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Removal of Methylene Blue Dye from Aqueous Solution using Mango Seed Kernel–derived Activated Carbon

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JIMMA, ETHIOPIA

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A THESIS SUBMITTED TO SCHOOL OF GRADUTE STUDIES JIMMA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIRMENTS FOR THE DEGREE OF MASTERS OF SCIENCE IN CHEMISTRY

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We, the undersigned, members of the Board of Examiners of the final open defense by Abdo Mohammed have read and evaluated his thesis entitled “Removal of methylene blue dye from aqueous solution using mango seed kernel–derived activated carbon” and examined the candidate. This is, therefore, to certify that the thesis has been accepted in partial fulfillment of the requirement of the Degree of masters in chemistry.

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I hereby declare that this M.Sc. Thesis is my original work and has not been presented for a degree in any other University, and all sources of material used for this thesis have been duly acknowledged.

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LIST OF ABBREVIATION AND ACRONYMS

AC	Activated Carbon
ASTM	American Socity for Testing and Materials
ATSDR’s	Agency for Toxic Substances and Disease Registry
C_e	Concentration at equilibrium
FTIR	Fourier Transforms Infrared
GAC	Granulated Activated Carbon
K_1	Pseudo first order rate constant (min-1)
K_2	Pseudo second-order rate constant (g/mg min)
K_f	Constant measuring of adsorption capacity
KL	Langmuir constant related to free energy of adsorption (L/mg)
MB	Methylene Blue
MSK	Mango seed kernel
MKP	Mango kernel powder
n	Freundlich indicative of the intensity of adsorption
PAC	Powdered Activated Carbon
Pzc	Point of zero charge
q_e	Amount of MB dye adsorbed at equilibrium (mg/g)
Q_m	Maximum adsorption capacity (mg/g)
q_t	Amount of MB dye adsorbed at time t (mg/g)
UV-Vis	Ultra Violet Visible Spectrophotometer
WHO	World Health Organization

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ABSTRACT

Dyes removal by adsorption using modified activated carbon is by far the most common and effective method for wastewater contaminants removal. The aim of this study was to remove MB dye from aqueous solution using modified mango seed kernels as adsorbent. The lignocellulosic-based dried mango seed kernel modified with 50% H_2SO_4 and 40% H_3PO_4 was followed by heating in an electrical furnace at 500ºC for 2 hr for enhancement of MB adsorption from the aqueous solution. The surface characterization of raw MSK and MKAC before and after adsorption was carried out by proximate analysis, FTIR, XRD and SEM analysis. FTIR results showed different functional groups like aldehydes, ester, amide group and carboxylic acid were observed at different wave numbers. The batch adsorption studies were also carried out at optimum condition: adsorbent dose 0.2 g/L, initial MB concentration 10 mg/L, contact time 60 min, pH 8 and shaking speed 150 rpm . It was observed that the maximum adsorption efficiencies of the MKAC with 50% H_2SO_4 and 40% H_3PO_4 were found to be 91.5% and 89.3% at room temperature, respectively. UV-Vis spectrophotometer technique was used for the measurement of concentration of dye before and after adsorption of MB at maximum wave length (λmax) of 665 nm.. The linear form of Langmuir and Freundlich models were applied to represent adsorption isotherm. The calculated equilibrium data of MB fitted Langmuir isotherm models with maximum adsorption capacity (qmax) for 50% H_2SO_4 and 40% H_3PO_4 were 10 mg/g and 5.8 mg/g respectively. Pseudo second-order kinetic model was found to be well fitted to the data obtained from R^2 value.

KeyWords: *Adsorption, MB dye, wastewater, mango kernel activated carbon and pollutants*

CHAPTER ONE

1.INTRODUCTION

1.1 Background of the Study

Industrial, agricultural, and domestic activities of humans have affected the environmental system, resulting in drastic problems such as global warming and the generation of wastewater containing high levels of pollutants. Water treatment became nowadays a very important topic concerning environment protection. The industrial wastewaters are characterized by the presence of high quantities of organic and mineral pollutants [1].

Synthetic dyes are widely used for textile, pulp and paper, plastic, rubber, cosmetic printing and pharmaceutical industries. About 7 X 10^5 tones/year dyes are produced annually in the global market. It is estimated that about 2% of these dyes are discharged into the water system with most of the sources generated from textile industries [2]. With mass production of synthetic dyes and mass discharge of synthetic dye-containing wastewater, effective treatment of dye-containing wastewater has gained more attention for the past decades [3].

Agricultural products used for the preparation of activated carbons are organic materials that are rich in carbon [4]. Therefore, the development of methods to reuse waste materials as activated carbons is greatly desired and offers a promising future. Agricultural wastes, such as jathropha, corn cob, coconut shell, oil palm fiber, date stone, wood sawdust, olive stones and etc are of interest as activated carbons because of their high mechanical strength and hardness. These properties can be explained by high lignin, high carbon and low ash content [5]. In addition, conversion of agricultural wastes to value added product such as activated carbon is a sufficient method to solve environmental problem.

Degradation of synthetic dyes is difficult because of their complex aromatic structure and nature of the leadcompounds. Besides, the intermediate and byproducts of most of dye chemicals are considered to be harmful to aquatic organisms due to their toxicity and carcinogenic activity [6]. Therefore, efficient and cost-effective treatment processes of dye-containing wastewater need to be developed .

The presence of high levels of MB in the environment may cause long-term health risks to human and ecosystems.Therefore it is mandatory to reduce their concentration levels in drinking water, wastewater and water used for agricultural and recreational purposes must be reduced to the allowable concentrations recommended by national and international health authorities such as the World Health Organization (WHO). Current Environmental Protection Act (EPA) permissible drinking water standard for dyesare 5 mg/L [3,7].

There are various chemical and physico-chemical methods for the treatment of wastewater such as chemical precipitation, electrochemical reduction, ion exchange, biosorption and adsorption [8]. The choice of treatment depends on effluent characteristics such as concentration, pH, temperature, flow volume, economics involved and social factor like standard set by the government agency.Out of those methods, adsorption is emerged as one of the most promising technique. It is generally preferred for the removal of MB due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness [9]. Even if the use of AC is still very popular for adsorption of dyes, but are quite expensive and the regeneration of the carbon is not always possible. Activated carbon has been chosen as an adsorptive media for the removal of MB, by many researchers [5,10].

Mangoes are tropical fruits that grow on extremely large trees. Top five producers of mangoes in the worlds are Hindi, China, Thailand, Mexico and Indonesia and in Africa's are Egypt, Nigeria, Sudan, Kenya and Niger. Mangoes are consumed worldwide, and there has been an increasing demand in the past few decades. However, fruits have the highest wastage rate of all foods [11]. A mango's peel and seed consist up to forty percent of its total fruit weight. Since mangoes are abundant in a multitude of countries, a large amount of waste is produced and difficult to dispose of [12]. Places such as Africa face economic issues, and do not have sufficient clean water. Nevertheless, Africa has become one of the bigger producers of mangoes due to its geographical advantage [13].The mango industry has been growing rapidly in many other places as well.

In the present study, mango seed kernel, which is the bio waste products, of mango was used as a raw preparing activated carbon. Mangos produce a large amount of solid waste. To enhance the value of precursor for this bio waste, preparation of activated carbon had been attempted. Thus producing activated carbon from mango seed kernel not only helps in terms of waste minimization but also helps in reduction of pollution.

The aim of this study is to develop inexpensive and effective dyes adsorbents from one of plentiful agricultural bi-product mango seeds kernel. For seek existing commercially adsorbent materials. The adsorption processes were studied from isotherm and kinetic points of view.

1.2. Statement of the Problem

AC is a well-known versatile product used for many applications. It is used to remove pollutants from gases and liquids and for purification in several industrial processes. Micro pollutants generally enter water through discharge from various processes including food, dye, textile, plasticand paper, chemical and petrochemical industries.The presence of organic pollutants in water has attracted much attention in recent decades because of their potential mutagencity, carcinogenicity and toxicity. Moreover, it leads to undesirable effects on color, odor and taste of drinking water. It has been demonstrated that conventional treatment processes are ineffective in removing micro pollutants [14].

AC has been the most popular adsorbent for removal of MB dye from wastewater throughout the world due to its highly porous texture and large capacity to absorb pollutants [15]. However, adsorbent-grade activated carbon is cost-prohibited and regeneration of the used carbon is not straight forward [16]. Therefore, it is no longer an attractive choice of adsorbent for small-scale industries due to cost inefficiency. Many researchers have been conducted to develop inexpensive and effective adsorbents of dyes from plentiful sources of natural wastes in order to replace the conventional pollutant-removing methods available. Mango is one of the second potential fruit crop produced in Ethiopia next to banana, which is the first fruit crop produced in large quantity and produced mainly in Harari, West and East of Oromia, South people Nation and Nationality, and Amhara regional states.In Ethiopia, most varieties of mango available are Kent, Keitt, Tommy Atkins, and Apple mango and about 479,336 tons of mango fruit are produced annually [17]. Most of these mango seeds wastes are discarded or composted as they have no commercial purpose, resulting in environmental pollution. Hence, the utilization of these mango seeds as an adsorbent to remove MB dyes from industrial wastewater can greatly reduce the amount of waste released. Therefore, this study was attempted to answer the following basic research question:

- Which AC is better in its efficiency, H_2SO_4 modified or H_3PO_4?
- What is the optimum condition of each parameter for the removal of MB from aqueous solution using MKAC?
- What are the isothermal and kinetic models that fit adsorption?

1.3. Objectives of the Study

1.3.1. General Objective

The main objective of this study was to remove MB dye from aqueous solution using MSK modified with 50% H_2SO_4 and 40% H_3PO_4 as an adsorbent.

1.3.2. Specific objectives

1. To prepare and characterize activated carbon from the mango seed kernel.
2. To evaluate the optimum adsorption parameters.

~~3.~~ To examine the isotherm and kinetic models that best fit the sorption process~~.~~

1.4. Significance of Study

Dyes removal has become a serious environmental concern due to the nature of toxic and carcinogenic various cumulative dyes life forms. Discharged colored wastewater by some industries under uncontrolled and unsuitable conditions is causing significant environmental problems. One of the main concerns about colored effluent is not only its toxicity, but also its undesirable aesthetic impact on receiving waters. Since many dyes have an adverse effect on human beings, the removal of color from the effluent or process has appeared of importance for ensuring a healthy environment. Hence, the major significance of this study includes, but not limited to:

- Removal of MB dyes using waste material.
- Utilization of waste material, mango seed kernel, as low cost and effective adsorbent.

- ✓ The result obtained will provide background information how to treat the effluents from industries before discharging into water bodies.
- ✓ It would serve as a resource material to carry out further research on similar resource full samples

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Water Pollution

Water is one of the renewable resources essential for sustaining all forms of life, food production, economic development, and for general well being. It is impossible to substitute for most of its uses, difficult to depollute, expensive to transport, and it is truly a unique gift to mankind from nature. The fresh water ecosystems of the world comprise only about 0.5% of the earth's surface and have a volume of 2.84×10^5 Km^3 [18].

Water pollutants may be Organic and Inorganic water pollutant. Organic water pollutants: They comprise of insecticides and herbicides, organohalides and other forms of chemicals; bacteria from sewage and livestock's farming; food processing wastes; pathogens; volatile organic compounds etc.

Inorganic water pollutants: They may arise from heavy metals from acid mine drainage; silt from surface run-off, logging, slash and burning practices and land filling; fertilizers from agricultural run-off which include nitrates and phosphates etc. and chemical waste from industrial effluents [19].

Water pollution by dye is considered a serious environmental problem due to their toxicity, long persistence, bioaccumulation and biomagnifications in the food chain [1,9]. Nowadays water pollution by dyes is fast growing due to natural processes and increasing human activities which include textile, agriculture and manufacturing industries. Dyes are toxic pollutants released into the surface and ground water bodies as a result of different activities [2].

2.2. Pollutants

The term pollutant, in a broad sense, refers to a substance/material that changes the natural quality of the environment by physical, chemical, or biological means. Thus, we may have pollution in air, water, and soil. The three main activities that mankind indulges in are domestic, agricultural and industrial. In all of these activities, a large amount of fresh water is used, which is discharged as wastewater containing different pollutants depending on the type of activity. These may be various inorganic and organic chemicals and biological agents as well as heat and radiations [20]. Ideally, the temperature of water should be constant or undergo minimum variation. Because of its high heat capacity, water is used as a cooling medium. Thus, many industrial plants discharge water carrying away waste heat [20,21].

The high temperature of this wastewater not only affects aquatic life but is known to cause many chemical and bacteriological re-actions, such as formation of trihalomethane (THM) and higher corrosion activity. During the course of domestic, industrial, and agricultural operations, a number of chemicals are used or produced and often get mixed up with freshwater, which is then discharged as wastewater [13,17]. The chemicals present in wastewater may be in a dissolved or non-dissolved state. Non-dissolved substances are generally present as suspended solids in a dispersed form. The suspended solids make the water turbid and sometimes they may also slowly settle down with the formation of silt [22].The presence of suspended solids clogs water ways, flingup dams, and is harmful to aquatic life in many ways. The most common chemicals found in wastewater in a dissolved state and considered as potential pollutants are heavy metals, dyes, phenols, detergents,pesticides, polychlorinated biphenyls (PCBs), and a host of other inorganic and organic substances [23].

2.3. Dyes and their application

Dyes are basically chemical compounds that can connect themselves to surfaces or fabrics to impart color. The majority of dyes is complex organic molecules and is required to be resistant to many things such as the action of detergents. MB is a basic dye of thiazine group and is also known as Swiss blue and tetramethylthionine. It appears as a dark green powder that yields a blue solution when dissolved in water. MB has wide applications including cottons or wools dyeing, paper coloring, temporarily coloring hair, and coating for paper stock. It is also employed in ground water tracing, for the determination of specific surface area of activated sludge sewage and wastewater treatment [24].

2. 3.1. Classification of dyes

There are several ways for classification of commercial dyes. It can be classified in terms of structure, color and application methods [18]. However, due to the complexities of the color nomenclature from the chemical structure system, the classification based on application is often favorable [24]. Based on their particle charge upon dissolution in aqueous application medium dyes are classified as cationic (all basic dyes), anionic (direct, acid, and reactive dyes), and non-ionic (dispersed dyes). Reactive dyes are water soluble and 5–10% of the dyes go in the dye bath giving highly colored effluent causing serious troubles in the environment [25]. Additionally, reactive dyes that are chemically stable and having little biodegradability are likely to pass through conventional treatment plants untreated, so their elimination is of great importance. Due to their toxic effects, dyes have generated much concern regarding its use. It has been informed to cause mutagenesis, chromosomal fractures, carcinogenesis, and respiratory toxicity [14,25].

2.3.2.Methylene Blue and wastewater

The wastewater generated from many industries may contain a number of dyes and heavy metals which have significant toxic effects [26] and they are therefore considered as pollutants [20,21] requiring removal. The various industries that generate such water include the tanning, textile and paper. In most wastewaters, the concentration of MB dye present is much larger than the safe permissible limits (5%) and, therefore, they need to be removed [17, 27].

2.3.3. Methylene blue

MB ($C_{16}H_{18}N_3SCl$) is a hetero cyclic aromatic compound and is a basic dye. Hydrate is blue and exists in the form of three molecules of water per molecule of MB. MB ($C_{16}H_{18}ClN_3S \cdot 3H_2O$, molar mass: 319.85 g/mole, Sigma-Aldrich, USA) was used in powder form. MBs of various concentrations were prepared at a concentration of 1000 mg/L, and then diluted with distilled water to prepare a solution of the required concentration. The textile industry is one of the biggest users of water in the world. Colors, one of the most dangerous environment pollutants, are in the wastewaters of this industry, which pollutes the environment and human life [4,5]. The color MB with the chemical formula $C1_6H_{18}ClN_3S$, whose chemical structure is shown, blow.

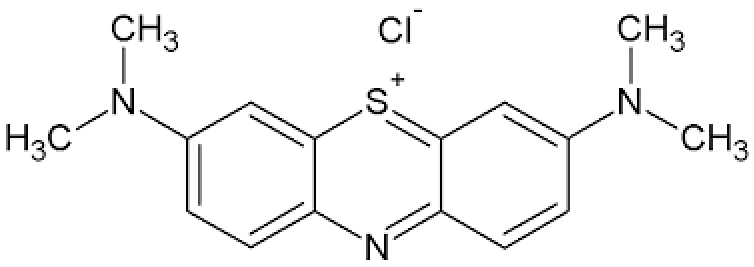


Fig.1 Chemical Structure of Methylene Blue (MB)

It is one of the most widely used cationic colors in the textile industry; it is used for dyeing wool, cotton, and silk cloth [28]. Owing to their complex structures, colors are often stable and resistant to biological degradation that is toxic, carcinogenic, and capable of mutagenesis. So re-discharge of colored wastewaters of different industries, such as textiles, papers, cosmetics, plastics, and leather, results in severe environmental problems because the toxicity of some dyestuff damages not only the natural landscape, but also the aqua ecosystems [9,15]. With regard to the increase of different types of pollutants in water resources and scarcity of healthy.

2.3.4. Impacts of Methylene blue on environment

The discharges of MB dye in to hydrosphere possess a significant source of pollution due to their recalcitrance nature. This will give undesirable color to the water body which will reduce sunlight penetration and resist photochemical and biological attacks to aquatic life [29]. In up-to-date data, more than 100,000 commercial dyes are known with an annual production of over 7×10^5 tones/ year [30]. Basically the exact data on the amount of dyes discharged from various processes in the environment are unknown. However, the release of essential amounts of synthetic dyes to the environment has posed challenges to environmental scientists. Basic dyes have high intensity of colors and are greatly visible even in very little concentration. The complex dyes are generally chromium based, which is carcinogenic. Dyes may affect the photosynthetic activity in aquatic life due to decreased light penetration and may also be toxic to some aquatic life due to, aromatics, etc.

Additionally it can also cause severe damage to human beings such as dysfunction of the kidney, reproductive system, liver, brain and central nervous system [31]. Similarly anthrax quinone based dyes are most resistant to degradation and remains color for a large time in effluents [31, 32].

2.4. Water Treatment

Water treatment is the process of removing undesirable chemicals, biological contaminants, suspended solids and gases from contaminated water. Water quality involves both aesthetic and health concerns depending on the contaminants present. Therefore, the purpose of water treatment is to produce safe aesthetically pleasant water. This ensures that the water be free of harmful chemicals and microbes as well as have an acceptable taste and odor [33].

2.5. Mango Seed

Mango belongs to the genus Angifera, consisting of numerous species of tropical fruiting trees in the flowering plant family Anacardiaceae. Mango trees (*Mangiferaindica*) reach 35-40 m in height, with a crown radius of 10 m. The leaves are evergreen, alternate, simple, 15-35 cm long and 6-16 cm broad. The fruit takes from 3-6 months to ripen. The ripe fruit is variable in size and color. It may be yellow, orange, red or green when ripe, depending on the cultivar. In the center is a single flat oblong seed that can be fibrous or hairy on the surface, depending on the cultivar [15,35]. Ripe mangoes are processed into frozen mango products, canned products, dehydrated products and ready-to-serve beverages [15]. After consumption or industrial processing of the fruits, a considerable amount of mango seeds is discarded as waste. Mango seed accounts for 35-50% of the fruit depending on the variety. Utilization of mango seed may be an economical way to reduce the problem of waste disposal from mango production. The mango kernel has a higher antioxidant and polyphenolic content than quantities of cellulose, and contains 34.2% of cellulose, 32.06% of hemicelluloses and 15.0% of lignin [21,36]. Mangoes are produced in over 90 countries worldwide. Asia accounts for approximately 77% of Global mango production, and the Americas and Africa account for approximately 13% and 9%, respectively [15,36].

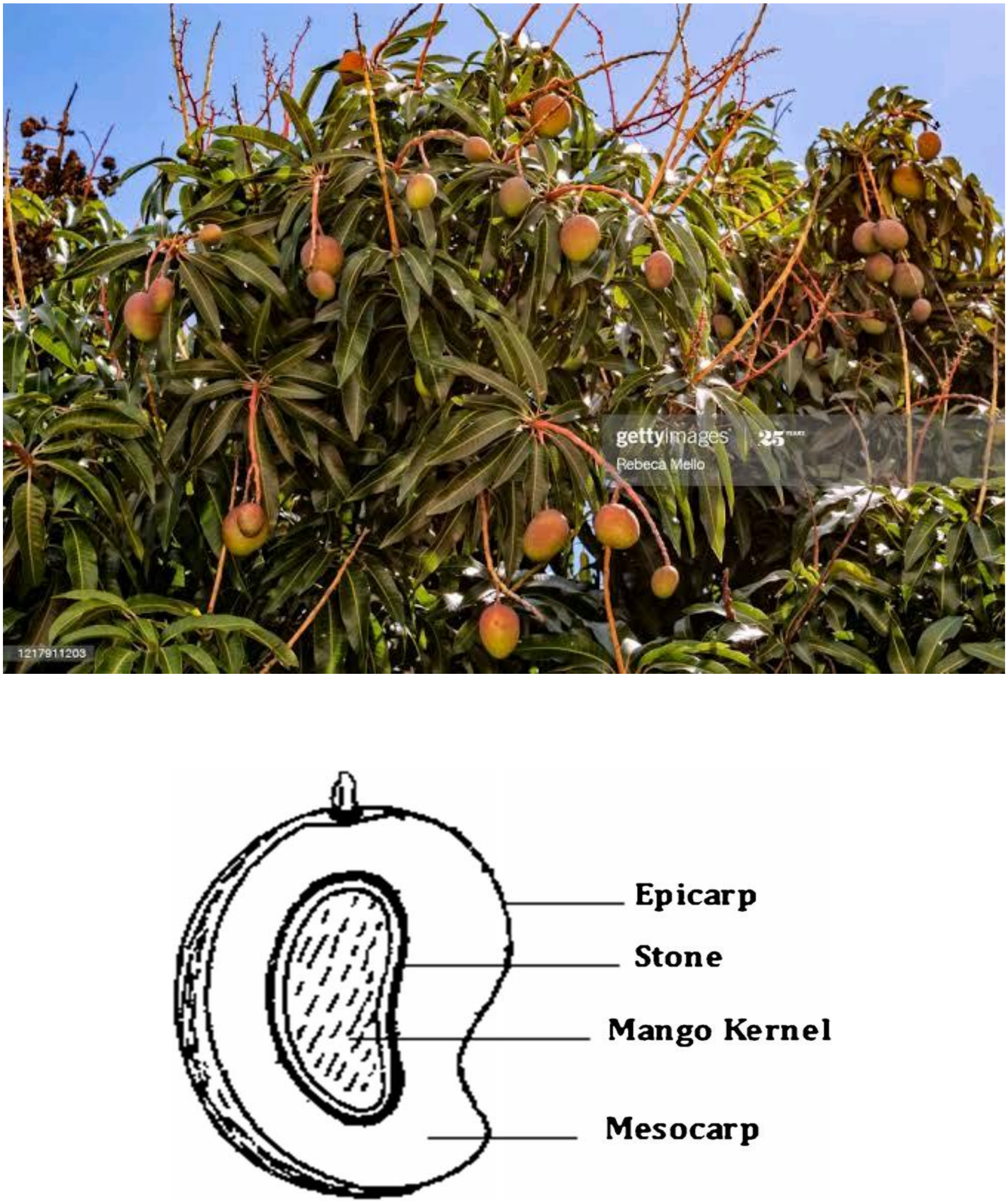


Fig. 2.Pictorial diagram of mango tree and fruit

2.6. Adsorption

2.6.1. Adsorption and Adsorption technology

“Adsorption” may be defined as the process of accumulation of any substance giving higher concentration of molecular species on the surface of another substance as compared to that in the bulk [25]. When a solid surface is exposed to a gas or a liquid, molecules from the gas or the solution phase accumulate or concentrate at the surface. Therefore the phenomenon of concentration of molecules of a gas or liquid at a solid surface is adsorption. “Adsorption” is a well established and powerful technique for treating domestic and industrial effluents. In water treatment, the most widely method is “adsorption” onto the surface of activated carbon [30]. Adsorption has long been used as a purification and separation process on an industrial scale. Highly porous adsorbents with good selectivity such as activated carbon have shown excellent ability in the removal of organic compounds such as dyestuffs, phenolics, endocrine-disrupting compounds, pesticides, pharmaceuticals and several metal ions [18, 20].

Adsorption can be a potential alternative to traditional treatment processes of metal ion removal [38]. The phenomenon of adsorption has been described in a wide range of non-living biomass like potato peel waste, orange peel [22]. And untreated coffee grounds as well as of living biomass like, microbial cell, moss, yeast, fungi, and algae [4,23]. The phenomenon of adsorption follows one of three general types, namely, diffusion, surface chemical reaction including ion exchange and surface complexation [25]. 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. For chemical surface reactions, several kinetic models are available depending on the adsorbate–adsorbent functional group order of reaction; examples include pseudo-first-order, pseudo-second-order and Elovich, Aram and Bingham models [39].

Adsorption techniques has become one of the most commonly used water treatment methods for removal of dyes from wastewater and water supplies [4,27]. Adsorption has distinct advantages over the conventional methods, the process does not produce sludge’s requiring further disposal, it could be highly selective, more efficient, easy to operate, can handle large volumes of waste waters containing low dye concentrations. The dyes sequestering ability of microorganisms such as yeast, bacteria, fungi and algae have been investigated and reported. Adsorption technology based on the utilization of dead biomass offers certain major advantages such as lack of toxicity constraints, non requirement of nutrient supply, and recovery of bound dyes species by desorption [12,37].

2.6.2. Adsorption principles

The basic principle of operation for carbon adsorption is the mass transfer and adsorption of a molecule from a liquid or gas into solid surface. Activated carbon is manufactured in such a way as to produce extremely porous carbon particles whose internal surface area is very large .This porous structure attracts and holds organic molecules as well as certain metal and inorganic molecules. Adsorption occurs because

1. The contaminant has low solubility in the waste
2. The contaminant has greater affinity for the carbon than for the waste
3. A combination of two

Two most common carbon adsorption processes are the granular activated carbon (GAC) which is used in packed beds, and the powdered activated carbon. The activated carbon adsorption process is one of the most frequently applied technologies for the removal of trace organic compounds from an aqueous solution. Adsorption is a surface phenomenon in which soluble particles from a solution are bonded onto a particular substrate. One of the most desirable properties of an adsorbent is a high surface to volume ratio. Activated carbon ratio ranging from 500 to 1000 m /g is a good adsorbent for effective removal of organic compounds [25, 40].

2.7. Adsorbents

An adsorbent is a substance usually porous in nature with a high surface area that can absorb substances onto its surface by intermolecular forces [40,41]. Adsorbent materials have an affinity to certain ions or ion groups and have shown high selectivity, resistance to degradation, high temperatures and high levels of radiation [42]. During adsorption, solutes distribute themselves between the adsorbent surface and the dispersing medium. Due to the presence of functional groups, sorbents can be derivertised to improve their efficiency and increase their adsorption capacity. Mostly activated carbon is used as an adsorbent. Adsorbents are used usually in the form of spherical pellets, rods, mouldings, or monoliths with hydrodynamic diameters between 0.5 and 10mm.They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption. The adsorbents must also have a distinct pore structure which enables fast transport of the gaseous vapours [43].

2.7.1. Characteristics of adsorbents

The selection of the adsorbent in the utilization of adsorption process is primarily dependent on the uptake capacity of the adsorbent for an individual substance as well as the contacting system design. Ideally, the adsorbent should satisfy four requirements, reasonably high surface area or microspore volume to achieve a high adsorption capacity. The pore diameter must be sufficiently large appropriate to the adsorbate molecule size. The appropriate surface functional group to attract the adsorbate, relatively large porous network providing access to the internal surface area -by diffusion. For the first aspect, the number of active sites is proportional to the surface area, or more precisely, the microspore volume due to its dominant contribution to the surface area; therefore, a larger surface area adsorbent is apparently advantageous in adsorption [6,25].

The functionality of the surface groups will create a positively, neutral or negatively charged surface capable of attracting the adsorbing species. The reasonably large porous network also plays a significant role as it allows a higher diffusion rate that is critical to adsorption kinetics and process design. It is important to determine the molecular dimensions of the pollutant adsorb ate and ensure that the activated carbon produced has sufficient pores of sufficient pore diameter to achieve the removal of the adsorbate. In addition, a large and cheap source of precursor is also required [44].

There are numerous adsorbents in commercial or laboratory use, and some common examples are activated carbons, Zeollite, silica and activated alumina .Other examples include bone char agricultural wastes or by-products, for example, wood meals, biogases, nutshells, rice husks, fruit stones or maize cobs, inorganic minerals, for example, bentonite, Fuller’s earth or clay, lignite, coconut shell, plastic wastes chitin/chitosan and aluminophosphate molecular sieves.

2.8. Types of Adsorption

2.8.1. Physical adsorption

Physical adsorption is the result of intermolecular forces of attraction between molecules of the solid adsorbent and the substance adsorbed. It is a readily reversible phenomenon. In industrial adsorption operations this reversibility is used for the recovery of adsorbent for reuse, for the recovery of adsorbed substance or for the fractionation of the mixtures.

2.8.2. Chemisorptions

Chemisorptions are the result of chemical interaction between the solid adsorbent and the adsorbed substance. The adhesive force and the heat liberated are much greater those that found in physical adsorption. The process is frequently irreversible. But they exhibit chemisorptions at high temperatures and sometimes both the phenomena may occur at the same time. Chemisorptions are of particular importance in catalysis.

2.9. Methods Used to Remove Water Contaminants

Common methods used to remove MB dye include ion exchange, chemical precipitation, ozone oxidation and adsorption.

2.9.1. Ion exchange

The ion exchange process is one of the most common techniques, which can effectively remove dyes from aqueous solutions through strong interactions between charged dyes and functional groups on ion exchange resins. This process involves the exchange of ions to form strong bonds between solutes and resins, thereby achieving effective separation. However, resins may be poisoned by unexpected constituents or rapidly exhausted by unexpectedly high loadings [45].

2.9.2. Chemical Precipitation

Chemical precipitation is a relatively simple wastewater treatment technique in which chemicals such as sulphides, hydroxides and carbonates react with organic and inorganic pollutants present in wastewater to form insoluble precipitates. Chemicals react with dissolved dye molecules to form insoluble precipitates and then can be removed. The general procedures involve the addition of chemicals into wastewater treatment to form the precipitate with dye molecules and waiting for the insoluble particles to settle. Then the wastewater can be decanted to separate the sludge. The most common chemical precipitation method for dye removal is hydroxide precipitation. Chemical precipitation is an efficient method for the removal of dyes from wastewaters, but generation of sludge and high chemical cost are the major hurdle for the application of this technology at industrial scale [46].

2.9.3. Ozone oxidation

It is a very effective and fast decolorizing treatment, which can easily break the double bonds present in most of the dyes. Ozonation can also inhibit or destroy the foaming properties of residual surfactants and it can oxidize a significant portion of COD. Moreover, it can improve the biodegradability of those effluents which contain a high fraction of non-biodegradable and toxic components through the conversion (by a limited oxidation) of recalcitrant pollutants into more easily biodegradable intermediates [44]. As a further advantage, the treatment does increase neither the volume of wastewater nor the sludge mass. Full scale applications are growing in number, mainly as final polishing treatment, generally requiring up-stream treatments such as at least filtration to reduce the suspended solids contents and improve the efficiency of decolonization.

Sodium hypochlorite has been widely used in the past as oxidizing agent. In textile effluent it initiates and accelerates azo bond cleavage. The negative effect is the release of carcinogenic aromatic amines and other wise toxic molecules and, therefore, it should not be recommended [47].

2.10. Synthesis of activated carbon

Activated carbon is an effective adsorbent material due to its large number of pores. These provide a large surface area relative to the size of the actual carbon particle and visible exterior surface. Its high degree of porosity and surface area makes it most versatile adsorbent to be used for effective removal of organic solids that have extraordinary large internal surface and pore volume [16,36]. Adsorption processes provide an effective alternative treatment approach for MB removal due to the lower initial cost, sludge free, clean, flexibility and simplicity of design, simple operation, easy recovery and insensitivity to toxic pollutants. Agricultural solid wastes can be used as an inexpensive precursor material with high carbon content [37].

Wastes or by-products of industries can be used, directly or after treatments, as adsorbents in adsorption processes. Any carbonaceous material with high concentration of carbon can be simply changed into activated carbon. Activated carbon can be produced by physical reactivation involving carbonization carried at temperatures in the range 600-900ºC in the absence of oxygen or oxidation by exposing the carbonized material to oxidizing atmospheres at temperatures above 250˚c. Chemical activation involves pretreatment of the raw material with an acid, strong base, or a salt, followed by carbonization at lower temperatures of between 450-900°*c* [36, 48].

Chemical activation uses lower temperatures and shorter time and hence preferred to physical activation. During the carbonization process, the incomplete combustion tremendously increases the surface of carbon by the removal of hydrocarbons or tars. The processing of activated carbon basically involves selection of raw material, carbonization and activation. For the selection of an appropriate raw material for preparation of porous carbon, several factors are taken into consideration. Industrially, inexpensive material with high carbon and low inorganic (that is low-ash) content is preferred as raw material for the production of activated carbon. High density of the precursor and sufficient volatile content are of considerable importance [12, 37].

2.11. Mechanism of adsorption

To understanding the mechanisms of the solute adsorption onto the solid surface is essential for certain removal of contaminants from aqueous solution. The surface chemistry of the adsorbent and its effect on the adsorption process is generally investigated in order to interpret the solute adsorption. Fourier transform infrared (FTIR) spectroscopy is a useful tool for studying the interaction between an adsorbate and the active sites on the surface of the adsorbent [49].

Both cellulose and hemicelluloses contain the majority of oxygen functional groups which are present in the lignocelluloses material such as hydroxyl, ether and carbonyl, while lignin is a complex, systematically polymerized, highly aromatic substance that acts as a cementing matrix that holds between and within both cellulose and hemicelluloses units. Parameters like pH, surface functional groups and pores size play very important roles in determining the adsorption mechanisms. Metal ions may form complexes with surface functional groups of the adsorbents such as cellulose–OH and phenolic–OH through ion exchange reactions. At lower pH, the functionality of these groups is not changed. At higher pH, these groups begin to neutralize changing their activity and binding properties. In order to understand how solute binds to the activated carbon surface, it is essential to identify the functional groups responsible for their binding. Most of the functional groups involved in the binding process are found in cell walls. Plant cell walls are generally considered as structures built by cellulose molecules, organized in micro fibrils and surrounded by hemicelluloses materials, lignin and pectin along with small amounts of protein. During the activation process, these molecules are converted into graphitic carbon with some oxygen bonded functional groups. A lot of surface area is generated inside the molecule due to loss of volatile organic matters from the cell wall. Surface area and surface functional groups of activated carbons play the major role in adsorption processes [11, 50].

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Materials

The main raw materials used for this study were mango seed kernel (MSK).

3.2. Chemicals and Reagents

The chemicals that were used to perform this experiment were listed blow. All the chemicals that were used in experiments are analytical grade.

Table 1. Chemicals and reagents

no	chemicals	Formula	Conc.purity	CAS _no_	Prod.Country
1	Sulphuric acid	H_2SO_4	98% concn	7664-93-9	German
2	Phospheric acid	H_3PO_4	85% concn	7664-38-2	US
3	Hydrochoric acid	HCl	35% , 0.1 M	7647-01	India
4	Sodium Hydroxide	$NaOH$	98%, 0.1 M	1310-73-2	India
5	Methylene Blue	$C_{16}H_{18}N_3SCl$	0.1%	61-73-4	UK

3.3. Instruments and Charactrization Methods

The instruments which were used for this experiment was tubular furnace, XRD, UV-Visible spectroscopy, FT-IR, thermo-shaker and ultrasonic cleaner. Equipment which was used for this experiment were electronic balance, volumetric flask, measuring cylinder, dropper, filter paper wattman no 1, Test tubes, Beakers, and pH-meter. The morphologies of the produced activated carbons are obtained by JSM-5900LV SEM. The iodine number method is applied to characterize the adsorption capacity of the produced carbon. XRD analysis is performed on XSAM800 spectrometer. The FTIR spectrometer was used for qualitative estimation of the surface functional groups. The spectra are recorded from 400 to 4,000 cm^{-1}[51].

3.4. Sample collection and pre-treatment

The mango seeds were collected from the Jimma town juice cafeteria and it was sun-dried for 72 hrs. Thereafter, the mango stones were broken-up to retrieve the fleshy mango kernels. The kernels were solar dried and then crushed in the disintegrator mesh (BSS) to obtain desired particle size. Then the MKP washed twice or thrice to remove soluble and insoluble materials and dried in an oven at 60 °C for 2 hr.

3.5. Preparation of activating agent

Preparation of the activating agent, it were prepared 51.03 mL of 98% H_2SO_4 was added to 48.97 mL of distilled water to obtain 50 % of 1oo mL H_2SO_4 activating agent and 141.15 mL of 85% of H_3PO_4 were added to 158.85 mL of distilled water by drop wise and were obtained 300 mL of 40% H_3PO_4 activating agent.

3.5. Preparation of activated carbon

Chemical activation of the precursor was done with 50% H_2SO_4 in 1:1 IR (impregnation ratio, that is 50 mL of 50% H_2SO_4 with 50g of MKP) and 40% H_3PO_4 was impregnated in ratio of 3:1 IR (300 mL of 40% H_3PO_4 with 100g of MKP) . The impregnation ratio is defined as the ratio of (the volume of chemical activating agent) to the precursor. The resulting both chemical-loaded samples were carbonized in a furnace at 500ºc for 2 hrs. The products were washed thoroughly with distilled water until the pH becomes 7 to remove residual organic and mineral matters, and then dried at 75ºC. In all experiments, heating rate was kept constant. Then powdered mango kernel activated carbon was kept in airtight containers experimental use [52].

3.6. Preparation of adsorbate

The Stock solution of MB containing 100 mg/L was prepared by dissolving 0.1g of MB powder in 1000 mL distilled water respectively. From the stock solution (100 ppm) serial test solutions of MB containing 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L and 25 mg/L (ppm) were prepared and calibration curve was generated from the prepared concentration of 5-25 mg/ L [42].

3.7. Proximate analysis of MSK

The proximate analysis of a substance is a means of determining the distribution of products obtained when the sample is heated under specified conditions. According to ASTM D121, proximate analysis is the determination of moisture, volatile matter, fixed carbon, and ash content by prescribed methods [53].

3.7.1. Determination of moisture content

The moisture content was found by oven-drying test method ASTM D2867-17. The moisture content of the sample was determined by weighing 17.9096 g of sample into a pre weighed crucible 24.0153 g and drying it in an oven at a temperature of 105 ± 5 °C till the constant weight dry matter was obtained. The percentage moisture content was computed as follows:[53].

$$\text{Moisture content (\%)} = \frac{W_1 - W_2}{W_1} X100 \qquad (1)$$

Where:

W1 = weight of sample before drying (gram), W2 = weight of sample after drying (gram)

3.7.2. Ash Content

The ash content of raw MSK and MKAC produced was determined by the standard test method for ash content- ASTM D2866-94.14.528 g of raw MSK sample was weighed and taken in a crucible. It was then heated to 650 °C for 3hr. During this test the crucible was left open. The heating was done in a furnace. The crucible is cooled to room temperature in a desiccator and the percentage weight of the sample remained was considered as ash content. In this test, the amount of residual substance is equal to the ash present in the sample [54]. The % ash content of the sample was calculated as follows:

$$\text{Ash content (\%)} = \frac{w_2}{w_1}\text{x}100 \qquad (2)$$

Where: W1 = weight of dry sample before heating (g), W2 = weight of ash (g).

3.7.3. Determination of volatile matter

The percentage of volatile matter of the MSK and AC samples was determined by the standard method ASTM D5832 – 98 [54]. 16.4218 g of raw MSK sample was weighed and placed in a closed crucible covered with lid. It was then heated up to 900℃ for exactly 7 min in a furnace using in Jimma Agricultural Collage lab according to the American Society for Testing Materials ASTM . The crucible was then cooled in a desiccators and weighed. The weight of the sample before heating and after heating was used to determine the amount of volatile matter present in the sample.

$$\text{Volatile \%} = \frac{100(100(B-F)-M(B-G)}{(B-G)(100-M)} \qquad (3)$$

G = Wt of empty crucible with lid= 25.2800 gm
B = Wt of empty crucible + lid + sample (before heating) = 41.7018 gm
F = Wt of empty crucible + lid + sample (after heating) = 34.5447 gm
M = Moisture content in 11.6%

3.7.4 Fixed Carbon Content

The fixed carbon content is determined by subtracting the sum of percentage compositions of moisture content, volatile matter content, and ash content form 100. The value obtained is the amount of fixed carbon present in the sample expressed in percentage [54].

$$\text{Fixed carbon (\%)} = 100 - (\text{\% moisture} + \text{\% volatile matter} + \text{\% ash}) \qquad (4)$$

3.8. Point of zero charge

Point of zero charge of the MKAC Sorbents was measured by the batch equilibrium technique in 0.1M $NaNO_3$. Six series of test solutions 25mL were prepared in conical flask by varying initial pH of the test solution from pH 2 to 12. And 0.2g of the MKAC with H_2SO_4 and H3PO_4 adsorbent was added to each test solutions. And the solutions were shaken for 24h at 150 rpm in room temperature 27°C. Finally, was measured the final pH of each test solution. The point of zero charge was then determined from the Δ pH values in y-axis was plotted against the initial pHi (x-axis). The point of intersection of the resulting curve with the x-axis gave the pHpzc [55].

3.9.Batch Studies

The adsorption of dyes on activated mango seed kernel was studied by batch technique. The batch experiments werecarried out at room temperature by shaking a mixture of 0.2g of mango kernel powder and 25mL of MB solution in water bath shaker, at agitation rate of 150 rpm for 1hr until equilibrium wasreached unless otherwise stated. All samples were carried out in duplicate under the same conditions and the average results were taken. After agitation, the powder was removed by filtration using filter paper. The concentration of MB in the filtrates as well as in the control samples was determined by using UV-Visible spectrometer.

$$\text{MB removal (\%)} = \frac{Co - Ce}{Co} x\ 100 \qquad (5)$$

Where; Co, Initial concentration of MB (mg/L)

Ce , Concentration of MB at equilibrium state (mg/L)

3.10. Parameters that will be used for determination of MB adsorption

3.10.1. pH variation

pH is an important parameter that influences the adsorption process and it was conducted with pH values of 2, 4, 6, 8 and 10. A 0.2 g/L of adsorbents dose was agitated with 25mL of 10 mg/L MB solution and at constant time of 60 min. A 0.1M NaOH and 0.1M HCl were used to adjust the pH of the solution. The amount of MB adsorbed was determined by UV-visible spectroscopy Plot of percentage removal against pH wasdrawn to show the effect of pH value on removal of MB concentration.

3.10.2. Contact time

A 0.2 g/L of activated carbon was agitated with 25mL of 10 mg/L(10ppm) MB and in pH value 8 and at time interval of 20, 40, 60, 80 and 100 min. The amount of MB adsorbed was determined using UV-Visible spectroscopy.

3.10.3. Dosage of adsorbent

The effect of adsorbent dosage was determined using 0.05 g/L, 0.1 g/.L, 0.15 g/L, 0.2 g/L and 0.25 g/L of MKAC was agitated with 25mL of 10mg/L of MB solution ,each in turn at optimum contact time of 60 min and at pH 8.The studies were done at room temperature of 25°C at constant shaking speed.The amount of MB adsorbed was determined by UV-visible spectroscopy,.

3.10.4. Initial Concentration of MB

A 0.2 g of the adsorbents was agitated with 25mL of 5mg/L, 10 mg/L, 15 mg/L, 20 mg/L and 25 mg/L (25 ppm) and pH of 8. The temperature was maintained at 25ºC of uniform shaking speed.The studies were carried out at an optimum contact time of 60 min for maximum adsorption to be realized. The results obtaining were used to plot adsorption isotherms and to determine the adsorption capacity.

3.11. Equilibrium Adsorption Isotherms

This study wasdone with the optimum pH of MB. In order to understand theadsorbate-adsorbent interaction, optimization of the use of adsorbent and its adsorption capacity towards a particular adsorbate is necessary for studying the adsorption isotherm. Adsorption capacity of activated mango kernel towards MB determined by plotting the amount of MB adsorbed by the biomass (qe) against equilibrium concentration (Ce) in solution. The adsorption equilibrium data were fitted to both the Freundlich and Langmuir adsorption isotherm model.The equilibrium sorption of the MB were carried out by contacting 0.2 g of the adsorbents derived from mango kernel with 25mL of 10 mg/L of different concentrations from 5 mg/L to 25 mg/L in 100mL plastic containers placed in a water bath rotator shaker for 60 minutes. The mixture wasfiltered and the filtrate was analyzed for MB dye concentration [18,25].

3.12. Adsorption equilibrium

Adsorption is the adhesion of substances onto the surface of adsorbent solid. It is the formation of gas, liquid or solid to the surface of a solid or less frequently a liquid [46].

Adsorption occurs at solid-solid, gas–solid, liquid–liquid and liquid–gas interfaces. An isotherm is a functional expression for the variation of adsorption relative to the concentration of adsorbate in the bulk solution at a constant temperature. It describes the relation between the adsorbate retained by the activated carbon and the adsorbateequilibrium constant. This graphical representation shows the relationship between the amounts adsorbed by a unit weight of adsorbent for example activated carbon and the amount of adsorbate remaining in a test medium of equilibrium [47].

Sorption isotherm is based on data that is specific for each system and the isotherm must be determined for every application. The major factors in determining the shape of an isotherm are;- the number of compounds in the solution, the relative adsorb abilities of the compound , the initial concentration of the solution, the degree of competition among solutes for adsorption sites and the characteristics of the specific carbon [47] .

According to Letterman adsorbate are held on the surface by various types of chemical forces such as hydrogen bond, dipole-dipole interactions and Van der Waal's forces. In adsorption equilibrium the rate at which the materials adsorb onto the surface is equal to the rate at which they desorbs. The adsorption can be on a monolayer as explained by Langmuir or on a multilayer as explained by Freundlich. The adsorption capacity of activated carbon may be determined by the use of adsorption isotherms. Freundlich isotherm used in heterogeneous surface is used to measure adsorption from solution in environmental engineering and specifically drinking water treatment applications. For a single solute system this isotherm is more convenient. The amount of MB dye at equilibrium qe is calculated from the mass balance equation [48] given by;

$$qe = (Co - Ce)V/W \qquad (6)$$

Where: qe is equilibrium concentration, Co is initial adsorbate concentration, Ce is equilibrium concentration of the adsorbate, V is volume of solution of the sample and W is the dosage.

3.12.1. Langmuir adsorption isotherm

The Langmuir adsorption isotherm describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent and after which no further adsorption takes place. The Langmuir represents the equilibrium distribution of MB between the solid and liquid phases. The Langmuir isotherm is valid for monolayer adsorption onto surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. Based on these assumptions, Langmuir represents the following equation [49];

$$\mathrm{Qe} = \frac{Qo\,\frac{K}{Ce}}{1+\frac{K}{Ce}} \qquad (7)$$

Langmuir adsorption parameters are determined by transforming the Langmuir equation (7) to linear form;

$$\frac{1}{Qe} = \frac{1}{Qo} + \frac{1}{QoKLCe} \qquad (8)$$

Where: Ce is the equilibrium concentration of adsorbate mg/L, Qe is the amount of adsorbate adsorbed per gram of the adsorbent at equilibrium (mg/g), Q0 is maximum monolayer coverage capacity (mg/g) and $K_L$is Langmuir isotherm constant (L/mg) [11,47]. The values of Qo and K_L are computed from the intercept and slope respectively of the Langmuir plot of 1/qe versus 1/Ce. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L which is a dimensionless constant referred to as separation factor or equilibrium parameter [50].

$$R_L = \frac{1}{1+KLCo} \qquad (9)$$

Where; Co =highest concentration

3.12.2. Freundlich Adsorption isotherm

Freundlich equation is given by;

$q_e = \text{K}f ce^{1/n}$ (10)

Where;

K_f is constant measuring adsorption capacity **Ce** is the equilibrium concentration of the adsorbate in solution and **we** is equilibrium surface coverage (amount of adsorbate adsorbed per unit weight of adsorbent).

This equation describes non-linear adsorption in a narrow range of adsorbate concentration. The Freundlich equation can be reduced to linear form as;

$\text{Log } q_e = \log kf + \frac{1}{n}\log C_e$ (11)

Where: Qe is the amount at equilibrium (mg/g), Ce is the equilibrium concentration of the adsorbate such as MB and kf and **n** are Freundlich constants, **n** gives an indication of how favorable the adsorption is and kf is the adsorption capacity of the adsorbents. kf can be defined as the adsorption or distribution coefficient and represents the quantity of MB adsorbed onto biosorbents for a unit mg equilibrium concentration [17,48].

The slope 1/n ranging between 0 and 1 was a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [49]. A value for1/n < 1 indicates a normal Langmuir isotherm while 1/n > 1 is indicative of cooperative adsorption. A plot of log qe against log Ce gives a straight line with slope 1/n and log kf as intercept. Freundlich model agrees with Langmuir equation and experimental data over moderate range of concentration.

3.13. Adsorption kinetic study

The study of adsorption kinetics in wastewater treatment is important as it not only provides valuable insight into the reaction pathways and the mechanism of sorption reactions, but also describes the solute uptake rate, which in turn control the residence time of sorbate uptake at the solid-solution interface. The kinetics data obtained from adsorption of MB dye onto mango seed kernel were studied by using two common kinetic models, which are the pseudo-first order kinetic model and pseudo-second order kinetic model. The best fit model was selected based on the linear regression, correlation coefficient (R^2), which is a measure of how well the predicted values from a forecast model match with the experimental data [19, 51] .

3.13.1. Pseudo first order kinetic model

The pseudo-first order kinetic model assumes that the rate of occupation of sorption sites is proportional to the number of unoccupied sites. The pseudo-first order equation was expressed in equation (12)

$$\frac{dq}{dt} = k1(qe - qt) \qquad (12)$$

Where: qe is Amount of adsorbate adsorbed at equilibrium (mg/g), qt is the amount of MB dye adsorbed at time t (mg/g), k1 is pseudo first-order rate constant (min^{-1}). By applying the boundary conditions of t = 0 and t = t and correspondingly qt = 0 and qt = qt and integrating equation (12).

$$\log\left(\frac{qe}{qe-qt}\right) = \frac{K1t}{2.303} \qquad (13)$$

The resultant equation (13) in linear form was:

$$\text{Log}(q_e - q_t) = \log q_e - \frac{K1}{2.303} \qquad (14)$$

2.13.2. Pseudo-second order kinetic model

The pseudo second order is based on the assumption that the rate limiting step may be chemical sorption involving valence forces through sharing or exchange of electrons between MB dye and adsorbent. The pseudo-second order kinetic rate equation was expressed as:

$$\frac{dqt}{dt} = k_2(qe - qt)2 \qquad (15)$$

Where:k^2 is the pseudo second-order rate constant (g/mg min). Integrating equation (15) and applying the boundary conditions of t = 0 and t = t and correspondingly qt = 0 and qt = qt gave:

$$\left(\frac{1}{qe-qt}\right) = \frac{1}{qe} + K^2 \tag{16}$$

Equation (16) was rearranged to obtain a linear form:

$$\frac{t}{qt} = \frac{1}{h} + \frac{1}{qe}t \tag{17}$$

Where: $h = k_2 \, qe^2$ (mg/g min) is the initial sorption rate.

CHAPTER FOUR

4.RESULTS AND DISCUSSION

4.1. Characterization of Mango Seed Kernel

4.1.1. Proximate analysis of MSK

According to ASTM D121, proximate analysis is the determination of moisture, volatile matter, fixed carbon, and ash content by prescribed methods. It is a means of determining the distribution of products obtained when the sample is heated under specified conditions. Proximate analysis of the raw MSK and AC were measured and calculated using the method in equations (1,2,3 and 4).

A. Moist % = $\frac{W_1 - W_2}{W_1} X100$= 17.9096 - 15.9996/17.9096 = 1.91/17.9096 = 11.6%

B. Ash % = $\frac{w_2}{w_1}$ x100 = (0.353g/14.528 g) x 100 = 2.43%

C.Volatile % = 100(100(B-F) - M(B-G))/ ((B-G)(100-M)

=100(100(41.7018-34.5447) – 11.6 (41.7018-25.2800))/ (41.7018-25.2800)(100-11.6)

=100(100 x7.1571) -11.6 (16.4218)/16.4218 x 88.4 = 36.18%

D. Carbon content (FC) % = 100 - (% M+ % Ash + %Volatile)

FC% =100 – (11.6%+2.43%+ 36.18%) = 100 - 50.21= 49.79 %

Table: 2. Proximate analysis of raw MSK and MKAC

Parameters	Normal (%)	40% H_3PO_4	50% H_2SO_4
Moisture content	11.6	6.23	4.89
Ash content	2.43	1.67	1.55
Volatile content	36.18	17.58	14.47
Carbon content	49.79	74.52	79.09

As it could be observed from Table (2) Proximate analysis of raw MSK and acid treated MSK activated carbon; difference estimated after undergoing activation process, the volatile matter content decreased significantly whereas the fixed carbon content increased in both activated samples. This due to the pyrolytic effect at 5000c temperature where most of the organic. The ash content for both acids treated with activated carbon showed a slight decrement as compared to the ash content of raw MSK. The ash content is a reflection of the amount of inorganic substituent present and was obtained as 2.43 %, 1.67% and 1.55% for raw MSK, PAAC and SAAC, respectively. The ash content of most AC from agricultural products is within 0.2 to 13.4 % H_2SO_4 [52].

Volatile matter is due to the residual organic compounds in the prepared adsorbent. The volatile matter obtained was 36.18 %, 17.58 % and 14.47 % for raw MSK, PAAC and SAAC respectively. It shows that the fixed carbon content of activated carbon prepared from MKAC is high while the moisture, volatile and ash content are the least. Due to its high fixed carbon it is preferred adsorbent with respect to another and ash content lower values favor the good adsorption characteristics. It was revealed that the carbon content is reasonably good enough to make MSK as a good low-cost adsorbent .

4.1.2. Point of zero charge of the adsorbent

The value of pH affected a net zero charge on a solid in the absence of specific biosorption is called the pHpzc. The point of the curve at which it crosses the X-axis was taken as the point of zero charge of the adsorbent MSK. The surface charge of adsorbents was further examined by comparing the pHpzc and pH of the adsorbent samples. The pHpzc was found to be 4.8 and 6.0 for the physically treated MKAC by 50% H_2SO_4 and 40% H_3PO_4 respectively, as represented in Fig.3. This is a convenient index of a surface when the latter becomes either positively charged or negatively charged ion as a function of pH. When the pH of the aqueous solution is below the pHpzc, the surface of the adsorbent will become positively charged. Meanwhile, the surface of the adsorbent will become negatively charged when the solution pH is greater than zero point of charge. Similar works were reported in the literature to determine point of zero charge of mangrove bark Sorbent, an agricultural waste [53]

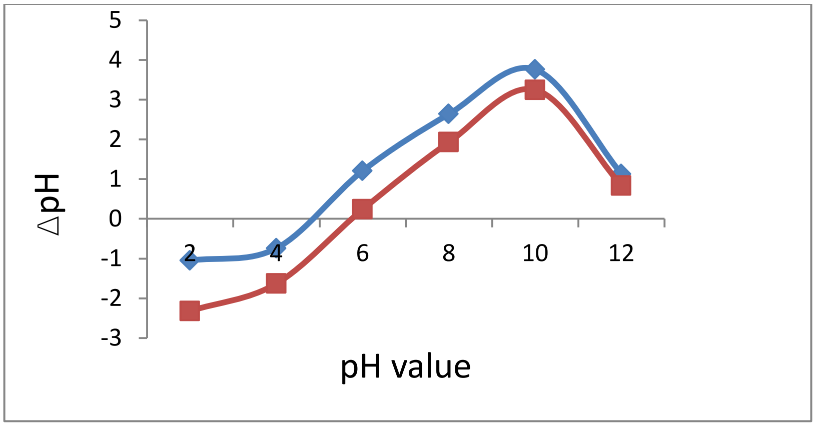


Fig:3. Plot of pHpzc of MKAC in H_2SO_4 and H_3PO_4.Initial pH vs ΔpH

4.1.3. FT-IR Spectroscopy

The surface functional groups of the sulphuric acid treated MSK based activated carbon before and after adsorption were estimated by Fourier Transform Infrared (FTIR) spectroscopy (FTIR-65, Perkin Elmer) analysis. FTIR spectra of samples were recorded within the range of 400–4000 cm^{-1}. The transmission spectra of the samples were recorded using the KBr pellet. The analysis was done in Jimma University College of Natural Sciences Department of Chemistry.

Several IR bands appearing in the FTIR spectrum of MKAC before adsorption (Fig. 3) and after adsorption was shown in Fig.4, that were assigned to various functional groups, in accordance with their respective wave number (cm^{-1}) position. The main reason for the absorption peak at 1203 and 1207 cm-1 is the stretching vibration of C-O, ester was assigned before and after absorption. However as sharp band was observed at 1369 cm^{-1} and 1338 cm^{-1} due to CN str aromatic 2° amine and 3° amine . The band at 1574 cm^{-1} and 1582 cm^{-}1 indicate the presence of amide N-H bend. Ester O-H str , carboxylic acid and the carbonyl (-C=O) stretching vibration occurred at 1718 cm^{-1} and 1746 cm^{-1}. Finally the very weak peak at about 2357 cm^{-1} and 2994 cm^{-1} corresponds to the stretching vibration of C=C conjugated , C≡C and C-H str alkane were appeared [37].

After the dye adsorption, the peak at 1338 cm^{-1} shifted to higher wave length of 1369 cm^{-1} and 1718 cm^{-1} shifted to 1746 cm^{-1} and the peak 2357 cm^{-1} shifted to a higher wave length of 2994 cm^{-1} that indicates the amine, amide and ester (CN, N-H and O-H) groups of adsorbent were involved in the adsorption of MB dye.

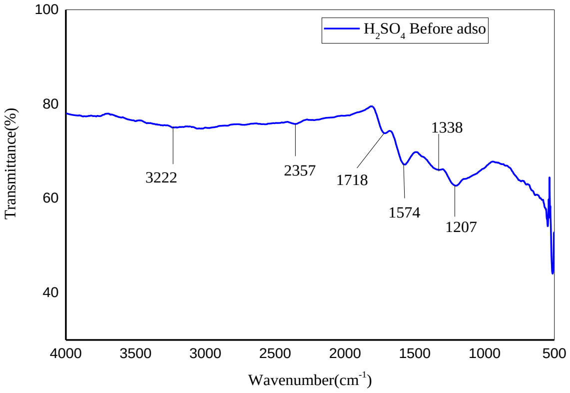


Fig 4. FT-IR spectra of MKAC with H_2SO_4 before adsorptions

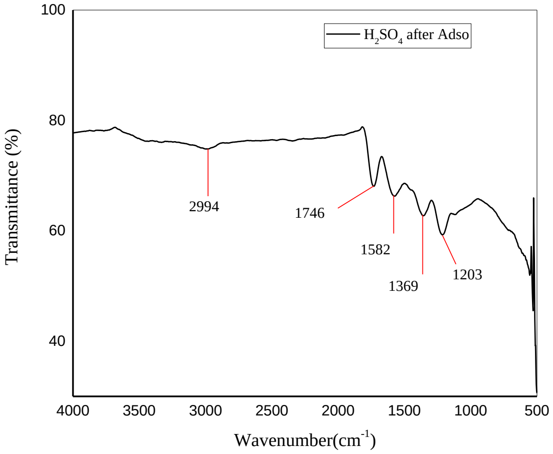
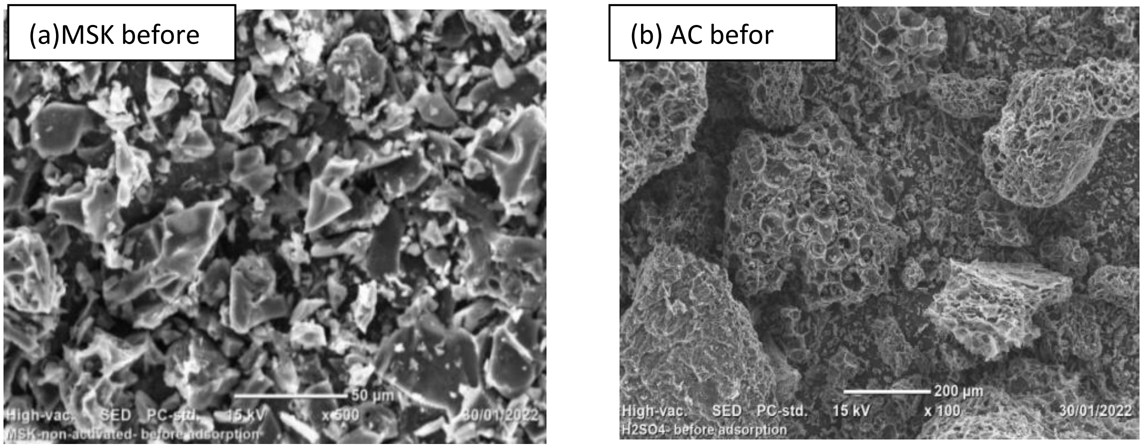


Fig: 5. FT-IR SPECTRA of MKAC with H_2SO_4 after adsorption

4.1.4. Scanning electronic micrograph studies (SEM)

In this study, the SEM analysis conducted using of raw MSK and sulphuric acid treated activated carbon before and after adsorption taken. After activation process, it can be seen in figure 5 (b) before adsorption, the SEM image of sulphuric acid treated activated carbon shows almost homogeneous type pores structure distributed on the surface and well developed pore structure. Whereas, the surface morphology of the raw MSK in Fig**. 5** (a) has no holes and enough porous structure. Therefore, the SEM image reveals that MB may be adsorbed onto the MKAC surface and the accessible pore domains of the carbonaceous surface the SEM image of MKAC after adsorption shows comparatively irregular shape than before because the active site of carbon occupied by methylene blue. From this analysis result revealed that, the activation process of MKAC was effective in creating well-developed pores, resulting in the large surface area activated carbon with good porous structure. The surface morphology of MKAC after MB adsorption reveals a change in the topography of the adsorbent, as evidenced by the appearance of reduced pore structure, holes and smoother surface features due to the adsorption of MB in (Fig**.**6 (a) and (b) . From this experimental analysis result sulpheric acid is an effective activating agent for locally built well-structured, large pore size activated carbon for the removal of methylene blue in aqueous solution [39] .

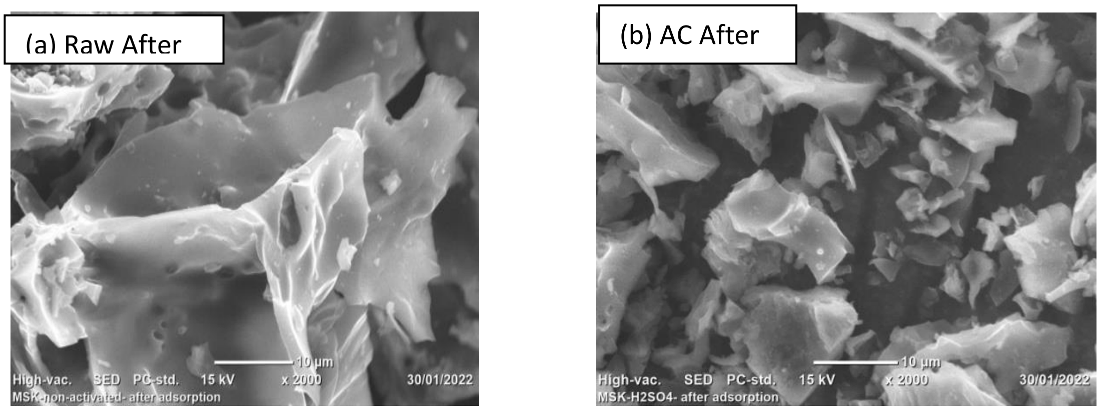


(a) at x 500 zoom

(b) at x 200 zoom

Fig: 6. SEM Image of MSK (a) Non activated and (b) Activated before Adsorption

The sample and pole lens distance was maintained at 25 mm while images were recorded at 5 to 20 kV acceleration voltage.



(a) at x 2000 ZOOM (b) at x 2000 ZOOM

Fig: 7. SEM Image of MSK (a) Non activated and (b) Activated after Adsorption

4.1.5. X-ray diffraction studies

X-ray diffraction (XRD) technique is a powerful technique to analyze the crystalline and amorphous nature of the material under investigation. In crystalline material, well defined peaks are observed, whereas in noncrystalline, or amorphous material shows broad peaks instead of sharp peaks. Fig.7 (a) shows that well defined peaks are observed in the adsorbent of MKAC and non-activated before adsorption.. XRD studies show change in crystallinity of the adsorbent due to adsorption [40].

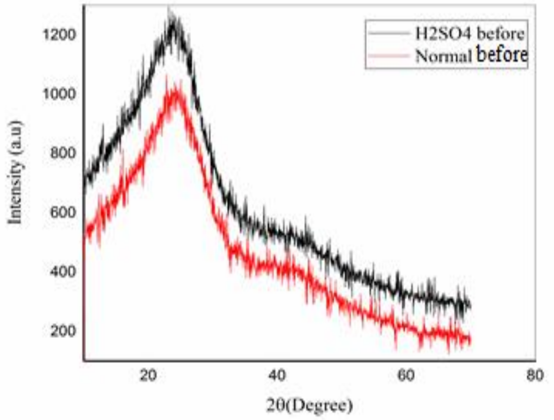


Fig: 8. XRD image of MKAC and normal MK

4.2. Adsorption studies

4.2.1. Effect of Adsorbent dose

The effect of the adsorbent dose was studied at room temperature by varying the adsorbent amounts from 0.05 to 0.25 g. For all these runs, initial concentration of MB, pH, agitation speed and contact time was kept constant. Fig:8 shows that adsorption efficiency of different doses of MKAC as adsorbent. The result revealed that adsorption efficiency for removal of MB increased with adsorbent dose in the range from 0.05- 0.15 g/L and showed little variation with by further increment.This is due to limited availability of adsorbate species for a relatively larger number of surfacesites on the adsorbent at higher dosage of adsorbent [40]. It is reasonable that with higher dosage of adsorbent, there would be greater number of exchangeable sites for MB. Therefore, the maximum removal efficiency of MB was obtained at on MKAC dose of 0.2 g is 91.5% and 89.3% for AC with H_2SO_4 and H_3PO_4. In all subsequent studies, 0.2 g of MKAC was taken. In the case of adsorption capacity, the reverse trend was observed as the dose of the adsorbent increased i.e., the adsorption capacity decreased as the dose of the sorbent was increased. Since adsorption capacity is expressed as the mass of MB adsorbed per unit mass of the adsorbent, its value decreases when the mass of the MB adsorbed gets smaller for the same increase in the mass of the adsorbent [41].

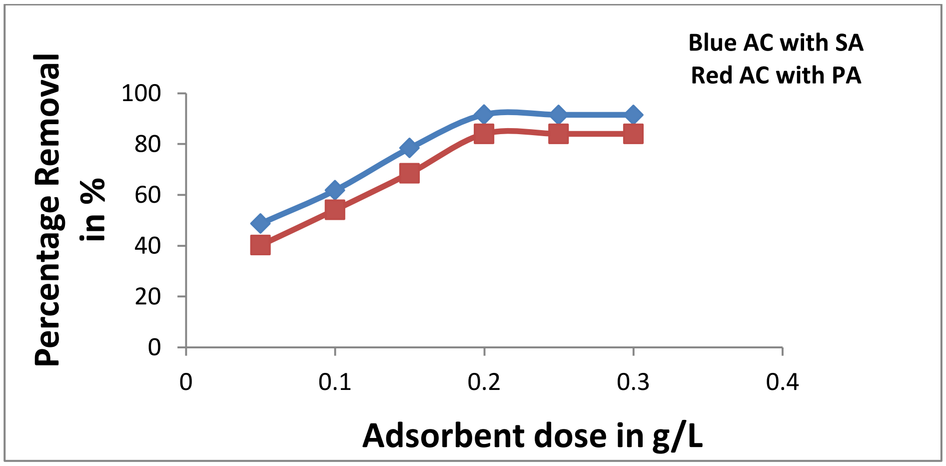


Fig: 9 plot of adsorbent dose vs Removal efficiency in % by MKAC

4.2.2. Effect of Initial MB concentration

The effect of initial MB concentration between (5 and 25 mg/L) on the adsorption of MB onto the MKAC 0.2g/L and pH 8 was studied. The adsorption capacity of MKAC increased with increasing initial MB concentration and percent of adsorption decreased with the increase in initial MB concentration, just as also shown in Fig10. It means that the adsorption is highly dependent on initial concentration of MB. It was high percentage removal of MB observed in 5mg/L was 92% and 88% for AC H_2SO_4 and H_3PO_4 respectively.It is because of that, at lower concentration, the ratio of the initial number of MB molecules to the available surface area is low and subsequently the fractional adsorption becomes independent of the initial concentration. However, at high concentration the available sites of adsorption becomes fewer and hence the percentage removal of MB is dependent upon the initial concentration [42].

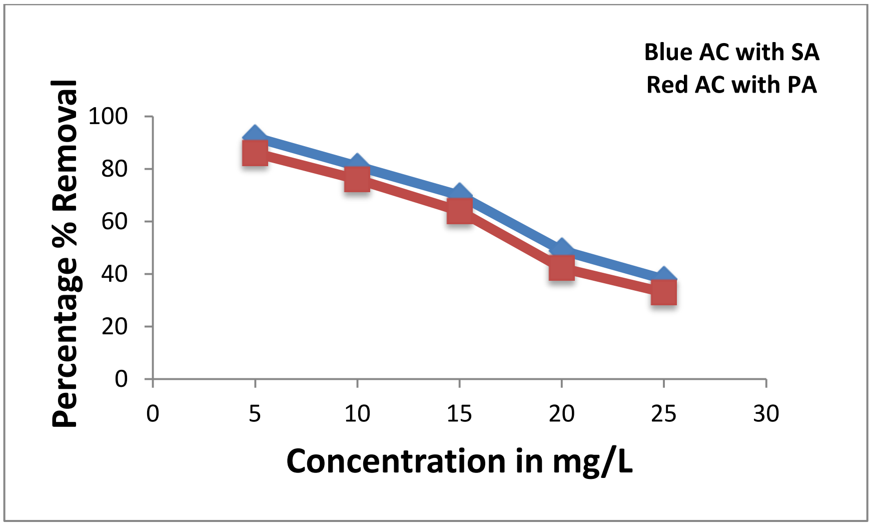


Fig:10 . Effect of initial concentration on removal of MB by MKAC with H_2SO_4 and H_3PO_4

4.2.3.Effect of Contact Time

A 0.2 g/L of activated carbon was agitated with 25mL of 10 mg/L (10 ppm) MB in 20, 40, 60, 80 and 100 minutes. The amount of MB adsorbed was determined using UV-visible spectroscopy. The adsorption process was fast at the beginning due to availability of large area, then the process were slowing down as more pores are filled with molecules. The adsorption capacity increased from 0.64 mg/g to 1.09 mg/g for MB by MKAC with 50% H_2SO_4 and from 0.68 mg/g to 1.11 mg/g for MB by MKAC With 40% H_3PO_4as time increased from 20 to 60 min. The maximum removal efficiency was found at 60 min and 10 mg/L concentration shows the comparison of adsorption capacity for the two MKAC at the same concentration was 89.2% and 87.9% for MKAC With 40% H_3PO_4 and 50% H_2SO_4. It shows that MB by MKAC With 40% H_3PO_4 is more adsorbed per unit mass than MB by MKAC with 50% H_2SO_4, the difference in AC [44].

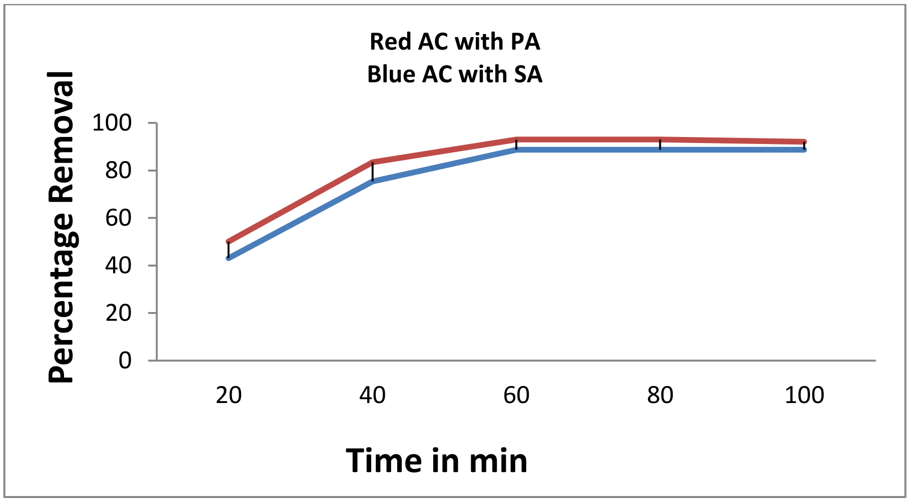


Fig:11. Plot of time vs Percentage Removal of Mb

4.2.4.Effect of pH of solution

The pH of the dye solution plays an important role in the whole adsorption process, particularly on the adsorption capacity [42]. Fig 11 shows the effect of pH on the adsorption of MB onto the MKAC at an initial concentration of 10mg/L MB and the amount of adsorbent (0.2 g/L) at 150 rpm agitation speed and at 298K. If the pH of the dye solution was changed from 2 to 8, the adsorption capacity of MKACwas raised from 1.8 to 2.9mg/. In the process of adsorption, at a lower pH, the adsorbent surface is positively charged, favoring adsorption of anionic contaminants. Because MB is a cationic dye, positive charge which occupied the feasible adsorption position competes with dye molecules, resulting in a lower adsorption of dyes;while at a higher pH, negatively charged surface facilitates adsorption of cationic contaminants [45]. High removal percentage at pH 8 was 89.8% and 876.6% for AC with 50% $H_2SO_4$and 40% H_3PO_4 respectively. However, as the pH increases the binding sites start deprotonating and more negatively charged surface becomes available. This in turn facilitates a much greater MB uptake and cations binding capacity increases as pH increases [46].

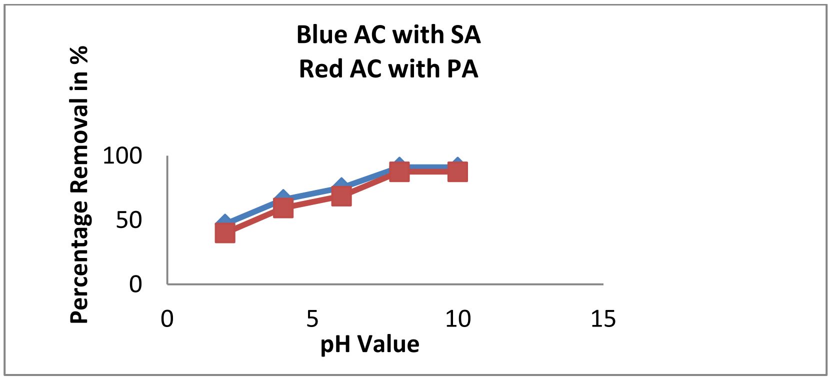


Fig: 12.pHvs Percentage Removal in % MKAC with H_2SO_4 (S.A)andH_3PO_4 (P.A)

4.3. Adsorption Equilibrium

Adsorption isotherm is needed to explain the adsorption process and to determine the adsorption efficiency of an adsorbent. Out of the different adsorption isotherm models, Langmuir’s and Freundlich models have been preferred by most of the studies concerning about adsorption. The present experiment also used Langmuir’s and Freundlich equations to explain the adsorption mechanism of the adsorbent considered [47].

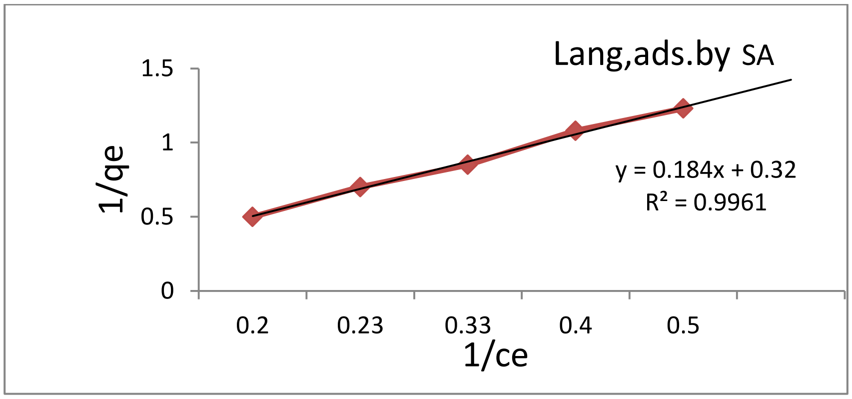
4.4 Adsorption Isotherms

The study was carried out by using 0.05 g, 0.1 g, 0.15 g, 0.2 g, and 0.25 g of activated carbon prepared from mango kernel. Fig.8 shows the relationship between the quantity of MB dye adsorbed per gram of adsorbent and the equilibrium liquid phase concentration at room temperature. Adsorption equilibrium isotherm models were used to describe the adsorption process and the results obtained were analyzed using different isothermal equations [48].

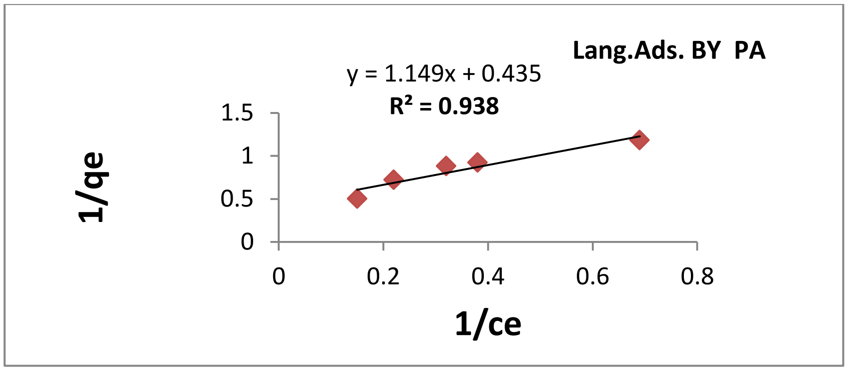
The graph obtained by Langmuir equation shows that the relation between1/Ce in the x axis and 1/qe in the y axis. On the other hand, the graph of the Freundlich equation showed that the relationship between log Ce in the X axis and log qe in the y axis.

4.4.1. Langmuir isotherm model

The Langmuir adsorption isotherm model was primarily designed to describe gas-solid phase adsorption is also used to quantify and contrast the absorptive capacity of various adsorbents [49]. It accounts for the surface coverage by balancing the relative rate of adsorption and desorption (dynamic equilibrium). Adsorption is proportional to the fraction of the surface of the adsorbent that is open while desorption is proportional to the fraction of the adsorbent surface that is covered [50].



(a)



(b)

Fig: 13. Languimer adsorption isotherm of MB with (a) AC with SA and (b) with PA

According to figure (12 a)

Y-intercept (1/qm) =0.100, qm =10

Slope ($1/K_L$qm) = 2.323, $K_L$qm =0.43 and K_L =0.043

R_{La} =1/ (1+K_LCo), 1/(1+0.043x10) mg/L = 1/2.43 =0.41

Where, Co is the initial adsorbate concentration (mg/L) and KL is the Langmuir isothermconstant (L/ mg^{-1}).

The maximum adsorption capacity (qm) of MKAC with H_2SO_4 was calculated from the intercept was10 mg/g for MKAC with H_2SO_4. That is one gram of MKAC with H_2SO_4 can absorb 10.0 mg of MB dye. And one gram of MKAC with H_3PO_4 can absorb 5.8 mg of MB dye. The essential characteristic of the Langmuir isotherm may be expressed in terms of the dimensionless separation parameter RL, which is indicative of the isotherm shape that predicts whether the adsorption system is favorable or unfavorable [49]. From the experimental data RL= 0.41 for MKAC with H_2SO_4 and 0.28 by MKAC with H_3PO_4, the value lies between zero and one, which indicates a favorable adsorption. This means that the activated carbon prepared from mango kernel is a favorable adsorbent for the removal of MB dye [51].

4.4.2.Freundlich isotherm model

Freundlich isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption. Freundlich equation does not consider all sites on the adsorbent surface to be equal rather it assumes that, once the surface is covered, additional adsorbed species can still be accommodated [52].

Fig. 13, Freundlich adsorption isotherm for MB by MKAC with H_2SO_4 Plotting log ce versus log qe gave a straight line with a slope of 1/n and intercept of log kf Fig.(13).

According to Figure (13) for AC with H_2SO_4

Slope 1/n = 0.543, n =1.84,Y- Intercept log kf = - 0.18

Constant kf = 0.66 . From Freundlich equation, the values of 1/n and n were obtained as 0.543 and 1.84, respectively.

Table: 3. Languimer and Freundlich Isotherm constant of MB adsorption

Isotherm	Langmuir Isotherm				Freundlich Isotherm		
Activator	qm (mg/g)	K_L (L/mg)	R_L	R^2	K_f (mg/g)	1/n	R^2
H_2SO_4	10	0.043	0.41	0.983	0.66	0.453	0.976
H_3PO_4	5.8	0.16	0.28	0.938	0.69	0.533	0.925

qmax = maximum adsorption capacity (mg/g), b(KL) = constant related to binding energy, R^2 = Correlation coefficient, RL =separation factor, Kf=Freundlich adsorption capacity, n = Freundlich constant related to intensity of adsorption

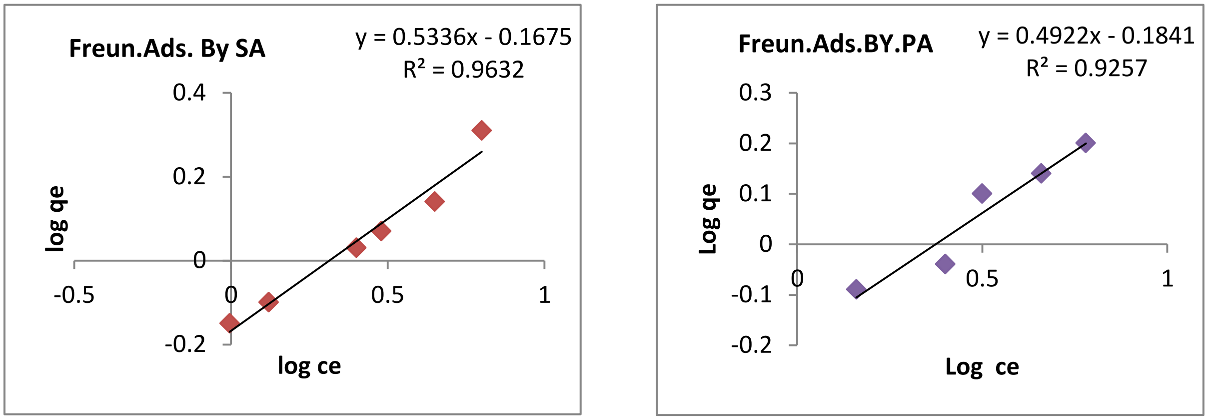


Fig :14.Freundlich Adsorption isotherm of MB (a) for AC with SA and (b) AC for PA

4.5.Adsorption Kinetics

Adsorption kinetics, that describes the solute adsorption rate, is animportant characteristic in evaluating the efficiency of adsorption. The adsorption data (at pH 8) for MB concentration of 10 mg/L is shown in Fig.(14**)** 0.2 g of MKAC was taken for this study. The plot shows that the adsorption MB with different contact time consists of two phases; an initial rapid phase where adsorption was fast and a second slower phase where adsorption equilibrium uptake was achieved. In adsorption process identification of the slowest step or rate determining step is very crucial. Previously several researchers used different kinetic models, such as Lagergren’s pseudo first order, pseudo second order, Elovich kinetic equation and parabolic diffusion model, in order to predict the mechanism involved in the adsorption process [50,53].

Currently, the Lagergren’s pseudo first order and pseudo second order models have been widely used for adsorption systems due to their good representation of the experimental data for most of the adsorbent adsorbate systems [54]. Therefore, the two kinetic models were applied.

4.5.1.The pseudo- first order model

The pseudo- first order model can be represented in the following Form.

$dqt/dt = k_1(qe - q\ )$ (8)

Where k_1 is the rate constant, qe and qt are the amounts of the MB adsorbed (mg/g) at equilibrium and at any time t, respectively. This equation can be integrated to yield a linearized form at initial conditions where qt = 0, t = 0 and at any time t,

$\log\ (q_e\ -q_t = \log\ q_e - (k_{1/2.303})t$ (9)

where, q_t = t and t = t.

In this equation, the rate of adsorption is assumed to be proportional to the difference between the adsorption capacity at equilibrium (qe) and the adsorption capacity at time t (qt).

The pseudo- first order kinetics is applicable if the plot of log(qe - qt) against t shows linear relationship. A straight line plot of log (qe-qt) versus t was used to determine the rate constant, k_1 and correlation coefficient, R^2 [55,56].

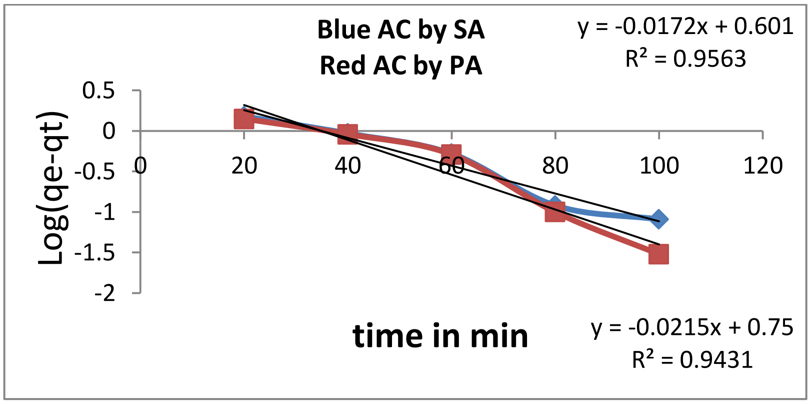


Fig.:15. Plot of pseudo- first order kineticsmodel of MB for AC with SA and PA

The graph for both MKAC gave unsatisfactory fit with the Pseudo first order kinetic model, implying the process of adsorption has no first order kinetics. And also the values of k_1 (L/min^{-1}) and qe (Cal) in mg/g of MB predicted from those plot are $-1.82\ x10^{-4}$ for H_2SO_4 AC and $-2.11\ x\ 10^{-4}$ for H_3PO_4 AC, and qe (Cal) in mg/g are 1.82 and 2.11 mg/g and has lower R^2 value. The result shows that the pseudo-first order rate equation did not adequately describe the adsorption result of MB.

4.5.2.Pseudo second-order kinetics model

The Pseudo-second order kinetic model was tested in the same way by rewriting the equation in its linear form and plotting the appropriate variables. The equation that describes the pseudo second order model is given in the following linear form:

$$\frac{t}{qt} = \frac{1}{k2qe2} + \frac{1}{qe}t \qquad (10)$$

The constants, qe and K_2, were computed from the slope and intercept of t/qt versus t linear plot, respectively.

Equation (10) was rearranged to obtain a linear form:

$$\frac{t}{qt} = \frac{1}{h} + \frac{1}{qe}t \qquad (11)$$

Where: h = k_2 qe2 (mg/g min) is the initial sorption rate.

Pseudo second order rate constant (k_2), h and the equilibrium adsorption capacity (qe) can be determined experimentally from the slope and intercept of the plot t/qt versus t. The plot t/qt versus t should give a straight line if pseudo second order kinetics is applicable [57].

The plot of the linearized form of the pseudo second order reaction of MB dye on adsorbent surface is shown in fig 15.

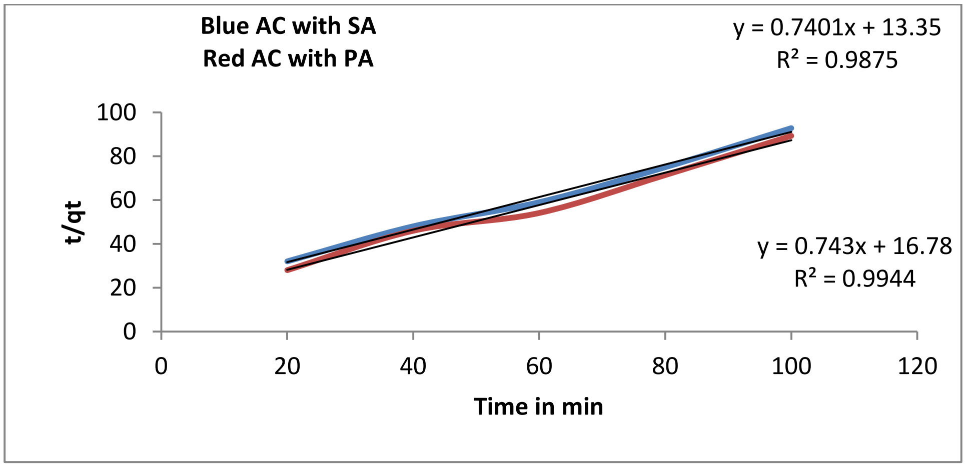


Fig: 16. Pseudo second order kinetics for MB adsorption with H_3PO_4 andH_2SO_4

The plot of t/qt versus t for pseudo second order rate equation yields a good straight line as compared to the plot of pseudo first order and higher R^2 value. This suggests that the adsorption of MB by MKAC follows the pseudo-second order model, which relies on the assumption that chemisorptions is the rate limiting step [58].

Table:4 Pseudo first and second Kinetic order of MB Adsorption

MKAC	Pseudo first order kinetic model				Pseudo second order kinetic model			
Activator	Intercept	qe in mg/g	K_1	R^2	h	Qe in mg/g	K_2	R^2
H_2SO_4	0.601	1.824	$-1.7x10^{-4}$	0.956	0.069	1.35	0.038	0.994
H_3PO_4	0.75	2.11	$-2.1x10^{-4}$	0.943	0.068	1.377	0.036	0.987

qe (Cal) = calculated equilibrium adsorption capacity (mg/g),

K1 = pseudo first order rate constant (L/min)

R2 = correlation coefficient

k2 = pseudo second order rate constant (g $mg^{-1}min^{-1}$)

h = initial adsorption rate mg/g min)

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

The present study shows that, the adsorption capacities of the MKAC in 50% H_2SO_4 and 40% H_3PO_4 forms were investigated for the removal of MB dye under a batch adsorption system. Characterization adsorbents were performed using the pHpzc, proximate analysis, FT-IR, SEM and XRD analyses. Different reaction parameters affecting the adsorption process were optimized, including the contact time, pH, initial dye concentrations and adsorbent dose. The optimal pH for favorable removal of MB dye was 8. The change adsorbent dose and initial MB concentration had an effect on the removal of MB dye. The adsorption equilibrium was reached in approximately after 60 min. The amount of RL value showed that MKAC can be used for dye removal. The adsorption capacity and kinetics for the adsorbents investigated were well described by the monolayer adsorption model of the Langmuir isotherm and the chemisorptions model of pseudo-second-order kinetics. The results presented in this study clearly reflect that the MKAC with 50% H_2SO_4 adsorbent is more efficient than 40% H_3PO_4 adsorbent. Hence charcoal prepared from waste materials, MSK was found to be cost effective in removing MB dye from aqueous solutions.

5.2 Recommendation

The following recommendations were made from this study. Activated carbon prepared from the mango seed kernel was found to have a good potential in removing MB dye from its aqueous solution. The stages of treatment could then be adopted based on the efficiency of the mango kernel in recovery and reuse. Furthermore, a continuation of tests on the adsorption of real effluents onto mango kernel should be undertaken to allow an easier implementation of this adsorption process on a larger scale in developing countries.

Futurity; Other characterization of the MSK should be done, using more advanced techniques such as

- BET; to visualize the surface area and pore structure of the material.
- Elemental analysis of the adsorbent
- Finally, Performance of this adsorbent further optimization study could be conducted using different method.

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7. APPENDICS

Append 1A, How to Prepare 40% of 300 mL H_3PO_4 from 85% of H_3PO_4 Its density 4.71 g mL-1 , MW = 98 g/mole .The no of mole of PA present in 1L of PA is; Mass of soln of 85% PA = volume x density = 1000 mL x 4.71 g/mL = 4710 g Mass of 85% PA = % PA x mass of soln = 0.85 x 4710 g = 4003.5 g

No of mole of 85% PA = mass of PA/molar mass of PA = 4003.5g/98 g mole^{-1}= 40.85 mole

- Want to prepared 40 % of 300 mL H_3PO_4 (PA)
- Mass of 40% PA = % PA x mass of soln = 0.4 x 4710 g = 1884 g

No of mole of 40% PA = 1884 g /98 g mole -1= 19. 22 mole

- By using the dilution method was obtained 40 % of PA
- M1V1 =M2V2 , V2= 300mL, M2= 19.22 and M1= 40.85 mole
- V1= M2xV2/M1 = 19.22 mole x 300mL/40.85 mole = 141.15 mL
  - ❖ 141.15 mL of 85 % of H_3PO_4 was taken and added to 158.85 mL of distilled water, finally was obtained 40 % of 300 mL of H_3PO_4 .

Append 1B, To prepared 50 % of 100 mL H_2SO_4 , from 98 % of H_2SO_4. Its density 1.84 g mL-1, MW 98g mole-1, the procedure is the same to preparation of 40% H_3PO_4 .

- By using dilution method to prepared 50 % of 100 mL of H_2SO_4 .
- M1V1= M2V2 , V2= 100mL, M2= 9.39 mole, M1= 18.4 mole , V1 = ???
- V1= M2 x V2/M1 = 9.39 mole x 100 mL/18.4mole= 51.03 mL
  - ❖ 51.03 mL of 98 % H_2SO_4 was taken and added drop wise to 48.97 mL of distilled water, finally was obtained 100 mL of 50 % H_2SO_4

Appen. 2 The result of MB adsorption isotherm by MKAC with H3PO$_4$

Adsorbent dose in g	Residual Concent. Ce in (mg/L)	Adsorption capacity qe (mg/g)	Percentage removal in %	1/ce	1/qe	Log ce	Log qe
0.05	5.98	2.01	40.2	0.15	0.5	0.78	0.30
0.1	4.58	1.39	54.1	0.22	0.72	0.66	0.14
0.15	3.15	1.14	68.5	0.32	0.88	0.5	0.1
0.2	2.62	0.92	91.5	0.38	1.1	0.42	-0.04
0.25	2.62	0.92	91.5	0.69	1.18	0.16	-0.07

Append 3: The result of Mb adsorption isotherm By MKAC with H2SO$_4$

Adsorbent dose in g	Residual Concent. CeIn (mg/L)	Adsorption capacity qe(mg/g)	Langmuir		Ferundlich		perc.Remo
			1/ce1/qe		log celogqe		in %
0.05	5.87	2.06	0.2	0.5	0.77	0.31	41.3
0.1	4.43	1.39	0.23	0.7	0.65	0.14	55.7
0.15	3.01	1.17	0.33	0.85	0.48	0.07	69.9
0.2	2.5	0.94	0.4	1.1	0.4	-0.03	89.3
0.25	2.5	0.94	0.4	1.1	0.4	-0.03	89.3

Appen:4 Effect of intial Concentration on removal of MB BY H_2SO_4

Intial MB Con. Mg/L	Risdual Conc. in mg/L	Adso.Capac. In mg/g	Removal Percentage %	1/ce	1/qe	Log ce	Log qe
5	0.8	0.56	92	2.5	1.78	-0.097	-0.25
10	1.1	1.14	89	1.1	0.88	0.041	0.06
15	3.0	1.63	80	0.5	0.61	0.48	0.21
20	10.8	1.29	46	0.1	0.78	1.03	0.11
25	16	1.13	36	0.06	0.88	1.204	0.05

Appen 5: Effect of intial MB conce. 0n Logce,Logqe& % Removal By H_3PO_4

Co in mg/L	Ce in mg/L	Qe in mg/g	Perc.Removal .in %	1/ce	1/qe	Logce	Logqe
5	0.6	0.11	88	1.67	-0.96	-0.22	-0.96
10	1.5	1.06	85	0.67	0.94	0.18	0.025
15	2.4	1.58	83	0.45	0.63	0.38	0.198
20	10.1	1.24	49.5	0.09	0.806	1.004	0.09
25	15.4	1.21	38	0.06	0.83	1.19	0.08

Appen 6: Effect of pH of solution on ce, qe and perc.Removal of MB by H_3PO4

pH value	Ce in mg/L	Qe in mg/g	1/ce	1/qe	Log ce	Log qe	Perc.Remo. in %
2	6	0.5	0.17	2.0	0.78	-0.30	40
4	2.8	0.9	0.36	1.1	0.45	-0.05	72
6	2.2	0.98	0.45	1.02	0.34	-0.01	78
8	1.3	1.09	0.41	1.06	0.39	-0.03	87.6
10	1.3	1.09	0.19	1.67	0.71	-0.22	87.6

Appen:**7** of the effect of time, on adsorption of MB By H_2SO_4

Time in min	Ce in mgL	Qt in mg/g	Remo.effic in %	1/ce	1/qt	Logce	Logqe
20	4.72	0.64	52.8	1.55	1.55	.67	-0.19
40	3.12	0.86	68.8	1.14	1.16	.49	-0.065
60	1.21	1.09	87.9	0.19	.92	.083	0.04
80	1.22	1.1	87.8	0.2	.91	.086	0.041
100	1.22	1.1	87.8	0.2	.91	.086	0.041

Appen 8: Effect of time on 1/ce, 1/qt&perc.Removalof MB by H3PO_4

Time in min	Ce value in mg/L	Qt value in mg/g	1/ce	1/qt	Log ce	Log qt	Perc.Remo.in %
20	4.6	0.68	0.23	1.47	0.66	-0.17	54
40	3.05	0.87	0.33	1.15	0.48	-0.06	69.5
60	1.10	1.11	0.91	0.9	0.04	0.05	89.2
80	1.11	1.1	0.92	0.91	0.05	0.06	89.2
100	1.11	1.1	0.91	0.91	0.05	0.06	89.2