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HYDROTHERMALLY ACTIVATED BANANA PEELS FOR ADSORPTION AND KINETICS STUDIES ON MALACHITE GREEN DYE

BY

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BU/UP/2021/1683

A DISSERTATION SUBMITTED TO THE DEPARTMENT OF CHEMISTRY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR OF SCIENCE EDUCATION DEGREE OF BUSITEMA UNIVERSITY

MAY, 2024

DECLARATION

I Namalike Mariam declare that the information here is my original work unless where reference has been cited. The work has never been submitted to any other institution for any award or publication.

Signature.. Date.26TH JULY, 2024

Namalike Mariam

APPROVAL

This work has been supervised and approved by Dr. Kigozi Moses.

Signature.. Date..26/08/2024..........................

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DEDICATION

I dedicate this project to my supervisor, the Chemistry Department of Busitema University, my beloved parents and siblings, my lovely son, my fellow year three students 2023/2024, and Chemistry laboratory technicians.

ACKNOWLEDGEMENT

I would like to sincerely thank my supervisor Dr. Kigozi Moses for his efforts, guidance and words of encouragement. I thank the Chemistry laboratory technician, Madam Amado Mary for her advice and assistance during the process of doing my practical work, the entire staff of Chemistry Department for their advice, the management and staff of Busitema University.

I extend great thanks to my beloved parents, my brothers Wambede Mudasiru and Wambede Abudallah with my friend Walumu Fahad for their support throughout the course. I also appreciate Anyobu Philips, Opollot Henry Joseph, Nangoli Cranimer and Watwati Bruno for their electronic support.

I also appreciate Kitayi Solomon for his welfare during the practical process, my colleagues; Nabutsale Esther, Wazemba Boniface, Anyait Salome, Abukwi Patience, Tibenda Christine, Namasoko Jerald, Akello Norah, Mateya Constant, Mulabi Erukam, Alowo Florence, Okello Ivan for their advice, cooperation and team work.

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ACRONYMS

UV-Vis: Ultra-violet Visible Spectrometer

C_e: Equilibrium concentration

x: Amount of malachite green dye adsorbed per adsorbents

m: Maximum amount of malachite green dye adsorbed per adsorbents

pH: Hydrogen potential

qt: amount of malachite green dye adsorbed on hydrothermally activated banana peels at time

AB: Activated biomass

qe: amount of malachite green dye adsorbed at on hydrothermally activated banana peels equilibrium

ABSTRACT

In this study, hydrothermally activated banana peels powder was used as an adsorbent for removal of malachite green dye from aqueous solutions. The influence of pH, equilibrium time and initial concentration of malachite green dye on amount of malachite green dye adsorbed were investigated. Studies showed that the amount of malachite green dye increased with increasing bulk solution pH, initial concentration of malachite dye and then decreased with increase in equilibrium time. The experiments showed that the highest removal of malachite green dye was at pH 5, contact time 20 minutes and initial concentration 559mg/L. The experimental data were analyzed using Langmuir and Freundlich adsorption isotherms, pseudo-first order and pseudo-second order kinetic models. It was shown that the adsorption of malachite green dye onto hydrothermally activated banana peels powder could be described by the Freundlich adsorption isotherm and pseudo-second order kinetic model, suggesting that the adsorption process is presumable a physisorption

CHAPTER ONE

1.0 INTRODUCTION

1.1:BACKGROUND

The treatment of wastewater nowadays has become a great area of concern by many researchers due to the sudden decrease in the quality of fresh drinking water, which could result from contaminants from the aqueous phase. Because of their broad application in several industrial activities, many industrial effluents including textile companies, plants, food producers, dye factories, electroplating factories release waste water containing dyes leading to the contamination of various water sources (Gupta, Ali, Saleh, Nayak, & Agarwal, 2012). Dyes refer to a group of complex organic materials that are intended to be stable and non-biodegradable. These dyes enter the environment as a result of several industrial processes. The textile industry alone accounts for two thirds of the dye stuff production, about 10-15% of the dyes used come out in the effluent (Thompson et al., 1987). Dyes contamination in waste water results into problems in various ways; the availability of dyes though in very low quantities, is highly visible and undesirable. The effluents from industries manufacturing and consuming dyes are highly colored, have high chemical and biological demands, (COD and BOD) respectively, and contain suspended solids.

Direct discharge of such effluents into the environment may cause formation of toxic carcinogenic breakdown products, also affects the colour of the receiving streams and its aesthetic value. Toxicity rates were found to be highest among basic and diazo direct dyes (Ablikim et al., 2008). Colour interferes with the penetration of sunlight through water, reducing the rate of photosynthesis, inhibiting the growth of aquatic biota and interfering with the solubility of gas in water bodies(Banat, Nigam, Singh, & Marchant, 1996). This demands for the efficient methods for the removal of dyes from waste water. Among the different anionic, cationic, non-ionic, and zwitterionic classes of dyes, cationic dyes are more toxic than anionic ones. (Ghaedi et al., 2011)

The various methods for treating waste water containing dyes are; coagulation and flocculation, electrochemical treatment, chemical oxidation, liquid-liquid extraction and adsorption(Wang, Boyjoo, Choueib, & Zhu, 2005). Though some of these techniques were m reported to be powerful in decolorizing waste water, adsorption has been proven to be a very effective technique for separation. Therefore it is now considered to be a superior technique among other techniques for treatment of waste water in terms of initial cost, simplicity of design, ease of operation and insensitiveness to toxic substances (Parimaladevi & Venkateswaran, 2011).

More than 10,000 dyes are widely used in various industries such as textile, paper, and others. Malachite green dye is most commonly used. It is an organic compound with molecular formula, $C_{23}H_{25}ClN_2$ applied as a dye. Its structural formula is shown in Figure1.1.1 below.

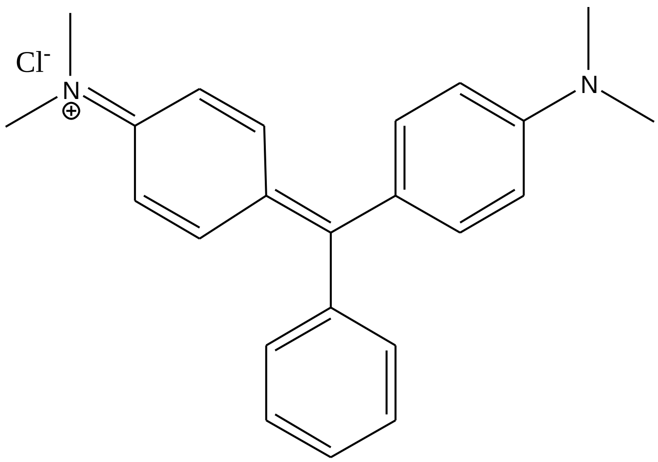

Figure 1.1: Chemical structure of malachite green dye

Malachite green dye is traditionally used as a dye for materials such as leather, silk and paper (Raducan, Olteanu, Puiu, & Oancea, 2008). Though important, malachite green dye is highly for species living in water such as fish and mammals. It is toxic in nature and it level of toxicity increases with exposure time, temperature, and concentration. It leads to mutagenesis, chromosomal fractures and toxicity of the respiratory system, among others. During the ancient days, malachite green dye was largely applied in fish farming due to its cost and good efficiency treating and preventing external fungal and parasitic infections in fish (Hashimoto, Paschoal, De Queiroz, & Reyes, 2011). Researchers found that it harms human beings if inhaled or ingested by the body and also causes irritation when contact with the skin.

Hence there is need to remove malachite green dye from waste water before it is discharged back to the environment.

There are several techniques employed in the removal of malachite green dye from waste water and these include; coagulation, flocculation, oxidation/advanced oxidation, precipitation, combined chemical and biochemical processes, ozonation, aerobic and anaerobic digestion, irradiation, adsorption, membrane treatment, (Bekçi, Seki, & Cavas, 2009), bio sorption, fungal decolonization, ion exchange (Tewari, Singhal, & Arya, 2018).The choice of the method to be used depends on effluent characteristics like temperature, pH, concentration of malachite green dye in waste water, costs involved and social factor set by government agencies. In this study, adsorption method was used. Adsorption is the most effective technique as it is cheap, fast, and simple (Tewari et al., 2018).

Adsorption refers to attracting and retaining molecules of a substance on the surface of a liquid or solid, resulting in higher concentration of the molecules on the surface. Adsorption is a phase transfer process that is widely used to remove substances from fluid phases (Benjamin, 2002). In waste water, adsorption has been proved to be an efficient method for removing dye molecules by adsorption onto solid surfaces. Solid surfaces are characterized by energy rich active sites that are able to interact with solutes in adjacent aqueous phase due to their electronic and spatial properties (Guillet-Nicolas, Ahmad, Cychosz, Kleitz, & Thommes, 2016). Typically the active sites have different energies that is to say the surface is energetically heterogeneous.

In adsorption theory, the basic terms shown in Figure 1.1.2 are used. The solid material that provides the surface for adsorption is called an **adsorbent;** the species that will be adsorbed is called the **adsorbate** (Schwarzenbach, Gschwend, & Imboden, 1993). For this study, the adsorbent will be hydrothermal activated banana peels and malachite green dye will be used as the adsorbate. By changing the properties of the aqueous phase (such as concentration, pH and temperature), adsorbed species can be released from the surface and transferred back into the aqueous phase. The reverse process of adsorption is called **desorption.** The surface area of the adsorbent is a key parameter since adsorption is a surface process (Schideman, Marinas, Snoeyink, & Campos, 2006). This study will examine the effects of pH, contact time and adsorbate concentration on malachite green dye adsorption.

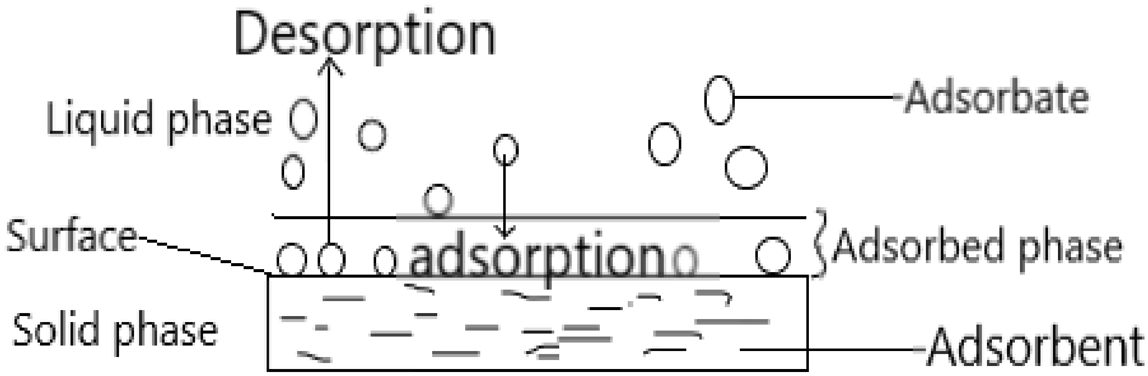

Figure 1.2: Basic terms of adsorption.

As explained earlier, adsorption describes the enrichment of adsorbate on the surface of adsorbents. Contrary, absorption is the transfer of a substance from one bulk phase to another bulk phase. In this case, the substance is enriched in the receiving phase and not on its surface (Benjamin, 2002).

An example of absorption is the dissolution of gases in liquids. In natural systems, some materials with complex structures can bind substances from the aqueous phase on their surface and also in the interior of the material. In such cases, it is quite difficult to distinguish between absorption and adsorption (Polson, 1950).

Hence, the term sorption is the general term preferred to describe the transfer between liquid and solid in natural systems. The term sorption consists of adsorption and absorption. The term sorption is also used for ion exchange processes on mineral surfaces (Digiano, Baldauf, Frick, & Sontheimer, 1978).

1.2 STATEMENT OF THE PROBLEM

The use of activated biomass (AB) as an adsorbent in removing malachite green dye from waste water is prevalent. Different kinds of biomass are available but are quite expensive. For this reason, a low cost, highly available adsorbent must be developed which can easily be obtained without a complicated process. In this study, hydrothermal activated banana peels were used as an adsorbent since they are not expensive to develop and can easily be obtained from the environment.

Since the government of the republic of Uganda banned the importation of second hand clothes from foreign countries to Uganda, Ugandans shall resort to making their own clothes by coloring locally produced cotton using various dyes to gets several colored clothes. With this, there will be increased use of dyes which are later discharged together with the effluent and may end up in fresh water sources, affecting aquatic biota and human life. Therefore, there will be need to remove these dyes from waste water before being discharged back to the environment to minimize their effects on aquatic biota and human beings. For this study, malachite green dye will be removed from wastewater.

1.3 OBJECTIVES

1.3.1 General objective

To determine the ability to absorb of malachite green dye on hydrothermally activated banana peels.

1.3.2 Specific objectives

I. To activate banana peels and characterize them

II. To set up the adsorption experiment.

III. To study the effect of pH, contact time, adsorbate concentration on the removal of malachite green dye from waste water by adsorption

IV. To carryout kinetics of the adsorption of malachite green dye on hydrothermal activated banana peels.

1.4 SIGNIFICANCE OF THE STUDY

The study demonstrated the suitability of hydrothermally activated banana peels as an effective adsorbent for removal of malachite green dye from wastewater.

1.5 JUSTIFICATION OF THE STUDY

The discharge of waste water containing malachite green dye to the environment causes harm to both aquatic biota and human life. In aquatic environments, malachite green dye can be toxic to fish, invertebrates, and other aquatic organisms. It can interfere with the respiratory system, cause tissue damage, and affect reproduction in fish and other aquatic species. Additionally it can persist in the environment and bio accumulate in organisms leading to long-term impacts on aquatic ecosystems. In terms of human life, there are concerns about the potential carcinogenic and mutagenic properties of malachite green dye. Exposure to malachite green dye has adverse effects, including skin irritation and potential risks of cancer among others.

Several researchers have developed different adsorbent materials such as graphenes oxide, and activated carbon got from other biomass like orange peels, neem sawdust, pineapple peels for the removal of malachite green dye but a small population adopts them due to their high costs of preparation, low availability and inability to be recycled.

Banana peels when adopted as an adsorbent for the removal of malachite green dye from waste water, a large population can easily access it since it's readily available within the environment and involves low costs of preparation.

1.6 SCOPE OF THE STUDY

The study was be performed in Busitema University chemistry laboratory where the apparatus were arranged and used for analysis. Some materials like bananas peels were got from the Nagongera town council.

CHARPTER TWO

2.0 LITERATURE REVIEW

Various researchers have carried out adsorption studies using low-cost adsorbents (Sud, Mahajan, & Kaur, 2008). The adsorbent was prepared from Prosopis cinerania sawdust an agro-industry waste, treated with formaldehyde and sulphuric acid and used for the removal of malachite green dye in a batch reactor (Garg, Amita, Kumar, & Gupta, 2004). Papinutti et al. (2006) used wheat bran to remove malachite green dye and this was found to be an effective adsorbent since it contains polysaccharides like starch and cellulose and is a useful carbon source. Maximum adsorption capacity was 240mg/g. Kumar et al (2006) proposed a method for removing malachite green dye using Pithophorass sp., a fresh water algae with the maximum dye uptake sobserved at pH 6. The adsorbent had an adsorption capacity 42.2mg/g with removal of 98.8%. The data followed first-order kinetics. Oil palm trunk removed malachite green dye from an aqueous solution. The maximum dye removal was 82% at pH 10. They found that adsorption of the dye was unfavorable at pH less than 4 which was attributed to two reasons ; First, as the pH of the system decreased, the number of negatively charged adsorbents decreased and amount of positively charged surface increased . Secondly, an excess in H^+ lower adsorption of malachite green dye took place at acidic pH (Hameed & El-Khaiary, 2008). Rahman et al. (2005) conducted similar studies with activated carbon derived from bamboo, rice husks, or spent tea leaves. Rice husks treated with phosphoric acid, sodium hydroxide, and nitrogen was used to remove malachite green dye. They found that maximum carbonization temperature for effective adsorption was 773K and the corresponding adsorption capacity was 80mg/g. The derived activated carbon also gave good removal efficiency. Neem saw dust was also used as an adsorbent to remove malachite green dye from aqueous solution. The neem sawdust was collected from local timber industry, boiled with dilute hydrochloric acid for 30 minutes, distilled with water and then dried. It was sieved finely to particle sizes of 50, 80 and 100 mesh sizes significantly influencing the adsorption kinetics. The adsorption capacity was directly proportional the surface area totally exposed and inversely proportional to the particle diameter. Adsorption of malachite green dye increased from 66.75% to 75.78% with reduced adsorbent particle size from 50 to 100 mesh at pH 7.2 for a solution of 12mg/g concentration. Adsorption rate increased with agitation speed, the adsorption process was endothermic in nature (Khattri & Singh, 2009).The adsorbent could not be used on large scale because of limited availability and high cost. Chowdhury et al. (2011b) used rice husks treated with NAOH to remove malachite green dye in batch study. The adsorption capacity increased with dye concentration from 10 to 100mg/L because enough driving force was provided to overcome all the mass transfer resistance.

Bio adsorbents were synthesized by Song et al. (2015) using triethylamine as the modifying agent. The modified adsorbent was 632.98% more efficient than the unmodified one. Maximum adsorption capacity was 697.8mg/g in 6 hours at pH 5.08. The adsorption data fitted with the Freudlich model(Song et al., 2015). A continuous fixed- bed reactor for malachite green dye removal was designed by Das et al. 2016. They used pine apple leaf powder as an adsorbent, and the adsorption efficiency was higher at a low flow rate as compared to a high flow rate due to more residence time. The break through time increased with increased bed height due to more of adsorbent and hence, higher intake of the dye. The data fitted well with Thomas model (Das et al., 2016).

2.1 HOW ADSORPTION OCCURS

Adsorption is a phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid resulting into higher concentrations of the molecules on the surface. The process of adsorption is due to the presence of unbalanced forces of attraction or free valences at the surface of the solid or liquid phases. The unbalanced forces of attraction have a tendency to attract and retain ionic or molecular species which come into contact with the surface of the adsorbent (Kuennen, Van Dyke, Crittenden, & Hand, 1989).

2.2 TYPES OF ADSORPTION

There are mainly two types of adsorption and these are based on the kind of attractive forces existing between the adsorbent and the adsorbate that is physical adsorption and chemical adsorption (Sepulveda, Castellan, Hankinson, & Cocke, 1984).

2.2.1 Physical adsorption or physisorption

When weak Vander Waals forces of attraction exist between the absorbate and adsorbent, the process is called physical adsorption or physisorption. It occurs with formation of a multi-layer of adsorbate on the adsorbent. Physical adsorption has a low enthalpy of adsorption that is 20-40kJmol^{-1}. This takes place at low temperature below the boiling point of the adsorbate. As the temperature increases in the bulk, the process of physisorption decreases. The process can easily be reversed by heating or lowering the pressure(Sepulveda et al., 1984).

2.2.2 Chemical adsorption or chemisorption

When the forces of attraction between the adsorbate and the adsorbent are chemical forces of attraction or chemical bond, this process is called chemical adsorption or chemisorption. It has high enthalpy of adsorption that is 200-400KJmol^{-1}. This process can occur at all temperatures. With increase in temperature, it first increases and then decreases. This type of adsorption cannot be reversed (Helfferich, 1962).

2.3 KINETICS OF MALACHITE GREEN DYE ADSORPTION ON HYDROTHERMALLY ACTIVATED BANANA PEELS

In the present study, adsorption capacity is one of the most vital parameter because it determines how much contaminant can be removed from the solution that is to be cleaned, by unit mass of adsorbents. However, not only high specific surface area and high adsorption high capacity of the adsorbent developed play a key role in fast adsorption of noxious impurities; the kinetics process may also strongly constrain the application of the developed material as an efficient adsorbent. Small kinetic adsorption significantly increases the removal time of the impurity from the liquid phase which directly makes the adsorption process unfavorable.(43). In this work, various kinetic models including the pseudo-first order and the pseudo-second order kinetic models were used to test the experimental data.

CHAPTER THREE

3.0 METHODOLOGY

3.1 MATERIALS AND REAGENTS

Measuring cylinder, pH meter, Heater, Thermometer, Stop watch, Centrifuge, Glass beakers, Volumetric flasks, Stirrer, Spatula, Autoclave reactor, Oven, Analytical balance, FTIR, UV-Vis spectrophotometer, Thermally isolated magnetic stirrer, Potassium hydroxide, Deionized water, Distilled water, Filter funnel, Malachite green dye.

3.2 PREPARATION OF ADSORBENT

Bananas were purchased from Nagongera town council market and peeled. The banana peels were washed thoroughly with distilled water in order to remove surface dirt and any other impurities, cut into small pieces and then dried in an oven at 100 ^{0}C for 24 hours to remove moisture content. After complete drying, the dried sample were crushed and sieved to be of uniform particle size.

3.2.1 Hydrothermal activation of banana peels.

20g of banana peels precursor was dispersed in 100mL of distilled water in a beaker, and KOH was added in the ratio of 1:1. The mixture was sealed into a Teflon vessel inserted in the autoclave, which was subjected to heating at 180 ^{o}C for 24 hours. After this period of time, the autoclave was cooled to room temperature. The reaction mixture was consisting of a liquid solution and a solid phase (hydrochar). The hydrochar was collected in a glass beaker for separation, washed thoroughly with distilled water to pH 7 and then dried at 100 ^{o}C for 12 hours.

3.2.2 Characterization of banana peels.

The infrared spectra for the hydrothermally activated banana peels sample for the determination of functional groups present were recorded with FT/IR-6600typeA spectrometer model in the region 4000.6 cm^{-1} – 399.193 cm^{-1}.

3.3 PREPARATION OF ADSORBATE

Stock solution of malachite green dye was prepared by dissolving 1g of malachite green dye powder in 1000mL of distilled water. The desired concentrations of the dye 15 samples of malachite green dye solution will be prepared by dissolving 165.5g of malachite green dye crystals in 500mL of distilled water placed in a glass beaker to make 1.0M solution. Solutions of concentrations lower than 1.0M such as 0.625M,

3.4 ANALYSIS

Five samples were used while varying every parameter of the study. The adsorption process was performed in glass beakers where the mixtures of hydrothermally activated banana peels powder and a solution containing malachite green dye were stirred to maximize the chances of contact between the adsorbate and the adsorbent. In each experiment, 0.5g of the adsorbent was used. The resultant solutions at the end of the adsorption period were obtained by filtering the mixture using a centrifuge. Experiments were conducted at room temperature. The time was measured by a stop watch, pH was measured by a pH meter, and the mass of hydrothermally activated banana peels powder and malachite green dye was measured by analytical balance. Every experiment was left to stand for 1hour except those of the effect of contact time which were left to stand for 20, 40, 60, 80 and100 minutes. After adsorption, the remaining concentration of malachite green dye in solution was determined using UV-Vis at 620nm

The results when considering individual parameters were tabulated in various tables. The %age removal of malachite green dye by hydrothermally activated banana peels were calculated for each variable in the experiment using the expression:

$$\% \text{ removal} = \frac{Ci-Cf}{Ci} \times 100$$

Where C_i and C_f are the concentrations of malachite green dye before and after adsorption respectively, (C_i - C_f) is amount of malachite green dye adsorbed. Different graphs showing the variation of amount of malachite green dye adsorbed with initial dye concentration, pH and contact time were plotted using Microsoft excel to enable the researcher to explain the relationships.

3.4.1 **Effect of pH on malachite green dye adsorption on hydrothermal activated banana peels.**

Malachite green dye solutions were adjusted to the pH of 2, 3, 4, 5 and 6 using sodium hydroxide solution or hydrochloric acid before each of them was being mixed with the adsorbent. The pH of solutions was measured using a pH meter.

3.4.2 **Effect of contact time on malachite green dye adsorption on hydrothermally activated banana peels.**

The malachite green dye solutions were left in contact with the adsorbent for 20, 40, 60, 80 and 100 minutes. In this analysis, all the solutions had the same pH, adsorbent and adsorbate concentration.

3.4.3 **Effect of adsorbate concentration on the malachite green dye adsorption on hydrothermally activated banana peels.**

The adsorbate concentrations were varied using a factor of 2 from 0.00027M to 0.00135M that is solutions of 0.00027M, 0.00054M, 0.00081M, 0.00108M and 0.00135M were considered. Dilution law was applied to make solutions below 0.0024M from 0.0024M solution.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 EFFECT OF CONTACT TIME ON MALACHITE GREEN DYE ADSORPTION ON HYDROTHERMALLY ACTIVATED BANANA PEELS

The variation of amount of malachite green dye adsorbed with contact time between the adsorbate and the adsorbent is illustrated in table 4.1 and figure 4.1 The amount of malachite green dye adsorbed was measured at given contact times for the same initial malachite green dye concentration. From figure 4.1, the graph shows that the amount of malachite green dye adsorbed generally decreases with increase in contact time. This may probably be due to the sticky nature of banana peels in solution which tends to bind the adsorbent particles together making some adsorption sites to remain hidden thus few sites are available for adsorption. During the first 60 minutes, the amount of malachite green dye adsorbed decreased gradually. The gradual decrease may be due to the less time allowed for contact between malachite green dye and adsorption sites on hydrothermally activated banana peels, thus the adsorbent particles were free and mobile to remove the adsorbate from solution.

Table 4.1: Variation of amount of malachite green dye adsorbed with contact time

Initial [$C_{23}H_{25}ClN_2$] = 67.90598mg/L

Contact time(minutes)	Amount of malachite green dye adsorbed(mg/L)	% removal of malachite green dye
20	67.86641	99.94172
40	67.66855	99.65035
60	67.47069	99.35897
80	66.8771	98.48485
100	66.08566	97.31935

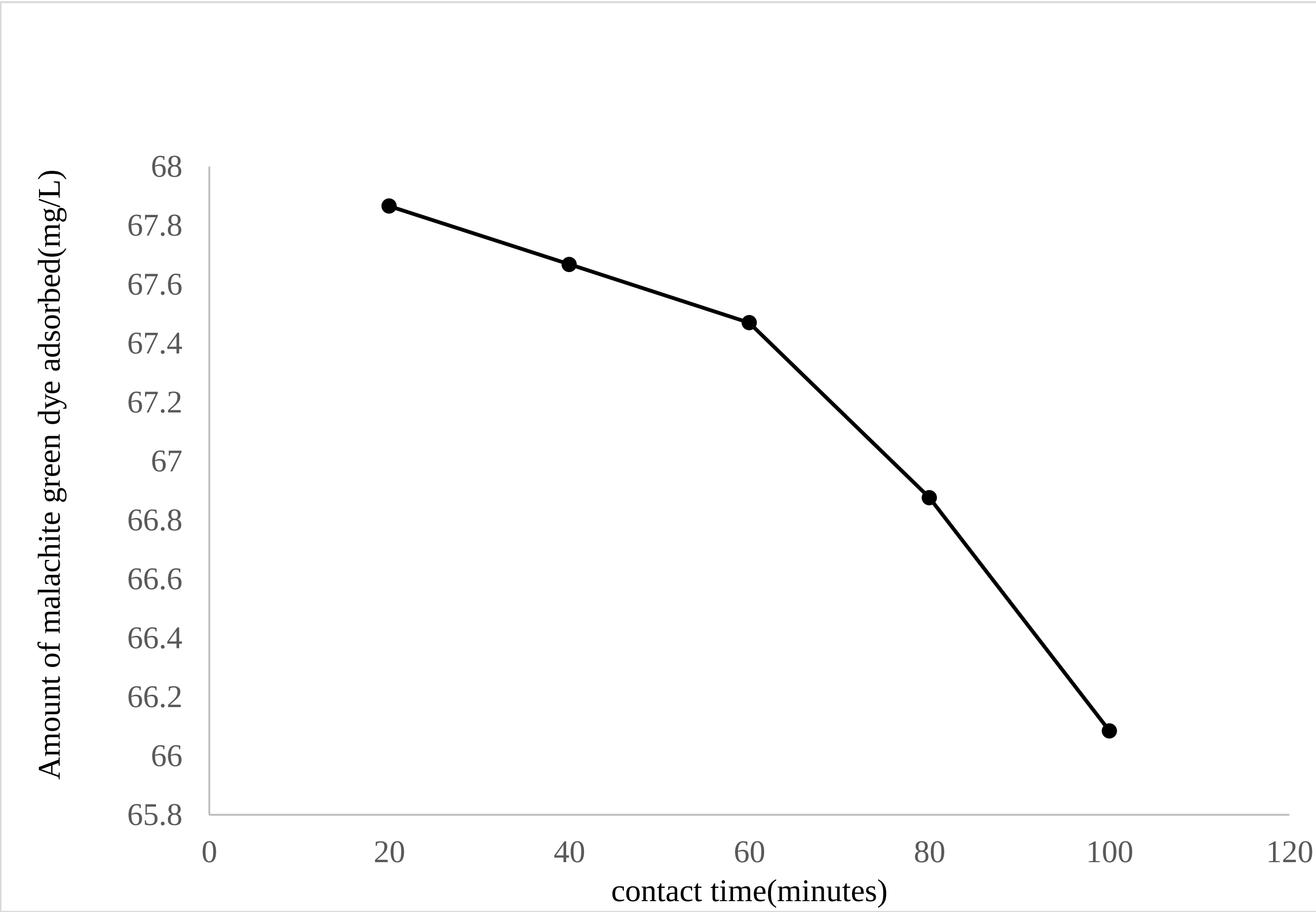

Figure 4.1: Effect of contact time on malachite green dye adsorption on hydrothermally activated banana peels.

4.2 EFFECT OF pH ON MALACHITE GREEN DYE ADSORPTION ON HYDROTHERMALLY ACTIVATED BANANA PEELS

The influence of pH on malachite green dye adsorption on hydrothermally activated banana peels is shown in table 4.2 and figure 4.2 The amount of malachite green dye adsorbed increased with increase in pH, however at pH 6 the amount of malachite green dye adsorbed was low than expected.

The low amount of malachite green dye adsorbed in strongly acidic medium where pH value was less than 3 is attributed to the fact that the adsorbent surface possessed a species with a positive charge that is hydrogen ion. The lower the pH, the higher the concentration of hydrogen ions in solution which intensively competes with malachite green dye for the active sites resulting in decreased amount of malachite green dye adsorbed.

As observed from figure 4, the competitiveness of hydrogen ions with malachite green dye for adsorption sites becomes weaker as the pH increases since the hydrogen ions tend to be removed in neutralization as the solution becomes alkaline. When the pH was 5, the amount of malachite green dye adsorbed was significantly high and hence, the optimum pH for the adsorption of malachite green dyes from waste water should be established at pH 5.

At higher pH values above 5, sodium ions from sodium hydroxide accumulate in solution, thus competing for the adsorption sites with malachite green dye, leading to decrease in the amount of malachite green dye adsorbed.

Table 4.2: Variation of the amount of malachite green dye adsorbed with pH.

pH	Amount of malachite green dye adsorbed(mg/L)	% removal of malachite green dye
2	9.299479	7.66471
3	69.05358	56.91455
4	96.55629	79.58252
5	116.5403	96.05349
6	110.8023	91.3242

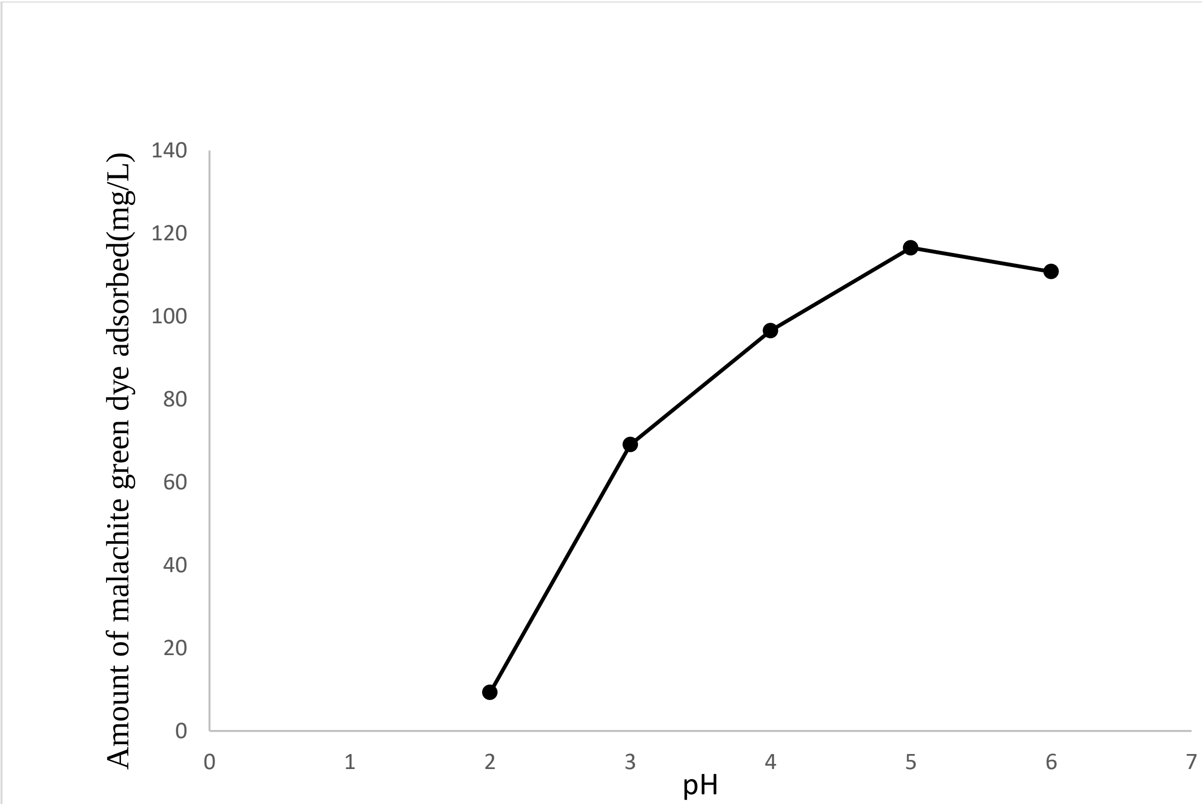

Figure 4.2: Effect of pH on malachite green adsorption on hydrothermally activated banana peels.

4.3 EFFECT OF INITIAL MALACHITE GREEN DYE CONCENTRATION ON MALACHITE GREEN DYE ON HYDROTHERMALLY ACTIVATED BANANA PEELS

The effect of initial dye concentration on adsorption of malachite green dye is shown in table 4.3 and figure 4.3. Figure 4.3 shows that the amount of malachite green dye adsorbed increased with increase in initial dye concentration. This can be attributed to the high concentration of hydrothermally activated banana peels used which provided many adsorption sites sufficient enough for removal of malachite green dye from waste water even at high concentrations. The general increase could also be due to large surface area offered by hydrothermally activated banana peels powder used as an adsorbent. However, the decrease in the amount of malachite green dye adsorbed from 278.9844 mg/L to 197.0698mg/L may be due to saturation of the adsorption sites hence decrease in the amount of malachite green dye adsorbed at higher dye concentrations.

Table 4.3: Variation of the amount of malachite green dye adsorbed with initial dye concentration.

s	Concentration of malachite green dye after adsorption(mg/L)	Amount of malachite green dye adsorbed(mg/L)	% removal of malachite green dye
154.3713	35.25888	119.1125	77.1597
326.1149	107.2804	218.8345	67.10351
372.8102	136.5638	236.2463	63.36907
473.3237	194.3393	278.9844	58.94156
558.9976	361.9278	197.0698	35.25414

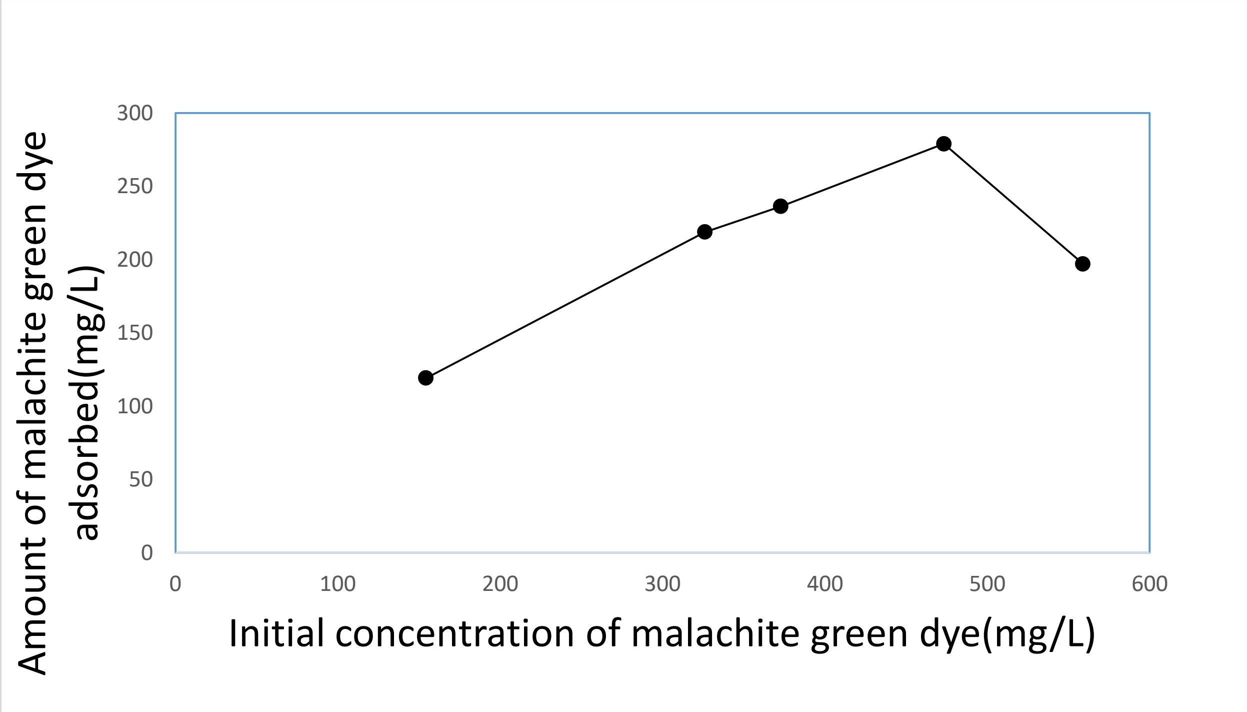

Figure 4.3: Effect of initial dye concentration on malachite green dye adsorption on hydrothermally activated banana peels.

4.4 ADSORPTION ISOTHERMS

Adsorption isotherms were studied which are the presentation of the solute adsorbed per unit of adsorbent, as a function of equilibrium concentration in the bulk solution at constant temperature. In order to optimize the design of adsorption system to remove malachite green dye from waste water, it is important to establish the most appropriate correlation for equilibrium curve. Two isotherm equations have been tested in this study: Langmuir and Freundlich.

4.4.1The Langmuir isotherm

The Langmuir model (Langmuir, 1918) is based on the assumption that maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate molecules in the surface plane. The Langmuir isotherm is given by:

$$q = \frac{aC}{1 + aC}; q = \frac{x}{m}$$

The linear form of the Langmuir equation can be expressed as shown below:

$$\frac{c}{x} = \frac{1}{b} + \frac{aC}{b}$$

Where C is the concentration of malachite green dye in solution, q is the fraction of malachite green dye adsorbed, x is the amount of malachite green dye adsorbed per adsorbent, m is the maximum amount of malachite green dye adsorbed per adsorbent, a and b are Langmuir constants.

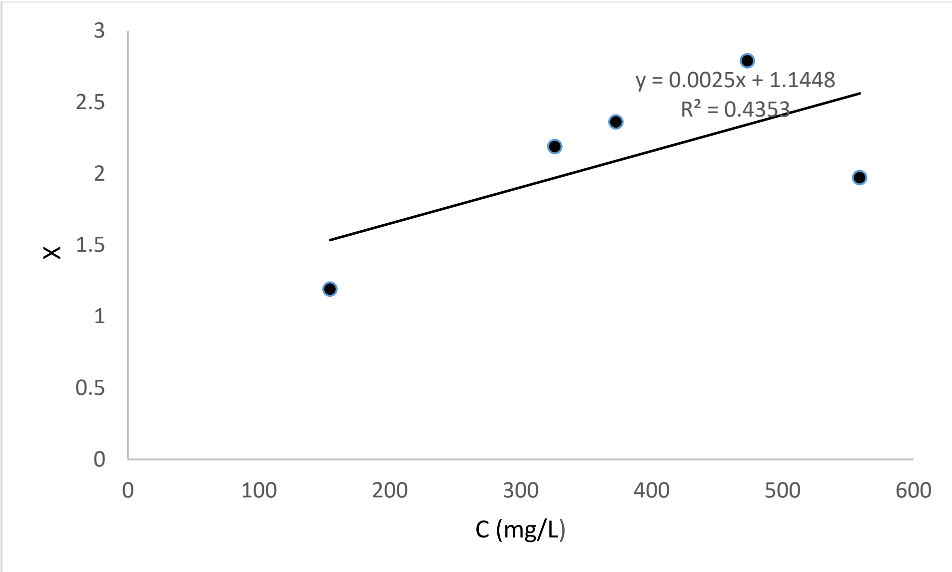

Figure 4.4.1: Graphical representation of x against concentration of malachite green dye

4.4.2 The Freundlich isotherm

The Freundlich isotherm model (Freundlich, 1906) is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface and assumes that different sites with several adsorption energies are involved. Freundlich adsorption isotherm is the relationship between the amount of malachite green dye adsorbed per unit mass of adsorbent, q and the concentration of malachite green dye at equilibrium C.

$$q = KC^{1/n}$$

Where K and n are Freundlich constants, the characteristics of the system. K and n are the indicator of adsorption capacity and adsorption intensity respectively.

The Freundlich isotherm equation may also be written in the form;

$$\log q = \log K + \frac{1}{n}\log C$$

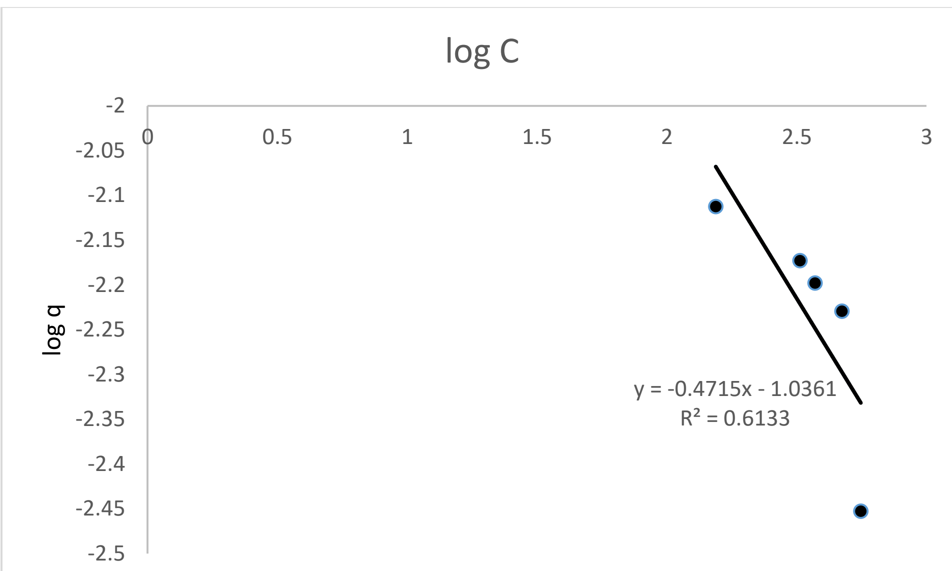

Figure 4.4.2: Graphical representation of Freundlich adsorption isotherm for malachite green dye

4.5 ADSORPTION KINETICS

4.5.1 The pseudo-first order kinetic model

The pseudo- first order equation is expressed as follows (44):

$$\frac{dqt}{dt} = k_1 (qe- qt) \quad (1)$$

And the integrated form as; (Y. Chanie, I. Diaz, E. Perez, J.2015).

$$\log(qe - qt) = \log(qe) + k_1t \quad (2)$$

Where q_t and q_e are amounts of malachite green dye adsorbed on BP at time t and at equilibrium, respectively, k_1 is the rate constant that will be determined by plotting values of $\log(qe - qt)$ against t where k_1 and qe will be determined from the slope and intercept respectively.

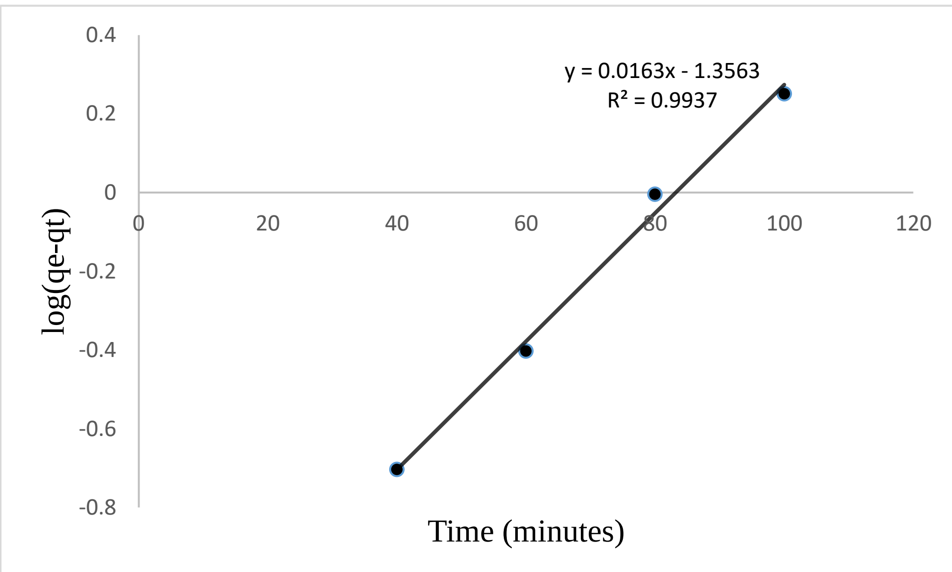

Figure 4.5.1: Graphical representation of log (q_e- q_t) against time

4.5.2 The pseudo-second order kinetic model

In the adsorption processes, the change in the concentration of reactant or product per unit time is used to determine the rate of reaction in the chemical process. Therefore, the kinetic rate equations can be rewritten as follows

$$\frac{dqt}{dt} = k (qe- qt)^2 \quad (3)$$

According to 45, an integrated pseudo-second order rate law for boundary conditions of t = 0 to t = t and qt = 0 to qt = qt can be obtained by;

$$\frac{1}{(qe-qt)} = \frac{1}{qe} + kt \qquad (4)$$

Rearranging equation (4) to obtain a linear form;

$$\frac{t}{qt} = \frac{1}{k2qe2} + \frac{t}{qe}$$

Where t is the reaction time (min); k_2 is the equilibrium rate constant of pseudo-second order adsorption (g $mg^{-1}min^{-1}$); q_t is the amount of adsorbate at time t (mg g^{-1})

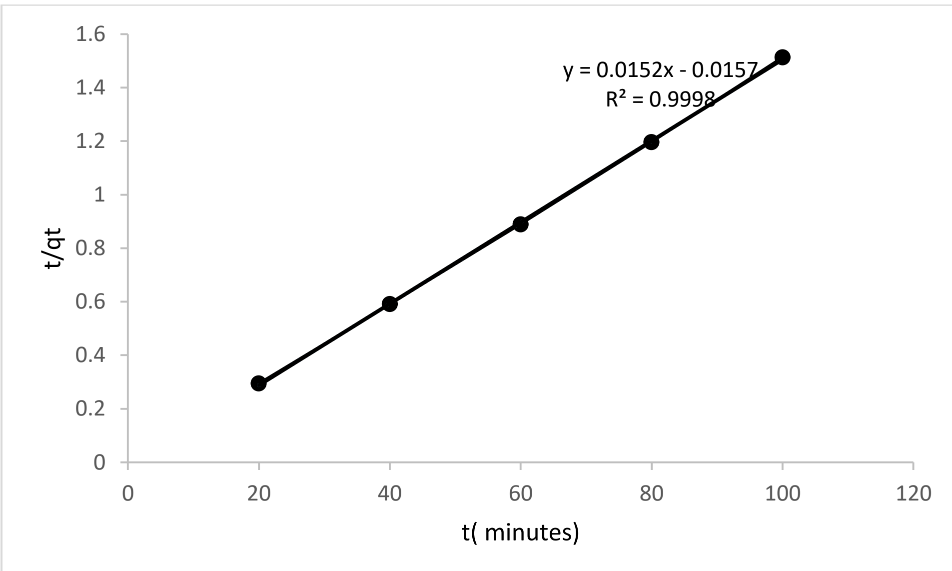

Figure 4.5.2: Graphical representation of t/q_t against time

4.6 CHARACTERISATION OF HYDROTHERMALLY ACTIVATED BANANA PEELS

The FTIR spectrum was used quantitatively to examine the nature of the surface and functional groups which are present in hydrothermally activated banana peels sample. Figure 4.6.1 shows the typical FTIR of hydrothermally activated banana peels. Various peaks were observed which indicates the presence of multiple functional groups in the sample. A broad peak between 4000cm-1 and 3000cm-1 is due to free hydroxyl of polymeric compounds. A medium peak between 3000cm-1 and 2500cm-1 is due to C-H stretching in alkanes. The peak observed between 2000cm-1 – 1500cm-1 is attributed to C=O stretching vibrations of carboxylic acids or esters. The peak between 1500cm-1 – 1000cm-1 is due to C-N bonds. Since banana peels contain hydroxyl and carboxyl groups, the adsorption of malachite green dye on hydrothermally activated banana peels may have been due to the interaction of the hydrogen ions in the hydroxyl and carboxyl groups of banana peels with the nitrogen of the amino group in malachite green dye through hydrogen bonding.

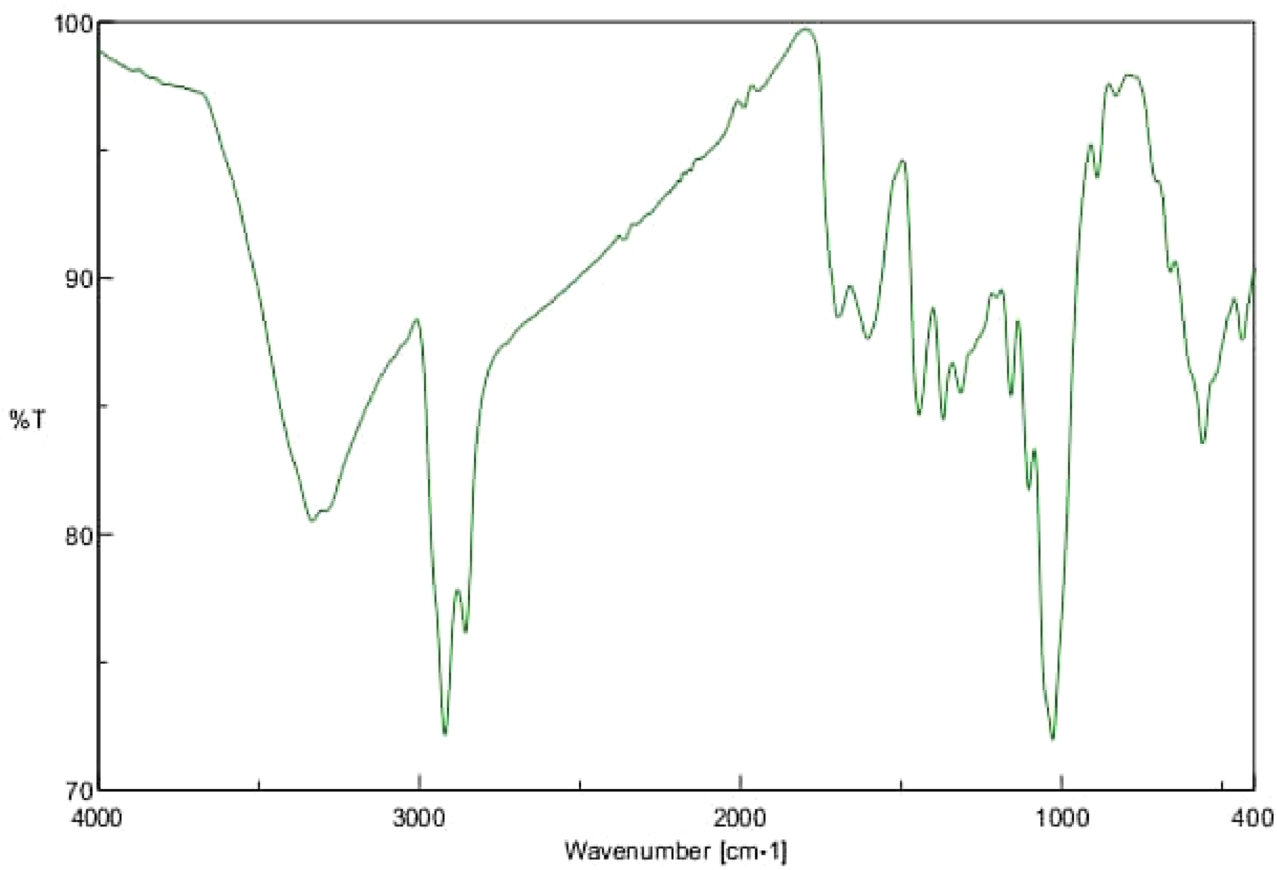

Figure 4.6: FTIR spectrum of hydrothermally activated banana peels.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS.

Based on the results, it can be concluded that optimum pH for adsorption of malachite green dye from waste water 5 and the optimum contact time for adsorption of malachite green dye to occur is 20 minutes. The adsorbent dose used in this study was enough to adsorb malachite green dye even at their high concentrations. The equilibrium data was analyzed using Langmuir and Freundlich adsorption isotherms. The Freundlich isotherm model was found to be suitable for characterizing the adsorption mechanisms occurring in the adsorption of malachite green dye onto hydrothermally activated banana peels in comparison with the Langmuir adsorption isotherm model. The kinetics of malachite green dye adsorption was carried out by pseudo-first order and pseudo-second order kinetic models. The adsorption mechanisms of malachite green dye adsorption onto hydrothermally activated banana peels followed the pseudo- second order kinetic model compared to the pseudo-first order kinetic model. Therefore it can be concluded that the adsorption process of malachite green dye onto hydrothermally activated banana peels is chemisorption. This indicated a strong interaction between the adsorbate and the adsorbent hence, the rate of adsorption was proportional to the square of the concentration of the adsorbate.Following the FTIR results, hydrothermally activated banana peels is a poly-functional material with the following functional groups; hydroxyl, carboxyl, and amino groups.The study indicated the suitability of the adsorbent used (hydrothermally activated banana peels) for removal of malachite green dye from waste water. This was evidenced by its high adsorption capacity for malachite green dye.

5.2 RECOMMENDATIONS

Hydrothermally activated banana peels can be adopted as an adsorbent material for removal of malachite green dye from waste water since the results have demonstrated that it has high adsorption capacity for malachite green dye removal in solution. When using hydrothermally activated banana peels for removing malachite green dye from waste water, the following have to be put into consideration;

- pH of bulk solution should be maintained at about 5 to provide favorable medium for maximum malachite green dye removal.
- Little time should be allowed for adsorption process so as to maximize the malachite green dye removal from waste water.
- Higher adsorbent dose needs to be used to ensure that most malachite dye molecules are removed from waste water.

Further studies need to be conducted to investigate the effect of adsorbent dose, un activated adsorbent and temperature on adsorption of malachite green dye from waste water. There is also need to investigate whether hydrothermally activated banana peels can be effectively used for removal of other dyes from waste water apart from malachite green dye such as methylene blue, crystal violet which are also known to be hazardous to human health.

REFERENCES AND APPENDICES

REFERENCES

Ablikim, M., Bai, J., Bai, Y., Ban, Y., Cai, X., Chen, H., . . . Chen, J. (2008). Observation of Y (2175) in J/ψ→ η ϕ f 0 (980). *Physical review letters, 100*(10), 102003.

Banat, I. M., Nigam, P., Singh, D., & Marchant, R. (1996). Microbial decolorization of textile-dyecontaining effluents: a review. *Bioresource technology, 58*(3), 217-227.

Bekçi, Z., Seki, Y., & Cavas, L. (2009). Removal of malachite green by using an invasive marine alga Caulerpa racemosa var. cylindracea. *Journal of hazardous materials, 161*(2-3), 1454-1460.

Benjamin, L. S. (2002). *Interpersonal diagnosis and treatment of personality disorders*: Guilford Press.

Das, S., Ngene, P., Norby, P., Vegge, T., De Jongh, P. E., & Blanchard, D. (2016). All-solid-state lithium-sulfur battery based on a nanoconfined LiBH4 electrolyte. *Journal of The Electrochemical Society, 163*(9), A2029.

Digiano, F., Baldauf, G., Frick, B., & Sontheimer, H. (1978). A simplified competitive equilibrium adsorption model. *Chemical Engineering Science, 33*(12), 1667-1673.

Garg, V. K., Amita, M., Kumar, R., & Gupta, R. (2004). Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste. *Dyes and pigments, 63*(3), 243-250.

Ghaedi, M., Shokrollahi, A., Tavallali, H., Shojaiepoor, F., Keshavarz, B., Hossainian, H., . . . Purkait, M. (2011). Activated carbon and multiwalled carbon nanotubes as efficient adsorbents for removal of arsenazo (III) and methyl red from waste water. *Toxicological & Environmental Chemistry, 93*(3), 438-449.

Guillet-Nicolas, R., Ahmad, R., Cychosz, K. A., Kleitz, F., & Thommes, M. (2016). Insights into the pore structure of KIT-6 and SBA-15 ordered mesoporous silica–recent advances by combining physical adsorption with mercury porosimetry. *New Journal of Chemistry, 40*(5), 4351-4360.

Gupta, V. K., Ali, I., Saleh, T. A., Nayak, A., & Agarwal, S. (2012). Chemical treatment technologies for waste-water recycling—an overview. *Rsc Advances, 2*(16), 6380-6388.

Hameed, B., & El-Khaiary, M. (2008). Batch removal of malachite green from aqueous solutions by adsorption on oil palm trunk fibre: equilibrium isotherms and kinetic studies. *Journal of hazardous materials, 154*(1-3), 237-244.

Hashimoto, J. C., Paschoal, J. A. R., De Queiroz, J. F., & Reyes, F. G. R. (2011). Considerations on the use of malachite green in aquaculture and analytical aspects of determining the residues in fish: a review. *Journal of Aquatic Food Product Technology, 20*(3), 273-294.

Helfferich, F. (1962). Ion-exchange kinetics. 1 III. Experimental test of the theory of particle-diffusion controlled ion exchange. *The Journal of Physical Chemistry, 66*(1), 39-44.

Khattri, S., & Singh, M. (2009). Removal of malachite green from dye wastewater using neem sawdust by adsorption. *Journal of hazardous materials, 167*(1-3), 1089-1094.

Kuennen, R. W., Van Dyke, K., Crittenden, J. C., & Hand, D. W. (1989). Predicting the Multicomponent Removal of Surrogate Compounds by a Fixed-Bed Adsorber. *Journal-American Water Works Association, 81*(12), 46-58.

Parimaladevi, P., & Venkateswaran, V. (2011). Adsorption of cationic dyes (rhodamine B and methylene blue) from aqueous solution using treated fruit waste. *J. Appl. Technol. Environ. Sanit, 1*, 285-293.

Polson, A. (1950). The Some Aspects of Diffusion in Solution and a Definition of a Colloidal Particle. *The Journal of Physical Chemistry, 54*(5), 649-652.

Raducan, A., Olteanu, A., Puiu, M., & Oancea, D. (2008). Influence of surfactants on the fading of malachite green. *Central European Journal of Chemistry, 6*, 89-92.

Schideman, L. C., Marinas, B. J., Snoeyink, V. L., & Campos, C. (2006). Three-component competitive adsorption model for fixed-bed and moving-bed granular activated carbon adsorbers. Part I. Model development. *Environmental science & technology, 40*(21), 6805-6811.

Schwarzenbach, R. P., Gschwend, P. M., & Imboden, D. M. (1993). Vapour pressure. *Environmental Organic Chemistry*, 56-75.

Sepulveda, M., Castellan, R., Hankinson, J., & Cocke, J. (1984). Acute lung function response to cotton dust in atopic and non-atopic individuals. *British journal of industrial medicine, 41*(4), 487.

Song, D., Zhou, X., Peng, Q., Chen, Y., Zhang, F., Huang, T., . . . Wu, Q. (2015). Newly emerged porcine deltacoronavirus associated with diarrhoea in swine in China: Identification, prevalence and full-length genome sequence analysis. *Transboundary and emerging diseases, 62*(6), 575-580.

Sud, D., Mahajan, G., & Kaur, M. (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions–A review. *Bioresource technology*, *99*(14), 6017-6027.

Tewari, K., Singhal, G., & Arya, R. K. (2018). Adsorption removal of malachite green dye from aqueous solution. *Reviews in Chemical Engineering*, *34*(3), 427-453.

, M. E., Baxter, S. M., Bulls, A. R., Burger, B. J., Nolan, M. C., Santarsiero, B. D., . . . Bercaw, J. E. (1987). . sigma.-Bond metathesis for carbon-hydrogen bonds of hydrocarbons and Sc-R (R= H, alkyl, aryl) bonds of permethylscandocene derivatives. Evidence for noninvolvement of the. pi. system in electrophilic activation of aromatic and vinylic CH bonds. *Journal of the American Chemical Society*, *109*(1), 203-219.

Wang, S., Boyjoo, Y., Choueib, A., & Zhu, Z. (2005). Removal of dyes from aqueous solution using fly ash and red mud. *Water research*, *39*(1), 129-138.

Y. Chanie, I. Diaz, E. Perez, J. Chem. Technol. Biotechnol. (2015) (wileyonlinelibrary.com)

Freundlich, H. (1906). Over the adsorption in solution. *j. phys.chem.*, 57,385-471.

Langmuir, I. (1918). The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am Chem Soc.*, 40(8), 1361-1403.

APENDICES

Table 6.1 Calibration results for determining maachite green concentration using UV-Vis

Concentration(mg/L)	Absorbance (a.u)
0.00027	0.6
0.00054	1.189
0.00081	1.664
0.00108	2.181
0.00135	2.591

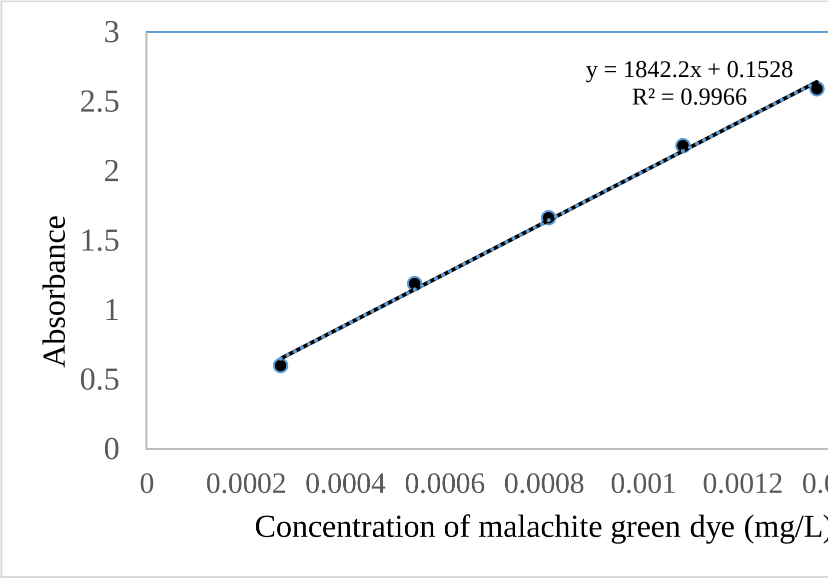

Figure 6.1: Calibration curve of malachite green dye

m= 100mg/L; x=$\frac{Ca}{m}$, Ca is the amount of malachite green dye adsorbed and m is the mass of adsorbent

Table 6.2: Results for analysis using Langmuir adsorption model.

C_a (mg/L)	X
154.371	1.19113
326.115	2.18835
372.81	2.36246
473.324	2.78984

Table 6.3: Results for analysis using Freundlich adsorption model.

C	Log C	q	Log q
154.371	2.188566	0.007716	-2.11261
326.115	2.513371	0.00671	-2.17325
372.81	2.571488	0.006337	-2.19812
473.324	2.675159	0.005894	-2.22958
558.998	2..74741	0.003525	-2.45279

Table 6.4: Table for analysis using pseudo-first order kinetic model

t (minutes)	q_e	q_t	$q_e - q_t$	Log ($q_e - q_t$)
20	67.86641	67.86641	0	∞
40	67.86641	67.66855	0.19786	-0.70364
60	67.86641	67.47069	0.39572	-0.40261
80	67.86641	66.8771	0.98931	-0.00467
100	67.86641	66.08566	1.78075	0.250603

Table 6.5: Table for analysis using pseudo-second order kinetic model

t (minutes)	q_t	t/q_t
20	67.86641	0.294697
40	67.66855	0.591117
60	67.47069	0.889275
80	66.8771	1.196224
100	66.08566	1.513188