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MAGNETIC CHARCOAL AS AN ADSORBENT FOR THE REMOVAL OF METHYLENE BLUE FROM WATER

A dissertation submitted to the Department of Chemistry, School of Science, College of Science and Technology, University of Rwanda, in partial fulfillment of the requirements for the Degree of Masters of Science in Environmental Chemistry.

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Kigali, September 2024

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I, Mrs. Marie Goreth UWIRAGIYE, hereby declare that this master's dissertation entitled ***"Magnetic Charcoal as an Adsorbent for the Removal of Methylene Blue from Water***" is my original work. It is submitted to the University of Rwanda for partial fulfillment for the award of the Degree of Master of Science in Environmental Chemistry at the University of Rwanda. This dissertation has never been submitted and will not be submitted elsewhere for any other degree or academic certificate award.

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I, Dr. Anaclet NSABIMANA, supervisor of this master's dissertation, confirm its originality and that it have been submitted for examination with our approval.

Dr. Anaclet Nsabimana

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DEDICATION

To the Almighty God.

To my spouse

Clement RUKUNDO

To my Parents,

NSABIMANA Sixtbert and MUKARURANGIRWA Alphonsine.

To Sisters,

Chantal UWUBURIZA and Yvonne UZAYISENGA.

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ABSTRACT

Choosing a particular wastewater treatment method should take into account both the environment and the economy in addition to its effectiveness to prevent two crucial ecological issues that affect the entire world. One that covers the full range of potentially harmful and irreversible effects on the many ecosystems and food web components. This puts additional strain on clean water delivery systems in both rural and urban areas. To maintain development within a circular economy, additional potable water must be drawn from the available freshwater reserves to fulfill rising water demands. Therefore, the primary goal of this research is to develop an environmentally friendly technique for eliminating the dye methylene (MB) via physicochemical process that involves adsorption on magnetic charcoal. Magnetic adsorbents were synthesized by mixing 4 g of activated charcoal (AC) with 13.1795 g of $FeCl_3$ and 6.9502 g of $FeSO_4.7H_2O$. FT-IR analysis was used to characterize the produced Fe-AC adsorbents. The magnetic AC (Fe-AC) that was created was successfully employed to remove MB from aqueous solutions. The effects of a number of variables, such as temperature, pH, adsorbent dosage, initial MB dye concentration, and contact time, were studied with regard to adsorption. These magnetic particles were recovered from the media by a straightforward magnetic process and employed as an adsorbent. Adsorption capacity increases with time and decreases as temperature rises. A UV-Vis spectrophotometer was used to determine how much MB was present in the solution. The maximal adsorption capacity was determined by the Langmuir isotherm model to be at 45 °C. The outcomes also demonstrate that the adsorption matches fictitious *pseudo* second-order kinetics. Magnetic charcoal, a new adsorbent, offers enormous promise for the removal of MB dye from aqueous solutions due to its advantages of being made affordably and having a high adsorption capacity.

Keywords: Methylene blue, magnetic charcoal, and adsorption.

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LISTS OF ACRONYMS AND ABBREVIATIONS

AC: Activated Carbon

FTIR: Fourier Transform Infrared spectroscopy

m: mass

M: molarity

MAC: Magnetic Activated Carbon

MB: methylene blue

pH: Hydrogen Potential

PPM: parts per million

rpm: rotation per minute

SEM: Scanning Electron Microscopy

TEM: Transmission Electron Microscope

q_e: the number of metal ions adsorbed by the adsorbent

V: volume

XRD: X-Ray Diffraction

XPS: X-Ray Photoelectron Spectroscopy

CHAPTER 1. GENERAL INTRODUCTION

1.1. Background

Severe environmental issues have been caused by the discharge of wastewater that has not been treated into natural sources of water together with a population that is expanding too quickly. Large amounts of chemicals, such as insecticides, antibiotics, heavy metals, and colors, fuel the whole economy every year. The majority of these pollutants is stubborn by nature and have a high level of persistence because of the potential harm to ecosystems that their unchecked release could cause [1]. In water sources, MB dye chemicals reduce the amount of dissolved oxygen, which blocks the water sources' access to sunlight. As a result of sea environmental dye bioaccumulations, harmful compounds may enter the human food chain. MB dye is a chemical that is very durable and has strong photolysis resistance, making it very persistent in natural environments. It has been demonstrated that some dyes are mutagenic and carcinogenic. Problems with the central nervous system, brain, liver, reproductive system, and kidneys are just a few of the human organs that MB dye poisoning can impact [2].

Multiple techniques are employed to lower the MB dye amount to the levels advised by the World Health Organization (WHO) because it might be difficult to eliminate MB dye complexes. Although these methods can be quite effective at getting rid of MB dye, they have the disadvantage of producing more trash. Wastewater should be recycled utilizing effective chemical, physical, and biological treatment techniques due to the scarcity of clean water supplies. Most techniques have several limitations, including high maintenance and operation costs, high energy and chemical consumption, process complexity, the inability to remove pollutants at low concentration, and the complete conversion of pollutants into biodegradable or less dangerous byproducts. Due to its ease of usage, one of the best dye-remediation techniques is adsorption [3].

To selectively adsorb pollutants, adsorbents with superior adsorption performance can be created and used to target adsorbate. After adsorption, adsorbents should be simple to collect and should do so promptly. Since magnetic components may be easily separated from mixtures using a magnetic field, the magnetic separation approach is a promising one.

Adsorption is often used to eliminate contaminants, notably MB dye, from water and wastewater because of its simplicity, high efficacy, advantages, and low cost [4].

1.2. Problem Statement.

Due to its possible toxicity and endurance, methylene blue (MB) dye in water bodies is a serious environmental problem. Therefore, technologies for removing MB from water must be developed that are efficient and long-lasting. This investigation's goal is to determine whether magnetic charcoal is a substance that can be used to adsorb methylene blue from water. The dye methylene blue (MB) pollutes water sources and endangers the ecosystem. The effectiveness, expense, and environmental impact of the current technologies for MB removal are constrained. The research suggests using magnetic charcoal as a potential adsorbent to eliminate MB. The study's objective is to assess the MB's ability to adsorb onto magnetic charcoal as well as the kinetics and factors that affect this process. The research will help to establish an effective and sustainable approach for removing MB from water, addressing environmental issues [5].

1.3. Objectives

1.3.1. General objectives

This study aims to determine how well magnetic charcoal works as an adsorbent for removing MB dye from water.

1.3.2. Specific objectives

i. To make magnetic charcoal out of charcoal.
ii. To assess magnetic charcoal's efficiency as a natural adsorbent for MB dye.
iii. To evaluate how adsorbent and adsorbate dosage, temperature, pH, time, and other variables affect the removal of MB.
iv. To study the reusability of the synthesized adsorbents.

1.4. Research question

Are magnetic charcoals effective adsorbents for MB dye in water?

Is magnetic charcoal an affordable and environmentally responsible adsorbent for MB dye?

1.5. Significance of the study.

The textile, printing, and pharmaceutical industries all frequently utilize the dye methylene blue. Its potential toxicity and detrimental effects on aquatic life make its presence in water and natural water bodies a serious environmental concern. To reduce these environmental dangers, it is essential to develop efficient removal techniques. The benefit of magnetic charcoal is that it has both magnetic and adsorption characteristics. Charcoal's magnetite content makes it simple to use magnetic fields to separate and recover the adsorbent from the aqueous medium. This quality makes removal easier and may lower the expense and effort required for the adsorbent's regeneration and reusability [4]. Agricultural waste, wood, and coconut shells are just a few examples of biomass sources that can be used to create charcoal, which is a plentiful and affordable material. Using charcoal serving as an adsorbent for the elimination of MB provides a sustainable and cost-effective alternative to conventional adsorbents. It is possible to alter the surface of charcoal to increase its selectivity and adsorption capability. Magnetic charcoal's characteristics can be modified using a variety of surface modification processes, including chemical processing or functionalization, to enhance MB adsorption efficiency. To maximize the removal efficiency, it is essential to investigate the adsorption kinetics and understand the factors, that affect the adsorption process, including pH, temperature, the starting MB concentration, and contact time. This information can help with the development and application of magnetic charcoal-based devices for the removal of MB [6].

CHAPTER 2: LITERATURE REVIEW

2.1. Overview of organic pollutants

Large amounts of organic compounds found in water and wastewater that come from sewage from homes, runoff from cities, industrial effluents, and agricultural waste are referred to as organic pollution. BOD, COD, and TOC in wastewater are indicators of organic contamination. The dissolved oxygen in water can be consumed at high rates during the breakdown of organic contaminants, which causes oxygen depletion and has detrimental effects on the stream biota [2].

2.2. Dyes

Many different dyes are employed for various industrial applications, and sizeable amounts are released into the environment as effluent wastewater. Due to their adaptability and chemical durability, azo dyes are the most common class of colorants used in the textile, printing, cosmetics, tattooing, and consumer goods sectors. However, once these colors are discharged into water bodies, their permanence and non-biodegradability lead to pollution. Some azo dyes are extremely poisonous, mutagenic, and carcinogenic. Dye wastewater discharge comprises a significant amount of harmful chemicals. The azo dyes make up around 70% of all the dyes in terms of weight. Azo dye intermediates, or aromatic amines, offer a major health risk to people since they are mutagenic and carcinogenic. [7].

Many different businesses utilize dyes and pigments, and the dyeing process releases a significant amount of these coloring agents into the effluent water. These substances provide a rising risk to aquatic life due to their propensity for cancer and toxicity. To remove color, many physicochemical techniques have been explored, including coagulation, adsorption, filtering, precipitation, and oxidation [8]. Furthermore, dye pollution is a significant category of pollutants, and it is even visible to the human eye. A dye molecule is made up of two essential parts: the chromophores, which are in charge of creating the color, as well as the auxochromes, which support the chromophores, as well as boost the molecule's affinity for fibers and make it soluble in water. Dyes possess a wide range of structural variety and different classifications.

Several dye characteristics depend on their use and are broadly categorized into acid-based dyes. It is a sulfonic, carboxylic, or phenolic organic acid sodium salt. Water dissolves it and has a preference for amphoteric fibers. It is utilized for food, paper, leather, nylon, wool, and makeup [9]. Here are some common types of dyes:

1. *Direct Dyes*: These dyes can be applied to the material directly and do not require a mordant (a substance that aids in fixing the dye to the material). They are water-soluble. For coloring cotton, rayon, and other cellulosic textiles, direct dyes are frequently employed.
2. *Acid Dyes*: Protein fibers like wool, silk, and nylon are colored using acid dyes. Since they are water-soluble, an acidic environment is necessary for optimal dye uptake. When applied to protein-based materials, acid dyes can give vivid and colorfast effects [10].
3. *Basic Dyes*: Basic dyes, often referred to as cationic dyes, have a positive charge and are used to color objects that have a negative charge, like paper, certain kinds of plastics, and acrylic fibers. Typically, basic colors are applied in an aqueous solution.
4. *Disperse Dyes*: Synthetic fabrics like nylon, polyester, and acetate are typically colored using disperse dyes. Although these dyes are poorly soluble in water, they can be spread throughout the fiber matrix when heated and combined with dispersing agents. High-temperature dyeing techniques are often used to disperse color [9].
5. *Vat Dyes*: To become soluble in water, vat dyes must undergo a reduction procedure. Cellulosic fibers like cotton and linen are dyed with them. Vat dyes are renowned for their fading resistance and high colorfastness.
6. *Reactive Dyes*: Reactive dyes have good wash and light fastness qualities because they create a covalent link with the fiber molecules. These colors are frequently used to color cellulosic fabrics like cotton, and other textiles are frequently dyed with these colors.
7. Solvent Dyes: These dyes are not soluble in water, but they are soluble in organic solvents. Plastics, waxes, and materials having hydrocarbon bases are typically tinted using them. In industrial settings, solvent dyes are often used and come in a variety of colors.
8. *Natural Dyes*: Plant materials like roots, leaves, flowers, and bark are used to make natural dyes. They have been used to color textiles for ages. The natural dyes indigo, madder, turmeric, and cochineal are a few examples. Compared to synthetic dyes, natural dyes produce distinctive colors and are thought to be more environmentally beneficial.

It's crucial to keep in mind that these are generic categories of dyes and that there are several subtypes and variations with unique characteristics and uses within each category. Our daily lives depend heavily on dyes since they give us access to a huge variety of colors and shades for a variety of materials [7].

2.3. Methylene blue dye

A synthetic dye with a rich blue hue called methylene blue has been employed in industry, biology, and medicine for a variety of uses. Here are some important details regarding methylene blue: Methylene blue, commonly referred to as methylthionine chloride, is a member of the thiazine dye family. The chemical formula of it is $C_{16}H_{18}ClN_3S$, and it has a MW of 319.85 g/mol. MB has a bright blue color when dissolved in water and appears as a dark blue powder or crystal. It has limited solubility in organic solvents but is soluble in water [9]. Applications in Medicine and Biology: Methylene blue has several applications in medicine and biology. In histology and microscopy, it is used as a staining agent to make cells and tissues more visible. Methylene blue is a deep blue synthetic dye that has been used for a variety of tasks in biology, medicine, and other fields. It is also utilized in several diagnostic processes and as a biological dye in research investigations. Methylene blue is used medicinally for many therapeutic purposes. Methemoglobinemia, a disorder in which red blood cells have diminished oxygen-carrying capacity, has been treated as a drug. Methylene blue can also be used as a surgical dye and as an antidote for cyanide poisoning. Methylene blue has been utilized as a disinfectant and an antiseptic due to its antibacterial characteristics. It can stop some parasites, fungi, and bacteria from growing [10].

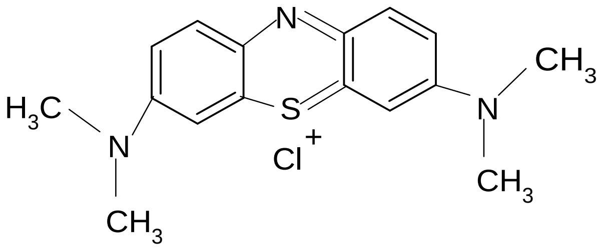


Figure 1: Structure of methylene blue molecule

2.4. Dyes removal methods

Three categories—biological, chemical and physical purification processes—can be used to categorize the many techniques employed to clean up sewage or environmental fluids [5].

2.4.1. Biological purification

- Bioremediation: This method uses microorganisms to break down or change contaminants into less dangerous ones, such as bacteria or fungi. It is frequently used to clean up polluted soil, water, or air.
- The biological treatment process known as the "activated sludge process" is employed in wastewater treatment facilities. The organic matter in the activated sludge is broken down by microorganisms, resulting in the production of carbon dioxide, water, and biomass.
- Phytoremediation: This method uses plants to clean up pollutants in soil, water, or the air. Through the roots, leaves, or stems of these plants, contaminants can be absorbed, accumulated, or degraded [11].

2.4.2. Chemical purification

- Coagulation and flocculation: To destabilize suspended particles, chemicals like alum or ferric chloride are added to water or wastewater. This procedure aids in the formation of flocs, which are bigger particles that are simple to filter or sediment.
- Chemical Precipitation: Chemicals are employed to turn dissolved pollutants into insoluble precipitates that can then be isolated via settling or filtration.
- Ion Exchange: Ions are exchanged between a solid resin and a liquid solution in this procedure. It is used to swap out undesirable compounds' ions for desired ones. [3], [5].

2.4.3. Physical purification

- Filtration: To separate solids or particle matter, a substance is passed through a medium or filter in this procedure. Depending on the particular application, many filter types, including membrane filters, activated carbon filters, and sand filters, can be employed [12].
- Distillation: To separate and cleanse liquids, distillation makes use of the various constituents' boiling points. The more volatile component of the mixture is heated to vaporization, which is followed by condensation and collection.

- Centrifugation: This process uses centrifugal force to separate materials with various densities or particle sizes. It is frequently used to separate components in mixes according to their densities or to separate solids from liquids [13].

2.4.4. Adsorption method

Adsorption, a surface phenomenon, decreases both organic and inorganic pollutants occur when an absorbable solute-containing solution comes into touch with a surface-structured media. In adsorption operations, the solute held (on the solid surface) is referred to as the adsorbate, such as H_2, N_2, and O_2 gases. Alternatively, the solid on which it is maintained is referred to as the adsorbent, such as charcoal, silica gel, or alumina [13]. A process called adsorption occurs when a substance accumulates on a surface in increasing quantities of a certain molecular species. On activated charcoal, the gases oxygen, nitrogen, and hydrogen adsorb. Remembering that adsorption and absorption are two different processes is also important. Adsorption phenomena are defined as the buildup of adsorbate at the gas-solid or liquid-solid interface. Because the Vander Waals connections between the adsorbent and adsorbate are typically weak, adsorption is reversible [14].

2.4.4.1. Types of Adsorptions

There are two forms of adsorption based on the forces that interact between adsorbate and adsorbents.

1. **Physical adsorption:**

Physisorption is another name for this kind of adsorption. Weak Van der Waals forces exist between adsorbents and adsorbed materials, which is the cause. For instance, H_2 and N_2 can be absorbed by coconut charcoal. This sort of adsorption, which is a weak phenomenon, a multi-layered process, and which occurs all over the adsorbent, is brought about by physical forces. Effects of physisorption on surface area, temperature, pressure, and adsorbate type. Low activation energy (20–40 kg/mol) is seen [11].

2. Chemical adsorption

This type of adsorption is also known as chemisorption. This is caused by powerful chemical forces that bond adsorbate and adsorbents together. We can use iron as an example, which generates iron nitride on its surface when heated to 623 K in N_2 gas. Adsorption of a gas onto a substance is a spontaneous exothermic reaction. The amount of heat emitted when a unit mass of a gas is adsorbed on a surface is known as the heat of adsorption. Chemical forces are responsible for the extraordinarily strong adsorption of this kind. This form of adsorption almost always takes place in a single layer. On the adsorbent, chemisorption takes place at reaction hubs and is extremely selective. The influences of surface area, temperature, adsorbate type, and activation energy (40–400 kJ/mol) on chemisorption are all significant. Furthermore, Chemisorption is when an attraction results from chemical bonds that are strong in nature. The nature of wood charcoal makes it effective for both chemical and physical sorption [14].

2.4.4.2. Factors affecting adsorption.

Adsorption capacity (rather than surface area) is related to pore size and volume, which are more than or equivalent to the size of the adsorbate molecules. The adsorption increases with larger adsorbate molecules as long as there is no size exclusion preventing the molecules from entering the pore system. The absorbability of organic molecules onto activated carbon increases as the polarity (solubility and hydrophilicity) of the adsorbate decreases. a significant amount of the adsorbate are removed from the aqueous phase is the outcome of the increase in adsorbent dosage. A larger adsorbent dosage, nevertheless, could result in limited adsorption volume, which stays undesirable after a financial standpoint. As a result, the dosage should be kept to a minimum. Because there are more activated sites available for adsorption at the beginning of the process and those sites have a significant concentration gradient, adsorption is an active process [14].

Typically, the following dependent parameters are of utmost importance for adsorption by magnetic activated carbon: Materials and preparation technique; adsorbent's nature, comprising the amount of ash, the surface area, the distribution of pores, the volume of pores, the size of the particles (granular or powered), the functional groups, and the polarity; Adsorbate type, including molecular size, functional groups, and polarity; adsorbent dose; contact time; starting adsorbate concentration; pH; temperature; and ionic strength [13].

Hydrogen ion concentration: The degree of adsorption depends on the pH of the solution in which it occurs.

Because hydrogen and hydroxide ions adsorb rather heavily, the pH of the solution affects how other ions adsorb. In addition, the high concentrations of H_3O+ ions in the solution compete with metal ions for the active sites on the adsorbent material at low pH levels, lowering the adsorbents' capacities [6].

Temperature: At higher temperatures, dye removal is typically more effective. Over the range of temperatures that are encountered in water and wastewater, temperature impacts on adsorption equilibrium are typically not significant. As a result, minor temperature changes have little impact on the adsorption process [11].

2.4.4.3. History and Advancements of Magnetic Adsorbents

Iron-based materials are widely used as magnetic particles because unpaired electrons in the 3D orbitals of Fe atoms have strong magnetic moments. Fe, magnetite (Fe_3O_4), and other magnetic minerals are used in the adsorption process and magnetite ($Fe_2O_4$is widely used. The creation of magnetic material adsorbents requires precise control more than crystal formations, particle sizes, and forms. Even though both Fe and Fe_3O_4 have substantial sensitivity to magnetic fields, Fe_3O_4 is more frequently employed in literature due to its superior stability. Fe_3O_4 particles become super paramagnetic at nanometer sizes [2]. The many hydroxyl groups on the surface of Fe_3O_4 can produce positive or negative charges in aqueous solutions by being protonated or deprotonated by altering the pH. Through electrostatic interactions, Fe_3O_4 can be utilized as an adsorbent to extract ionic species from water. As an adsorption site for complexation with negatively charged species or the electron-rich functional groups of some organic contaminants, the Fe atom in Fe_3O_4 also serves this purpose. Fe_3O_4's surface can also be altered to enhance functionalization and shield the magnetic core from degradation. The benefits of using magnetic adsorbents are as follows: Using an external magnetic field makes removing them from bulk solutions simple. Their biocompatibility makes them environmentally friendly, and they are recyclable. In addition to applications for environmental cleanup magnetic adsorbents have been utilized in analytical chemistry's so-called magnetic solid-phase extraction sample preparation procedure.

The samples are cleaned up and pre-concentrated using the core analysis approach to help with monitoring for organic and anionic contaminants [4].

The adsorbent's magnetism makes separation by a magnetic field outside of the body simple. It can remediate a huge amount of wastewater quickly and produces no impurities when compared to other treatment methods like flocculation. Magnetic adsorbents have been used for biomedical, organic, and inorganic contamination cleanup, as well as dye and heavy metal removal. A renowned sustainable cleanup method is magnetic AC because the used adsorbent may be recycled. Additionally, the used adsorbent can be reactivated and the adsorbed material recovered by regeneration or reactivation.

Because the magnetic AC can be recycled numerous times, the operation is both inexpensive and environmentally friendly. Wastewater cleanup is less expensive and takes less time thanks to AC magnetization [7].

2.4.4.4. Type and characteristics of adsorbent

Adsorbents, according to the source, can be broadly classified into:

1. Organic adsorbents: These materials, which include zeolites, clay minerals, charcoal, red mud, sediment, soil, ore minerals, etc., are naturally occurring adsorbents. They are easy to obtain and plentiful. To improve their adsorption capacity, they are simply modifiable [3], [15].
2. Synthetic adsorbents: These adsorbents are made from raw materials such as sewage sludge, agricultural waste, household trash, industrial waste, and polymeric adsorbents, among others. In comparison to natural adsorbents, they are pricey [2], [5].
3. Bio-adsorbents: Most of the plant and agricultural wastes used in wastewater treatment are used as adsorbents. They can be divided into two groups: non-living biomass, which includes things microbiological biomass, which includes bacteria, fungi, and yeast; algal

biomass, such as bark, lignin, shrimp, krill, squid, crab, and shell; and other types of biomass. Agricultural wastes such sawdust, mango, orange, and almond peels, tea waste, parthenium powder that has been dried, sugarcane bagasse, peanut shells, sunflower stalks, banana peels, rice husks, and corn cobs, and gram husk are promising bio-adsorbents [1]. Bio-adsorbents contain a wide range of other materials in addition to cellulose, hemicellulose, lignin, and extractives, such as lipids, starches, hydrocarbons, simple proteins, tannins, etc.

Due to the presence of hydroxyl functional groups, cellulosic biomaterials have strong adsorption potential. In terms of waste treatment, cellulose can be chemically changed to create a variety of derivatives

Esterification is a method used to modify cellulose through grafting, etherification, oxidation, and halogenation. The goal of the modification is to increase the adsorption capabilities in comparison to the initial cellulose[3], [16].

2.4.5. Adsorption isotherms

Graphs of the adsorption isotherm are frequently used to study the adsorption process. The graph between the amount of adsorbate x adsorbed on the surface of an adsorbent m at constant pressure and temperature is known as the adsorption isotherm. One of the most often utilized isotherms in adsorption is that produced by Freundlich and Langmuir [14]. The Freundlich adsorption isotherm, the amount of gas adsorbed per unit mass of adsorbent as a function of pressure is generally predicted using an empirical model. Additionally, it can be used to compare the concentration of adsorbate on a solid surface to that in a solution. According to equation 1.

$$q_{e=k_f \times C_e} 1/n \qquad (1)$$

The characteristics of the adsorbent and adsorbate define and n, which are the Freundlich adsorption isotherm constants. The values of the constants and n can be found using the plot of the linear adsorption isotherm form (lnqe vs. lnCe), as stated in equation 2.

$$.\ lnq_{e=lnK_f} \ + \frac{1}{n} lnC_e \qquad (2)$$

The Langmuir isotherm is a model that was created with the assumption that there would be dynamic equilibrium, fixed and equivalent adsorption sites, no intermolecular interactions, the formation of monolayers on the adsorbent surface, and no intermolecular interactions [13]. In equation 3, the Langmuir isotherm is displayed.

$$qe = \frac{bQ_m C_e}{(1+bC_e)} \tag{3}$$

Where q_e symbolizes the amount adsorbed at equilibrium time (mg/g), Q_m and b are Langmuir constants that depend on the maximum monolayer adsorption size and adsorption equilibrium constant that relates to the energy of adsorption, respectively. C_e is the equilibrium concentration (mg/L), A linear plot of $\frac{1}{q_e}$versus $\frac{1}{C_e}$ allowed the determination of q_m and b from the intercept and slope [13]. Q_m (mg/g) and b (L/mg) can be obtained from the plot of the linear adsorption isotherm form $\frac{1}{q_e}$ and $\frac{1}{C_e}$ is given in the equation 4.

$$\frac{1}{q_e} = \frac{1}{Q_m} + \left(\frac{1}{C_e} \times \frac{1}{bQ_m}\right) \tag{4}$$

In this work, the best fit of the data was verified using Freundlich and Langmuir adsorption isotherms. The correlation coefficient square (R2) is calculated. Was used to assess the accuracy and scope of each model. The portrayal improves as the value increases [14]. The dimensionless equilibrium parameter R is frequently used to explain additional Langmuir isotherm model analysis with the following equation 5.

$$R_L = \frac{1}{1+bC_o} \tag{5}$$

The percentage of methylene blue removal may be calculated by the following formula

$$\mathrm{R} = \frac{(C_o - C_e) \times 100}{C_O} \tag{6}$$

Where,

R stands for removal efficiency or removal percentage.

The starting concentration, C_O, is given in mg/L. After adsorption, Ce represents the final concentration in mg/L.

One method for calculating adsorption efficiency is as follows: [1]

.

$$q_e = (\frac{C_o - C_e}{m})v \qquad (7)$$

Where q_e : the amount of methylene blue adsorbed by magnetic charcoal.

v : The volume of the sample

m: Mass (g) of magnetic charcoal taken.

C_e: The residual concentration at equilibrium

C_o: The initial concentration of the methylene blue

2.4.6. Adsorption kinetics

Two kinetic models, such as pseudo-first-order and pseudo-second-orders, were utilized to calculate the adsorption rate and the amount of time needed to attain equilibrium for the adsorption [1**].**

2.4.6.1 *Pseudo*-First-Order Kinetics

Lagergren's first-order rate equation is used to assess the sorbent's rate of adsorption onto the sorbate [17].

$$\ln(q_e - q_t) = lnq_eK_1t \qquad (8)$$

Where qe and qt are, respectively, the amounts of (mg g1) adsorbed at equilibrium and time t.

First order rate constant (min1) is k1. The slope and intercept of the linear plots of ln(q e-qt) vs. t at different concentrations are used to derive the values of K1 and qe.

2.4.6.2. *Pseudo*-Second-Order Kinetics

The adsorption on the surface, which involves chemisorption, is assumed to be the rate-controlling step in the pseudo-second-order equation, while the removal from a solution is caused by interactions between the two phases' physicochemical properties. [17]

$$.\frac{t}{K_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (9)$$

$h = K_2 {q_e}^2$ where h is the initial adsorption rate (mgg^{-1}min^{-1}) and K_2(g mg^{-1} min^{-1}) is the adsorption rate constant for the *pseudo*-second-order reaction[18].

2.5. Magnetic recovery

Secondary contamination results from the wastewater's typical disposal with sludge after being treated with activated carbon (AC). As a result, its applications in many industries are restricted by the challenges associated with wasted AC separation and regeneration. Regeneration is a crucial step because it stops secondary contamination and restores the magnetic composites' removal effectiveness. Magnetic separation has several advantages over the customary methods for recovering adsorbents, including centrifugation, cross-flow filtering, and membrane filtration. This method recovers far faster than conventional methods, is easier to use, may handle environmental concerns, is more energy-efficient, and is more selective. The magnetic separation procedure can be easily performed thanks to the magnetic core of the adsorbent composite. One important advantage of using a magnetic separation technique is that the magnetic field can pass through most materials, including glass and plastic. Magnetic separation, a non-intrusive approach, avoids direct physical contact with the adsorbents during the dye removal process, preventing any potential water pollution [19].

CHAPTER 3. MATERIALS AND METHODS

3.1. Adsorbent preparation

3.1.1. Sampling

1kg of charcoal was collected from the Bugesera market. The charcoal was transported to the laboratory of the Chemistry Department at the University of Rwanda, College of Science and Technology for further analysis.

3.1.2. Chemicals and reagent

Chemicals that were used in this research were analytical grades, Iron (II) and iron (III) chloride, sodium hydroxide, hydrochloric acid, calcium chloride, and methylene blue were used as supplied without any further purification.

3.1.3. Materials

All instruments and apparatus used in the experiment are an electronic weight balance to measure weight, a pH meter to measure pH, an Oven to dry samples, a shaker to shake the samples in dyes solutions, a mortar and pestle to grind the prepared carbon; and magnet to isolate the adsorbent; UV-visible spectrophotometer to find out absorbance.

3.1.4. Preparation of magnetic charcoal (adsorbent).

The charcoals were activated using solutions of 25% calcium chloride and dried at 210 ˚C for 24 hours (h) [10].13.1795 g of $FeCl_3$ and 6.9502 g $FeSO_4.7H_2O$ was dissolved in 400 mL distilled water; 4 g of AC was added to the resulting solution and vigorously stirred. Thereafter, 100 mL 5 M NaOH was added slowly with constant stirring at 70 ˚C for 30 minutes. After being activated with 25% calcium chloride solutions, the charcoals were dried at 210°C for 24 hours (h) [10]. $FeCl_3$ weights of 13.1795 g and 6.9502 g. As a precipitate formed, the mixture's hue shifted from brown to black. A magnet was used to separate the black precipitate, and impurities were repeatedly rinsed away using a 50% ethanol solution. The resulting materials were dried for three hours in an oven set at 100°C. The substance created in this way was known as activated charcoal-magnetic. The magnetic Nano composite powder that was obtained was kept at room temperature [20].

3.1.5. Process of synthesis of magnetic charcoal

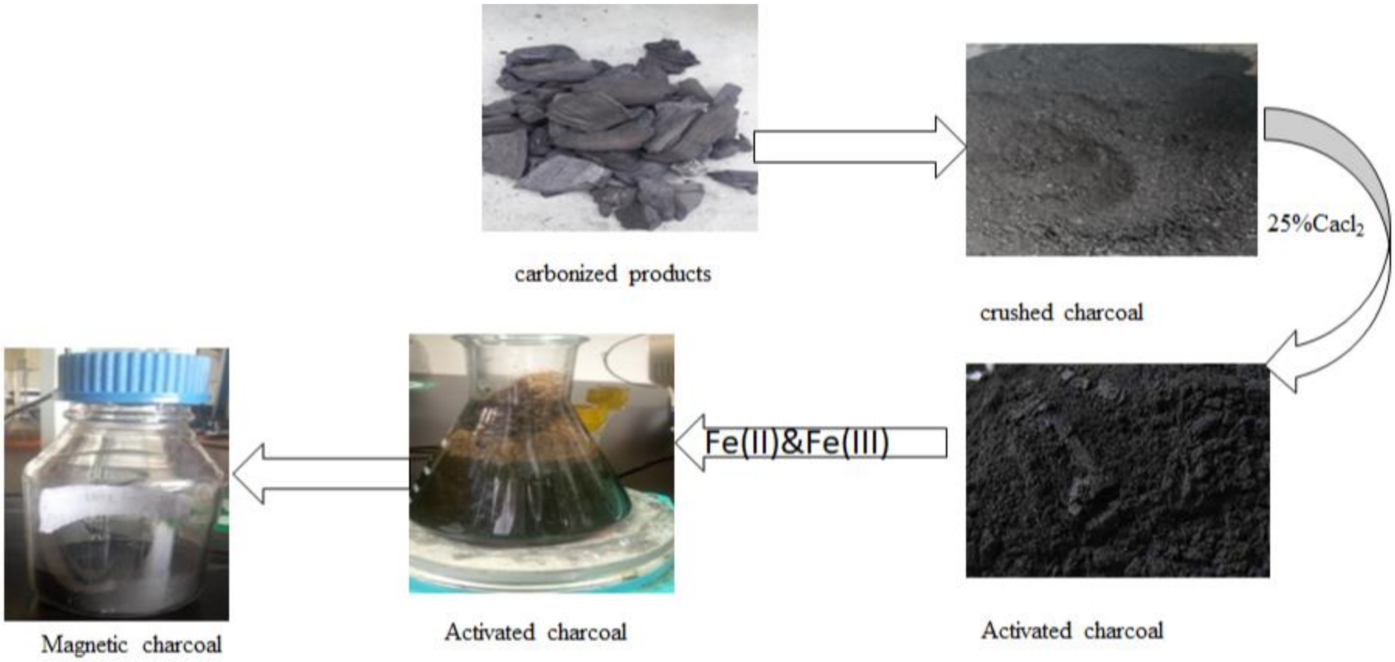


Figure 2: Process of magnetic charcoal synthesis

3.2. Characterization of adsorbent

Fourier transforms -Infrared spectrophotometry (Bruker Alpha II, 111131, Germany) was used for the identification of functional groups that are present in the adsorbents and diamond crystal ATR accessory is present. Moreover, the adsorbent's FT-IR spectra were captured between the wavelengths of 4000 to 400 cm^{-1}[13].

3.3. Adsorbates

The biology lab at the University of Rwanda's College of Science and Technology provided the methylene blue (MB) dye, which has the chemical formula $C_{12}H_{18}ClN_3S.XH_2O$. The necessary quantity of MB was then diluted with distilled water to create 1g/l MB stock solutions. Initial concentrations for several test samples [17].

3.4. Instrumental analysis

The characterization of adsorbents and identification of functional groups that are present in adsorbents were done using Fourier Transform Infrared (FT-IR) equipment.

The concentration of dyes (methylene blue) was then measured employing a UV-Vis spectrophotometer, which gauges the amount of light that enters a sample and compares it to the amount of light that exits the sample.

3.4.1 UV-Visible spectrophotometer

Using a UV-Vis spectrophotometer, dye (methylene blue) solution solutions were examined. The compound solution is put in a suitable transparent container that doesn't absorb light in the area being examined, and the container is then used as a spectrophotometer to expose the solution to UV-Visible radiation. The concentration of the dyes (methylene blue) was discovered using a UV-Vis spectrophotometer [21]. According to Beer's law, the relationship between solution concentration (C) and absorbance (A) is straight forward. Based on the solution's linear regression equation and Lambert's law, the plot of absorbance vs. concentration provides the calibration curves (line) that were utilized to determine the solution's unknown concentration.

$$A = log\frac{p_o}{p} = \varepsilon lC \tag{16}$$

Where P_o and P refer to the radiation directed at a sample solution transmitted radiation from the sample, respectively while, l and ε are the length of the cuvette cell and molar absorptivity coefficient, respectively. As a result, the equilibrium concentration of methylene blue was calculated using a UV-Vis spectrophotometer. After being washed, dried, and filled with distilled water (the reference solution), the empty cuvette cell was prepared. The standard solution of 10 ppm of methylene blue was then placed inside the cuvette chamber, where it was measured at a fixed wavelength of 665 nm. The standard and sample readings were done at a fixed wavelength. The data collected were used to establish calibration curves for methylene blue by applying Beer’s Lambert low to determine the equilibrium concentration of methylene blue [4].

3.4.2. FT-IR spectrometer

The FT-IR spectrometer’s diamond crystal plate was cleaned using acetone solvent and wiped dry with a piece of tissue paper by following the instructions in the FT-IR manual. Before doing the background spectrum measurement, the crystal plate was given time to dry.

The dried powdered adsorbent sample was placed on a diamond crystal plate and the anvil tip was allowed to make contact with the sample so that IR beams could flow through it. The FT-IR spectra were then generated and appeared on the computer screen.

3.5. Adsorption process

Experimental trials were carried out to determine the lot adsorption kinetics and to look into the underlying mechanisms of MB adsorption. The removal of MB is subject to on a number of process variables, including the initial concentration of MB, the dose of the adsorbent, time, pH, and process temperature; as a result, their individual and interacting effects were carefully investigated. A dye solution with varied initial MB dye concentrations (10–50mg/L in a glass container) was mixed with various adsorbent dosages (0.7, 0.25, and 1.4g/L). In an orbital shaker, these mixtures were agitated at 200 rpm and 25 °C. At various periods, samples were taken out of each conical flask. An UV-Vis spectrophotometer was used to portion the quantity of MB elimination at each time interval at wavelength max = 665nm..

3.5.1. Study of the initial concentration of adsorbate effect

There were made solutions with 10 mg/L to 50 mg/L of MB. The following parameters: pH, temperature, contact time, agitation rate, and adsorbent dosage. Following these settings, the impact of the initial methylene blue concentration on adsorption was more readily apparent. We used a fixed volume of each methylene blue solution in the individual adsorption trials and added 0.2 g of magnetic charcoal. Thoroughly combine the solution and charcoal, and then waited for 30 min for the adsorption to take place. We collected samples from each experiment after 30 minutes. The samples were then examined using UV-Vis spectroscopy, to ascertain the remaining concentration of methylene blue. We measured the absorbance of the samples at 665 nm of methylene blue absorption. We created a graph that contrasted the initial and residual methylene blue concentrations. To spot any trends or patterns, the data was evaluated [5].

3.5.2 Study of the magnetic charcoal dosage effect

Various weights of magnetic charcoal (0.7–1.4 g) and solutions of methylene blue with a set concentration of 50 mg/L, pH, temperature, contact time, and agitation rate were placed in separate containers.

30 minutes were given for the mixture to absorb after careful mixing. Each adsorbent was used in varied amounts for the trials, ranging from 0.74 to 1.4g. The mixture was shaken at 200 rpm for 30 minutes with a fixed pH of 7 and 5 mL of 50 ppm methylene blue solutions at 25 °C to bring about equilibrium. Samples from each experiment were taken after 30 minutes and examined using UV-Vis spectroscopy, to ascertain the remaining concentration of methylene blue. The absorbance at 665 nm of the samples was calculated. A graph of the residual methylene blue concentration versus the dosage of magnetic charcoal was plotted and then examine the data to look for any trends or patterns[7].

3.5.3. Study of the temperature effect

Adsorption experiments a range of temperatures (25, 35, 40, and 45 ^{o}C) were used for the experiments in a thermostat. Three glass bottles containing 5 mL of methylene blue solution having constant concentrations of 50 ppm and constant dosage for adsorbent 0.2 g were added respectively. The mixture was placed in a temperature-controlled shaker with and shaking speed of 200rpm for 1 hour. Other parameters such as pH, magnetic charcoal dosage, contact time, agitation rate, and initial concentration of methylene blue remained constant to ensure reliable comparisons for all experiments. A fixed 5mL of the methylene blue solution was added to 0.2 g of magnetic charcoal. The solution and charcoal were mixed thoroughly to allow the adsorption to occur for 30 min at the desired temperature Using UV-Vis spectroscopy, the samples from each experiment were gathered and examined to establish the residual methylene blue content. Measured the samples' absorbance at 665 nm. The residual methylene blue concentration against temperature was plotted on a graph, and the data were examined to look for any trends or patterns [9].

3.5.4. Study of the pH effect

In order to determine its effects on the ability of magnetic0.1M HCl and 0.1M NaOH solutions were used to modify the pH and the pH of the solution was precisely measured using a pH meter. Magnetic charcoal was used to absorb methylene blue solution, and a constant mass of 0.2 g of this material was added to 5 mL of the 50 ppm solution. For each sample, an equal amount of adsorbents was applied.

After that, the glass bottles were shaken at 200 rpm for 30 minutes. Glass 30-minute bottles were removed from the shaker and employed an external magnetic field to separate the water and magnetic charcoal. A UV-Vis spectrophotometer was used to measure the equilibrium concentration of methylene blue in the filtrate at wavelength intervals between 400 nm and 800 nm [10]. Then different values of absorbance and wavelength of individual pH of the solution were obtained. A graph of the residual concentration of methylene blue against pH was plotted and the data was analyzed to observe any trends or patterns.

3.5.5. Study of the contact time effect

0.2g of magnetic charcoal and 5 mL of 50 ppm methylene blue solutions were added to four glass bottles. At a temperature of 25^{o}C and 200 rpm, the mixture was shaken. The range of minutes was 10-180. To enable the adsorption to take place, the solution and charcoal were completely combined. Using UV-Vis spectroscopy, the samples from each experiment were gathered and examined to establish the residual methylene blue content. Absorbance was measured at 665 nm. The residual methylene blue concentration against temperature was plotted.

CHAPTER 4. RESULT AND DISCUSSION

4.1. FTIR characterization of charcoals

The FT-IR spectrometer’s diamond crystal plate was cleaned using acetone solvent and wiped dry with a piece of tissue paper by following the instructions in the FT-IR manual. Before doing the background spectrum measurement, the crystal plate was given time to dry. The dried powdered adsorbent sample was placed on a diamond crystal plate and the anvil tip was allowed to make contact with the sample so that IR beams could flow through it. The FT-IR spectra were then generated and appeared on the computer screen.

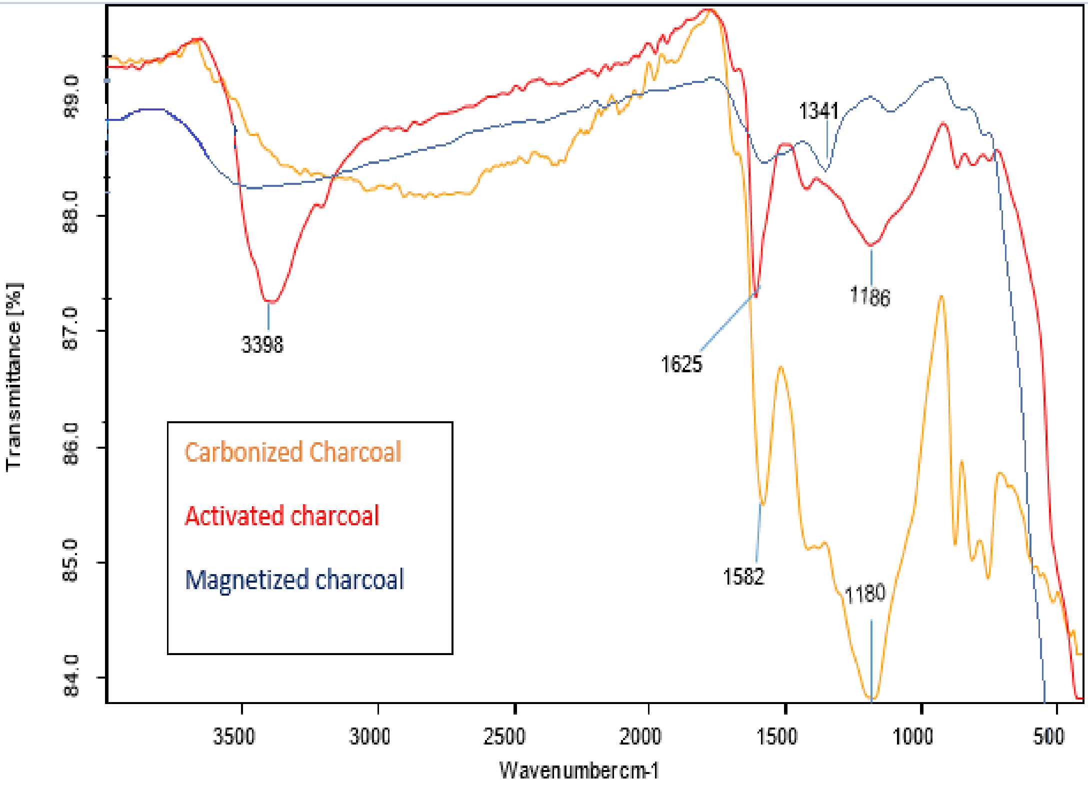


Figure 3: The FT-IR spectra results of carbonized, activated, and magnetic charcoal adsorbents.

The infrared spectrum of all charcoals is shown in Figure 3. From 4000 to 400 cm^{-1} wavenumber range was investigated. The spectra show large adsorption bands between 3400 and 3200 cm^{-1} as a result of the lengthening of the -OH bond brought on by alcohols, carboxyl, or phenols. A C=C bond is present at 1625 cm-1. 1186 and 1180 cm-1 correspond to the C-O symmetry stretching of primary alcohol, while 1582 cm-1 and 1341 cm-1 correspond to the C=O stretching vibration[21]. Functional elements on the surface of the charcoal, such as aromatic rings, hydroxyl groups, and carboxyl groups, are principally responsible for the adsorption of MB. When producing magnetic charcoal, materials like wood or agricultural waste are employed as precursors, and these materials frequently include aromatic carbon compounds. The cationic methylene blue molecules can engage with these aromatic rings through -stacking interactions, electrostatic interactions, and hydrogen bonding, which results in adsorption. Through hydrogen bonding, the hydroxyl groups (-OH) on the surface of magnetic charcoal may aid in the adsorption of MB. The cationic MB molecules can form hydrogen bonds with hydroxyl groups, which make it easier for them to bind to the charcoal surface. On occasion, the surface of magnetic charcoal may have carboxyl groups (-COOH). These groups can provide additional adsorption sites for the positively charged methylene blue molecules. Adsorption may be aided by the electrostatic affinity between the cationic MB and negatively charged carboxyl groups [22].

4.2. UV-Vis spectrum of methylene blue

The measurement of methylene blue content in the presence of magnetic charcoal perfumed by using UV-vis. A wavelength at which the absorbance measurement was performed was fixed upon scanning methylene blue and its UV-Vis spectrum is presented in Figure 4. It is seen that maximum absorbance was observed at a maximum wavelength of 665nm. Similar findings were reported in other literature [23].

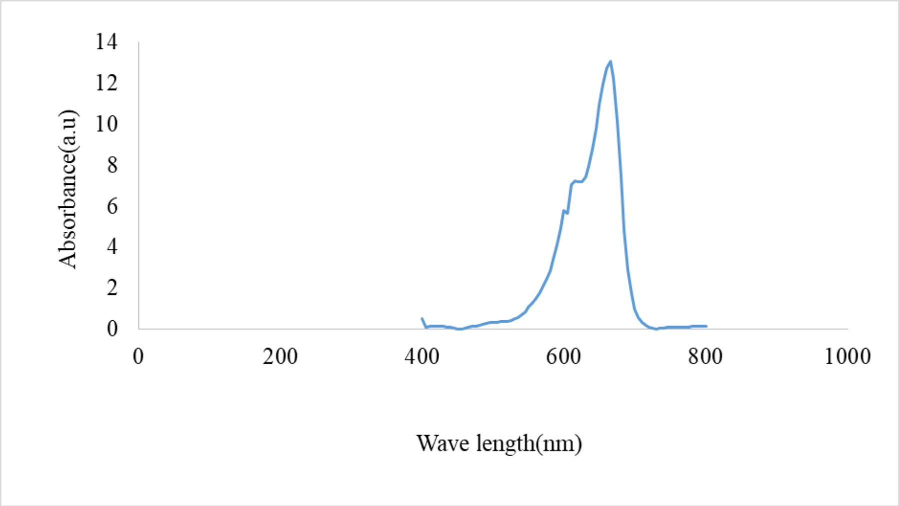
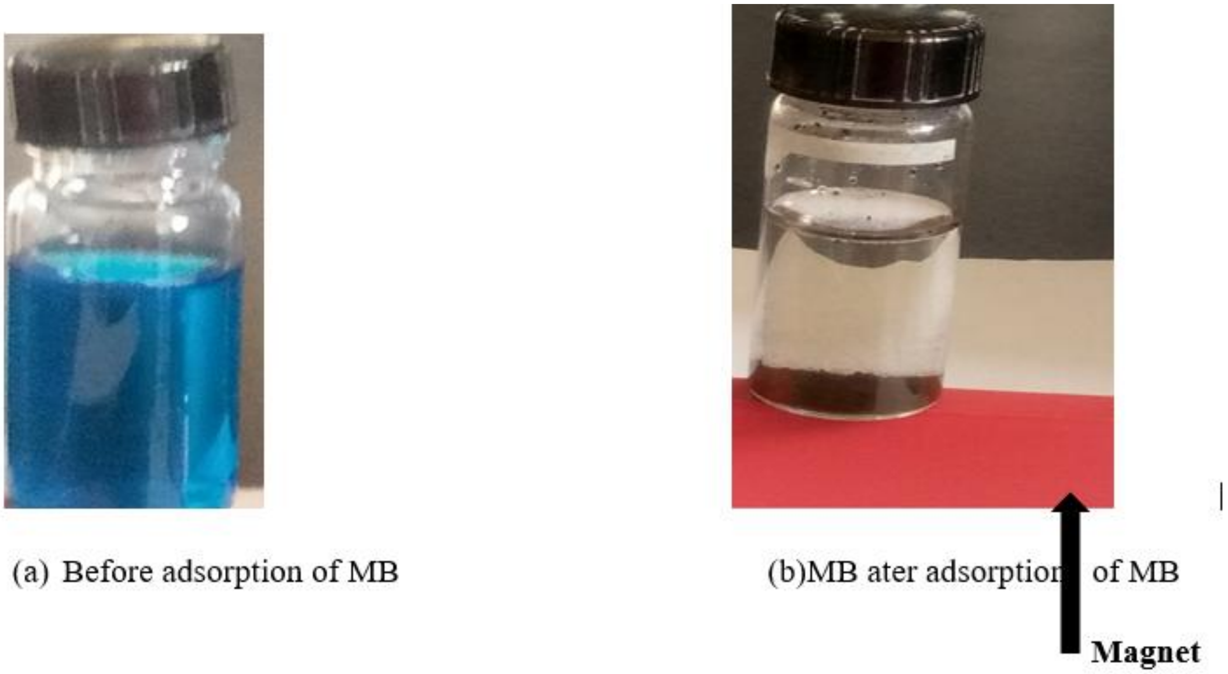


Figure 4: UV-Vis spectrum of methylene blue

4.3 Adsorption of Methylene blue by magnetic charcoal

Adsorption of methylene blue by magnetic charcoal refers to the process of removing methylene blue dye molecules from a solution using magnetic charcoal as an adsorbent material. This process involves the physical adherence of methylene blue molecules to the surface of the magnetic charcoal particles, leading to a reduction in the concentration of the dye in the solution.


(a) Before adsorption of MB

(b)MB ater adsorption of MB

Figure 5: Adsorption process of methylene blue before (a) and after (b)

4.3.1. Effect of temperature

Temperature hurts adsorption capacity, adsorption capability decreases as the adsorption temperature increase. Adsorption is an exothermic reaction, according to the laws of thermodynamics. This indicates that when adsorbate molecules (methylene blue) bind to the surface of the adsorbent (magnetic charcoal), heat is generated. The system's thermal energy rises together with the temperature. By disrupting the attraction interactions holding the adsorbate molecules to the adsorbent surface, the increased thermal energy makes it simpler for the molecules to desorb or separate from the surface. Consequently, when more molecules are desorbed from the adsorbent surface, the overall adsorption capacity declines. The temperature has an impact on the kinetics of adsorption as well. Higher temperatures can often increase the rate of mass transfer between the bulk solution and the adsorbent surface due to increased molecular mobility and collision rates.

While it could appear to be helpful for adsorption, it might also result in quicker desorption rates. Higher temperatures can cause desorption to exceed adsorption, which lowers total adsorption capacity.

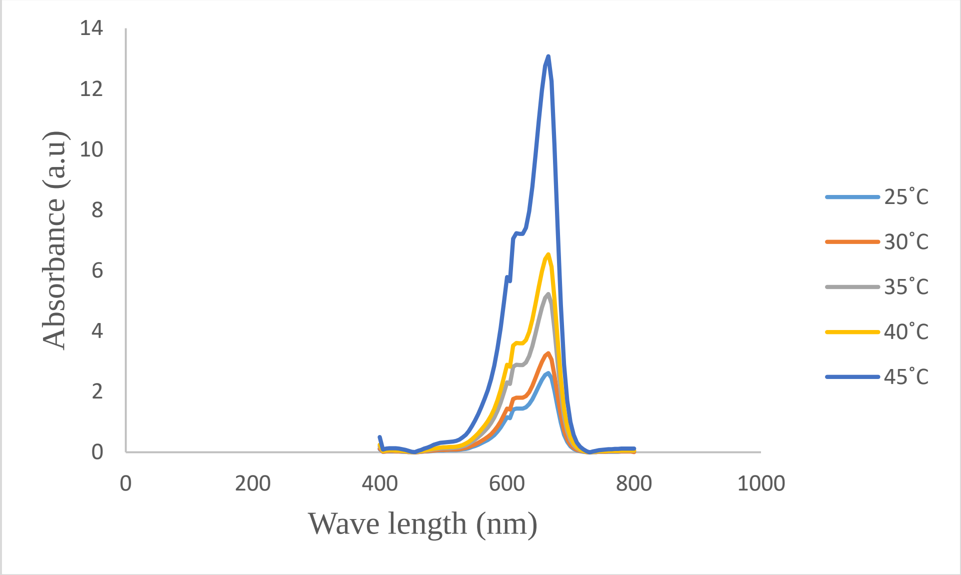


Figure 6: Effect of temperature on the adsorption of MB.

4.3.2. Effect of adsorbents dosage

With an increase in adsorbent bulk, dye removal efficiency increases. There are more active sites on the adsorbent surface as a result of the increased availability of adsorbent. The significant rise in dye removal efficiency at the initial dosage increment may be due to the presence of a significant number of active sites that allow for a significant surface area on the adsorbent. At low dosage concentrations of magnetic charcoal, the number of available adsorption sites is relatively limited compared to the amount of methylene blue in the solution. As a result, the absorbance will increase rapidly at the beginning of the adsorption process, as the methylene blue molecules quickly bind to the available sites on the sparse surface of the adsorbent.

As the dosage concentration of magnetic charcoal increases, more adsorption sites become available on the adsorbent surface. The rate of adsorption may slow down compared to the low dosage concentration, leading to a less steep increase in absorbance. At this stage, there are still a significant number of unoccupied adsorption sites available for methylene blue molecules to bind. At high dosage concentrations of magnetic charcoal, there is a surplus of adsorption sites relative to the amount of methylene blue present in the solution. As a result, the rate of adsorption further decreases and the absorbance increases more gradually. The adsorption process may approach saturation, and the absorbance may reach a plateau, indicating that the adsorption capacity of the magnetic charcoal has been maximized.

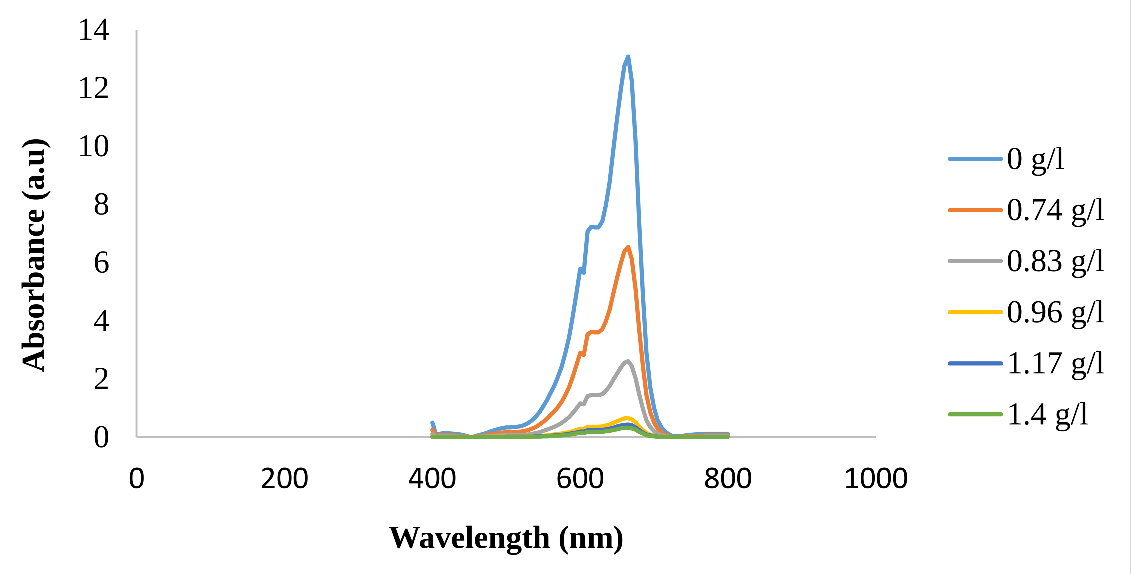


Figure 7: Effect of adsorbent dosage on the adsorption of MB.

4.3.3. Effect of adsorbate initial concentration

As initial dye concentrations increased, methylene blue removal declined. The link between the effective sites readily available on the surface of the magnetic charcoal adsorbent and the methylene blue concentration determines this effect of initial dye concentrations. On the adsorbent surface, there were many vacant effective sites at low concentrations, and as the initial dye concentration rose, fewer of the necessary effective sites for the adsorption of methylene blue molecules were present. Therefore, the dye removal decreased because the adsorbent's surface area was insufficient to handle the additional dye that was available in solution. At low initial dye concentrations, there are plenty of available adsorption sites on the magnetic charcoal surface relative to the number of methylene blue molecules in the solution. As a result, the absorbance will increase rapidly as methylene blue molecules quickly bind to the available sites on the adsorbent surface.

As the initial dye concentration increases to a moderate level, the available adsorption sites on the magnetic charcoal surface start to become occupied. The rate of adsorption begins to slow down, and the increase in absorbance becomes less steep.

At high initial dye concentrations, the adsorption sites on the magnetic charcoal surface become increasingly limited in comparison to the large number of methylene blue molecules in the solution. Consequently, the adsorption rate decreases further, and the absorbance increases more gradually. Eventually, the adsorption process may approach saturation, leading to a plateau in the absorbance.

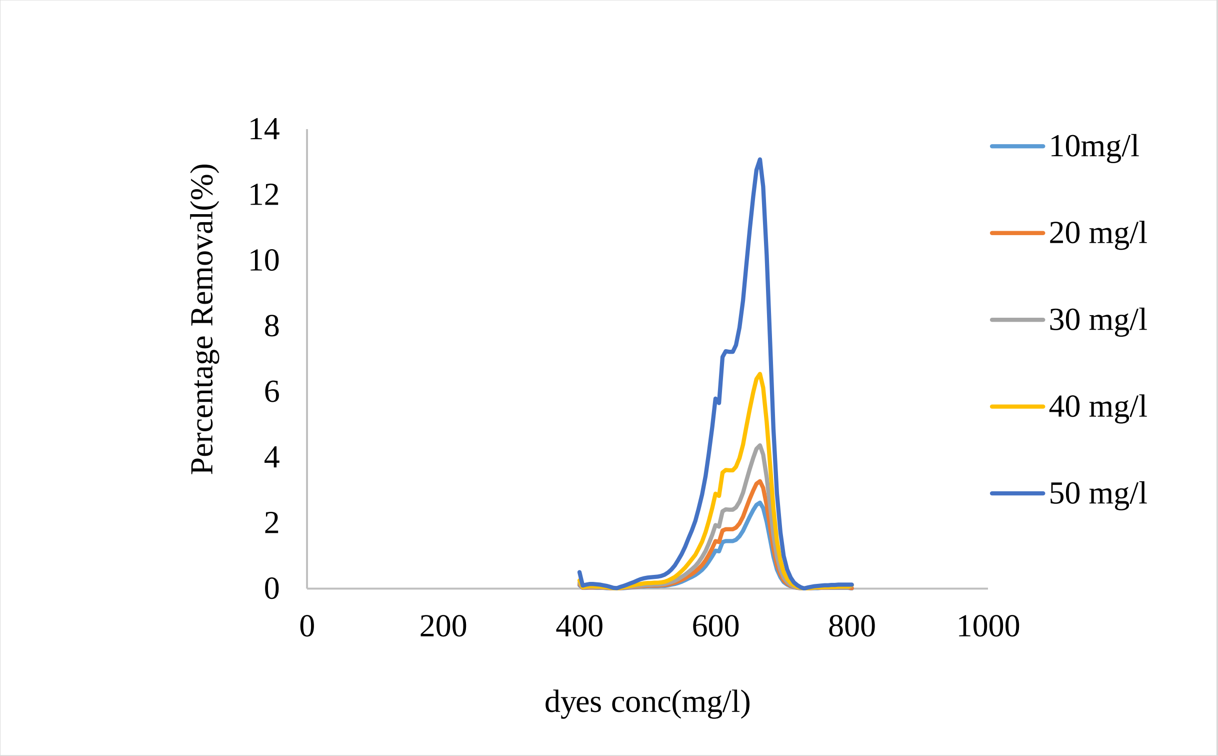


Figure 8: Effect of dye concentration on the adsorption of MB.

4.3.4. Effect of pH

The Figure below can also be explained based on the observations of the effect of the initial pH of methylene blue on magnetic charcoal. The presence of carbonyl and hydroxyl functional groups on the surface of the adsorbent makes the removal of the dye more favorable for lower pH settings (about pH=2) and higher pH values (around 9). The functional groups on the adsorbent surface become polarized in acidic environments, resulting in electrostatic contact, hydrogen bonding, and van der Walls interaction. Physisorption based on hydrogen bonding and van der Walls interaction can both be used to explain why dye adsorbs on the surface of magnetic charcoal. Electrostatic interaction coming from polarized functional groups on the adsorbent's surface that were brought about by the solvent. The charge on the surface, a crucial component of electrostatic interaction, is influenced by the solvent's composition. The dye is essential in nature; it should be noted. The surface charge of the adsorbent (magnetic charcoal) is strongly influenced by the pH of the solution. At different pH levels, the surface functional groups of the magnetic charcoal may become protonated or deprotonated, altering the overall surface charge. These changes in surface charge can affect the electrostatic interactions between the magnetic charcoal and the methylene blue molecules.

Methylene blue is a cationic dye, meaning it carries a positive charge in a solution. The adsorption process of methylene blue by magnetic charcoal involves electrostatic interactions between the positively charged methylene blue molecules and the charged sites on the adsorbent surface. The pH of the solution can significantly influence these electrostatic interactions, as it determines the degree of ionization of both the adsorbent and the dye. At different pH values, the concentration of H+ and OH- ions in the solution changes, affecting the competition for adsorption sites on the magnetic charcoal surface. The presence of a higher concentration of H+ or OH- ions can compete with methylene blue for binding sites, influencing the overall adsorption capacity. The speciation of methylene blue in solution is influenced by pH. At certain pH ranges, methylene blue may undergo deprotonating, forming different molecular species with varying affinities for the adsorbent surface. The literature claims that the varied degree of polarization of activated carbon in response to pH fluctuations is explained by the amphoteric property of the surface. Therefore, for chemisorption to take place, the charge on the activated carbon must be negative. The least amount of adsorption occurs in a very basic environment, such as pH 12, as shown in the graphic bellow.

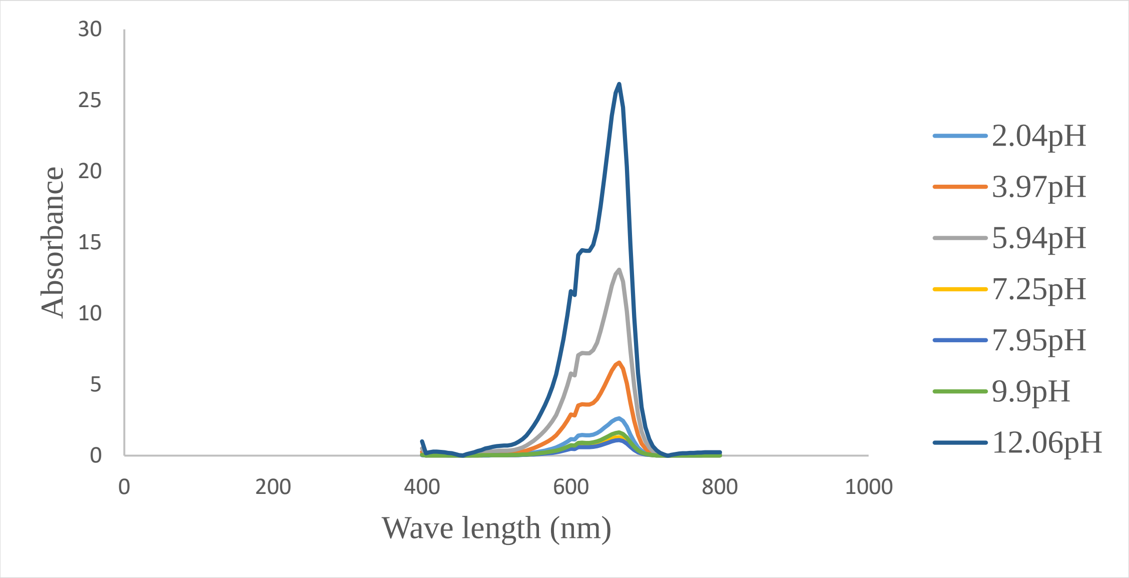


Figure 9: Effect of pH on the adsorption of MB.

4.3.5. Effect of time

The graph shows how adsorption rises more rapidly in the beginning and falls as we get closer to the saturation limit. Because the final dye concentration did not appear to significantly increase after this time restriction, the equilibrium can be presumed to have been formed after 100 minutes. The active sites may be saturated, which prevents further adsorption, as the culprit. Rapid adsorption (initial phase): During this phase, the absorbance increases quickly as a large number of available adsorption sites on the magnetic charcoal surface are occupied by methylene blue molecules.

Gradual adsorption (transitional phase): As the adsorption a progress, the rate of adsorption slows down because fewer vacant adsorption sites are available for methylene blue molecules to bind to. The rate of change in absorbance decreases as the system approaches equilibrium.

Equilibrium adsorption (plateau phase): At this stage, the adsorption process reaches equilibrium, where the rate of adsorption becomes equal to the rate of desorption. The absorbance remains constant as the adsorption and desorption processes balance each other, indicating that no further significant adsorption of methylene blue is occurring.

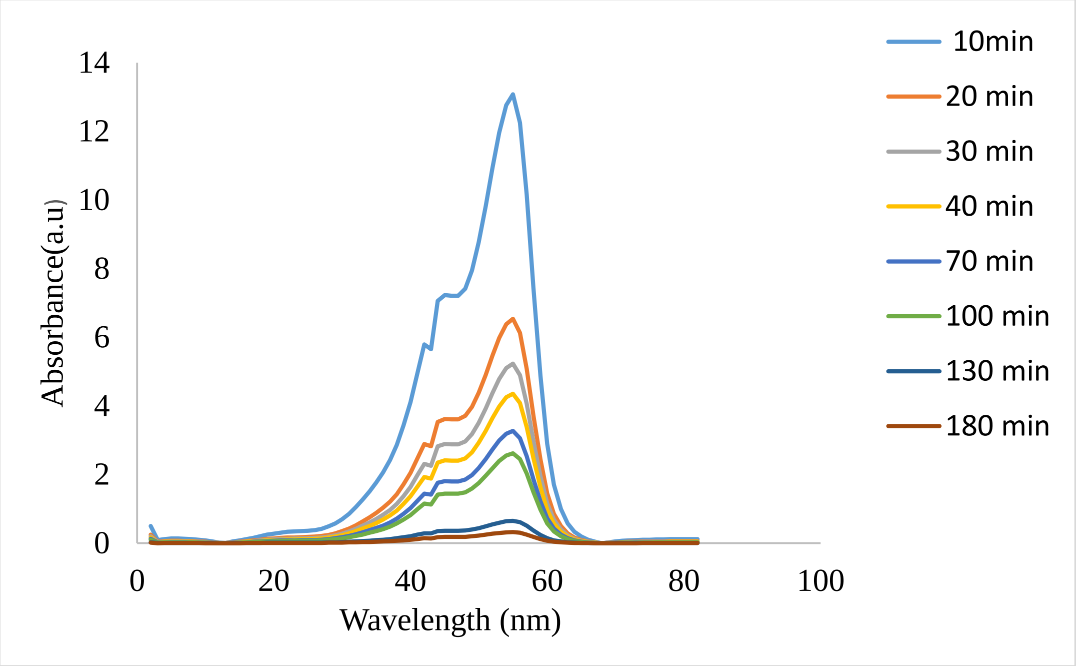


Figure 10: Effect of time on the adsorption of MB.

4.4. Adsorption kinetics

The mass transfer of adsorbate from the fluid phase to the surface of the adsorbent is what is known as adsorption in physical terms [23]. To determine how effective the process is, it is required to investigate the adsorption mechanism, which can be accomplished by examining adsorption kinetics. The significance of MB adsorption onto waste wood adsorbents was investigated using pseudo-first-order and pseudo-second-order models [12]. Based on the results of the regression correlation coefficient R2, the best-fit model was chosen. Also known as a pseudo-first-order analysis of the adsorbate-adsorbent interactions' mechanism of action.

Table 1: Adsorption parameters obtained from kinetic studies

Pseudo -First Order Model			*Pseudo* -Second Order model		
kl (min-1)	qe (mg/g)	R2	k2	qe (mg/g)	R2
-7*10^-5	1.22	0.239	-0.062	17.88	0.997

The pseudo-second order kinetic models for the adsorption of MB from aqueous solution by magnetized charcoal are shown in Figure 8 and Table 1. The pseudo-second order kinetic model had a higher linear correlation coefficient (R2>0.997) than other kinetic models, and it fit the experimental data better.

Indicating that pore diffusion is not the only element impacting the rate, the findings of the linearized pseudo-first order equation significantly depart from a straight line as well [11]. First-order kinetics in this case displayed low correlation coefficients. On the other hand, the linearized pseudo-second order model demonstrated a linear connection for MB into magnetized charcoal when t/q was plotted against t. Additionally, the pseudo-second order kinetics parameters are qe 11.96 mg/g and k1 -0.132 min-1 with R2 values of 0.997. This demonstrates that the pseudo-second order model more properly describes the adsorption kinetics. Second-order kinetics were found to have higher regression coefficient R2 values than first-order kinetics [12].

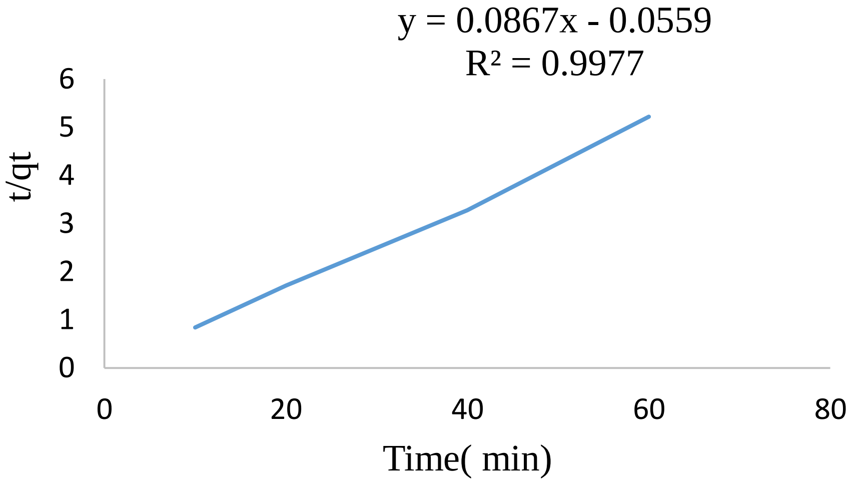


Figure 11: *Pseudo*-second order kinetic for MB onto magnetized charcoal

4.5 Adsorption isotherms

Adsorption isotherms can be used to characterize how dye concentrations interact with an adsorbent's surface[18]. This can help in enhancing the adsorbent surface for the dyes that are removable and they are among the requirements for knowing the adsorption system. Additionally, the values of the isotherm constants can be used to forecast the maximum adsorption capacity and to describe the adsorbent's affinity and surface characteristics [10]. Using Freundlich and Langmuir's isothermal models, the experimental equilibrium data were examined to define the MB dye's adsorption on magnetized charcoal. The Freundlich isothermal model indicates heterogeneity of the adsorbent material and multi-layer coverage of the adsorbate, whereas the Langmuir model assumes monolayer coverage of the adsorbate on a homogenous adsorbent surface [14].

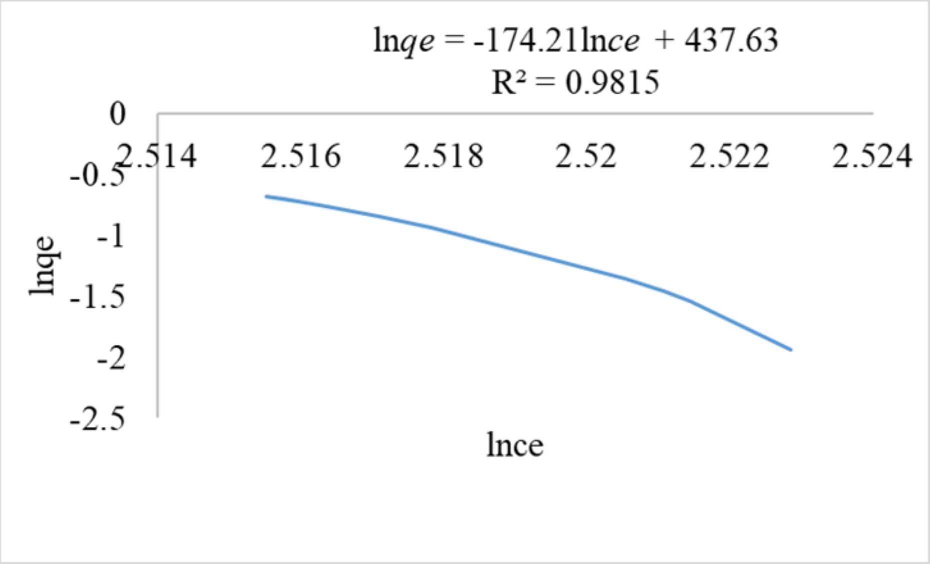


Figure 12: Freundlich isotherm for the adsorption of MB onto magnetized charcoal

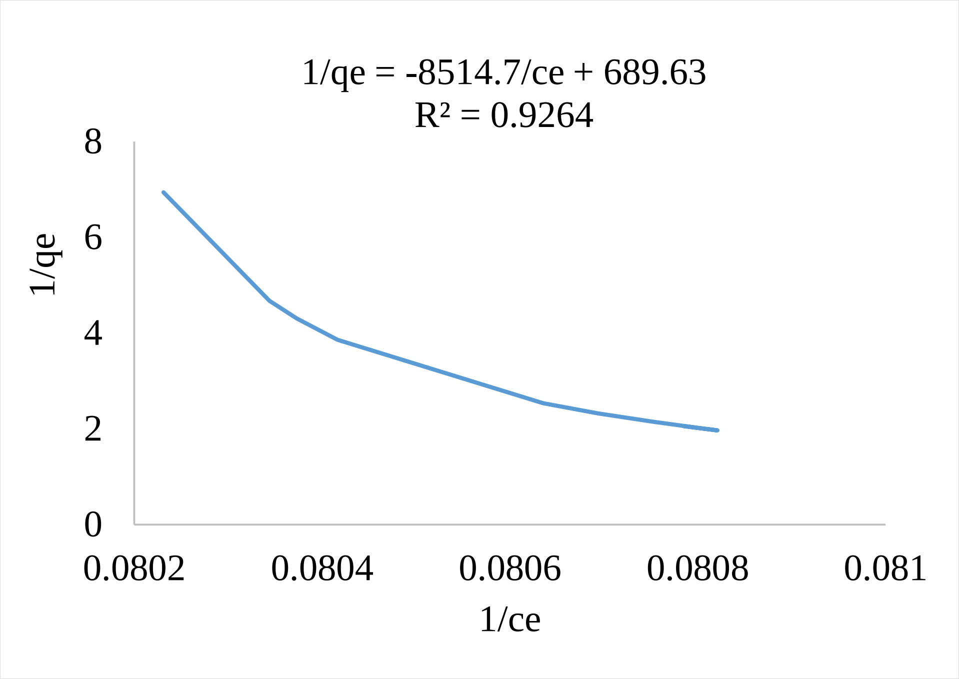


Figure 13: Langmuir isotherm for the adsorption of MB.

The graph of the Langmuir isotherm revealed that the slope was -8514.7, th intercept was 689.63, and R2 was 0.9264. The equation is given by lnqe=-174.21lnC_(e)+437.63 on the graph of the Freundlich isotherm, and R2= 0.9815, which is quite near to 1. Thus, both models do a good job of describing the system. For the adsorption of MB onto magnetized charcoal.

Table 2: Langmuir isotherm and Freundlich for the adsorption of MB onto magnetized charcoal.

Adsorbent	Methylene blue						
	R^2	Slope	Intercept	K_L	R_L	*Kf*	
Magnetized charcoal	Langmuir	-8514.7	689.6	-12.3	-0.0016		
	0.9264						
	Freundlich						
	0.9815	-174.2	437.6			1.14x10^10	

4.6 Thermodynamic study

The adsorption process's thermodynamic research is more helpful in determining the type and frequency of the adsorption reaction. Typical changes in free energy (G), enthalpy (H), and the.

In the experiment, the following equations were employed: You may find the values of H and S by plotting lnK against 1/T and comparing the slopes and intercepts of the linear straight. At various temperatures and starting dye concentrations, the values of G were calculated and are displayed in Table 3 along with the values of H, S, and G. The adsorption of MB dye onto magnetic charcoal at various temperatures (30, 35, 40, and 45^{o}C) was investigated using initial dye concentrations of 50 mg/l and 0.02g of the magnetized charcoal adsorbents in 50mL of the dye solution shaken at 200 rpm for 30 min.

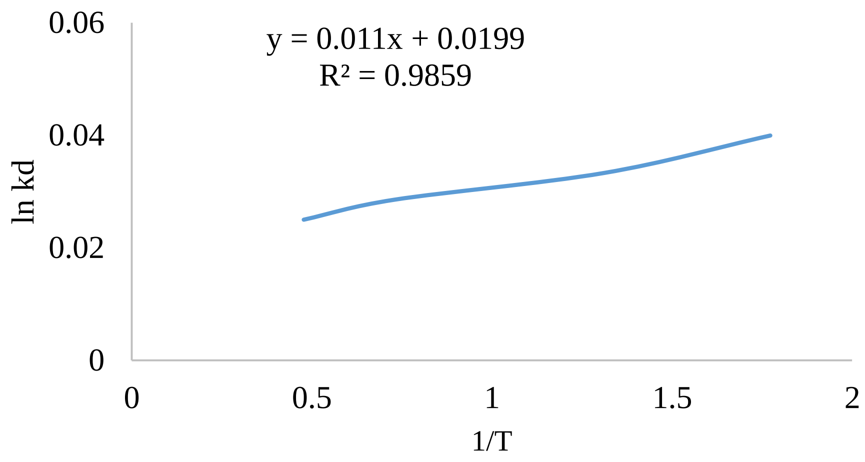


Figure 13: Plot of lnK_dversus $\frac{1}{T}$for adsorption of MB dye.

Table 3: Thermodynamic parameters for the adsorption of the MB dye onto the magnetized charcoal adsorbent.

$\Delta S°$ (KJ mol^{-1}K^{-1})	**$\Delta H°$(KJ mol^{-1})**	**$\Delta G°$ (KJ mol^{-1})**			
		298K	303K	308 K	313K
0.165	-0.091	-368.5	-327	-212	-158.7

According to the negative standard enthalpy change (-H), the interaction of the MB dye adsorbed onto the magnetized charcoal was the exothermic reaction, which is by the impact of temperature. The positive standard entropy change (+S) has drawn attention to the rise in randomness that occurred at the dye solution interface during the adsorption phase. The negative value of the standard free energy change (-G)[11] indicates that the adsorption of the MB dye is a spontaneous reaction. Regarding their thermodynamic behavior, the Spirogyra species that were treated and those that were not exhibited very different results. Spontaneity was characterized by a negative value of G during the adsorption of MB. For Spirogyra sp. in both its raw and pretreated forms, the value of ΔH° was negative such behavior demonstrated the exothermic nature of MB adsorption, and the randomized character of the solid-liquid adsorption interface was reflected by the positive value of ΔS° [16].

4.7. Reusability study of magnetic charcoal

In order to reduce the cost of the adsorption technology and recover contaminants from wastewater, repeating applications for five cycles of methylene blue adsorption tests have been conducted to evaluate the stability and potential for the reuse of magnetic charcoal as an adsorbent. Because of the powerful external magnet, separating the solid and liquid phases in each step has become much simpler. In the graph of Figure 14, the adsorption capacities of magnetic charcoal were displayed. It peaked at 97% for the first run, then fell to 96% and reduced by 3% for the next three runs. The decline in removal effectiveness may be brought on by some magnetic charcoal that was still tightly bonded to the surface.

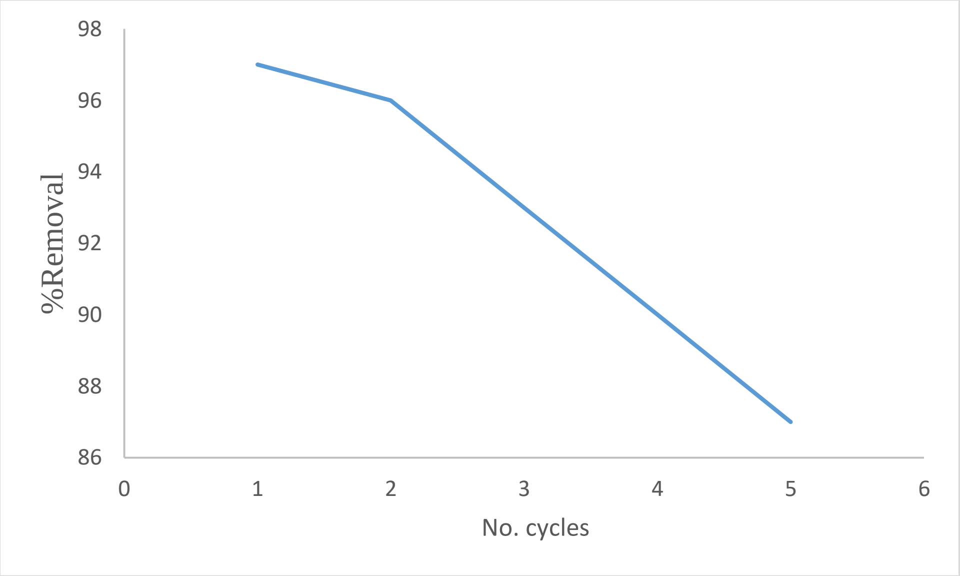


Figure 14: Percent removal of methylene blue by magnetic charcoal with consecutive five repeated cycles.

Experimental conditions: methylene blue initial concentration 50 mg/l, mass of magnetic charcoal 0.2 g, solution volume 10 mL, at pH 7 and 25 ^{o}C.

CHAPTER 5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This dissertation's research examined the effectiveness of magnetic charcoal as an adsorbent for organic contaminants in water. In order to do this, the produced adsorbents were examined using FTIR, and the adsorption tests were carried out using UV-Vis. It has been demonstrated that the adsorbent has the potential to be utilized in MB removal. This substance is inexpensive and safe for the environment. In the process of treating water, magnetic charcoal has a surprising advantage over other adsorbents. This study's dye adsorption process comprises ingredients, characteristics, adsorption specifics, and steps for magnetic recovery and separation. Utilizing magnetic materials speeds up the separation and recovery process.

Based on the findings of the experiments, it was discovered that the quantity of adsorption capacity increases with decreasing MB dye concentration and increases with increasing magnetic charcoal concentration. A high-efficiency removal of 96.55% of the dyes was accomplished with 1.4g. According to FTIR analysis, the functional groups were found to be the root of the adsorption discrepancies. Additionally, when we plotted the results for the Langmuir and Freundlich models for the adsorption isotherm, we saw that the regression coefficient was very near to 1. Consequently, both models can be used to fit the experiment's data. The regression coefficient for the Langmuir isotherm was 0.92 as opposed to 0.98 for the Freundlich isotherm, making it less accurate. Magnetic-activated carbon hence shows potential as an adsorbent. Due to its limited application, it is critical to pay careful attention to the properties and manufacturing processes of magnetic activated carbon. To the benefit of society, adsorbents with exceptional MB dye removal adsorption efficacy and reusability will be successfully sold for large-scale dye removal.

5.2 Recommendation

Based on the obtained results and conclusions, the following recommendations can be suggested:

i. People working in industries especially all those who work in textile industries use magnetic charcoal to protect human health.
ii. More investigations should be done for other organic pollutants, especially those which are persistent organic pollutants.
iii. Further studies may focus on the use of other characterization techniques like SEM, TEM, and nitrogen adsorption/desorption among others to study the morphology and size of synthesizednanoparticles.

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