

JIMMA UNIVERSITY
COLLEGE OF NATURAL SCIENCES
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DEPARTMENT OF CHEMISTRY



THESIS
ON
REMOVAL OF DYES FROM AQUEOUS SOLUTION USING LOCALLY AVAILABLE
ADSORBENT: BARLEY (*Hordeum vulgare*) BRAN AND *Ensete ventricosum* MIDRIB OF
LEAF

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FEBRUARY, 2021

JIMMA, ETHIOPIA

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Declaration

I, the undersigned, declare that this thesis entitled: (Removal of dyes from aqueous solution using locally available adsorbent: barley (*hordeum vulgare*) bran and *ensete ventricosum* midrib of leaf) is my original work and has not been presented for a degree in any other University and that all source of materials used for the thesis have been duly acknowledged.

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Date_____

Abstract

*The dis-charge of textile effluents in to water bodies has become a serious environmental problem. Based on this idea, focusing the environmental issue and economic point of view, the use of, low cost and eco-friendly agricultural by-products were investigated for removal of methylene blue from aqueous solution. In this study, the usage of Barley (*Hordeum vulgare*) bran & *Ensete ventricosum* midrib of leaf as adsorbents for the removal of methylene blue dye from aqueous solution has been investigated. Some physico-chemical properties of the adsorbents were determined, such as porous characteristics, surface area, surface functional group & point of zero charge. The batch adsorption studies of methylene blue carried out by Barley bran & *Ensete ventricosum* midrib of leaf independently and three main factors such as contact time, effect of pH & effect of initial concentration were used to optimize the best of adsorption efficiency for methylene blue removal adsorption processes. The surface area measured by Sear method was 26.2 m²/g and 20.344m²/g respectively, for both adsorbent. The optimum adsorption of methylene blue on Barley bran & *Ensete ventricosum* midrib of leaf were 96.3% & 97.4%, at pH 5.07 & natural pH 5.66, adsorbent dose 0.1g, concentration of methylene blue 10mg/L, contact time 4 h & 1 h, respectively. The experimental result has been fitted well by Langmuir isotherm model for both barley bran & *Ensete ventricosum* midrib of leaf. Moreover adsorption kinetics were determined using pseudo first order and pseudo second order models and it was found that the adsorption process follows the pseudo second order model for both barley bran & *Ensete ventricosum* midrib of leaf. The adsorbents used were locally available and could be taken as low-cost adsorbents for the removal of cationic (basic) dyes in wastewater treatment. Thus, this low-cost, effective removal method may solve the problem of industrial wastewater through adsorptive removal of dye.*

*Keyword: Adsorption, Barley bran, *Ensete ventricosum* midrib of leaf, Methylene blue.*

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Acronyms

BB	Barley bran
EVML	<i>Ensete ventricosum</i> midrib of leaf
MB	Methylene blue
FTIR	Fourier Transformer Infrared spectroscope
PH	Power of Hydrogen
PZC	Point of zero charge
MO	Methyl orange
EBT	Erichrome Black T
MG	Malachite green
BG	Brilliant green

1. INTRODUCTION

1.1. Background of study

Wastewater generated by textile plants is linked to one of the major problems of water pollution. It contains a mixture of different dyes, auxiliaries, additives, and additional chemicals that were added during textile production processes, causing serious environmental concerns. However, the main problematic pollutants from textile factories in the aquatic environment are dye mixtures.¹ For instance, the contamination of water bodies by synthetic dyes has created a serious environmental problem all over the world. A considerable amount of dyes are released into the aquatic ecosystems through wastewater streams of industries such as textile, carpet, leather etc.² Industries produce wastewater containing organics with a strong color, where in the dyeing processes the percentage of dye lost wastewater is 50% of the dye because of the low levels of dye-fiber fixation.³

Discharge of these dyes in to water bodies affects the people who may use these effluents polluted water for living purposes such as washing, bathing and drinking. Therefore, it is very important to verify the water quality of the effluents, especially when even just 1.0 mg/L of dye concentration in drinking water could impart a significant color, making it unfit for human consumption.³ The presence of dyes in water in trace amount is undesirable because most of them are toxic, mutagenic and carcinogenic. Dyes also prevent light penetration and thereby reduce photosynthetic activities of water streams and disturb the aquatic equilibrium.⁴ The problems become high due to the fact that the complex aromatic structures of the dyes render them ineffective in the presence of heat, light, microbes, and even oxidizing agents and degradation of the dyes become difficult.⁵

Dyes can be classified as anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (dispersive dyes).⁵ MB dye is an organic cationic dye and a heterocyclic compound with chemical formula $C_{16}H_{18}N_3SCl$. The decomposition of MB leads to the evolution of hazardous gases like nitrogen oxides, carbon dioxide, carbon monoxide, and sulfur oxides which may cause diarrhea, pre-cordial pain, gastritis, allergic dermatitis, and cancer. Long term exposures of MB

can cause methemoglobinemia, nausea, anemia, and hypertension.⁶ Therefore, it is important to remove MB dye from the effluents, before discharging in to environment.⁷

MB dye has been found to be the most suitable substrate in synthetic textile fiber industries.⁸ However, such extensive use often causes problems in the form of colored waste water, and adequate treatment is required for its removal before discharging into water bodies. The chemical structure of MB is complex; it is difficult to fade away from exposed light and water, and therefore, it is very difficult to remove it from wastewater using commonly used techniques.⁸ Therefore, these constitute a serious threat to human health and water quality, and thus become a vital issue. In a colour removal, the industries involvements are required to treat effluents containing dyes before they are discharged into water bodies. Thus, the scientific community shoulders the responsibility of contributing to the wastewater treatment by developing effective dye removal technique.⁵ Wastewater effluents contain dyes which may cause environmental pollution.⁹ Since the removal of dyes from wastewater is considered an environmental issue and government legislation requires textile wastewater to be treated.¹⁰ Therefore there is a constant need to have an effective process that can efficiently remove these dyes.

Due to the environmental and health concerns associated with the wastewater effluents,⁹ many treatment processes have been applied for the removal of dyes from wastewater.¹¹ Typical treatment methods include such as: physical, chemical and biological water treatment.¹² Comprising adsorption, coagulation/flocculation, advanced oxidation processes, ozonation, membrane filtration, electroflotation, electrokinetic coagulation, electrochemical destruction, ion-exchange, precipitation¹³ and reverse osmosis have also been found to be impressive in removing dye contaminants from wastewater.¹⁴ Because of danger, high cost and high energy requirement, researchers use adsorbents obtained from agricultural waste for the removal of such contaminants.¹⁵

Among the conventional methods, adsorption has been found to be good treatment technology for dye removal. Fundamentally, adsorption technology is flexible, simple for design, relatively easy of operation, cost-effective, high efficiency, recyclability, and environmentally friendly.¹⁶

Commercial activated carbon is the universal adsorbent but it is very expensive to use in real applications in many nations across the globe.¹⁶ This has motivated the search for low-cost, efficient, high carbon content, and renewable materials for use as sorbents and has led to a growing interest in the use of nonconventional and locally available materials such as natural materials and agricultural wastes.¹⁷ Non-conventional activated carbon has been produced from local materials such as cassava peel, cotton, orange peel, the bark of *Morinda tinctorial*, the bark of the *Vitex negundo*, bagasse fly ash, wheat straw, sawdust, avocado seed and crocus sativus leaves etc.¹⁶

1.2 Statement of problem

Removing the colour of wastewater is an issue of concern for both aesthetics and health. Color removal from textile effluents on a continuous industrial scale has been given much attention in the last few years, not only because of its potential toxicity, but also mainly due to its visibility problem. The industries are required to treat effluent containing dyes before they are discharged to water bodies. Thus, the scientific community takes on the responsibility of contributing to waste treatment through the development of an effective dye removal technique.⁵ That is why this study was interested to remove the MB dye from aqueous solution by using locally available & affordable adsorbents prepared from BB & EVML. There are several promising techniques for removal of dyes from wastewater such as: physical, chemical and biological methods which were widely used to treat wastewater, containing dyes.¹⁸ Physicochemical and electrochemical treatment methods such as photochemical, sono-chemical, electrochemical, coagulation and flocculation, bio-degradation, membrane separation, photo-fenton processes, oxidation or ozonation¹⁹ have been reported in the literature. However, in developing countries, such methods remain unaffordable and, in some cases, tend to produce secondary waste by-products.¹⁹ Amongst these technologies, the adsorptive removal process is revolutionary, a cost-effective and easy-to-use alternative with reliable performance. Of countless sorbents used for the mentioned purpose, the most pertinent is the activated carbon, which unfortunately is accessible at high prices and is limited in amounts.²⁰ Several reviews have compiled works dedicated to removing exhausted dyes from effluent water using low-cost adsorbents, e.g. natural minerals or biological species, agricultural byproducts, wastes from various industrial processes.^{21,22} Among them, some have shown certain degrees of MB dye adsorption capacity. Barley bran and *Ensete ventricosum* midrib of leaf are locally available, cost effective & eco-friendly agricultural by-products. In general, the selection of an adsorbent mainly include: the adsorption capacity, inexpensive, availability, production technology etc. When the agricultural by-product adsorbents are prepared and screened, it is expected to remove MB dye from wastewater effectively.

1.3 Objective of study

1.3.1 General Objectives:

The general objective of this study is to assess the selection of adsorbent through screening of different agricultural byproducts & utilization of selected adsorbents; barley bran and *Ensete ventricosum* midrib of leaf as a low cost adsorbent.

1.3.2 Specific Objectives

- To screen out adsorbents for removal of MB dye from aqueous solution by locally available agricultural by-products.
- To characterize the surface functional group of barley bran and *Ensete ventricosum* midrib of leaf adsorbents.
- To evaluate adsorption capacity of barley bran and *Ensete ventricosum* midrib of leaf prepared adsorbent in removal of methylene blue.
- To optimize batch adsorption parameters for enhanced MB removal from aqueous solution.
- To determine the kinetics of MB dye removal by barley bran and *Ensete ventricosum* midrib of leaf from aqueous solution.

1.4 Significance of study

This study encourages the usage of agricultural by-products which are available around us as low-cost, ecofriendly etc. Consequently, the study, provide information to search previously non-used agricultural by-product which are available around, as waste to remove dye such as: MB from wastewater. It could also provide initiation to search solution on problems existing, around us. The method will have benefits for the removal of MB dye from industrial wastewater for the reduction of contributors of environmental pollution. And this will provide an opportunity for the researchers with information to use agricultural by-product for the adsorption process.

2. REVIEW LITERATURE

2.1. Dyes

Dyes as colorful substances have been utilized by humans since 3500 BC in various applications using natural extracts of flowers, fruits, certain insects, etc.²³ These natural dyes constitute a very limited range of colors and are produced in low quantities. However, after the discovery of synthetic colors by W. H. Perkins in 1856, a wide range of dyes are used in various fields to color their product such as paper, leather, rubber, textile, plastics, etc.²³ Synthetic dyes are developed and have replaced natural dyes gradually in different industries because their molecules are stable and can resist degradation upon contact with water, detergents, or any other washing agents.²³ They are widely used in textiles, printing, rubber, cosmetics, plastics, leather industries to color their products leads to the production of a large quantity of colored sewage. They constitute a significant group of pollutants as several industries discharge a huge amount of wastewater containing various dyes into natural water bodies.²⁴

Dyes are chemical compounds that have a complex aromatic molecular structure that attach to fabrics or surface shells to create colour. These structures are present in stable dyes, are very difficult to treat, and have low biodegradability. The depolarization of waste water from the textile and manufacturing industries is a major challenge for environmental managers because dyes are soluble in water and produce very bright colors in water with acidic properties. The textile and manufacturing industries are expected to employ more than 10,000 products available on the market (worldwide) dyes and the consumption of dyes in textile industry is more than 1000 tones/year and about 10-15% of these dyes are discharged into waste streams as effluents during the dyeing processes.⁹ The discharge of synthetic dye effluent into the environment affects its ecological status, causing several undesirable changes. Highly colored effluents can be very harmful to receiving water bodies, as the dyes have high water solubility even at low concentrations.²⁵ MB is a very commonly used synthetic dye and, as a result, is often found in industrial wastewater.²⁶

2.2 Classification of dye

Generally, the dyes used in the textile industry are basic dyes, acid dyes, reactive dyes, direct dyes, azo dyes, mordant dyes, vat dyes, disperse dyes and sulfur dyes, where azo derivatives are the major class of dyes that are used in the industry today.¹⁰ There are several ways for classification of commercial dyes. It can be classified based on their chemical structure into azo, anthraquinone, indigoid, nitroso, nitro, and triarylmethane dyes. Sometimes, they are classified by their application or by their solubility in water.²³ However, the classification based on application is advantageous before considering chemical structures in detail because of the complexities of the dye nomenclature from this type of system.²⁷ Dyes are also usually classified based on their particle charge upon dissolution in aqueous application medium; such as cationic (all basic dyes), anionic (direct, acid, and reactive dyes), and non-ionic (dispersed dyes).²⁸

2.1.1 Cationic dyes

They are also called basic dyes due to the presence of positive ions in the molecule's structure. Basic dyes are water soluble and they are highly visible in water even at very low concentration.²⁹ Basic dyes consist of monoazoic, diazoic and azine compounds.³⁰ They are used to colour wool, silk, nylon, mod-acrylic and polyester materials.³¹ Cationic functionality is found in various types of dyes such as cationic azo dyes, methane dyes, anthraquinone, di- and tri-arylcabenium, phthalocyanine dyes, polycarbocyclic and solvent dyes.³⁰

2.1.2 Anionic dyes

They have negative ions due to the excess presence of the OH⁻ ions in aqueous solution. Anionic dyes are water soluble and they include acid dyes, azo dyes, direct dyes and reactive dyes.^{32,33} Reactive dyes attach to their substrates by a chemical reaction (hydrolysis of the reactive groups in the water) that forms a covalent bond between the molecule of dye and that of the fibre.^{30,34} Their removal is the most challenging task as they produce very bright colours in water and show acidic properties.³⁵

2.1.3 Reactive dyes

They contain reactive groups such as vinyl sulphone, chlorotriazine, trichloropyrimidine, and difluorochloropyrimidine that covalently bonded with the fiber during the dyeing process.^{30,34} Moreover, azo dyes represent the largest class of reactive dyes used in the textile industry followed by anthraquinone and phthalocyanine classes.³⁵ Azo dyes have the largest variety of dyes and under anaerobic conditions, the dye's linkage can be reduced to form aromatic amines which are colourless but can be toxic and carcinogenic. It was estimated that 130 of 3,200 azo dyes in use can form carcinogenic aromatic amines during degradation process.³⁰

2.3 Methylene blue dye

MB is a cationic dye with heterocyclic aromatic chemical compound, consisting of dark green crystals which has a molecular weight of 319.85 g/mol, with a molecular formula of (C₁₆H₁₈N₃SCl).³⁶ MB has a net positive charge and the structure of this dye is shown in Fig. 1 which is commonly used for dyeing of cotton, wool and silk. About 40% of the synthetic dyes like MB are toxic, mutagenic, and carcinogenic compounds that remained in industrial effluent and can cause severe public and environmental health problems.¹⁶ The accidental contact of MB with eyes can cause serious problems, being potentially responsible of permanent injury to humans and animals. In addition, its inhalation may cause breathing difficulties and its ingestion produces burning sensation & nausea. Due to this researcher give the attention to the removal of MB from waste water using activated rice husk, banana leaf, activated banana stem, broad been shell, groundnut shell, papaya leaf etc.^{37,38,39,40} Hence, the treatment of polluted streams containing this dye is a mandatory task to significantly limit these negative effects.⁴¹

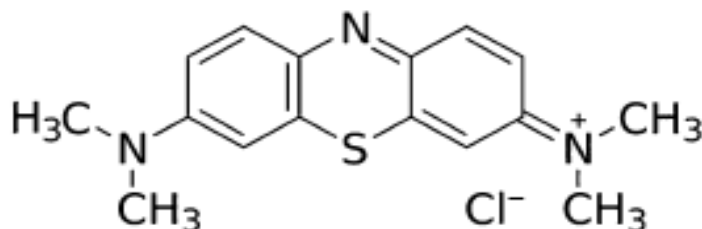


Figure 1 the structure of methylene blue dye⁴²

2.4 Textile industrial wastewater and Environmental Pollution

Pollution of natural waters with waste water arising from various industries has become a serious problem globally. Textile industries are large industrial consumers of waters as well as producers of wastewaters with the increased demand for textile products leading to increase in the generation of textile wastewater, which makes the textile industry one of the main sources of severe pollution problems worldwide. Industrial effluents represent an important source of chemical pollutants responsible for the water quality deterioration after their discharge into the environment. The major concern with color is its aesthetic character at the point of discharge with respect to the visibility of the receiving waters. Dyes are fundamentally organic compounds that bond chemically to the surface of the fabric to impart color which is termed as coloring agents. Effluents from the textile factory commonly contain high concentrations of organic and inorganic chemicals and are characterized by high Chemical Oxygen Demand (COD), Biological Oxygen Demand (BOD), Total Dissolved Solids (TDS), pH, Total Suspended Solids (TSS) values, and low dissolved oxygen (DO) value as well as strong color. Among those contaminants, the presence of colored substances in wastewaters means an important public concern due to their impacts.⁴³ The major pollutant in textile industrial wastewater is a dye which is highly visible even in small amounts (< 1 ppm) in the environment that can cause aesthetically unpleasant and toxicologically harmful. In general, the dye is toxic and hazardous chemicals in the environment, particularly in the water bodies and biosphere. In addition, the dye can cause dysfunction of the kidneys, reproductive system, liver, brain, and nervous system of human beings.

Approximately, 100,000 different types of dyestuffs are available on the global market but the annual production rate is about 7×10^5 t.^{16,40} About 2–50% of the dyestuffs quantity is released into the ecosystem as generated industrial wastewater due to various applications of basic and reactive dyes. However, this subject represents a major environmental problem due to environmental impact on the quality of water.⁴⁰ MB is the most commonly used substance for dyeing cotton, wood and silk. It can cause eye burns which may be responsible for permanent injury to the eyes of human and animals. Although MB is seen in some medical uses in large quantities, it can also be widely used in coloring paper, dyeing cottons, wools, coating for paper

stocks, etc. Though MB is not strongly hazardous, it can cause some harmful effects. Acute exposure to MB will cause increased heart rate, vomiting, shock, Heinz body formation, cyanosis, jaundice and quadriplegia and tissue necrosis in humans .⁴⁴.

2.5 Toxicity effects of dyes

The basic dyes have high color intensity and are highly visible even at very low concentrations. Most organic dyes pose acute challenges to the ecological system, as they are toxic and have carcinogenic properties, making water contaminated by dyes that inhibit aquatic life.⁴⁵ Dyes can affect photosynthetic activity in aquatic life because of the decrease in light penetration and may also be toxic to certain aquatic lives because of the presence of metals, aromatic etc.²⁸ In addition, dyes are also carcinogens, mutagens and teratogens in a variety of microbiological fish species. Additionally, it may also cause serious damage to humans such as dysfunction of the kidney, reproductive system, liver, brain and central nervous system. Similarly, anthraquinone-based dyes are more resistant to degradation and long-lasting colour in⁴⁶ effluents. The reagent dyes are soluble in water and 5 to 10% of the dyes go into the dye bath giving a highly colored effluent causing severe problems in the environment. 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.²⁸

2.6 Some Techniques to remove colors

Different physical, chemical and biological techniques have been developed to remove toxic dyes from wastewater and water reservoirs. The conventional methods for the treatment of colored wastewater are physical, chemical and biological treatments. However, these technologies have advantage and disadvantages. At large scale, most of these conventional methods are not applicable Because of the high cost and disposal problems as large amount of sludge is been generated at the end of the process.⁴⁷

Physical treatment: includes membrane-filtration process, reverse osmosis, electrolysis and adsorption techniques.³⁰ The major drawback in this technology, especially membrane filtration

is limited life time before membrane fouling occurs and as such the cost of periodic replacement must thus be included in any analysis of their economic viability. Among all the physical treatments, adsorption process has been reported to be the most effective method for water decontamination.^{48 49}

Chemical treatment: The major agents of chemical treatment of dye wastewater are coagulants/flocculants.^{30,48 49} It involves the addition of substances such as calcium, aluminum, or ferric ions in to the effluent, as such flocculation is induced.⁴⁸ Generally, chemical treatment has economic feasibility and efficiency, but major drawback is that, the cost of chemical are expensive and price fluctuation in market due to high demand and the rate at which chemicals are being produced. Moreover, even though it's efficient, the overall disadvantage of chemical treatment is the production of sludge at the final stage of the treatment which is pH dependent and brings about disposal problem.^{49 50}

Biological treatment: Biological treatment of wastewater is an alternative and most economical method as compare to physical and chemical methods. Biodegradation methods such as adsorption by (living or dead) microbial biomass, fungal decolorization, bioremediation systems and microbial degradation are commonly used in the treatment of industrial effluents.

Microorganism such as yeasts, bacteria, fungi and algae are able to accumulate and degrade different pollutants, but due to some technical constraints their applications is often restricted.^{49,}
⁵⁰ Biological treatment may be aerobic and anaerobic.^{30,50} But the major drawback is that, it requires substantial land area and is constrained by sensitivity toward diurnal variation as well as toxicity of chemicals.³⁰ The following table, show some removal techniques.

Table 1 some of treatment techniques of colour⁴⁷

Physical methods	Chemical methods	Biological methods
Adsorption	Fenton reagent techniques	Aerobic degradation
Ion exchange	Ozonation	Anaerobic degradation
Filtration	Photocatalytic methods	
Coagulation/flocculation		

2.7 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 organic dyes from wastewaters, but generation of sludge and high chemical cost are the major hurdle for the application of this technology at industrial scale.⁴⁷

2.8 Coagulation–flocculation

Coagulation and flocculation are an essential part of drinking water treatment as well as in wastewater treatment plants. The principle is to destabilize the dispersed solid particles in water by reducing their surface charge and gathering them to form larger particles. Its procedures can be divided into three steps: flash mixing, coagulation and flocculation. Firstly, coagulants are added with violent mixing. Then, the coagulants act to reduce or neutralize the surface charge of finely dispersed particles. After that flocculants and gentle mixing are used to bring the fine particles close together and to form larger particles. Sedimentation is usually applied to remove the larger particles afterwards. Various types of coagulants and flocculants have been used for wastewater treatment. Sometimes coagulant aids are also added to enhance the treatment process. Coagulants can be metal salts, polymers or some naturally occurring materials. In recent years, researchers have used calcium chloride, aluminum sulphate, polymeric aluminum sulphate, polyaluminium chloride and polyaluminium chloride sludge, and other naturally occurring materials as coagulants to remove dyes from water.⁴⁷

2.9 Ion exchange

Ion exchange is basically a reversible chemical process wherein anion from solution is exchanged for a similarly charged ion attached to an immobile solid particle. Ion exchange shares various common features along with adsorption, in regard to application in batch and fixed-bed processes and they can be grouped together as “sorption processes” for a unified treatment to have high water quality. Ion exchange has been fruitfully used too for the removal of colours. By far the largest application of ion exchange to drinking water treatment is in the area of softening, that is, the removal of calcium, magnesium, and other polyvalent cations in exchange for sodium. Various studies have been carried out using ion exchange for the removal of dyes.²⁷

2.10 Membrane Process

The membrane separation process is more, well known from industrial viewpoints for decolourization, of wastewater treatment and sea water desalination. In a membrane separation process, particles are isolated on the premise of their molecular size and shape with the utilization of extraordinarily composed semi-permeable membrane. The semi-permeable membrane is frequently a thin, nonporous or porous polymeric film, ceramic, or metal material or even a liquid or gas. The membrane must not dissolve, disintegrate or break. Reverse osmosis utilizes a semi-permeable membrane which removes total dissolved solids by applying pressure exceeding the osmotic pressure of the solution. In electro dialysis, anion selective and cation selective membranes are placed in alternate layers and electric field is applied to move the ions in water through these membranes. The shortcomings of these methods are that they are not selective and remove all or part of the dissolved ions present in the water, produce concentrated brine which must be disposed of properly to prevent pollution and are relatively energy intensive and consequently expensive to operate. Membrane fouling by colloidal material and certain dissolved salts is also another problem associated with these methods.⁵¹ Reverse osmosis, nanofiltration, dialysis, and electrodialysis are examples of this technique.⁵² The table below shows the advantage and disadvantages of physical and chemical treatments.

Table 2 advantage& disadvantages of physical & chemical treatment⁵⁰

Physical/chemical Methods	Method description	Advantages	Disadvantages
Fenton reagents	Oxidation reaction using mainly H ₂ O ₂ -Fe(II)	Effective decolorization of both soluble and insoluble dyes	Sludge generation
Ozonation	Oxidation reaction using ozone Gas	Application in gaseous state: no alteration of volume	Short half-life (20 min)
Photochemical	Oxidation reaction using mainly H ₂ O-UV	No sludge production	Formation of by-products
NaCl	Oxidation reaction using Cl ⁺ to attack the amino group	Initial and acceleration of azo bond cleavage	Release of aromatic Amines
Electrochemical destruction	Oxidation reaction using Electricity	Breakdown compounds are nonhazardous	High cost of electricity
Activated carbon	Dye removal by adsorption	Good removal of a wide variety of dyes	Regeneration difficulties
Ion exchange	Ion exchange resin	Regeneration: no adsorbent loss	Not effective for all dyes
Electrokinetic coagulation	Addition of ferrous sulphate and ferric chloride	Economically feasible	High sludge production
Membrane filtration	Physical separation	Removal of all dye types	Concentrated sludge Production

2.11 Adsorption Process

Adsorption is a surface phenomenon with common mechanism for organic and inorganic pollutants removal. When a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure, liquid–solid intermolecular forces of attraction cause some of the solute molecules from the solution to be concentrated or deposited at the solid

surface. The solute retained (on the solid surface) in adsorption processes is called adsorbate, whereas, the solid on which the solute is retained is called as an adsorbent. This surface accumulation of adsorbate on adsorbent is called adsorption.⁵³ This creation of an adsorbed phase having a composition different from that of the bulk fluid phase forms the basis of separation by adsorption technology. The exact nature of the bonding depends on the details of the species involved, but the adsorption process is generally classified as physisorption (characteristic of weak Van der waals forces) or chemisorption (characteristic of covalent bonding).⁵³ Adsorption has great potential for MB removal because of its cost effectiveness, ease of operation, high removal capacities, and ability to reuse the adsorbent. These characteristics encourage researchers to continue to explore adsorbents for additional potential. Figure 2 shows the schematic of the detailed mass transport in the adsorption process.⁵²

Adsorption is a three-step process

- (a) External mass transfer, i.e. the transfer of MB dye from aqueous solution to the external surface of the adsorbent, which is called molecular diffusion or film diffusion;
- (b) Adsorption of MB dye onto particle surfaces;
- and (c) Intra-particle diffusion, i.e. the transfer of adsorbed MB dye molecules to the internal surfaces of the adsorbent particles

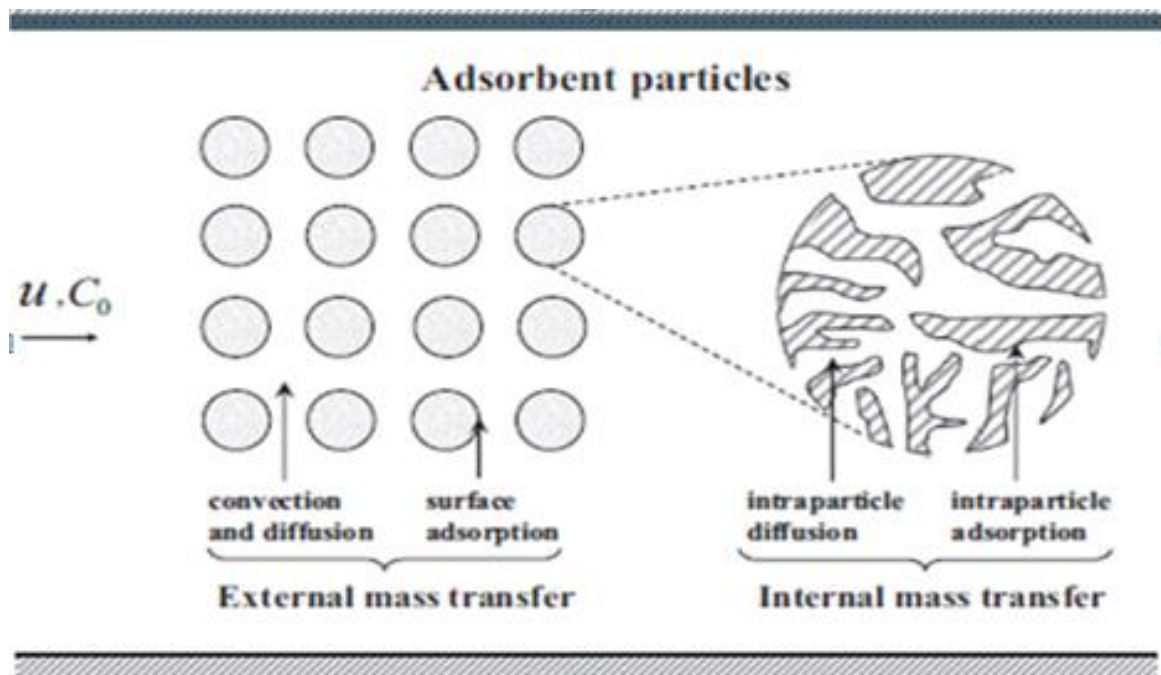


Figure 2 schematic expression for the three steps of adsorption process⁵⁴

2.11.1 Modes of Adsorption

The adsorption of molecules to a substrate is often described as Physisorption or chemisorption depending on the strength of the interaction between the substrate and adsorbate. The two modes are schematically shown below in Figure 3

Physisorption is a broad term that describes all weak electrostatic interactions including, Van Der Waals interactions, dipole-dipole and London forces and have a low heat of adsorption that is only slightly greater than heat of sublimation of the adsorbate.⁵⁵ The formation of these weak physisorbed interactions between the adsorbate and substrate typically range from 0.2 to 4.0 kJ/mol.^{56,57} These bonds are considered the weakest of interactions and can be easily broken.

Chemisorption occurs when the adsorbate becomes covalently bound to the substrate via the sharing or transfer of electrons, with interactions that are typically two orders of magnitude stronger than that of physisorbed species. The formation of chemisorbed substrate-adsorbate bonds can originate from physisorbed interactions and hydrogen-bound species, making the rate of condensation dependent upon the rates of both physisorption and chemisorption.^{55,56,57}

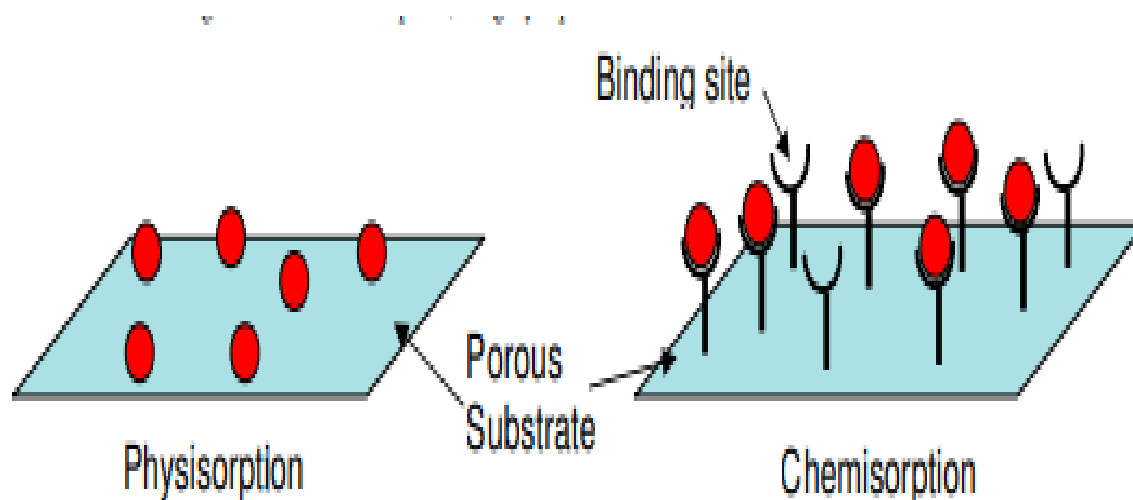


Figure 3, schematic expression for the two modes of adsorption⁵⁶

2.11.2 Activated carbon

The most commonly used adsorbent is activated carbon a substance which is quite similar to common charcoal. Actually, the active carbon is much more efficient because of its high porous character. The high porous character is generated by treating carbon to steam and high temperature (1300°C) with or without oxygen in the presence of inorganic salts (physical method). The carbon may be of petroleum coke, bituminous coal, lignite, wood products, and coconut/peanut shells. At high temperature, parts of carbon are oxidized in CO₂ and steam. The gases are evacuated and micro fractures and pores are generated in the carbon structure. It dramatically increases the carbon surface area, making a useful material for the removal of contaminants. In some cases, the carbonaceous matter may be treated with a chemical activating agent such as phosphoric acid, zinc chloride and the mixture carbonized at an elevated temperature, followed by the removal of activating agent by water washing (chemical method). Active carbon uses the physical adsorption process, whereby Vander-Waals attractive forces pull the solute contamination out of the solution and onto its surface.

The efficiency of the adsorption depends on the nature of the carbon particle and pore size, surface area, density and hardness as well as the nature of the contaminants (concentration, hydrophobicity, polarity and solubility of the contaminant and contaminant attraction to the carbon surface). There are two different forms of activated carbon in common use, granular activated carbon (GAC) and powdered activated carbon (PAC). Physically, the two differ as their names suggested by particle size and diameter. The reusability of the carbon is done primarily with the GAC as PAC particles are too small to be reactivated.⁵⁸

2.12 Factors affecting adsorption

Many factors affecting the adsorption process such as: Contact time, pH of the solution, initial concentration, nature of adsorbate, shaking speed & temperature.

2.12.1 Contact time

Independent of other parameters, contact time plays a vital role in the adsorption process. The adsorption of adsorbate increases with increasing contact time until equilibrium is achieved. Only very slight improvement occurs after equilibrium is achieved. This occurs because the active sites of the adsorbent are vacant during the initial stage and adsorption can take place rapidly, but the number of remaining active sites of the adsorbent are decreased after equilibrium and these sites are occupied with difficulty due to the repulsive forces between the solute molecules on the solid and the bulk phase.⁵²

2.12.2 pH of the solution

pH is a measure of acidity or basicity of an aqueous solution. Solution pH influences adsorption process by affecting both aqueous chemistry and surface binding sites of the adsorbent. At low pH values, surface of the adsorbent becomes positively charged because of protonation of the functional groups on adsorbent surface.⁵⁹ So adsorption of cationic adsorbate decreases because of electrostatic repulsion between adsorbate and protonated adsorbent. As the pH of the dye solution increases, deprotonation of positively charged groups on the adsorbent occur. Electrostatic attraction between negatively charged sites on the adsorbent and adsorbate cations cause increase in adsorption.^{59,60} As a result, the cationic species adsorption increases and anionic species adsorption shows a decrease.³⁰

2.12.3 Initial concentration

A given mass of sorbent material can only adsorb a fixed amount of dye hence the initial dye concentration of an effluent is one of important factor to be studied. The effect of dye initial concentration can be conducted by shaken adsorbent-adsorbate solution until equilibrium using fixed the adsorbent dosage with different initial dye concentration for different time intervals. The effect of increment in dye initial concentration will increase the adsorbent loading capacity.⁶¹

2.12.4 Adsorbate

The important factors affecting the adsorption process is nature of adsorbate, the nature of adsorbate affects their physical properties, as adsorption increases by increasing the molecular weight of the adsorbate material. They are also affected by their chemical properties in the existence of active groups in the composition of the adsorbate material, and the capacity of adsorption increases by increasing the concentration of the adsorbate material.⁶⁰

2.12.5 Effect of agitation speed

In the batch adsorption process, agitation speed plays a significant role in influencing the external boundary film and the distribution of the solute in the bulk solution. The influence of agitation speed on adsorption of dye can be carried out by varying the speed of rotation of adsorbate–adsorbent solution and samples withdrawn at different intervals, by keeping other parameters constant. Generally, removal of dyes increases with increase of agitation speed. Increasing agitation speed decreases the boundary layer resistance of the transfer of adsorbate molecules from the bulk solution to the adsorbent surface. Due to this, reason the adsorbate is forced towards the adsorbent surface and it leads to an increase in the diffusion of adsorbate into the surface of the adsorbent.⁵

2.12.6 Temperature

The effect of temperature varies according to the type of adsorption and the nature of the adsorbent and adsorbent. The adsorption of heat is increased by the exothermal process; in the endothermal process the contrary is achieved. The adsorption increases with higher temperatures, where the kinetic energy of the adsorbed molecules increases and thus increases its ability to enter the solid phase pores and their rapid spread, and this may be within a specific range of temperatures.⁶⁰

3. MATERIALS AND METHODS

3.1 Materials

3.1.1 Chemicals

Powder of MB (Nice), HCl (37% Riedel-deHaen, Germany), NaOH (90%, BDH, England), NaCl (s.d fine-CHEM Limited) and distilled water were used in this work for different purposes during laboratory work. Powder of MB was used to prepare MB dye solution as modeling contaminant with distilled water. HCl (37% Riedel-deHaen, Germany) & NaOH (90%, BDH, England), were used to pH adjustment. NaCl (s.d fine-CHEM Limited) was used for determination of pH_{pzc} & surface area determination. Distilled water was used for preparation of all solutions and dilutions, during the laboratory work. Working standard solutions of lower concentration were prepared by dilution method from 1000 mg/L standard solution.

3.1.2 Instrumentations

UV-Vis Spectrophotometer (Model SPECORD 200/PLUS, analytikjena, Germany), pH meter (Bante instrument, pH 902P, USA), thermostat water bath (Model GrantGLS400, England), FTIR spectrophotometer (Model Perkin Elmer Spectrum two), digit balance, oven (mode GENLAB WLDNES, England) were used through this work.

3.1.3 Preparation of different adsorbents for screening

Before the selections of the utilized two adsorbents, a number of locally available agricultural by-products & wastes namely Barley bran (BB), *Erythrina abyssinica* also locally called Korch (KO) Pea shell (PE), Tella residue (TL), Avocado kernel (AV), Coffee residue (CF), Charcoal (CH), Ash (AS) & *Ensete ventricosum* midrib of leaf (EVML) also called False banana (FB) were collected. Then, each was washed with tap water followed by distilled water, dried at room temperature, crushed with pestle & mortar, sieved with 11.81 inch particle size mesh and stored

in dry container for further screening study. The pretreatment steps are given in detailed for the selected two adsorbents in section 3.1.5.

3.1.4 Collection of adsorbents

In this study, barley bran and *Ensete ventricosum* (False Banana) midrib of the leaf were collected from Jimma town Ajip area.

3.1.5 Preparation of adsorbents

3.1.5.1 Preparation of Barley bran

The collected Barley bran was washed with tap water followed by distilled water and dried in air at room temperature. Then, it was crushed with mortar and pestle and sieved to particle size of 11.81 inches. Finally, it was stored in dry and air tight container for further use in MB dye adsorption studies.

3.1.5.2 Preparation of *Ensete ventricosum* midrib of leaf

The *Ensete ventricosum* mid rib of leaf required in this study was obtained locally from *Ensete ventricosum* leaf that was used during baking of traditional bread. The precursor was first washed to remove dirt particles from its surface, cut into small pieces and was dried in sunlight and again washed with distilled water and dried in an oven at 80 °C until complete drying reach. The dried sample was then ground and sieved to mesh sizes 11.81 inches. Then, 50 g of the adsorbent sample was added in to reagent bottle containing 250 mL of 0.1M HCl acidified distilled water and shaken for 6 h to remove the colour of adsorbent and decanted wisely. Then, the adsorbent was washed (3-5) times repeatedly to remove acidity. Then, the adsorbent was dried overnight in the oven at 80 °C and stored in an air tight container for further MB adsorption studies.

3.1.6 Characterization of adsorbents

Barley bran and *Ensete ventricosum* midrib of leaf prepared adsorbents surface functional groups were characterized by FTIR (Model Perkin Elmer Spectrum two) in the scanning range of 4,000–400 cm^{-1} . The pH of the adsorbents was measured using pH meter (Bante instrument, pH 902P, USA). The surface area of adsorbents was also determined by using the Sear method.⁶²

3.1.6.1 Proximate analysis

Moisture content, ash content, volatile matter and fixed carbon content of the adsorbents were also studied.

3.1.6.2 The moisture content

The thermal drying method was used to determine the moisture content of agricultural by-product prepared adsorbent Barley bran and *Ensete ventricosum* midrib of leaf. The dried adsorbent samples of 1.0 g each was added into a crucible which was placed in an oven at a constant temperature of 110 °C for 2 h. Then, the sample was cooled in a desiccator to room temperature and weighed. Then, the difference between the initial and final mass of Barley bran and *Ensete ventricosum* midrib of leaf prepared adsorbent were considered to be the moisture content of the material.⁶³ The moisture content in percentage (%) was computed using Eq. (1).

$$MC(\%) = \frac{W_1 - W_2}{W_1} \quad 1$$

Where MC is the moisture composition of barley bran and *Ensete ventricosum* midrib of leaf prepared adsorbents, which are described in percentages, W_1 is the weight of Barley bran and *Ensete ventricosum* midrib of leaf prepared adsorbents before the application of thermal heating (g) and W_2 is the weight of the adsorbent samples after thermal drying (g).

3.1.6.3 Volatile matter

For volatile matter determination, 1 g of Barley bran and *Ensete ventricosum* midrib of leaf prepared adsorbents were placed in a preheated crucible and incinerated in the muffle furnace at 800 °C for 8 min with no contact of air under the standardized conditions.¹⁶ The adsorbents samples were then cooled in the desiccator and weighed. Finally, the volatile matter of Barley bran and *Ensete ventricosum* midrib of leaf prepared adsorbent were calculated using Eq. (2).

$$VM(\%) = \frac{W_1 - W_2}{W_1} \times 100 \quad 2$$

where VM (%) is the volatile matter of the Barley bran in percentage, W_1 (g) is the weight of the Barley bran and *Ensete ventricosum* midrib of leaf prepared adsorbents before heating the sample, and W_2 (g) is the weight of Barley bran and *Ensete ventricosum* midrib of leaf prepared adsorbents after heating.

3.1.6.4 Ash content

The ash content of Barley bran and *Ensete ventricosum* midrib of leaf were determined by the thermal drying method. Empty crucibles were preheated and weighed. Both Barley bran and *Ensete ventricosum* midrib of leaf prepared adsorbents of 1 g were added in these preheated crucibles and placed in the furnace which was ignited at 500 °C for 4 h. Then, the adsorbent samples were cooled at room temperature in the desiccator. Finally, the adsorbent samples were weighed and the ash content was calculated using⁶⁴ Eq. (3).

$$AC(\%) = \frac{W_1}{W_2} \times 100 \quad 3$$

where AC is the ash content of the Barley bran and *Ensete ventricosum* leaf mid-part prepared adsorbents, in percentage, W_1 (g) is the weight of the Barley bran and *Ensete ventricosum* midrib of leaf prepared adsorbents before the heating process and W_2 (g) is the weight of the ash after ignition process.⁶⁵

Finally, the fixed adsorbent carbon (FC) of Barley bran and *Ensete ventricosum* midrib of leaf prepared adsorbents were calculated from the summation of all the percentages of moisture content, ash content, and volatile matter content which was subtracted from 100%. Eq. (4) was applied to calculate the fixed adsorbent materials of the Barley bran and *Ensete ventricosum* midrib of leaf prepared adsorbent.⁶⁴

$$FC\% = 100\% - (MC\% + VM\% + AC\%) \quad 4$$

3.1.6.5 Study of pH of Adsorbents

1.0 g of Barley bran & *Ensete ventricosum* midrib of leaf was weighed and transferred into a 500 mL beaker and then 100 mL of distilled water was added and stirred for 1 h using magnetic stirrer. The mixture was allowed to stabilize and then the pH was measured.⁶²

3.1.6.6 Surface area determination

Sears' method was used for the determination of surface area of the adsorbents.^{66,62} 1.0 g of the each adsorbent was weighed. Then, 30 g of NaCl was added and the volume was made up to 40 mL with distilled water. The pH was raised from 4 to 9 with 0.1 M NaOH. The experiment was carried out in triplicate for each adsorbent. Then, the surface area (S) was calculated from equation Eq. (5)

$$S(m^2/g) = 32V - 25 \quad 5$$

V (ml) is the volume of base (0.1M NaOH) required to rise pH of adsorbents mixture 4-9

3.1.6.7 Studies on point zero charge (pHPZC)

In pHPZC determination, 0.01 M and 0.1 M NaCl solutions were prepared and their pH was adjusted in the range of 3–12 by adding 0.1 M NaOH or 0.1 M HCl. Then, 40 mL of 0.01 M NaCl and 0.1M NaCl each was put in polyethylene plastic vials containing 0.1 g of the prepared

Barley bran adsorbent, separately. These, vials were put on a horizontal shaker at 200 rpm for 48 h and final pH of the solutions was measured by using pH meter. Graphs were then plotted for pH final versus pH initial.⁴⁴ The same procedure was followed for determination of pH_{PZC} for the adsorbent prepared from *Ensete ventricosum* midrib of leaf.

3.1.6.8 Surface Functional Group Determination

The surface functional groups of the Barley bran and *Ensete ventricosum* midrib of leaf prepared agricultural by-product adsorbents, before and after adsorption, were characterized by FTIR. The spectra of samples were recorded within range of 400 – 4000 cm^{-1} .⁴⁴ The transmission spectra of the samples were recorded using the KBr pellet at Jimma University material & engineering campus.

3.2 Screening tests

The preliminary screening experiments were performed to select adsorbents with better sorption capacity for MB removal. For this purpose, twelve (12) different adsorbents namely Barley bran (BB), *Erythrina abyssinica* also called Korch (KO), Pea shell (PE), Tella residue (TL), Avocado kernel (AV), Coffee residue (CF), charcoal (CH), Ash (AS), *Ensete ventricosum* midrib of leaf (EVML) also known as False banana (FB), activated korch (MKO), and activated avocado kernel (MAV) were tested for the sorption of MB. The testes were carried out under similar condition and each in duplicate, where the polyethylene containers labeled with the name of each adsorbent with 40 mL of 10 mg/L of MB solution and each containing 0.1 g of the adsorbent is agitated on shaker for 24 h. Consequently after selection of the two adsorbents, their uptake to anionic (methyl orange (MO), Erichrome black T (EBT)) & cationic dye (malachite green (MG), brilliant green (BG) was checked in addition to MB on their natural pH & contact time 24 h using the same concentration of dye (10mg/L & 20mg/L) for each of them in a duplicate .

3.3 Adsorption study

All batch adsorption studies were conducted in a set of 50 mL of polyethylene plastic containers containing 0.1 g of adsorbent and 40 mL of MB solutions with the initial concentrations of 10 mg/L without adjusting pH. The containers were capped and agitated in an isothermal water bath shaker at 200 rpm and 25 °C until the equilibrium was reached. Sample solutions were withdrawn at equilibrium to determine the residual concentrations. All samples were centrifuged with the speed of (2500 rpm) prior to analysis to minimize the interference of fine adsorbents during the analysis. The concentrations of MB dye in the supernatant solutions before and after the adsorption process were analyzed using a UV–vis spectrophotometer at its maximum wavelength of 665 nm.⁶⁷ Each experiment was performed in duplicate. The adsorption efficiency (%) of the adsorbents and MB uptake at equilibrium, q_e (mg/g) for selected adsorbents (Barley bran & *Ensete ventricosum* midrib of leaf) were calculated by using Eqs 6 and 7, respectively.

$$\text{Percentage removal (\%R)} = \frac{[C_o - C_e]}{C_o} \times 100 \quad 6$$

$$\text{Adsorption capacity } (q_e) = \frac{(C_o - C_e) * V}{m} \quad 7$$

Where:

C_o is initial methylene blue dye concentration

C_e is residual methylene blue dye concentration at equilibrium

m is mass of the adsorbent and

V is volume of the solution

Experiments were carried out to evaluate the adsorption parameters best function by varying one parameter while keeping other parameters constant. The effect of major parameters like contact time, pH, and initial MB concentration 10 mg/L were studied.

3.3.1 Contact time

In order to study the shaking time, 40 mL of 10 mg/L solution of the MB was taken in different polyethylene containers for the two adsorbents, Barley bran (BB) & *Ensete ventricosum* midrib of leaf (EVML), separately in duplicate. Pre-determined amount (0.1 g) of BB & EVML was added in each polyethylene container and was shaken in the water bath shaker at 200 rpm for various times from 5 min to 24 h & 1 min to 2 h. Then solution was centrifuged, filtered, and the absorbance was measured at λ_{\max} (665 nm) and the amount of MB adsorbed per gram of the adsorbent was calculated using the Eq (7).

3.3.2 Effect of pH

The effect of solution pH on the adsorption of MB on the adsorbent was studied by varying the solution pH from 2 to 12, which was prepared by adjusting the pH to the desired pH value by adding either 0.1 M NaOH or 0.1 M HCl. Then, 0.1 g of the adsorbents were added to the test solutions, separately and shaken for selected optimum time, 4 h for BB and 1 h for EVMRL, respectively. The experiments were done in duplicate and the residual MB concentration was analyzed in each experiment.

3.3.3 Effect of initial MB dye concentration

To investigate the effect of initial MB dye concentration, experiments were conducted by varying MB concentrations from 10 to 200 mg/L keeping adsorbent dose 0.1g and contact time 4 h for BB and 1 h for EVMRL, respectively.

3.4 Data analysis

3.4.1 Adsorption Kinetics

Pseudo-first-order (PFO) and pseudo-second-order (PSO) adsorption kinetics model were employed to evaluate the kinetics of the adsorption of MB dye using constant adsorbent dose of

0.1g and 10 mg/L of initial MB concentration. Residual MB concentration was measured at different time intervals (5 min to 24 h) & 1 min to 2 h for BB & EVML adsorbents, respectively by taking samples solution periodically. The non-linear expressions of the pseudo-first-order and pseudo-second-order models are given in Eq. (8) and (9), respectively

$$q_t = q_e (1 - \exp^{-k_1 t}) \quad 8$$

$$q_t = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad 9$$

where, k_1 (min^{-1}) is pseudo-first-order rate constant, k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) is pseudo-second-order rate constant, q_t and q_e are the adsorption capacity (mg/g) at any time t (min) and at equilibrium, respectively.⁴⁷ The adsorption affinity of the two adsorbent was assessed to have the information about the adsorption rate of the two adsorbent using the Eq. (10).

$$V_0 = K_2 q_e^2 \quad 10$$

To predict the potential rate-limiting steps in the adsorption processes, intra-particle diffusion models (Weber Morris model)⁶⁸ was also used Eq.(11) to analyze adsorption kinetics data.

$$q_t = k_p t^{0.5} + c \quad 11$$

Where, q_t is the amount of MB adsorbed on the adsorbents (mg/g) at time t , k_p ($\text{mg}/(\text{g} \cdot \text{min}^{0.5})$) is the intra-particle diffusion rate constant; and C (mg/g) is the intercept of the intra-particle diffusion model. If the rate-limiting step of MB removal is the intra-particle diffusion, the plot of q_t against the $t^{1/2}$ should be a straight line and pass through the origin.³⁷

3.4.2 Adsorption Isotherms

Adsorption isotherms were determined using the prepared BB & EVML adsorbents independently, at room temperature. Experimental data were obtained by mixing a constant

adsorbent dosage (0.1g) with a series of increasing MB concentration from 10 to 200 mg/L and 10 to 100 mg/L for BB & EVML adsorbents, respectively. The mixtures were agitated for 4 h and 1 h to ensure that equilibrium is reached for both adsorbents and then, the residual MB was determined after centrifuges. The equilibrium experimental data of MB adsorption were modeled using the non-linear forms of the Langmuir and Freundlich⁶⁹ isotherm models. The Langmuir isotherm assumes monolayer adsorption with adsorption can only occur at a finite number of localized sites that are identical and equivalent.⁶⁹ The non-linear form of Langmuir isotherm equation could be written as:

$$q_e = \frac{Q_{\max} b C_e}{(1 + b C_e)} \quad (12)$$

Where q_e (mg/g) are the amount of MB adsorbed per unit mass of sorbent) C_e (mg/L) is equilibrium concentration in solution or unabsorbed MB concentration in solution (mg/L), Q_{\max} (mg/g) is the maximum adsorption capacity based on the Langmuir equation; and b (L/mg) is the Langmuir constant⁷⁰. R_L is the essential characteristics of Langmuir isotherm can be expressed in terms of the dimensionless constant, separation factor or equilibrium parameter⁷¹, which is defined by the Eq. (13).

$$R_L = \frac{1}{1 + K_L C_o} \quad 13$$

Where, C_o (mg/L) is the initial MB concentration; and b (L/mg) is the Langmuir constant. The R_L values indicate the type of adsorption as either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).^{71,72}

Freundlich isotherm is a relationship describing the non-ideal and reversible adsorption.⁶⁹ The model assumes multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. The non-linear form of Freundlich adsorption isotherm is given in Eq. (14).

$$q_e = K_F C_e^{1/n} \quad (14)$$

Where, q_e (mg/g) is the equilibrium adsorption capacity; K_F ($\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$) is the adsorption coefficient based on the Freundlich equation; $1/n$ is the adsorption intensity based on the Freundlich equation.

In the Freundlich equation, the heterogeneity factor ($1/n$) is related to the capacity and intensity of the adsorption n is a measure of the deviation from linearity of adsorption. Its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of $n = 1$, the adsorption is linear; $n < 1$, this implies that adsorption process is chemical and $n > 1$ indicates physical process is a favorable and C_e is the equilibrium concentration (mg/L). The value of $1/n$ ranges from 0 to 1 and the closer this value to zero, the more heterogeneous the adsorbent surface.

3.4.3 Statistic test

The chi-squared test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from models. Besides the coefficient of determination, the nonlinear chi-square (χ^2) statistic test was used to identify the best model fit to the observed experimental data. The χ^2 is computed using Eq. (15) as described by ⁷³

$$\chi^2 = \sum (q_e - q_{e,cal})^2 / q_{e,cal} \quad (15)$$

Where $q_{e,cal}$ is the equilibrium adsorption capacity calculated from the model; and q_e is the experimental equilibrium adsorption capacity. A small χ^2 value indicates similarity of data between the modeled and the experimental data, whereas a larger χ^2 value implies variation between the modeled and experimental data.⁷³

3.5 Quality control

In order to determine the accuracy of the data collected, all batch tests were recorded and mean \pm SD values only were reported. Blank tests were carried out at the same time. All polyethylene bottles and laboratory items were washed with detergent, followed by repeated rinse with distilled water and soaked overnight in 10% HNO₃, then rinsed three times with distilled water and dried.

Experimental analyses were carried out using MB containing a working solution prepared from intermediate solution. The accuracy of the analytical techniques was verified by determining the standard deviation (SD) of the filtered sample analysis. Regression and chi-square analyses of experimental data were performed using Original 8 software. The correlation coefficient (R^2) and standard error in the evaluation of parameters were determined to characterize the accuracy of the optimal analysis of the data fit.

3.6 Adsorption cycle

The test of adsorption cycle on BB & EVML were done by keeping their optimum adsorption operating conditions like contact time & pH at constant initial concentration 10 mg/L of MB dye. The experiments were done by carefully decanting the supernatant MB solution & then leaving the adsorbent for some time in order to get dry before each cycle after the first cycle for both adsorbents (BB & EVML). The adsorption cycles were determined without desorption until the adsorption efficiency of adsorbent declines significantly.

4. RESULT & DISCUSION

4.1 Screening of locally available adsorbents

The preliminary screening experiments have been done to select adsorbents having high MB removal efficiency. For this purpose, twelve (12) different adsorbent namely Barley bran (BB), *Erythrina abyssinica* also locally known as Korch (KO), Pea shell (PE), Tella residue (TL), Avocado kernel (AV), Coffee residue (CF), charcoal (CH), Wood ash (AS), *Ensete ventricosum* midrib of leaf (EVML) also called False banana (FB), activated korch (MKO), activated False banana (MFB), and activated avocado (MAV) have been tested for the sorption of MB under similar condition. The adsorptive removal of MB is calculated and results are shown in Figure 4. As shown in Figure 4, most of the adsorbents, except wood ash and charcoal, were effective in removal of MB from aqueous solution. MFB & MKO removal efficiency were slightly higher than BB & EVML (FB). However, the modification of the two adsorbent, MFB & MKO were based on chemical specially, Sulfuric acid which made low pH of adsorbent and also there might be the leaching of this chemical during the adsorption process. The BB & EVML were natural & among the better adsorbent resulting high removal of MB 96.3 % & 97.4%, respectively. To the best of our knowledge, there is no any previous report on use of BB & EVML adsorbents for removal of dyes from aqueous solution. Moreover, the two adsorbents exhibit high MB removal efficiency, locally available, easy preparation, & relatively low cost. Therefore, BB & EVML were selected for further studies.

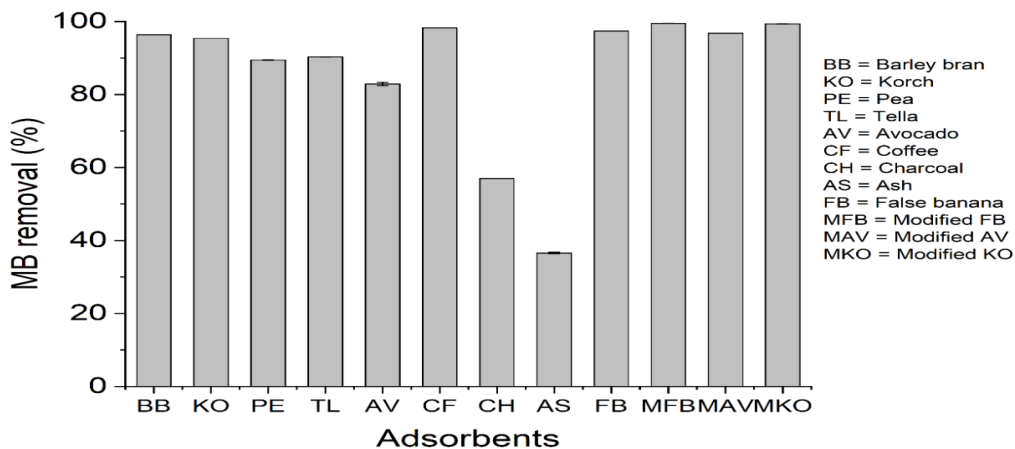


Figure 4 screening of sorptive removal of MB by different locally available adsorbents

On the other hand, the adsorptive capacity of adsorbents was assessed for an anionic dye methyl orange (MO), Erichrome Black T (EBT) and cationic dye malachite green (MG) and brilliant green (BG) with two different concentrations (10 mg/L and 20 mg/L) in their natural (non-adjusted) pH 5.62 & 5.68, 5.59 & 5.53, 4.82 & 4.55, 4.99 & 4.26, respectively for the mentioned dyes and concentrations. Here, the adsorption process of adsorbents BB & EVML on anionic dyes & cationic dyes were different. As studied in the adsorption process, the adsorption capacity of the two adsorbents BB & EVML were low for anionic dyes & high on cationic dyes Figure 5 A, B, C, D & E). These were because of the electrostatic interaction of adsorbent surface and adsorbate. As the experiment, result shows in Figure 5 below, the two adsorbent(BB & EVML) were favorable for cationic dye and unfavorable for anionic dye ^{77,78} These also provide supplementary information about the electrostatic interaction of adsorption processes between adsorbents & adsorbate used in this study. Therefore, the mechanism of dye removal was explained via the electrostatic interaction between the negatively charged surface of the adsorbents and the positively charged methylene blue dye adsorbat.⁷⁸

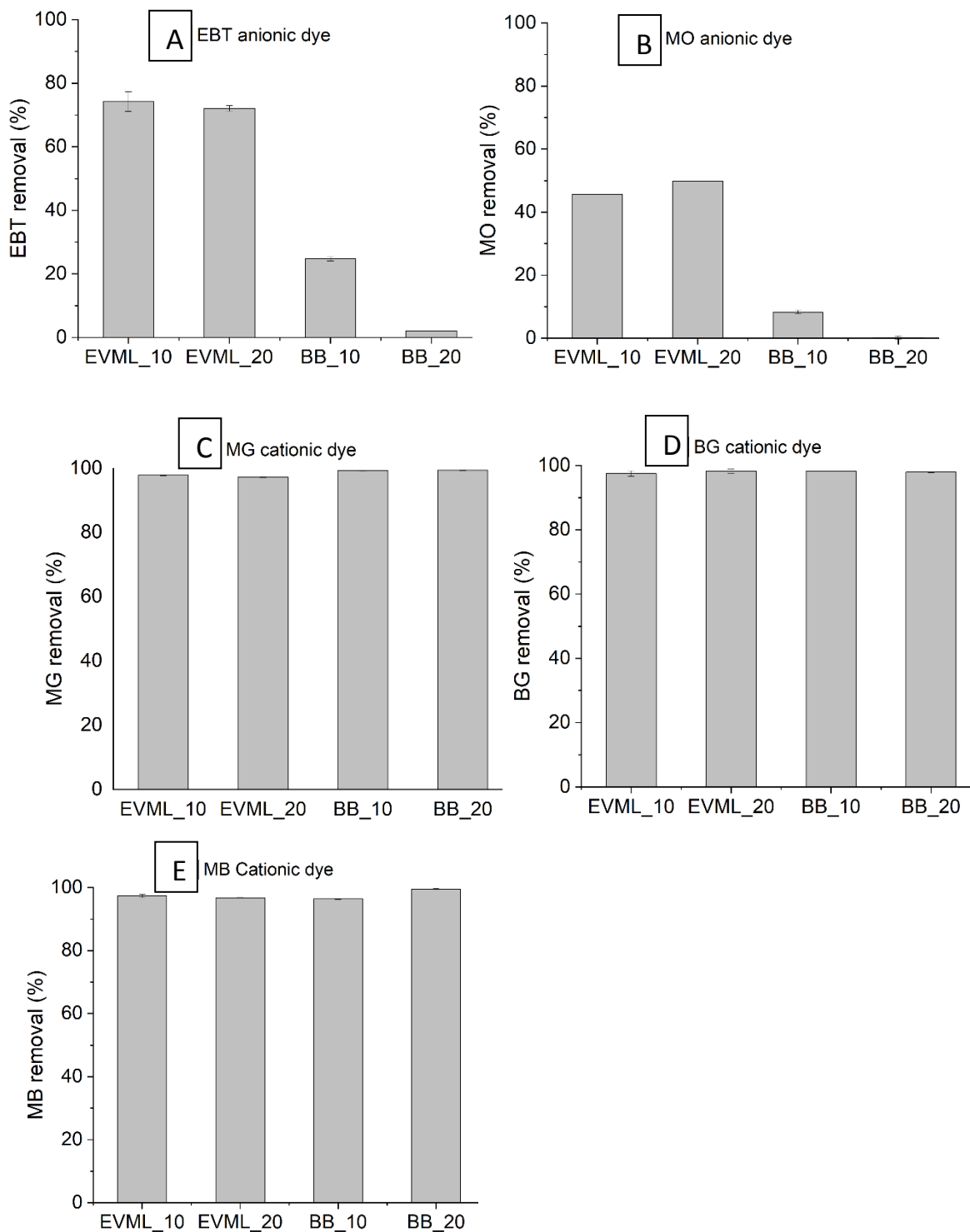


Figure 5 Test of adsorption performance of BB & EVML for (A) EBT, (B) MO, (C) MG, (D) BG & (E) MB dyes at initial concentration of 10 mg/L & 20 mg/L for each case

4.2 Characterization of adsorbent

4.2.1. Proximate Analysis

Proximate analysis was done for the prepared BB & EVML to analyze their different physicochemical characteristics such as moisture content, ash content and volatile matter. Table 3 summarizes some of the physico-chemical characteristics of BB & EVML. The moisture content of the BB & EVML was found to be equal & slightly lower than the value reported for raw fox nutshell.⁷⁴ From the experiment result moisture content of BB & EVML were 3% & 4%, respectively and has the influence in the adsorption efficiency when it's content become high. This happened due to the coverage of active binding sites with moisture which protect the attractive electrostatic interaction between adsorbate & adsorbent. The ash content is a reflection of the amount of inorganic substituent present. Here the % ash content of the adsorbent BB & EVML was 10.20% & 8.8% respectively. Volatile matter is due to the residual organic compounds in the prepared BB & EVML adsorbent with percentage content 72.4% & 76.7% respectively. The volatile matter obtained was higher than the value reported in the literature.⁷⁴ The percentage of fixed carbon of BB & EVML adsorbents were 14.4% & 10.5% respectively.

Table 3 physiochemical properties of BB & EVML adsorbents

Parameter	BB	EVML
Moisture content %	3	4
Ash %	10.2	8.8
Volatile	72.4	76.7
Fixed carbon	14.4	10.5
Surface area(m ² /g)	26.2	20.34
pH	6.47	4.53

4.2.2 Surface area determination

The surface area of the prepared BB & EVML adsorbents, were determined using the Sear Method of surface area determination. The obtained data are given in Table-3. The surface areas

for both the prepared adsorbents are relatively higher compared to the surface area reported in literature.⁸

4.2.3 Point of zero charge

Adsorption of MB on the adsorbent surface is primarily influenced by the surface charge on the adsorbent, which in turn is influenced by the pH of the solution. The pH at which the zero surface charge called the zero charge point is generally used to quantify or define the electrokinetic properties of a surface. The pH value used to describe pzc only for systems where H^+/OH is the ion analysis determining the potential. For this, the knowledge of pH_{pzc} would allow hypotheses to be made about the interaction between functional groups on carbon matter with ionic species in solution during contaminant adsorption. Because of the presence of OH-functional group, cationic dye adsorption is favored, when the pH of a solution is higher than the pH_{pzc} value, the adsorbent surface has a negative charge as the acidic groups are deprotonated and may therefore preferably interact with cationic species. In these circumstances, adsorbents may be an attractive strategy for absorbing cationic dyes from aqueous solutions.^{43,75} The pH_{pzc} BB & EVML were determined by plotting final pH-initial pH value ($pH_f - pH_i$) versus the initial pH value (pH_i) as displayed in Figure 6 (A) & (B). As observed the adsorbent surface charge could be positive at the pH less than pH_{pzc}. In this study, the pH_{pzc} of the BB & EVML adsorbents resulted to be 5.9 & 3.5, respectively. Therefore, the adsorption processes of cationic (basic) dye MB is enhanced at pH of greater than pH_{pzc}.

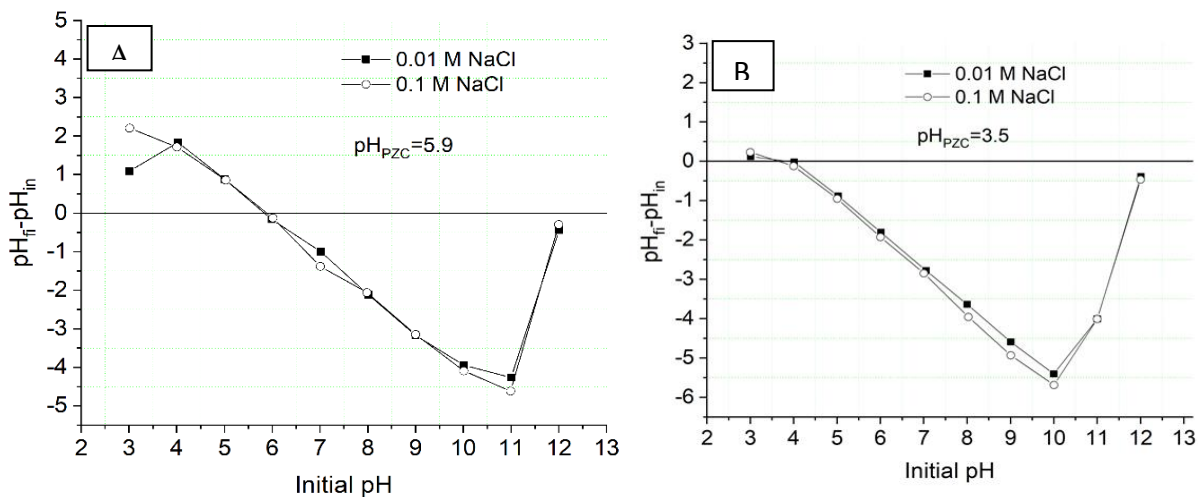


Figure 6 determination of pH_{pzc} of (A) BB & (B) EVML 0.1M NaCl & 0.01M NaCl solution adsorbent dose (2.5 g/L), speed of shaker (200 rpm).

4.2.4 FTIR analysis of adsorbent

The functional groups of BB and EVML were studied before and after MB adsorption by using FTIR spectroscopy. The spectrum showed the peaks around 3500 cm⁻¹ typical for hydroxyl group and it might be confirming the presence of alcohol and phenol groups for Figure A and carboxylic group for Figure B. The peak around near above 1600 cm⁻¹ can be assigned to the C=O stretching from the carbonyl groups. The adsorption peak observed around 1059 cm⁻¹ corresponds to the C-O band which is also an indicative of the presence of compounds containing carboxylic groups & hydroxyl groups in BB & EVML. The presence of these type functional groups for both samples was presented in Figure 7 (A) and (B). As observed, the shift of peaks & band width difference before & after adsorption tend to show the participation of functional groups of adsorbent surface on adsorption of MB for two adsorbent, BB & EVML. The results obtained confirm that the surfaces of the two samples were occupied by dye molecules and, as a result of this, the percent of transmission decreased after adsorption.³⁴

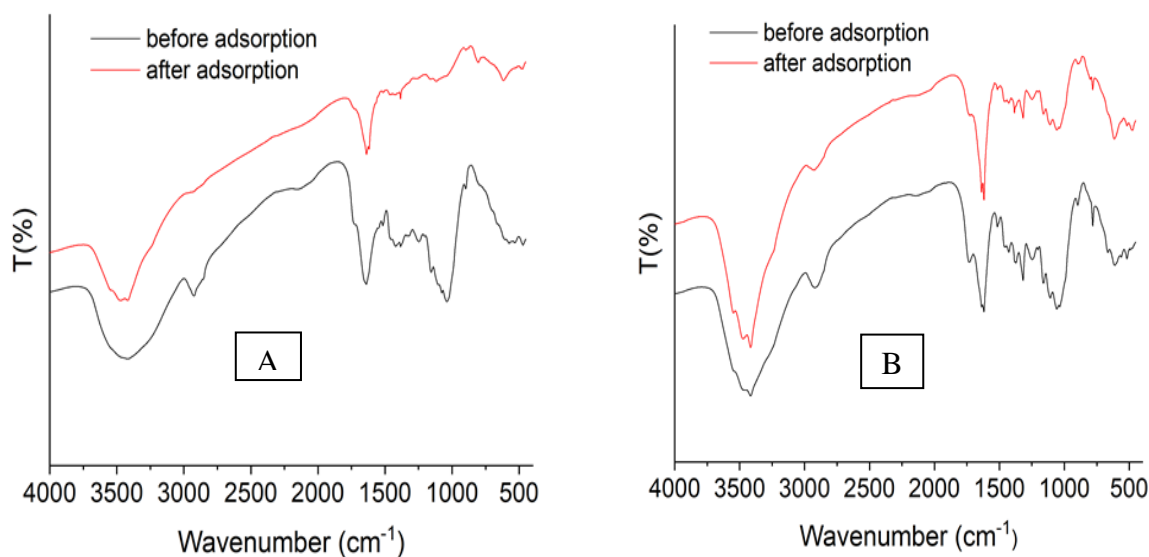


Figure 7 Fourier's infra-red transformation of (a) BB and (b) EVML before & after adsorption.

4.3 Adsorption study of MB

4.3.1 Effect of contact time

Contact time is one of the important parameter to evaluate the adsorption process between the two phases (adsorbate & adsorbent). Therefore, the two adsorbents, namely: BB and EVML were tested for the removal of MB from aqueous solution in the contact time of 1 min to 24 h respectively. The obtained results are presented in Figure 8 (A) and (B) which shows that as the contact time increases, adsorption capacity of both adsorbents increase. Thus, at beginning rapid adsorption capacity increment was shown with increasing time until 2 h in the case BB and 30 min in the case of EVML. Afterward, gradual increment was observed and maximum capacity of 63.2 mg/g and 35.5 mg/g was reached at the time of 4 h, 1h for BB and EVML, respectively. After this point the values of adsorption capacity gradually become, slower and no more significant change; which is taken as equilibrium time independently for BB and EVML. However, to ensure maximum adsorption at equilibrium, the equilibrium time for BB was set 4 h and for EVML 1 h for determination of all other adsorption parameters. Under this condition there was no change to the adsorption capacity with prolonging time. This was due to saturation

of surface active sites during initially and a lapsed time. Surface active sites available to highly saturated case have repulsive force interaction in between adsorbate adsorbed and adsorbate in the solution.⁴⁷ This situation occurs as the function of time for constant initial concentration (10 mg/L).

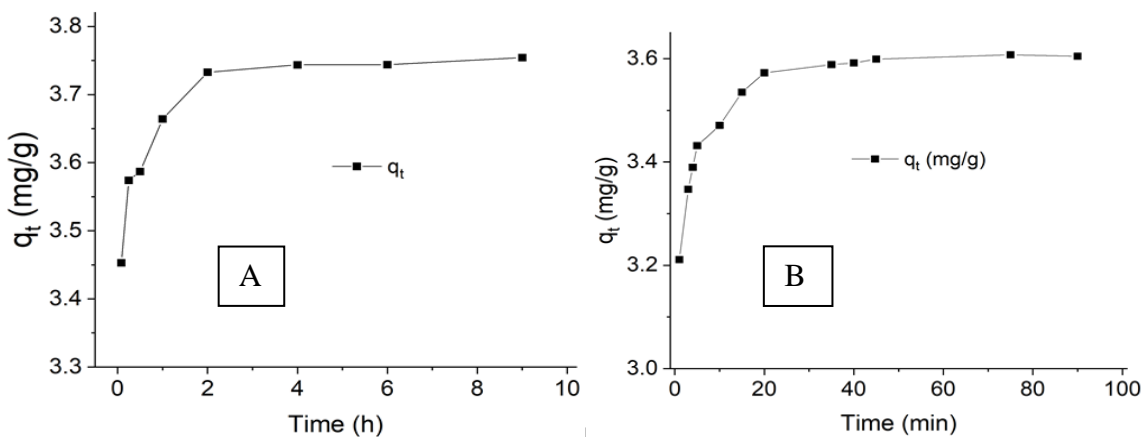


Figure 8 effect of contact time on MB removal by adsorbent (A) BB & (B) EVML, initial concentration (10mg/L) adsorbent dose (2.5g/L), speed of shaker (200rpm)

4.3.2 Effect of solution pH on MB dye adsorption by BB & EVML

The adsorption process was greatly influenced by change in initial pH of the solution. The pH effect of the solution usually depends on the ions present in the reaction mixture and the electrostatic interactions with the adsorption surface. Thus the pH of the solution influences aqueous phase chemistry and binding surface chemistry of the adsorbent.⁷⁶ The effect of initial solution pH on the adsorption of MB using BB and EVML adsorbent is depicted in Figure 9 (A) and (B). The pH variation causes the change in degree of ionization of adsorbate molecules and adsorbent surface properties.²⁸ As increasing initial solution pH range from 2 to 12 for both adsorbents, the adsorption capacity increases from 1.73 mg/g to 3.68 mg/g for BB and from 2.31 mg/g to 3.77 mg/g for EVML. The maximum adsorption capacity (q_e) was appeared at pH_i (5.066) and (5.660) with no significant change above the value mentioned for both adsorbent BB & EVML respectively. In general, the increment of adsorption capacity and attaining maximum value at which the adsorbents have negative surface charge due to the electrostatic interaction of

cationic MB dye and negatively charged surface functional group of adsorbent. Thus, the electrostatic interaction strength between the two charges is high when the surface of adsorbent develops more negative surface charge. This phenomenon was responsible for the observed maximum adsorption capacity at initial solution pH 5.66 for BB and natural (non-adjusted) initial solution pH 5.66 for EVML and the maximum amount of adsorbed was 3.68 mg/g and 3.77 mg/g, respectively. Similar work was reported on the adsorption of MB by Raw and Modified Waste Ash as Economical Alternative Bioadsorbent.⁶⁶ In this study adsorption of MB works in wide range of pH variation for EVML. This might be due to the extra OH group in the solution during the adjustment of the solution pH to basic media and further study will be needed.

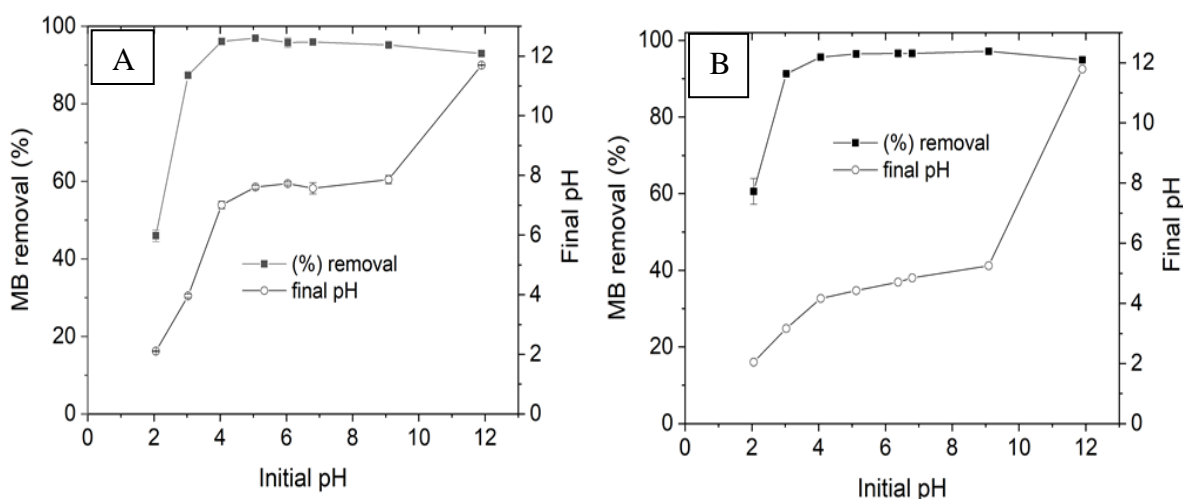


Figure 9 Effect of solution pH on the adsorption of MB on to (A) BB & (B) EVML, initial concentration (10 mg/L adsorbent dose (2.5 g/L), speed of shaker (200rpm).

4.3.3 Effect of Initial Concentration of MB Dye

The effects of the initial MB dye concentration were examined using a range of dye concentrations from 10 mg/L to 200 mg/L, for both BB & EVML adsorbents. The obtained data are presented in the Figure 10 (A) and (B) at room temperature, pH 5.066 and natural (non-adjusted) pH 5.66 of MB solution for BB & EVML respectively, adsorption capacity increased with the increase in MB dye concentration from 10 mg/L to 200 mg/L, where the adsorption capacity was 3.68 to 63.23 mg/g for BB and from 3.7 to 35.52 mg/g for EVML adsorbents. On the contrary, the percentage of dye removal efficiency was decreased for both adsorbents as the

initial concentrations of MB were increased. At a lower initial concentration of MB, there are vacant active sites on the adsorbing surface, and when the initial concentration of dye increases, the active sites necessary for the adsorption of dye molecules get occupied, where saturation of the active adsorbent sites is achieved.⁷⁸ Similar study was reported for removal of MB dye using banana leaf.⁷⁹

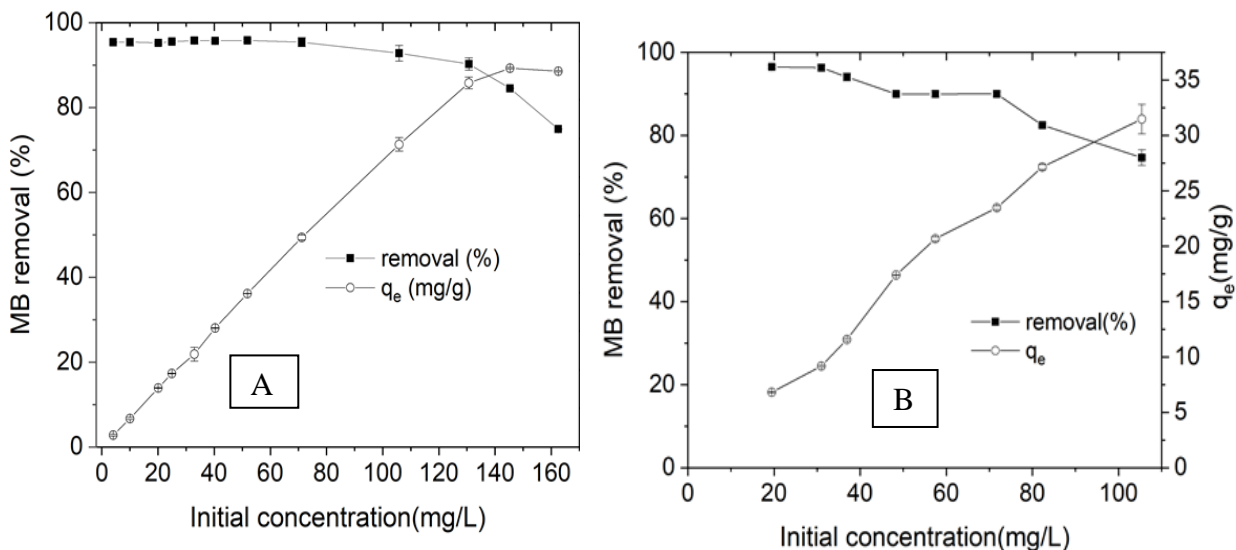


Figure 10 Effect of initial dye concentration by (A) BB & (B) EVML, initial concentration (10 mg/L) adsorbent dose (2.5 g/L), speed of shaker (200 rpm).

4.3.4 Adsorption kinetics

Kinetics models (pseudo-first-order (PFO) and pseudo-second-order (PSO)) were used to study the kinetics of the adsorption of MB on BB & EVML adsorbents. Both kinetics models were based on the assumption that the rate of occupation of sorption sites is proportional to the number of vacant sites. It is the fact that the extent of MB adsorption is rapidly increased at the initial stage and then increased gradually, and remains constant after 2 h for BB and 30 min for EVML adsorbents. However, the equilibrium adsorption of MB on BB was assumed to be 4 h and for EVML 1 h in order to allow ample time for maximum sorptions of MB on these adsorbents. The fast adsorption at the initial stage can be associated with the presence plenty vacant active sites initially, which are responsible for the rapid adsorption of MB on the adsorbents surfaces.

When equilibrium is achieved, the amount of MB dye migrates from the solution to the adsorbent and amount of MB dye desorbed from the surface of the adsorbent to the solution are in the state of dynamic equilibrium. The time required to attain this equilibrium process is termed as equilibrium time (t_e) and the amount of dye adsorbed on the adsorbent at this time implies equilibrium adsorption capacity (q_e). To study the mechanism involved in the adsorption process, the PFO and PSO kinetics models were used and the obtained results are shown in Figure 11 (A) & (B). The correlation coefficient (R^2) and the other parameters the kinetics studies of MB adsorption on BB and EVML are also shown in Table 4. As indicated in Table 4, the PSO model better than the PFO to model the experimental data because the PSO model has higher R^2 value and lower χ^2 value compared to that of PFO kinetics model for both BB and EVML adsorbents. Thus, MB adsorption on BB and EVML is assumed to be a chemisorption adsorption.

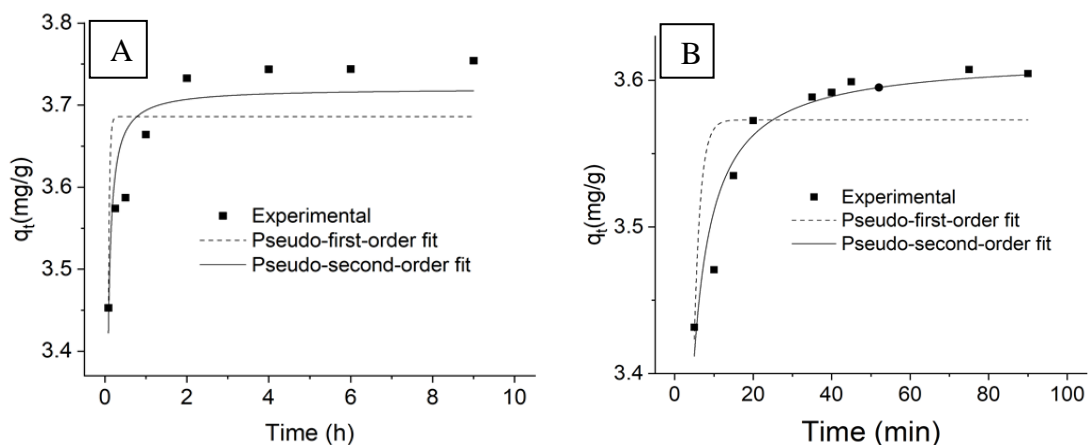


Figure 11 The kinetic models represented by the pseudo-first order and pseudo-second-order for (A) BB & (B) EVML, initial concentration (10mg/L), adsorbent dose (2.5 g/L), speed of shaker (200rpm).

Table 4 Pseudo-first-order and pseudo-second-order model parameters for methylene blue (MB) a BB & b EVML

Parameter	BB		EVML	
	PFO	PSO	PFO	PSO
Co(mg/L)	10	10	10	10
q _{e,exp} (mg/g)	3.744	3.744	3.607	3.607
q _{e,cal} (mg/g)	3.686	3.720	3.573	3.616
k ₁ (min ⁻¹)	33.057	-	0.635	-
k ₂ (g/(mg.min))	-	36.995	-	0.926
V ₀ (mg/(g.min))	-	511.95	-	12.11
R ²	0.56904	0.83729	0.56676	0.92953
χ ²	6.02×10 ⁻³	2.29×10 ⁻³	2.02×10 ⁻³	3.29×10 ⁻⁴

Adsorption affinity ($V_0 = K_2q_e^2$) provides information on the adsorption rate at the beginning of the adsorption process. The calculated value of V_0 for BB and EVML indicates that the adsorption of BB was about 42 times faster than that of EVML. The kinetic data was also explored using an intra-particle diffusion model. In order to study the relevance of the intra-particle diffusion model, the amount adsorbed, q_t , Vs. the square root of time, $t^{1/2}$, adsorption of dyes is mapped according to the theory proposed by Weber and Morris⁶⁸. That is, the diffusion mechanism of the MB molecules was examined by applying the Weber and Morris intra-particle diffusion model. If the rate-limiting step is the intra-particle diffusion, the plot of q_t versus $t^{1/2}$ should be a straight line and pass through the origin. However, in this work a plot does not pass through origin & show linearity of MB adsorption on both BB and EVML as shown in Figure 12 (A) & (B), that suggests intra-particle diffusion was not the only step that controlled the adsorption process. The adsorption of MB and its kinetics could be the overall effect of the external diffusion transport of MB, the intra-particle diffusion of the MB, and the adsorption of MB by the active sites on the adsorbents BB and EVML.^{68,80}

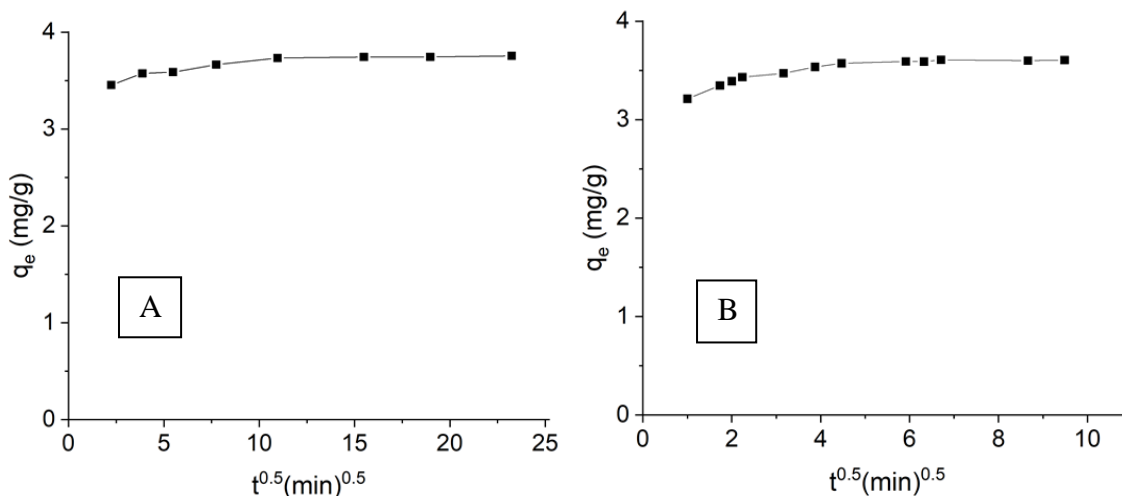


Figure 12 Intra-particle, diffusion model plot for (A) BB & (B) EVML, initial concentration (10 mg/L), adsorbent dose (2.5 g/L), speed of shaker (200rpm).

4.3.5 Adsorption equilibrium isotherm

Adsorption isotherm analysis is critically important in describing how adsorbed molecules interact with the adsorbent surface and highlight the distribution of adsorbate molecules between the liquid and solid phases based on the set of assumptions which are mainly relate to the homogeneity or heterogeneity of adsorbents, the type of coverage and possibility of interaction between the adsorbate species.⁸¹ In this study, the two commonly used isothermal models: the Langmuir and Freundlich isothermal models were used to model the equilibrium data of MB dye adsorption and the fitting curves are given in Figure 13 (A) & (B). The applicability of the isotherm equation was judged by the determination of correlation coefficients, R^2 ,⁸¹ & and the other parameters of isotherm also illustrated in Table 5. From the experimental results, the larger R^2 & the smaller χ^2 value observed for the Langmuir isotherm model. This reveals that the Langmuir isotherm model is better to model the experimental data for MB adsorption on BB & EVML adsorbents. The Langmuir isotherm⁷⁹ assumes monolayer adsorption with adsorption can only occur at a finite number of localized sites that are identical and energetically equivalent.

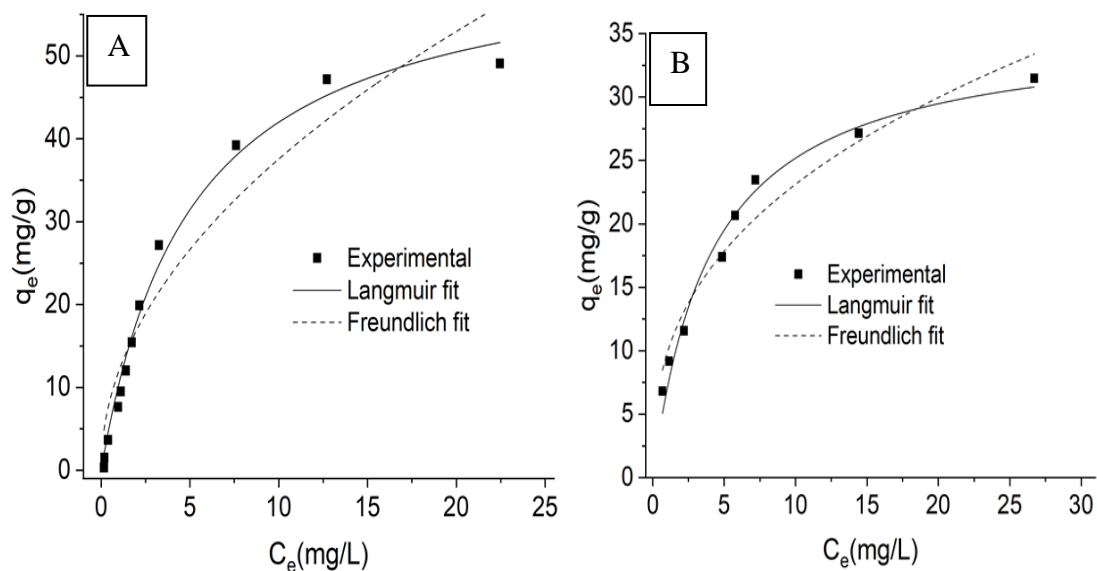


Figure 13 Langmuir & Freundlich isotherm model plot for (A) BB & (B) EVML, initial concentration (10mg/L) adsorbent dose (2.5 g/L), speed of shaker (200 rpm).

Table 5 Langmuir and Freundlich isotherm parameters for the adsorption of MB on BB &EVM.

Isotherm	Parameters	BB	EVML
Langmuir	q_{\max} (mg/g)	63.23	35.52
	b (L/mg)	0.1978	0.2438
	R_L	0.00123 – 0.0202	0.00232-0.0252
	R^2	0.98973	0.98029
	χ^2	3.43227	1.79086
Freundlich	K_F ((mg ^{1-1/n} L ^{1/n})/g)	11.998	9.784
	n	2.018	2.677
	R^2	0.9311	0.9579
	χ^2	23.0444	3.82589

4.3.6 Adsorption cycle

Adsorption cycle of adsorbents was the use of adsorbents without desorption more than one time. As observed in the Figure 14 (A) & (B), the adsorption efficiency of adsorbent BB & EVML become declined gradually & continuously starting the first cycle to last cycle. Here the adsorption of the two adsorbent declined gradually and remove until the saturation of active site. This was due to the high adsorption capacity of the two adsorbent & usage of the same initial concentration of MB (10mg/L) which tend to done for the cycles until the saturation. This was happened due to the loading of active binding sites with MB molecules and the ratio of competing active site decreases after each cycle.

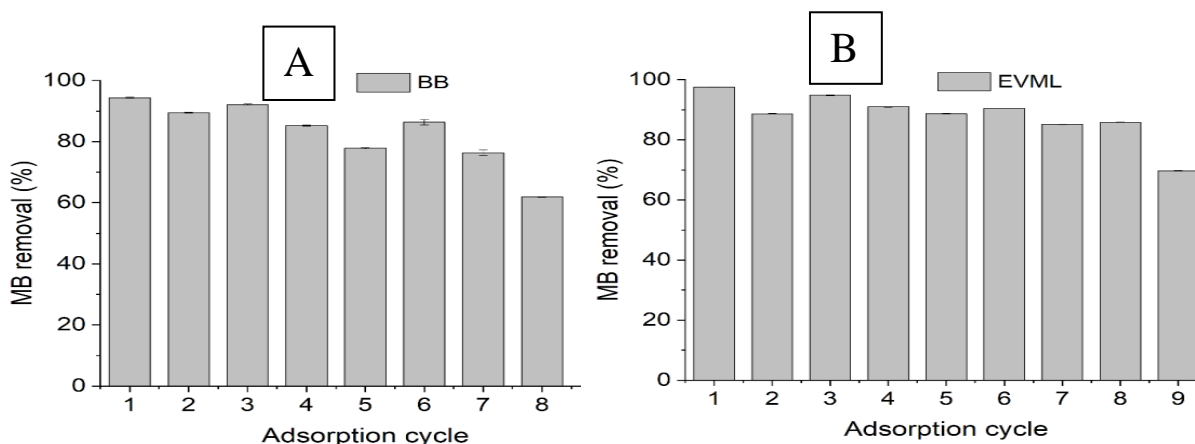


Figure 14 Test of adsorption cycle of MB on (A) BB & (B) EVML, initial concentration (10 mg/L), adsorbent dose (2.5 g/L), speed of shaker (200rpm).

4.3.7 Comparison of BB & EVML adsorption capacity with previously reported adsorbents for MB dye.

The adsorptive capacities of the adsorbents used in this work have been compared with those of others reported works in the literature and the values of adsorption capacity and the pH values was presented in Table 6 as shown below. Here experimental data of the present work were compared with reported adsorption capacity values of some adsorbents. Results of present work showed that the adsorbents (BB & EVML) have high adsorption capacity compared to wheat

shell, Neem leaf powder, & rice husk but mango leaf powder, rice husk, red mud activated graphite composite, potato peel & activated potato peel was observed as higher capacity than the present work. This might be, due to the carbon content, activation process & pore, development due to the basic morphology of the raw material.³⁷ Therefore, both BB & EVML can be considered to be comparable adsorbent for the removal of MB dye from aqueous solutions.

Table 6 comparison of MB adsorption capacity on BB & EVML Vs other reported literatures.

Serial No	Adsorbents	pH	Q _m (mg/g)	Optimum Time(h)	Dose (g/L)	Reference
1	Wheat shell	5-9	16.6	1	10	80
2	Rice husk	-	40.6	0.67	4	82
3	Mango Leaf powder	7-10	156.0	2	1.25	83
4	Red mud activated graphite composite	6	89.3	2	0.001	84
5	Neem leaf powder	5-8	8.8	-	-	50
6	Rice husk	10	13.5	2	2	85
7	Potato peel	8	47.6	-	-	86
8	Activated potato peel	12	41.6	-	-	86
9	Corn husk	6.2	30.0	0.25	1	87
10	Barley Bran	5.07	63.2	4	2.5	Present study
11	<i>Ensete ventricomus</i>	5.66	35.5	1	2.5	Present study

5. Conclusion and Recommendation

The aim of this work was to assess effective use of raw agricultural by-product adsorbents from BB & EVML for removal of MB from aqueous solution. The operational parameters such as contact time, pH, & initial MB concentration were found to have an effect on the adsorption capacity of adsorbent. At the optimum operation conditions, the adsorbents prepared from BB & EVML exhibited highest MB adsorption capacity of 63.23 & 35.52 respectively, for 10g/L of initial MB dye concentration. The FTIR spectra shift after adsorption process of MB showed that the functional groups were participated on adsorption process and had suitable site for MB binding. Adsorption isotherm and kinetic model were studied for the adsorption of MB from aqueous solution over BB & EVML adsorbent. The adsorption isotherm data were interpreted using Langmuir and Freundlich isotherm model. The process of adsorption follows Langmuir adsorption Isotherm than Freundlich isotherm. The characteristics parameters for each isotherm and related correlation coefficients were determined. And also adsorption kinetics were, studied by pseudo first order and pseudo second order models and it was found that the adsorption follows pseudo second order model for both adsorbent. Finally adsorbents, BB and EVML were potentially effective to adsorb MB from aqueous solution. Therefore, these adsorbents can remove MB dyes from textile wastewater. Thus, utilization of adsorbent from agricultural by-product is the best for environmental pollution control. The agricultural by-products prepared adsorbent, expected to economically effective & environmentally friendly in removal treatment of dye molecules. The adsorbents are suggested as: a, significant potential adsorbents, that could be an alternative treatment for basic (cationic) dye removal from aqueous solution; however, much work is necessary in the area of predicting the performance of adsorption process for the dye removal from real textile effluents. In addition, there is scope of study and research that can enhance uptake capacity of the adsorbents on MB dye.

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