505	0.107	1.06330366	3.93669634	78.73
10	1.01	0.244	2.418397626	7.581602374	75.82
15	1.516	0.418	4.139465875	10.86053412	72.40

Figure 9: Cut Fresh and Dried Pineapple Peelings

Figure 10: Powdered Dried Pineapple Peelings and Hydrochar

Figure 11: Researcher Doing Batch Experiments