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DEPARTMENT OF CHEMISTRY

THE REMOVAL OF DYE USING *ACTIVATED CARBON* PREPARED FROM *MANKETTI SEED SHELLS*: BATCH METHOD.

BY

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Approval form

The undersigned certify that the project entitled THE REMOVAL OF DYE WITH ACTIVATED CARBON PREPARED FROM MANLKETTI SEED SHELLS: BATCH METHOD was supervised, read and recommended to the Bindura University of Science Education.

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This work was submitted in fulfillment of the requirements of BACHELOR OF SCIENCE HONOURS DEGREE IN CHEMICAL TECHNOLOGY

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DEDICATION

I want to dedicate this work to the All-Powerful God, who is my source of motivation, fortitude, wisdom, insight, and understanding. I would also like to thank everyone who helped put this project together, including my family, friends, and myself. I'm grateful. THANK YOU.

ACKNOWLEDGEMENT

.

I want to express my gratitude to the following people: my supervisor, Prof. Matthew Mupa, whose expertise in the field guided me through my project for his help with this project, and. I also like to express my gratitude to the laboratory assistants at Bindura University of Science Education.

ABSTRACT

The common industries that make a significant contribution to the discharge of wastewaters that include detectable amounts of dye are the food, paint, leather, paper, and textile sectors. When dye effluent is dumped into bodies of water, it has a major negative impact on both people and aquatic life. Activated carbon adsorption has considered to be one of the most straightforward and efficient ways to remove dye from wastewaters out of all the available techniques. A research study is conducted to create activated carbon from Manketti seed shells and evaluate the material's effectiveness in removing methylene blue from an aqueous solution.

The bulk density, moisture content, methylene blue number, and iodine number of the activated carbon derived from Manketti seed shells were all measured. Evaluations were done on the effects of process variables such particle size, adsorbent dosage, and contact time. The findings demonstrated that powered activated carbon has a removal percentage ranging from 91.4% to 94.3%. As the initial dye concentration rose, so did the amount of dye that was adsorbed.

ABBREVIATIONS

AC	activated carbon
MB	methylene blue
PAC	powdered activated carbon
GAC	granular activated carbon
EAC	extruded activated carbon
BET	Brunauer Emmett-Teller
FT-IR	Fourier transform infrared
BOD	biochemical oxygen demand
COD	chemical oxygen demand
MC	moisture content
MSS	Manketti seed shells
AI	Active Ingredient

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Chapter 1: Introduction

Background

Environmental pollution has increased recently, mainly in poorer countries, and it is now prevalent throughout the world (Sciences et al., 2015) One of the contributing elements to environmental contamination is the release of liquid effluents by businesses engaged in the manufacture of paper, paints, cosmetics, leather, and textiles (El et al., 2020). The visible contaminants in these liquid effluents may include color or dye. An organic substance used for the purpose of adding color is called a dye. Companies in the textile, cosmetic, and paper industries manufacture over 700 000 tons of dye per year, and 50% of these dyes end up in surface water, having major negative consequences on the environment in 2013 (Ghaedi et al.) Over the past few years, the release of these dyes has caused significant environmental contamination that, even in minute amounts, is harming aquatic life and human health.

The dye compound methylene blue (MB), which has been used to represent dye compounds in aqueous solution, is described as an acid dye compound (Phihusut & Chantharat, 2017). The compound MB is frequently used in a variety of processes, such as fabric and paper dying. Additionally, MB as an environmental pollutant has the potential to harm ecosystems and the environment by raising COD and BOD levels, impeding photosynthesis, and causing bioaccumulation in surface water. Drinkable water quality is impacted by these colored chemicals. In order to properly dispose of the wastewater, color removal is therefore necessary.

Diverse, successful methods for removing dye from wastewater have been developed. (Narcisse et al., 2015) These processes include chemical coagulation, chemical oxidation (Sciences et al., 2015), electrolysis, membrane filtering (Phihusut & Chantharat, 2017), ozonation (Malik & Sanyal, 2004), photochemical degradation, adsorption by activated carbon, and biological therapy. Adsorption with activated carbon is one of the available methods that is simple, efficient, and affordable, although polypropylene and chitosan have also been discovered to be adsorbents. Due to their excellent surface area, high adsorption capacities, variety of functional groups, and thermo stability, AC have been widely utilized to remove dye from wastewaters. (Malik, 2004) Currently, businesses utilize activated carbon to remove dye from wastewater as a sorbent because of the exceptional adsorption properties.

Although the use of activated carbon as a sorbent has been restricted due to its high cost. As a result, numerous efforts have been made to look for low-cost adsorbents in an effort to lower the cost of therapy. If and only if sorbents are the most plentiful in the environment and need the least amount of processing, they are regarded as being inexpensive (Malik, 2004). Other options that have been shown to be effective as activated carbon sources include rice husk, plum kernels, nut shells, coconut shells bagasse, rattan sawdust, coffee grounds, olive stones, apricot stones, oil palm shells, soy meal hull, durian shell, lranian milk vetch, rambutan peel, and jute fiber (Ghaedi et al., 2013).

The objective of this study was to employ MSS to remove the methylene blue (MB) dye from aquatic settings. The impact of several factors, such as particle size, methylene blue number, contact time, adsorbent dose, iodine number, and initial dye concentration, was investigated on the effectiveness of dye removal. Due to their high adsorption capacity, significant surface area, micro porous nature, and chemical and thermal durability, activated carbons made from a variety of materials are frequently utilized as adsorbents.

The type of precursor used and the production method adopted determine the characteristics of AC. The production of AC can be done in two ways: chemical activation and physical activation. The physical activation process consists of a series of sequential steps where the precursor is first converted into char by being carbonized, and then the activation process is carried out using either steam, CO2, or a combination of both. In chemical activation, the precursor is impregnated with the chemical activators, and carbonization is carried out at various temperatures. This method results in immediate activation and carbonization, which changes the material both chemically and physically.

Problem Statement

Despite the contribution of plastic, photography, textile, paper, ink manufacturing industry as an important income source in many countries. After the continuous growth in world population, the demand for these products increased significantly (Robinson et al. 2001) Textile industry has been recognized as the most significant source of wastewater pollution, mostly related to the discharge of dyes that are mostly highly recalcitrant and toxic.

It is imperative to have highly effective methods for the eradication of pollutants from industrial effluents due to the major effects of the use of dyes in a significant number of sectors with strong growth. (Chowdhury et al. 2015). Otherwise, serious environmental (visual pollution, scarce penetration of light, and limit the photosynthetic zone in water bodies) and health (potentially mutagenic and/or carcinogenic) problems are to occur the environmental impacts brought by such industry cannot be overlooked

Significance Of The Study

Activated carbon adsorption is a somewhat successful, practical, cost-effective, and straightforward method for the removal of dye from wastewater compared to other methods. (Alhogbi et al., 2021).

Commercial based activated carbon is quite expensive to purchase especially for applications like water treatment, removal of dye and contaminants in wastewaters. The AC obtained from natural sources are considered since they are cost effective, readily available, and renewable and have good properties. Activated carbons can be economically employed for the removal of dye in wastewater if low-cost non-conventional supplies are utilized to manufacture them for a specific purpose. Due to the high cost of other techniques, there is an urgent need to use the one that is less expensive and readily available

.

Research Questions

- What distinguishes commercially generated activated carbon from AC made from MSS?
- Do the activated carbon from MSS have high adsorption properties as compared to the commercially produced AC?
- How the ash is content of the AC prepared from the MSS different from commercial based AC?
- How effective is the prepared activated carbon (AC) from MSS in the removal of MB in aqueous solution?

Aims

- To synthesize activated carbon prepared from readily natural raw material Manketti seed shells for the removal of methylene blue from aqueous solution.

Objectives

- To investigate the kinetics and equilibrium adsorption of Manketti seed shell-derived AC on Methylene blue.
- To create inexpensive activated carbon from the shell of the Manketti seed through chemical activation using sulfuric and phosphoric acids.
- To characterize the activated carbon from Manketti seed shells using FT-IR, Iodine number, moisture content, and methylene blue (MB) number.

CHAPTER 2: LITERATURE REVIEW

Manketti tree (Schiniziophyton ruatanenii (Schinz) Radcl. -Sm.)

In regions with high temperatures and little rainfall, manketti is frequently seen. The tree can mostly be found in Southern Africa, including the northern regions of Namibia, Botswana, western Zimbabwe, and southwestern Zambia. Featherweight tree, Elephant nut, Mongongo, Muoma, Mugongo, and Ungoma are some of the common names for the Manketti tree. The EUPHORBIACEAE family includes the tree.

After the wet season (April to May), which is when the fruits of the Schiniziophyton ruatanenii are gathered. 900 fruits or more can be produced year by each tree. The fruit has been utilized to make a very nutrient-dense oil, and the seed shells will eventually be used to make activated carbon.

Figure 1.0 Manketti Tree

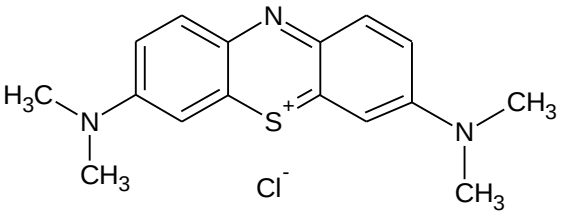
Figure 1.2 Manketti Tree And Its Fruit

Dyes

Dyes are colorants that last long on textiles and have a natural affinity. Synthetic dyes attained from inorganic or organic mixtures are mostly composed of two compounds that are auxochromes and chromophores (Alhogbi et al., 2021). The chromophore is the one that forms the color of the dye, while the auxochrome is in charge of the intensity of the color. Dye usually moves into the chemical molecular structure of the textile fiber to produce the end product color of the textile. Different types of dyes are used in manufacturing industries of textiles, paper, paints, and cosmetics. These include natural dyes for example indigo and synthetic dyes which are methylene blue and azo dyes.

Methylene blue, a synthetic heterocyclic aromatic dye that resembles a thiazine cationic dye, was initially created in 1876 as an aniline-based dye for the textile industry. One of the synthetic materials utilized in clinical therapy as an antiseptic and an antiseptic coloring was methylene blue. Paper, silk, nylon, viscose, wool, and cotton have all been colored with MB, and hair dyes briefly as well. The IUPAC designation for MB is [7-(Dimethyl-amino) phenothiazine-3-ylidene]-dimethylazanium chloride. Vitableu, Panatone, Demoidpillen, Desmoid Piller, and Urolene Blue are some of the generic trade names for MB.

Figure 1.3 Structure of the MB



MB has been used in veterinary pharmacy and humans for diagnostic and therapeutic procedures for instance as a redox coulometric agent, anti-haemoglobinaemic, antiseptic, disinfectant, stain in bacteriology, and a melanoma targeting agent. MB has also been used for treating methaemoglobinaemia which is caused by overexposure to drugs, industrial chemicals, for instance, nitrophenols, and environmental poisons for example cyanide composites and too many nitrates in well-water. MB has been used in paper dying and to tone up silk colors. MB is also applied to analytical chemistry, to govern anionic surfactants, in pH, and as a redox indicator reagent.

Environmental effects of dyes

- The residue water composition of the textile industry has high levels of chemical oxygen demand (COD) and biochemical oxygen demand (BOD).
- Cationic dyes affect both the animals and the human's eyes and skins.
- Dyes prevent light from penetrating through the water, leading to the reduction of the rate of photosynthesis and the dissolved oxygen levels, therefore, affecting the whole of aquatic life.
- Acts as carcinogenic, mutagenic, and toxic agents.
- Dyes can cause allergies
- Increased bioaccumulation of dyes in the soils, therefore can be transported to the public water supply chain.

Activated carbon

Activated carbon (AC) describes a class of amorphous carbonaceous materials that have high internal surface and high porosity. Generally, AC can be prepared from carbonaceous substances of any choice, and lately, bituminous coal and anthracite were found to be the major sources of AC. Commercially AC is made up of bone char, petroleum coke, woods, coal, lignite, and biomass sources. Mostly organic substances with high carbon content respectively can be starting materials ranging from synthetic polymers to convectional substances for example coconut shells, coal, and wood.

Commercial carbon grade, values for surface area classically vary in between the range of 500 and 1500m^2/g or as well as high as 3000m^2/g. Commercial AC can be put into 2 different groups that are the liquid and gas phases depending on their applications. The former is generally micro porous with a pore diameter of less than 2nm, the granular form has a pore diameter that varies from 2.36mm to, 833 mm or can be 8/20 mesh size, and the latter form is mesoporous with the pore diameter between 2 and 50mm and the powdered form has a pore diameter which ranges from 0,150 to 0,043 mm or can be 100/325. Powdered form and granulated AC were both proven to be effective in dye removal, metal recovery, decolorization, and adsorption of wastewater treatment.

Types of AC

- Powdered activated carbon (PAC)- generally have a particle size between 5 to 150 Å which are mostly used in liquid phase adsorption applications. PAC reduces processing expenses and is flexible in operation.
- Extruded activated carbon (EAC) is a type of carbon that is formed into cylindrical pellets with a particle size of 1 to 5 mm. EACs are made of heavy-duty carbon since they are extruded. EACs are practical to use and reusable. gas-phase processes
- Granular activated carbon (GAC)-has a 0.2mm to 5mm particle size range. GAC is frequently utilized in applications involving either liquid or gas phases. Because they outlast PACs, have increased strength, and are intelligent, GACs are well recognized.
- Impregnated carbon
- activated carbon cloths
- Bead activated carbon
- Activated carbon fibers
- Polymer coated carbon.

Figure 1.4. Types of AC

Properties of AC

AC is characterized based on physical and chemical properties. The physical properties include the ash content, bulk content, moisture content, particle density, pore volume, particle size distribution, and ball-pan hardness. The chemical properties include iodine number, methylene blue number, benzene number, carbon tetrachloride number, and surface area.

Ash content

Ash content of AC is the remains that are left after combustion of the matter in the AC that has completely been burnt. The remains denote the standard of the mineral substance. The ash content method is one way to gauge how much mineral oxide is present in the activated carbon produced on a weight basis. By converting the mineral components to the appropriate oxides at 800°C, ash content is determined. The amount of ash in the final product, activated carbon, which is typically composed of aluminum and silica, depends on where the raw materials came from. Typically, the ash concentration ranges from 2-3%W/W (for coconut shell-based AC), 5%W/W (for wood-based AC), and 8-15W/W% (for other types of AC) (coal-based AC). High levels of ash content may indicate that Ca, Al, Mn, or possibly Fe have been deposited on the AC or that sand is present. A percentage of the material that is amorphous, lifeless, inorganic, and useless is represented by the ash content of AC. Low ash content is necessary since the quality of the AC improves as ash content drops.

Bulk density/ apparent density

The mass of all the AC's innumerable particles divided by the volume that is occupied altogether is the bulk density, often called as the apparent density. Particle volume, internal pore volume, and inter-particle void volume make up the total volume. The adsorption per unit volume is affected by the bulk density of Ac rather than the absorption per unit weight.

Moisture content

The weight loss of the AC after heating it to 150 °C and then drying it to a constant weight is known as the moisture content (MC) of the AC (ASTM D2867) (typically after 3 hours). The total amount of moisture in the AC should ideally range from 3 to 6%.

Iodine number

A technique for figuring out the AC's adsorption capacity is the iodine number. Iodine adsorption from the solution is the method used to test the activated carbon's micro pore content. The unique range is 500 to 1200 mg/g, which is equivalent to 900 to 1100 m2 of carbon surface area per gram. The quality control criterion for the reactivation and production of activated carbon is the iodine number. According to ASTM D4607 standard, the iodine number is defined as the milligrams of iodine absorbed by one gram of material when the iodine residual content of the filtrate is 0.02N (0.01 mol/l).

Methylene blue number

MB number by definition is the maximum amount of dye adsorbed on 1.0 g of adsorbent. MB adsorption experiments are simple and are done to illustrate the adsorption capacity of the material being used. According to the dimensions of the methylene blue molecule, MB is mostly adsorbed

in mesopores, but small portions of MB are found in larger micro pores. The surface area of the AC has mostly been measured with the Brunauer Emmett-Teller (BET) method. This method employs nitrogen adsorption at different temperatures and pressures of liquid nitrogen. The unit of Activated Carbon area is m^2/g.

Adsorption properties

The elimination of dye from wastewater and the purification of materials in commercial enterprises have both shown the high efficiency of adsorption on AC. Adsorption, according to Aznar (2011), is a physicochemical process in which a solid, known as an adsorbent, Retains in the walls a certain kind of molecules, called adsorbents, that are contained in a gas or liquid. The commonly used adsorbents are activated carbons, synthetic resins, and silica.

Considerations of the adsorption process in terms of adsorbate -adsorbent.

- Particle size
- The affinity of the adsorbate
- Pore structure, size, and distribution
- Specific surface and porosity of the solid
- Partial pressure/ concentration of the adsorbate in the fluid phase.

Adsorption process

There are 3 types of adsorptions that is, surface chemical reaction together with ion exchange, surface complexation and diffusion. Diffusion processes are described in terms of pore diffusion, surface diffusion or a combination model of the two mechanisms; frequently, an external boundary layer film resistance is incorporated into these models. Depending on the order of the reaction between the adsorbate and the adsorbent functional group, many kinetic models are available for chemical surface reactions. Examples include pseudo-first-order, pseudo-second-order, Avrami, Bangham models, and Elovich. Many adsorption processes, particularly those involving the removal of heavy metals from wastewater, have been the subject of surface complexation mechanisms. This procedure uses hydrogen bonding or lone pair electron donation to coordinate the heavy metal ion with a variety of functional surface groups.

The type of adsorption mechanism therefore depends on the nature of the adsorbate and the properties of the adsorbent. Adsorption of dye onto adsorbents is a physical phenomenon in which dye molecules attach onto the adsorbent surface under the influence of van der Waals forces and hydrogen bonding. Each contact point in a continuous contact system is analogous to an equilibrium stage or theoretical plate, giving adsorption a distinct advantage because complete separation can be accomplished in a brief fixed-bed column. Due to their toxicity, high chemical stability, and tendency to prevent natural photosynthetic processes from occurring, colored/dye, pharmaceutical, or metal ion-containing effluents can cause considerable problems. Adsorption can considerably help with these problems.

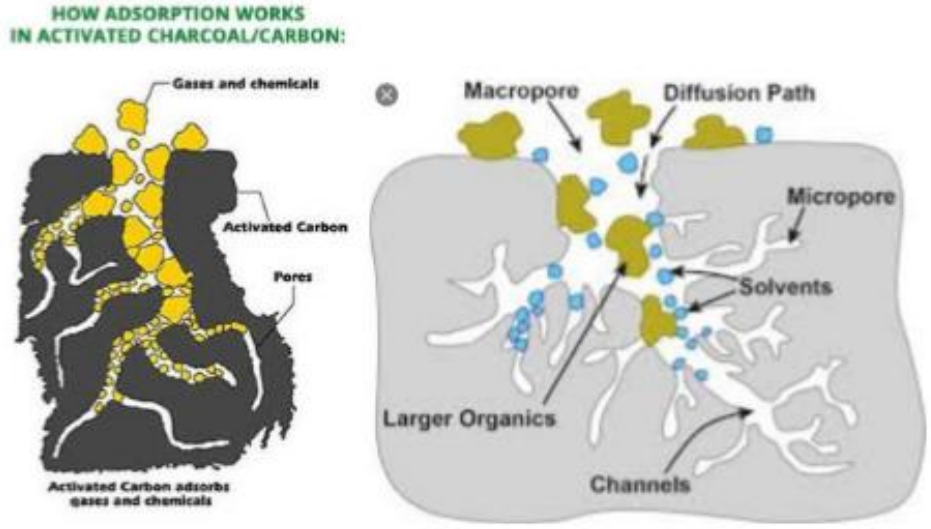
Pore Structure

Activated carbon is a coarse form of graphite that has a random or amorphous structure and is highly porous across a variety of pore sizes, ranging from apparent fractures and crevices to cracks and fissures of molecular diameter.

Adsorption, in which molecules of a liquid or gas are trapped by either an exterior or internal surface of a solid, is the primary scientific basis for the purification process using activated carbon. Similar to how a magnet holds iron filings, this phenomenon occurs. Activated carbon has a very high surface area within it (up to 1500 m2/g), making it the ideal substance for adsorption. Activated carbon can be created from a variety of basic materials that have a high carbon concentration. Both chemical and thermal procedures, which both call for the utilization of high temperatures, are used in the production process to transform the raw material into the finished adsorbent.

The surface morphology of activated carbon, which varies, is significantly influenced by the source material and manufacturing technique. Adsorption is made possible by the pore structure in combination with attraction forces. According to the nitrogen BET technique, the internal surface area of activated carbons is typically greater than 400 m2/g, and the volume of the pores is typically described as being greater than 0.2 ml/g. The IUPAC (International Union of Pure and Applied Chemistry) distinguishes three kinds of pores based on pore size: Macropores: (diameter > 50 nm) Mesopores: (2-50 nm diameter) (2-50 nm diameter) (2 nm in diameter) Micropores. The majority of the interior surface area is typically contributed by micropores. Macro- and mesopores are vital for kinetics and can be thought of as the roads into the carbon particle.

Figure 1.5. The AC's pore structure



Production of activated carbon

The raw material is first put through pretreatment processes like washing, drying, and heating before being used to make activated carbon next, carbonization and activation, two widely used methods for producing activated carbon, are used.

Carbonization process

Carbonization or pyrolysis is when the raw materials are thermally decomposed in a furnace under nitrogen (N_2) purge in an atmosphere that is inert with a temperature of less than 800℃. This is done to eliminate non-carbon species like O_2, H_2, and N_2 and to improve the fixed carbon content to yield bio char (Radenahmad et al., 2020). During the devolatilization process, the narrow pore structures of precursors start to develop which leads to the deposition of tarry substances formed as the temperature rises (Alhinai et al., 2018). In a few cases, this deposition may cause a collision of some tarry substances and the collapse of walls of pores that could lead to hydrocracking and carbon deposition Carbonization simply means the development of carbon.

The carbonization process involves condensation, dehydrogenation, isomerization, and hydrogen transfer. Elements such as sulfur, hydrogen, oxygen, and nitrogen are removed from the raw material through gasification. In raw materials, carbonization results in the removal of contaminants and the decay of organic matter. A pore structure is created when these volatile substances are discharged. The cycle of pyrolysis process will have to halt if no smoke is produced. Pore closure may occur at temperatures above 1000°C, although the process can be accelerated by adding more heat.

Activation process

Chemical activation

Chemical activation is the process of adding chemicals while the process is being activated. The substances employed in the activation are referred to as activators. The activators employed range from basic reagents like Na2CO3, NaOH, KOH, and K_2CO_3 to acidic and alkali ones like H_2SO_4, H_3PO_4, HCl, and ZnCl2. Compounds can be activated in one step using the thermal breakdown of raw materials and chemicals.

Due to lower temperatures needed and shorter activation times, chemical activation is one of the approaches that is preferred over the physical activation procedure. If the substance is wood, the wood must first be saturated with the activating reagent, which triggers the breakdown of the cellulose material. Following the impregnation procedure, the impregnated material is heated in a rotary kiln between 400 and 800℃ without the use of air. After the impregnation process is finished, the material is cooled, cleaned, and dried. The material is cooled, cleaned, and dried before activation.

The impregnation ratio determines the size of the carbon's pores; the bigger the impregnation ratio, the larger the pore diameter. The characteristics of the resulting activated carbon vary depending on the impregnation ratio, activation temperature, and gas composition.

Physical activation

Steam activation and pyrolysis, which involves heating in an inert atmosphere, are the two techniques used for physical activation. When a material is heated to a temperature of around 1100 °C, volatile chemicals leave the material and often just carbon in the form of char, with the original carbonaceous structure, is left. Shaft kilns, rotary kilns, fluidized beds, or multi-hearth furnaces are used for the steam activation process.

Why chemical activation is preferable than physical activation

- Normally gives a more porous structure.
- Results in a higher yield
- Need low activation temperature
- Chemical activation is a single-step activation process, therefore reducing the consumption of energy.

Benefits of physical activation over chemical activation and their drawbacks.

- Cleaning is required to eliminate chemical residues.
- The activating agents like NaOH and KOH are very hazardous, expensive to purchase, and corrosive, whilst $ZnCl_2$ is not environmentally friendly and has a problem when it comes to disposing of it.
- An increase in the processing cost due to the activating agents used.
- Health threats when it comes to the handling of activating agents. Therefore, there is a need for extra precautions.

In addition to chemical and physical activation, physiochemical activation is another immediate activation method (Chowdhury et al., 2013). There are two ways to manufacture activated carbons via physiochemical activation: pre-carbonization, which involves chemical treatment, and post-carbonization, which involves chemical treatment (Rashidi, 2017). The first method involves carbonizing the precursors, followed by the impregnation of bio char, thermal treatment in the presence of oxidizing gas, and high-temperature physical activation between 600 and 850°C. The second method involves carbonization in an inert environment and switching to oxidizing gas (Rashidi, 2017).

The first method involves carbonization of the precursors, followed by the impregnation of bio char, thermal decomposition in the presence of an oxidative gas, and high-temperature physical activation in the range of 600 to 850°C. Carbonization may also be done in an inert environment and then switched to an oxidizing environment (Rashidi, 2017). The second process, in contrast, requires that the precursors first go through chemical treatment before being heated and physically activated (Mohd Din et al., 2009).

Microwave (MW) activation

Due to its exceptional characteristics, including selectively, swiftly, even, and volumetric heating, indirect contact between the heating foundation and heated resources, and prompt and exact regulator, MW has replaced traditional methods of producing AC (Hoseinzadeh Hesas et al., 2013). The configuration of the process, the intensity of the MW radiation, the duration of the activation, the characteristics of the precursors, and interactions between the MW and chemical substances are the main working restrictions for microwave-supported activation (Ao et al., 2018). Dipole orientation and ionic transmission in MW heating make it simple for energy to be distorted into heat within the molecules.

When exposed to a high-frequency voltage, particles possessing either induced dipole moments or permanent dipole moments align in the direction opposite to the force being applied (Alslaibi, Abustan, Ahmad, & Foul, 2013). As a result, the example molecule's interior temperature increases significantly while its exterior temperature decreases, increasing its effectiveness and efficiency (Pathak and Mandavgane, 2015). One step (Deng et al., 2010) or two steps can be used to manufacture higher quality activated carbon via MW aided activation, which combines physical and/or chemical activation (Abbas and Ahmed, 2016)

Applications of activated carbon

- Purification of portable water – AC is commonly used to remove unwanted taste, bad smell and harmful pollutants.
- Remove precious metal catalysts after the synthesis of pharmaceutical active ingredients (AI)
- Removal of undesirable taste compounds and color precursor from processed fruit juices
- Removal of hydrogen sulphide (H_2S) in biogas
- VOC and siloxanes purifications
- Wastewater purification
- Removal of dye from textile, paper and paint industries
- Effective poison remover from the blood(Frequency et al., n.d.)

CHAPTER 3

3.1 REAGENTS

- Iodine solution
- sodium thiosulphate (Na_2SO4)

- starch solution
- methylene blue (MB)
- hydrochloric acid (HCl)
- Sulphric acid (H_2SO_4)
- Phosphoric acid
- distilled water

3.1.1 EQUIPMENTS USED

- Electrical oven
- Electrical muffle furnace
- UV-Vis Spectrometer
- Analytical balance
- pH balance
- Sample agitator
- FT-IR Spectroscopy
- Centrifugator

3.1.2 SAMPLE COLLECTION

MSS were brought from Matebeleland west where there are originally found. The seeds were approved by Prof Mupa.

3.1.3 Pretreatment of the MSS

To get rid of dirt and other pollutants, the MSS were cleaned first with running water and then with distilled water. The MSS was first washed, and then the seeds were first dried in the sun for a day and then in an oven at 110 °C.

3.2 SAMPLE PARTICLE SIZE REDUCTION

The MSS's hard shells required crushing with a massive granite stone. MSS were reduced down to approximately 1 mm in size. Different sieves with varying aperture diameters were used to separate the reduced MSS.

3. 2. 1 Synthesis of activated carbon using phosphoric acid as the activating agent

The precursor employed was MSS. The MSS was chosen for the synthesis of activated carbon after being dried, ground, and sieved to a particle size range from 0,5 mm to 1,0 mm. 200ml of phosphoric acid was used to impregnate 50g of MSS at varied concentrations of 60wt%, 70wt%, and 80wt%. The mixture was uniformly agitated for four hours at 85 degrees Celsius to guarantee that phosphoric acid could reach the MSS's inner core. Following mixing, the MSS were carbonized at a temperature of 500°C in the muffle furnace. The mixture was heated and then allowed to cool.

3.2.2 Preparation of Ac with H_2SO_4 as the activating agent

H_2SO_4 was combined in a 1:1 ratio with the MSS. For 24 hours, the mixture was kept on the shaker at room temperature. The sample was subsequently dried for 24 hours at 105°C in the oven. The sample was subsequently carbonized for 30 minutes at 650°C in a muffle furnace. To get rid of extra dehydrating agent and ash after the carbonization process, the product was rinsed with a 10-weight percent solution of HCl. The sample was subsequently cleaned three more times in deionized water and dried for 24 hours at 80°C.

Characterization of AC

3.2.3 Adsorption Experiments

Adsorption isotherms were performed in a series of 250 ml, and the adsorption equilibrium and kinetics were calculated using the batch method. The conical flasks contained 100ml of various MB concentrations. To the MB solutions, equal quantities of activated carbon in the range of 0.3g to 1.0g were added. The flasks were set up on a thermostatic water bath at various temperatures, and they were shaken and stirred for 45 minutes at 150 rpm. The centrifuge was used to separate the AC for 10 minutes at 3500 rpm. At 668 nm, Spectro photochemical analysis was used to determine the MB's residue (UV-VIS). When the absorbance exceeded 1.5, dilutions were made; the amount of MB that is removed is determined by

Percentage removal of MB is calculated by

$$\% \, Removal = \frac{Co - Ct}{Co} x \, 100$$

$$adsorption \, capacity = \frac{(Co - Ct)}{m} x \, V$$

Co- initial concentration

Ct- equilibrium concentration

m- Mass of the adsorbent

V- Volume used

3.2.4 Determination of the ash content

3g of AC was poured into ceramic crucibles after drying for 24 hours at 80 °C. The samples were heated for three hours at 650°C in the muffle furnace. The crucibles were weighed after cooling. Ash content is determined using

$$ash\ content = \frac{(weight\ of\ the\ crcible + ash\ sample\ ) - (weight\ of\ the\ crucible)}{(weight\ 0f\ the\ crucible\ with\ the\ \ sample) - (weight\ of\ the\ crucible)}$$

3.2.5 Determination of the Iodine number

10ml of 0.1M of iodine solution was put in the conical flask, and titrated with 0,1M sodium thiosulphate solution in the presence of 2 drops of 1wt% starch solution indicator until the solution became colorless. 0,05g of activated carbon was added to a conical flask with 15ml of 0,1M iodine solution. The mixture was shaken for 4 mins and filtered. 10ml of the filtrate was titrated with the standard sodium thiosulphate solution with 2 drops of starch indicator. The iodine number was calculated.

$$iodine\ number = V(Si - Sf)x\ C\ x\ M/(Si\ x\ g)$$

Whereby V- ml iodine

S_i – volume (ml) of $NaSO_4$ solution used for titration of 10ml Iodine solution

S_f -volume (ml) of $NaSO_4$ solution used for titrating the filtrate solution

g- Mass of the sample in grams

M- Molar weight of Iodine (126.9044g/mol)

C- Concentration of iodine

3.2.6 Determination of the bulk density

10ml graduated cylinder was weighed accurately. Sufficient amount of carbon was added with constant tapping up to 5ml mark. The bulk density was calculated.

$$bulk\ density = \frac{mass\ of\ AC}{volune\ of\ AC}$$

3.2.7 Determination of the moisture content

2g of activated carbon was weighed and placed in the heated oven of 105℃ for an hour. The heated AC was cooled in a desiccator and then weighed. The procedure of heating, cooling and weighing was repeated after every 30 minutes until the difference was plus or minus 0,01g. The moisture content was calculated.

$$moisture\ content\ = \frac{A - B}{A - C}$$

A- Mass of the crucible with the sample

B-mass of the crucible with cover + dry sample

C- Mass of the empty crucible

3.2.10 Determination of the percentage yield

Percentage yield is calculated by

$$percentage\ yield\ \% = \frac{mass\ of\ AC}{mass\ of\ raw\ naterial} \text{ x } 100$$

CHAPTER 4

Results and analysis

Characterization of the Activated carbon

Activated carbon prepared using $ZnCl_2$ as the chemical activating agent has turned out to the one with high percentage yield followed by the activated carbon prepared from phosphoric acid being the activating agent. Properties of activated carbon for instance iodine number, bulk density, moisture content, ash content and methylene blue number were observed and are shown in the table below. The range of iodine number was between1004.30-1080.48mg/g. The AC sample activated 60wt% H_3PO_4 at 500°C was observed with the highest iodine value of 1080.48mg/g.

The iodine number assesses the permeability inside the dimensions and can be used to estimate the surface area of the AC in m2/g (Mkungunugwa et al., 2021). The larger micropore structure of activated carbon, which can lead to the carbon having a large surface area due to the growth of its pore structure, has been linked to the material's higher iodine number. The observed iodine values allow for use in water treatment. Verla et al. It has been suggested that AC with an iodine content of 600 to 1100 mg/g be used for water treatment. The synthetic AC's iodine values were comparable to those of commercial AC sold in stores (1034.30.02mg/g). Comparing AC samples activated with H3PO4 to samples treated with H2SO4, the H3PO4-activated samples had higher carbon contents and higher iodine values. The variations in reactivity rates with the activating agents may provide an explanation for this.

When compared to other researchers' activated carbon, the activated carbon made from MSS is shown to have a high ash and moisture content. According to a study by Sharada et al., tamarind seed-derived AC has a moisture content of 2.9%, ash of 1.5%, a bulk density of 0.4g/cm3, an iodine number of 995mg/g, and a specific surface area of 912m2/g. Additionally, Mopoung et al. discovered that AC made from tamarind seeds activated with KOH had a carbon output of 54.09-82.03wt%.

Table 4.0 comparative results

Activation chemical	Percentage yield %	Moisture content	Ash content %	Iodine number	Bulk density
60wt% H_3PO_4	63.6	4.2	29.1	1080.48	0.33

70wt% H_3PO_4	61.3	3.6	27.5	1040.90	0.35
80wt% H_3PO_4	59.7	5.0	24.1	1025.89	0.36
H_2SO_4	56.8	8.3	14	1004.30	0.33

Figure 4.1 FT-IR spectrum of the AC with 60wt% H_3PO_4

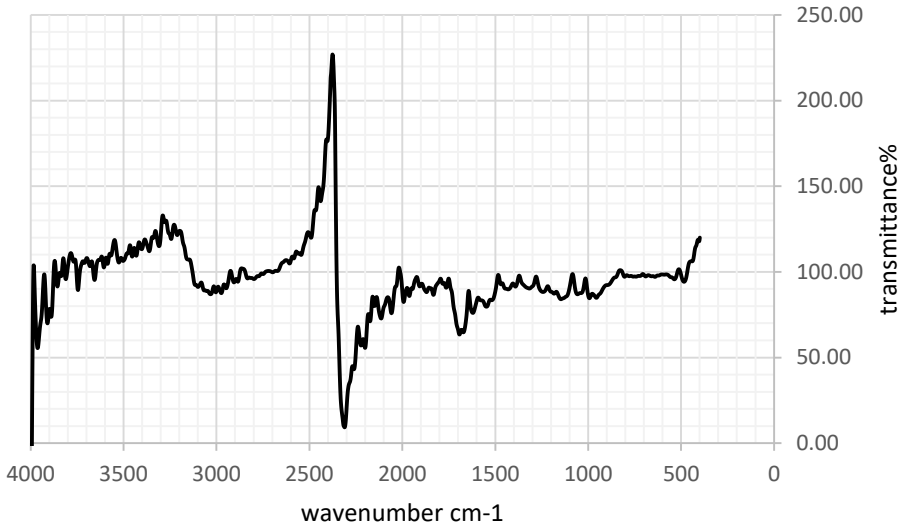


Figure 4.2. FT-IR spectrum for AC with 70wt% H_3PO_4

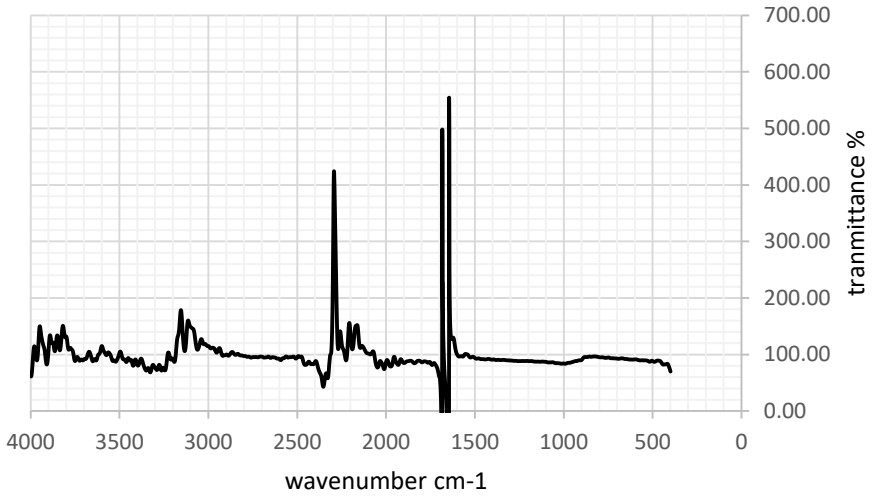
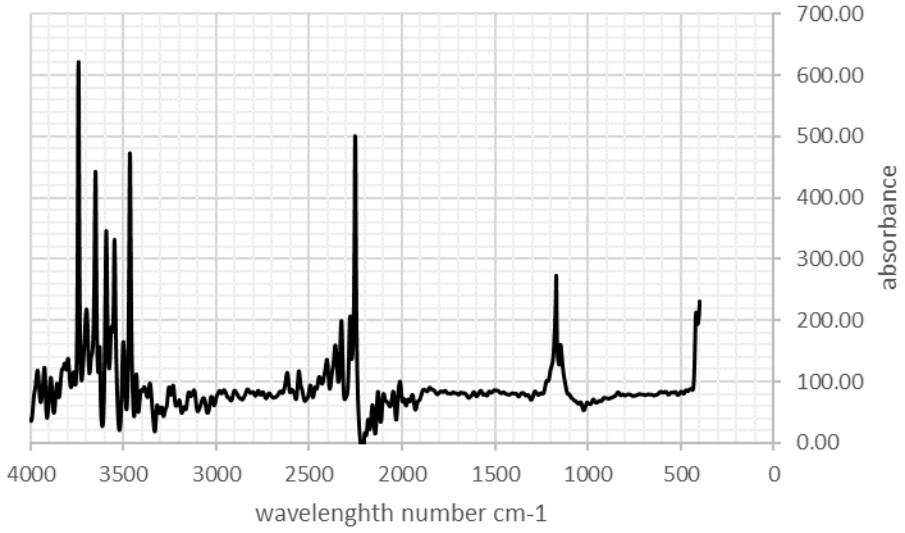


Figure 4.3. FT-IR for AC with H_2SO_4 as the activation chemical



FTIR Characterization

The results of the FTIR study are displayed in Figures 4.1–4.2. The functional groups and other chemical components present in the AC that are significant in its classification and prediction adsorption performance were found using FTIR analysis. An FTIR spectrum associated with a primary amine group (N-H) was found to be present in the surface properties of AC activated from sulphuric acid, and a tiny band at 2950 cm 1 indicated the presence of an alkane (Figure 4.3).

H_2SO_4 activated carbon, 60wt% H_3PO_4 activated carbon, and 70wt% H_3PO_4 activated carbon samples all displayed strong and broad bands at 3434-3400 cm-1. These might be attributed to the inter/intra-hydrogen bonding (O-H) stretching associated with the hydroxyl groups present in phenols, alcohols, and carboxylic structures. The spectra provide as an example of the N-H stretches. Strong bands found at 2905 cm-1 for the spectrum of 60 weight percent H3PO4 and 2918 cm-1 for the spectrum of sulfuric acid were attributed to the asymmetric C-H band found in alkyl groups. The stretched adsorption bands at 1146 cm-1 for the 60-weight percent H_3PO_4 spectrum may resemble the carboxyl group C=O present in esters, aldehydes, ketone groups, and acetyl derivatives, as well as the C=C stretching attributed to the alkynes C-C (2213 cm-1; 2174 cm-1) bands. The band at 1155 cm-1 H_2SO_4 attributed to the strong band of C-O.

Methylene blue removal from the solution

The active carbon made from MSS successfully removed the dye from an aqueous solution to produce a colorless solution, as shown in Fig. 4.4 below. It was discovered that MSS activated carbon may be used in industrial settings to remove color from wastewater produced by the textile, paper, photography, and paint industries. Municipalities can also use this activated carbon to purify water and get rid of bad odors and colors.

Figure 4.4. The removal of MB with the adsorbent AC

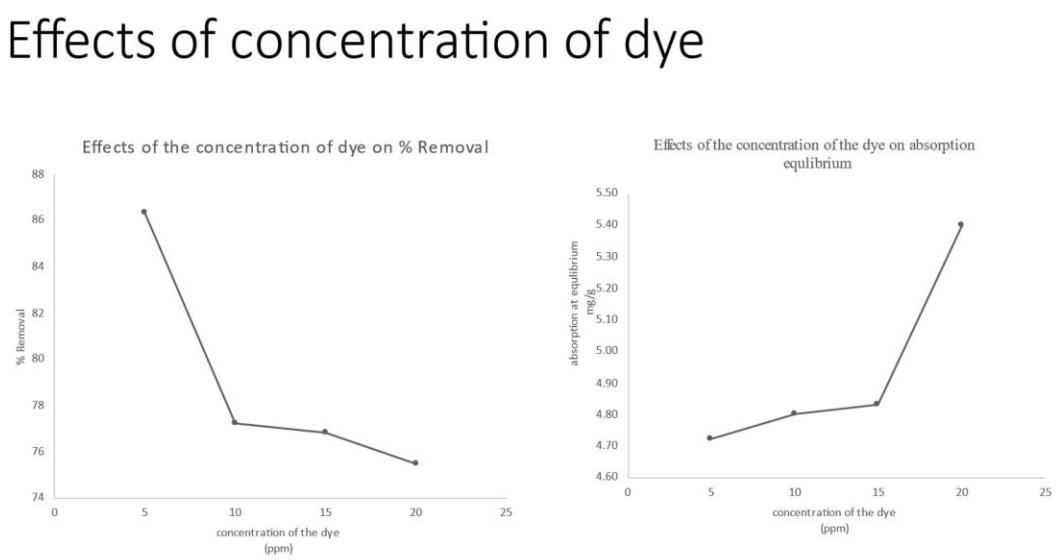


Figure 4.5. The effects of concentration of dye

Effect of the Concentration of MB

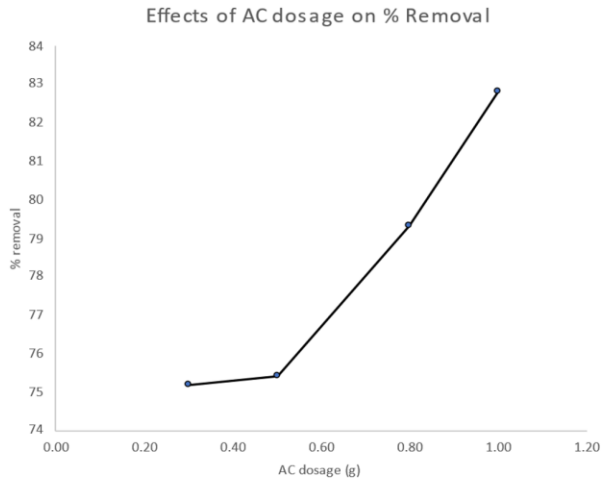
The impact of the various MB (5, 10, 15, and 20 ppm) concentrations on the rate of adsorption utilizing the MSS adsorbents was investigated. At room temperature (26 1 °C), the research was conducted with a continuous adsorbent dosage of 1g. Figure 4.5 shows a reduction in the percentage removal efficiency effect of MB concentration. As the concentration increased from 5 to 20 ppm, it was found that the percentage clearance of MB reduced from 86.3% to 75.5%.

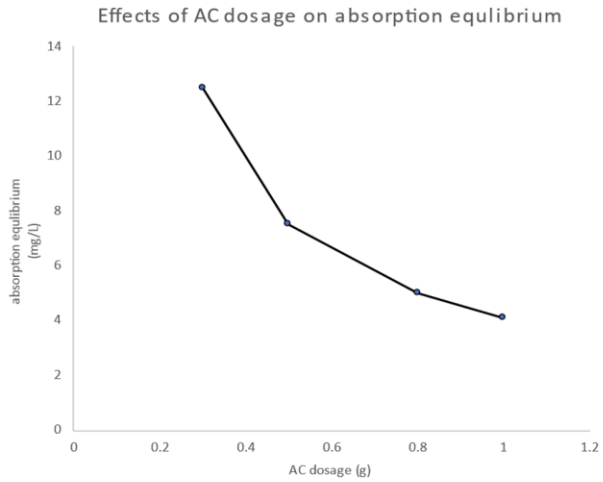
The decreased percentage of MB removal at increasing concentrations can be attributed to the fact that as concentration rises, more methylene blue molecules compete for the same number of available adsorbent particles, slowing down the rate at which they move from the bulk solution to the adsorbent surface.

As the concentration rises, so does the impact of concentration on the adsorption equilibrium

Figure 4.6. The effects of AC dosage

Effects of increasing the absorbent dosage





Effect of the AC dosage

According to Fig. 4.6, the proportion of MB removed by MSS adsorbent rose as AC dosage (0.3, 0.5, 0.8, and 1.0g) increased. To determine the capacity of AC utilizing different adsorbate concentrations, the effect of activated carbon dosage on the removal of methylene blue from the solution was examined. It was found that as the MSS adsorbent dosage was increased from 0.3 to 1.0 g, the amount of MB that was removed from the solution increased.

This indicates that as the adsorbent concentration rises, more sorption sites become accessible for the interaction of the sorbent with the bio solute, leading to a higher proportion of MB removal from the solution.

With an increase in the dosage of the adsorbent, the adsorption capacity of AC on the concentration of MB decreases. This may be caused by particle interactions, such as aggregation brought on by large adsorbent doses, or it may be caused by the sorption process unsaturation sorption sites. A decrease in the adsorbent's surface area and an increase in the diffusional path length would result from such aggregation.

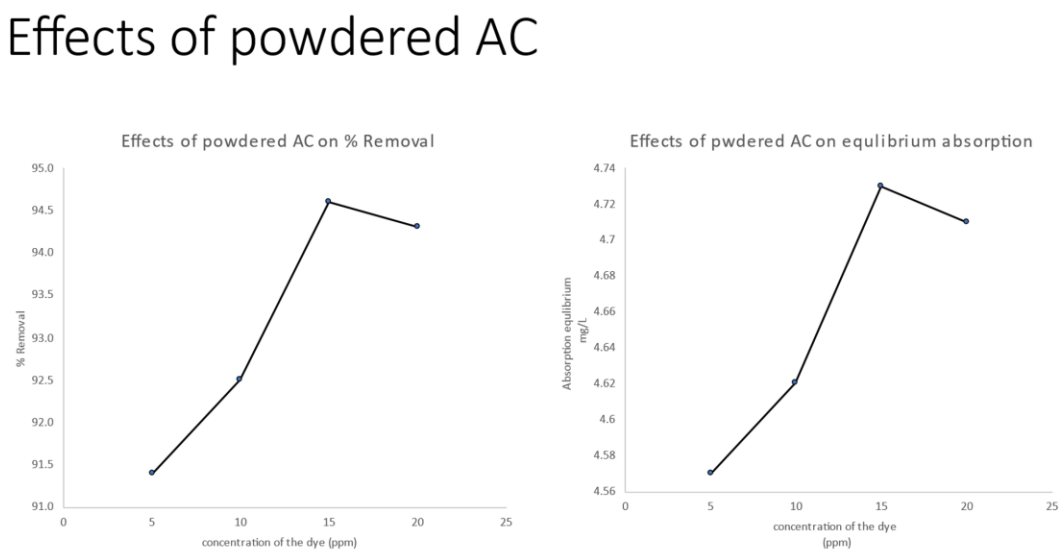
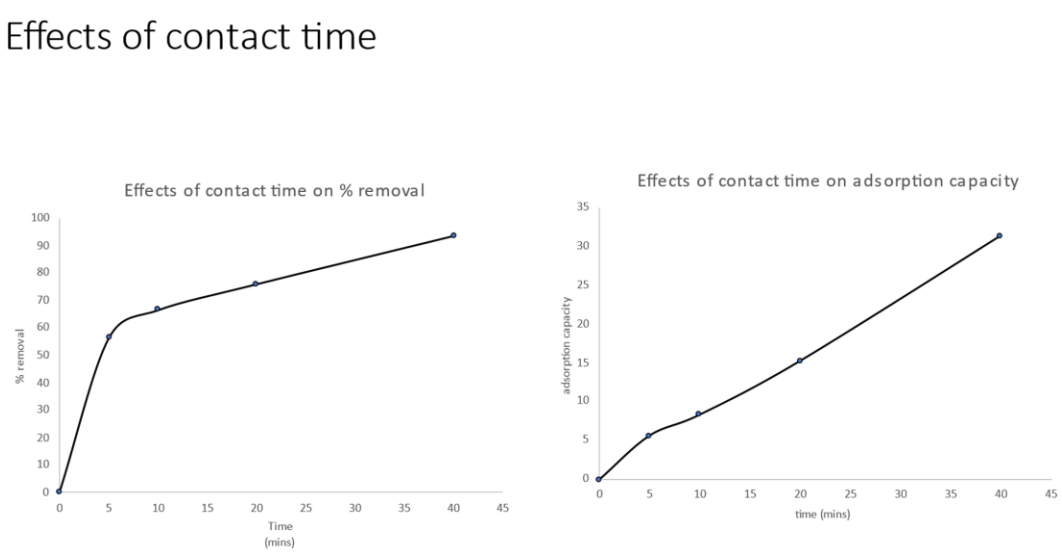


Figure 4.7. The effect of Powered AC

Effects of powdered AC

On the adsorption kinetics, the effects of particle size are very significant. Because smaller particles have a higher surface area than larger ones, it was found that the effects of powdered AC on the % elimination of MB increase with concentration. Surface area exposed to MB biosorption increases as particle size decreases and drops, respectively. This might be because the bio sorbent's pores are now more accessible to the adsorbate as a result of the particle size reduction.

Figure 4.8. Effect of Contact time



Effects of contact time

Since it can indicate the adsorption kinetics of the adsorbent and the specified concentration of the dye being removed, contact time is a crucial parameter. The percentage of MB removed rises as the contact duration grows; this could be due to the accessibility of the active sites. After 45 minutes, equilibrium was established. For the first five minutes of the reaction, there was a dramatic spike. As time passed, the adsorption capacity rose.

CHAPTER 5

CONCLUSION

In this research, activated carbon made from Manketti seed shells was used to study the adsorption of Methylene blue from an aqueous solution. The dye concentration, amount of adsorbent used, and temperature of the adsorption process were the key factors affecting how much MB was removed from the aqueous solution. Increasing contact duration, adsorbent dosage, and initial dye concentration were found to enhance the percentage of dye removal, while increasing contact time and initial dye concentration resulted in a decrease.

The current work demonstrates that the removal of MB from an aqueous solution by AC made from Manketti seed shells of inexpensive material was noticeably effective. The highest adsorption capacity value was similar to those for commercial activated carbon reported in other investigations. The outcome would be helpful for the creation and planning of textile dyeing wastewater as well as for the treatment of portable water to remove colors. Manketti seed shells are used as the raw material and are widely available for treatment.

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