DILLA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY

REMOVAL OF MALACHITE GREEN DYE FROM AQUEOUS SOLUTIONS BY USING ACTIVATED CORNCOB ADSORBENT

M.Sc. THESIS

BY

KELEMU HONJA

DILLA UNIVERSITY
AUGUST, 2020

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A THESIS SUBMITTED TO SCHOOL OF GRADUATE STUDIES DEPARTMENT OF CHEMISTRY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTERS OF SCIENCE IN CHEMISTRY (GENERAL)

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I the undersigned certify that I have read and evaluated this thesis entitled **"Removal of Malachite Green Dye from Aqueous Solutions by Using Activated Corncob Adsorbent"** prepared under my guidance by Kelemu Honja Anjelo. I recommend that it be submitted for defense as fulfilling the thesis requirements.

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EXAMINERS' APPROVAL SHEET

We the undersigned certify that the thesis prepared by Kelemu Honja Anjelo entitled **"Removal of Malachite Green Dye from Aqueous Solutions by Using Activated Corncob Adsorbent "** and submitted in partial fulfillment of the requirements for the degree of Master of **Masters of Science in Chemistry** (**General)** complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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AUTHOR'S DECLARATION

I, the undersigned, declare that this thesis, entitled **"Removal of Malachite Green Dye from Aqueous Solutions by Using Activated Corncob Adsorbent"** is my original work, that it has not been submitted to any other institution anywhere for the award of any academic degree, diploma or certificate, that I followed all ethical and technical principles of scholarship in the data collection, data analysis and preparation of this the report, and that all the sources that I have used or quoted have been indicated and acknowledged.

Name: _____

Signature: _____

Date: _____

BIOGRAPHICAL SKETCH

Kelemu Honja Anjelo was born in wolaita zone soddo zuria woreda bossa kacha kebele of southern nation and nationality regional state in 1981 E.C from his father Honja Anjelo and Mother Asnakech Dorena. He attended his elementary school education grade 1−8 in otona elementary and junior school, and also grade 9−10 in melka warer higher secondary school (afar region) and 11-12 (preparatory) in nemelefen high School (awash 7 kilo, afar region). After completion of his high school education, he joined dilla university from 2001−2003 E.C and awarded degree in chemistry. Finally he joined dilla university for postgraduate study and currently he is following his postgraduate studies at dilla university hopeful for M.Sc. degree in chemistry (general) in 2020 G.C academic year.

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LIST OF ACRONYMS AND ABREVIATIONS

ACC	Activated corncob
ASTM	America Society Testing Materials
FTIR	Fourier Transform Infrared Radiation
X/M	Iodine number
XRD	X-ray Diffraction
PCC	Powdered corncob
PHPZC	Point Zero Charge
UV	Ultraviolet
WHO	World Health Organization

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REMOVAL OF MALACHITE GREEN DYE FROM AQUEOUS SOLUTIONS BY USING ACTIVATED CORNCOB ADSORBENT

ABSTRACT

Presence of dyes in the aquatic systems has become a serious environmental problem. Concerning the environmental awareness and the economical point of view, the use of low cost and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing textile dyes from wastewater. To develop porous carbon, corncob was activated by chemical activation agent using H_3PO_4. The physicochemical characterization of the activated carbon was done by proximate analysis and iodine number. The effects of various parameters such as acid concentration, impegrination, carbonization temperature and activation time during activated carbon production were optimized. Their structural characterization also determined by XRD and FT-IR analysis. UV was used for the determination and monitoring of Dye ion concentration. The parameters were adsorbent dose, pH, contact time and Initial dye concentration. The optimum conditions for corn cobs activated carbon preparation were determined as impregnation ratio of 1.5, carbonization temperature of 450^oC, activation time of 120min, and acid concentration 65% by weigh. Batch adsorption was conducted to evaluate optimum condition which were optimum conditions of (pH = 10, adsorbent dosage = 0.3g and 0.2g, contact time = 150 and 120 minutes and initial of MG concentration = 10 mg/L) using PCC and ACC respectively. The sorption characteristic has been examined using various sorption conditions. It was found that the sorption process was very rapid; the equilibrium time was obtained at 120 min for PCC and 150 min in the case of ACC. The sorption yield increases with the increase of sorbent dosage with an optimum at 0.3g and 0.2g for PCC and ACC respectively. The optimum sorption was obtained at basic pH medium. The dye removal performance of ACC was compared with PCC. In order to understand the mechanism of the adsorption process, the sorption data were analyzed using Langmuir and Freundlich isotherm models. The Langmuir model provides the best correlation of the experimental equilibrium data. Finally, the rate of the adsorption process was investigated using

Pseudo-first order kinetics and Pseudo second-order kinetic models. Pseudo second-order kinetic model was found to be well fitted to the data obtained.

Keywords; *Dye, Adsorption, activated corncob, dye removal, textile wastewater*

1. INTRODUCTION

1.1. Background of the Studies

Water is a limited natural resource and fundamental for life and health (Dobriyal *et al.*, 2014). About 97.5% of all water on earth is salt water and the remaining 2.5% is fresh water. Only 1% of the earth‘s fresh water is accessible for extraction and human use (Corcoran, 2010). Water is important for life and for processing various materials in industry. Living organisms cannot exist without water, and almost all industries require water to operate. However, in the 21st century the growing population and industrial sector have contributed significantly to a reduction in quality of water and its availability through discharge of untreated wastewater to the environment; thus becoming the concern of many nations across the world (Yong, 2017).

Globally, every day more than two million tons of liquid wastes are released from point and nonpoint sources into both subsurface and surface water bodies without treatment (Corcoran, 2010). Water scarcity and water pollution are major global issues. Rapid population growth and the consequent increase in anthropogenic activities have resulted in high demand for scarce water resources, generation of large volumes of wastewater requiring treatment and diffuse pollution of surface and ground water sources (Yong, 2017).

Many industries, such as dyestuffs, textile, paper and plastics, use dyes in order to color their products and also consume substantial volumes of water. As a result, they generate a considerable amount of colored wastewater. It is recognized that public perception of water quality is greatly influenced by the color. Color is the first contaminant to be recognized in wastewater (Ramesh, 2013). The presence of very small amounts of dyes in water (less than 1 ppm) is highly visible and undesirable and may cause irregular coloration of surface waters as well as the pollution of the water with toxic compounds (Deokar & Sabale, 2014). Due to extensive application, synthetic dyes can cause considerable environmental pollution and are serious health-risk factors. Dyes may affect the photosynthetic activity in aquatic life due to reduced light penetration and may also be toxic to some aquatic life due to the presence of aromatics, metals, etc. in them (Wong *et al.,* 2013).

Many of the synthetic dyes are difficult to degrade naturally. Thus, they are often resistant towards light, temperature and naturally occurring bacteria. Amongst all, Malachite green (MG) is a popular dye and is used extensively. It also finds applications in medical sciences. MG is highly toxic to flora and fauna. It induces risk of cancer, acts as a liver tumor-enhancing agent and many other diseases. The dyes check the biological activity in aquatic lives. They also poses in human. It has mutagenic and carcinogenic characteristics. It can cause severe effects on nervous system, reproductive system, liver, brain and kidney (Kumar A, Prasad B & Mishra, 2008)

Various techniques can be applied for the removal of different classes of dyes from industrial effluents, prior to their discharge into the environment, such as chemical precipitation, ion exchange, coagulation-flocculation, advanced oxidation/reduction, along with the biological ones. Many of these techniques, even if very effective, can be expensive, due to their initial and operational high costs, generating sludge, requiring additional treatment and causing disposal problems.

Recently, sorption has become a subject of considerable interest, due to the advantages it provides, such as the possible utilization of different materials as adsorbents, cheap technological steps, easy maintenance, no special operational skills and local availability (Daniela S & Teodor M, 2010). Different sorbents have been conventionally used for the removal of dyes from aqueous solutions, whereas activated carbon has been widely used in the recent past due to the presence of different surface oxygen functional groups at its surface, its pore structure, and also for the high adsorption capacity. The properties of the activated carbons depend on the activation process and the nature of the precursor. Several biomasses have been tested as precursors in the production of activated carbon, including buriti shells Mauritia flexuosa L, waste tea, hazelnut husk, coconut shell, Diplotaxisharra , macadamia nut endocarp (Macadamia integrifolia), olive stones, chlorella-based algal residue, rice husk residue and coconut shells. However, studies in this field have not produced materials which meet all the demands of adsorption activity [8].

In the present studies, powdered corncob (PCC) and H_3PO_4 activated corncob (ACC), a non conventional agricultural-waste material has been indirectly used to prepare activated carbon for the removal of MG from its aqueous solutions.

1.2. Statement of the Problem

Environmental pollution is an inevitable consequence of economic development and people's desire to improve their quality of life. With the increasing demand of textile industries in Ethiopia discharge colored effluents is also increased. Ayka Addis textile manufacturing industry is one of the largest economic sectors in Ethiopia, which discharge 1,800m^3/day of dyes colored wastewater into the nearby water bodies. These colored effluents give undesirable perspective to the water streams where as some dyes and their metabolites pose toxic, carcinogenic and mutagenic effects (Nuriya, 2015).

Colour affects the nature of water and inhibits the sunlight penetration into the stream and reduces photosynthetic activity and disturbs aquatic equilibrium. Moreover wastewater containing dyes is difficult to treat, since dyes are recalcitrant organic molecules, resistant to biological degradation and are stable to light or any exposure due to their complex aromatic molecular structures. As a result, removal of dyes from wastewater has a considerable attention over the past decades to decrease their impact on the environment (Seeds & Sepehr, 2011).

Several physical, chemical and biological methods have been developed for the removal of synthetic dyes from wastewater. Most widely used methods for dyes removal are chemical precipitation, ion exchange, coagulation-flocculation and advanced oxidation/reduction are used for removal of dyes. But these methods are non time consuming and very expensive, due to their initial and operational high costs, generating sludge, requiring additional treatment and causing disposal problems (Kharub, 2012). Due to the high cost and disposal problems involved in the above said methods, further investigation of new techniques have been come up. Physical methods, mainly adsorption on various supports were recognized to be a promising and effective process to remove dyes from textile wastewaters. Exploration of good low cost and non-conventional adsorbents may contribute to the sustainability of the environment and offer promising benefits for the commercial purpose in future (Durairaj & Shankar, 2012).

The successful dye removal using low cost adsorbents has been carried out by several researchers. The most common low cost adsorbents used for the removal of dyes include rice husk (Dalai et al., 2015), fruit waste (Ozsoy & Leeuwen, 2010), bagasse fly ash (Azeb T,2017),

coconut shell (Wong et al., 2013) etc. Some of these materials have their own limitations and also there is usually a problem of collection of these wastes for their large scale application. This work aims to evaluate the potential of powdered corncob and H_3PO_4 activated corncob (ACC) as an efficient adsorbent material that is easily available in large quantity and economically feasible for removal of malachite green (MG) dye from textile industries. From this research different beneficiaries like authority, agricultural office, different industries.

1.3. Objective

1.3.1. General Objectives

The main objective of this research is to investigate the malachite green dye removal activity of phosphoric acid activated corncob from aqueous Solution.

1.3.2. Specific Objectives

- To prepare activated corncob and characterize adsorbent prepared from corncob.
- Optimize activated carbon preparation parameters.
- To determine the various physiochemical controlling factors affecting adsorption including pH, adsorbent dose, initial concentration of dye and time of contact.
- To analys the adsorptive capacity and equilibrium isotherm of adsorbent under batch adsorptive experiments.
- To study the kinetics of dye adsorption by the adsorbent.

1.4. Scope of the Study

The scope of this study includes; collection of raw material, modification, treatment and characterization and study of adsorption parameters. An adsorbent H_3PO_4 activated corncob (ACC) synthesized from raw corncob was selected to be used as an adsorbent in this study due to its good performance in adsorption, easily available and environmentally friendly. Proximate analysis was conducted following the standard test method for determination of iodine number of activated carbon. The result obtained was expressed in the percentage of ash, volatile matter and moisture contents and iodine adsorbed in mg/g. Wastewater containing malachite green also collected from Ayka addis textile industry of Ethiopia found in Addis Ababa for this work.

The character tics of powdered corncob and activated corncob were determined by XRD and FTIR. Determination of the malachite green concentration in the textile wastewater sample was analyzed with UV-Vis Spectrophotometer by determining absorbance at maximum wavelength using standard solution. After determination, batch experiments were conduct to look at the effects of pH, activated corn cob dosage, initial dye concentration and contact time on the sorption mechanisms involved in the removal process. The study includes determine the applicability of adsorption isotherm and adsorption kinetics models from the calculated parameters and it can be compared by judging correlation coefficients (R^2) values of the isotherm and kinetic data fitting to which models. Finally, the analysis of test results and figures of experiment was performed using origin 6 software.

1.5. Significance of the Study

A major challenge of many industries is finding solutions that equate to positive environmental and economic impacts regarding the treatment of their effluents (Takele. S, 2018). Textile industries wastewater containing organic pollutants. These pollutants are directly or indirectly discharged into the environment, causing serious environmental pollution and even threatening human life. Available water treatment methods are expensive. This study utilizes locally available material to make adsorbents for water treatment. Environmental pollution brought about by these waste would be minimized. Potential of the low cost adsorbent from maize cob to remove dyes from waste water will greatly help in reducing the number of people affected with cancer, nerve disorders and mental retardation.

The study can also provide fundamental information in the adsorption of dyes, from aqueous solution. Also for industries, it will help to elute their wastewater to the environment without Dye. And for the scientific community it will add scientific information and initiate for further investigation using phosphoric acid activated corncob.

2. LITERATURE REVIEW

2.1 Environmental Pollution

Environmental pollution due to development in modern industrial practice is one of the most significant problems of this century. Of this the contamination of water resources by hazardous pollutants has attracted much serious attention in the last few decades. This is particularly due to their toxic, acute and chronic health effects.

2.1.1 Water Pollution

The presence or introduction of undesirable materials in the earth which have destructive or toxic impacts is defined as Pollution. It is the presentation of contaminants in the surroundings which have adverse impacts. There are various manifestations of pollution which exist nowadays like air pollution, water pollution, and clamor pollution. The distinctive constituents of pollution which are called pollutants may be either contaminants which are as of now in nature or those which have been gone onto presence because of human exercises. Pollution may exist as any natural or inorganic materials or at times some form of energy like sound, light and so forth (Vijaya. L,2014). Water pollution has become one of the most dangerous threats to the environment in today's world. It is the degradation in quality of water resources-rivers, oceans, groundwater etc. because of human beings and their activities.

There are various ways by which water gets polluted, most important being the discharge of industrial waste water through spillage from into water bodies. The sewage discharge from homes is not subjected to proper treatment before being discharged to the environment. This serves as the main cause of pollution. Other causes include chemicals which are flowing on the surface due to various activities and fertilizers and pesticides release from the agricultural activities. Thus we can come to a conclusion that any kind of change in properties of water which may be physical, chemical or biological and which have harmful consequences is water pollution. The effects of water pollution are not just limited to human beings, but it is fatal for the entire ecosystem. Water comes from many sources like ground water, surface water that is why the cause of its pollution are different depending on the sources. Chemical, textiles, tannery

industries etc. cause high rate of pollution. The effluent containing heavy metals, chemicals, dyes, oils and many other harmful materials are discharged by the industries into the water bodies without proper treatment, thus leading to contamination of water bodies. The horrific effect of water pollution can be easily guessed by the fact that today, polluted drinking water has become a chief concern for mankind. There are more than 300 million cases of water-borne diseases every year with the number showing no signs of dwindling in the near future, which leads to the death of around 8 to 12 million people. In developing countries like India, Pakistan and Bangladesh more than 60 percent of harmful wastes are thrown into water bodies where they contaminate the water available for use. Approximately 600 persons in India die of water pollution related illness every day (Vijaya L, 2014). Due to these catastrophic effects of water pollution, it has become a matter of ultimate importance to find out different methods for treatment of waste water owing to the great importance of pure water for the existence of mankind.

2.2. Dyes

Dyes are ionic, aromatic organic compounds with structures including aryl rings with delocalized electron systems and also give color to the material. Mauveine, the first synthetic dye, was discovered in 1856 by William Henry Perkin (Gupta et al., 2015). Since then, thousands of new synthetic dyes have been produced. Unlike most organic compounds, dyes possess color because they absorb light in the visible spectrum (400 –700 nm), have at least one chromophore (color-bearing group), have a conjugated system, i.e. a structure with alternating double and single bonds, and exhibit resonance of electrons, which is a stabilizing force in organic compounds. When any one of these features is lacking from the molecular structure the color is lost. In addition to chromophores, most dyes also contain groups known as auxochromes (color helpers), such as carboxylic acid, sulfonic acid, amino and hydroxyl groups. While these are not responsible for color, their presence can shift the color of a colorant and they are most often used to influence dye solubility.

Nowadays, the total annual world dye production is estimated at about 7*105 tons, with more than 100,000 dyes available on the market. The largest consumer of these dyes is the textile industry accounting for around two thirds of its market. It is estimated that 10-15% of the dye is

lost during the dyeing process and released with the effluent (Banerjee & Sharma, 2013). Dyes are usually classified based on their particle charge upon dissolution in aqueous application medium such as cationic (all basic dyes), anionic (direct, acid, and reactive dyes), and non-ionic (dispersed dyes) (Yagub et al., 2014). Anionic dyes are highly water soluble and difficult to remove by conventional methods. Nonionic dyes, also known as disperse dyes, do not ionize in an aqueous solution and their fused aromatic ring structure makes them highly resistant to degradation. However, a few cationic dyes like methyl blue can be easily removed by adsorption and advanced oxidation processes (Ahmad et al., 2015).

2.2.1 Malachite Green Dye

Malachite Green (MG), tri-phenyl methane dye, $C_{23}H_{25}N_2Cl$, is basically a cationic dye (Fig 2.1). It is usually prepared by the condensation of benzaldehyde and dimethylamine to give leuco-malachite green (LMG). $C_6H_5CHO + 2\ C_6H_5N\ (CH_3)_2 \rightarrow C_6H_5CH\ (C_6H_4N\ (CH_3)_2)_2 + H_2O$. Then this compound is oxidized to a cation that is MG (Fig. 1): $C_6H_5CH\ (C_6H_4N\ (CH_3)_2)_2 + HCl + 1/2\ O_2 \rightarrow [C_6H_5C\ (C_6H_4N\ (CH_3)_2)_2]\ Cl + H_2O$. MG has been widely used for the dyeing of leather, wool, jute and silk, as a fungicide and antiseptic in aqua culture industry to control fish parasites and disease. MG is environmentally persistent and acutely toxic to a wide range of aquatic and terrestrial animals. It is highly lethal to freshwater fish, in both acute and chronic exposures. It causes serious public health hazards and also poses potential environmental problem. Both clinical and experimental observations reported so far reveal that MG is a multi-organ toxin. It decreases food intake, growth and fertility rates; causes damage to the liver, spleen, kidney and heart; inflicts lesions on the skin, eyes, lungs and bones; and produces teratogenic effects. MG is highly cytotoxic to mammalian cells and acts as a tumor enhancing agent. This dye may enter into the food chain and could possibly cause carcinogenic, mutagenic and teratogenic effects on humans (Azeb 2016; Makeswari & Santhi, 2013).

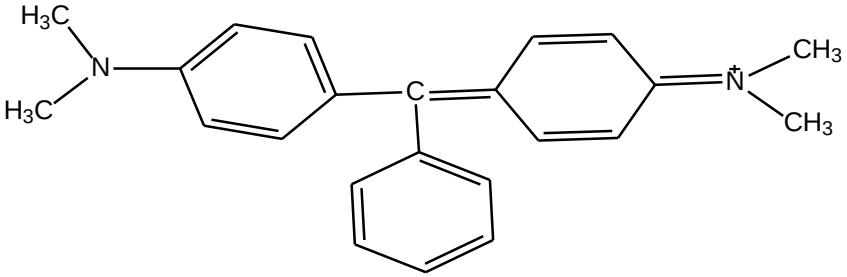


Figure 1: Molecular structure of Malachite green (Azeb G, 2016).

2.2.2 Impact on the Environment

Any industrial activities causes pollution in one form or the other so is the textile industry. Wastewater is the most environmentally damaging, and the wastewater from textile plants is classified as the most polluting of all the industrial sectors, considering the volume generated as well as its composition. The dyestuff lost through the processes of the textile poses a major problem for wastewater treatment (Malinauskiene, 2012).

Through the dyeing process, depending on the class of the dye, its loss in wastewaters could vary from 2% for basic dyes to as high as 50% for reactive dyes, leading to severe contamination of surface and ground waters. Color is the first wastewater contaminant to be recognized, since a very small amount of dye concentration in water (<1ppm) are highly visible that affects aesthetic merit, transparency and water-gas solubility. Moreover reducing light penetration through water decreases photosynthetic activity, generating oxygen deficiency and de-regulating the biological cycles of aquatic biota (Mohammadine El Haddad, 2013).

Many dyes are also highly toxic to the ecosystem and mutagens, meaning they can have acute to chronic effects upon organisms, depending on exposure time and dye concentration. For example, dye effluent has been connected to growth reduction, metabolic stress and death in fish, and growth and productivity in plants. Contamination therefore limits downstream human water use such as recreation, drinking, fishing and irrigation (Chequer, 2013). Therefore, wastewater containing residual dyes need to be treated before discharging to the receiving environment to keep the environment eco-friendly and sustainable.

2.3. Dye Removal Technologies

With the growing rate of industrialization, the emission of effluents from different industries poses serious threats to several living forms due to their adverse effects. The serious environmental impact and increase of public awareness in environmental protection, created a need to remove pollutants from wastewater before it is discharged into the environment. Currently there are several methods that can be used in the removal of dyes from industrial effluents. However, due to the variety of existent dyes and to the effluents complexity, not all methods have the same efficiency and each method has its limitations. Generally, the treatment

methods can be divided into three main categories namely physical, chemical and biological methods (Maria, 2014).

2.3.1. Physical Method

A number of different physical methods are used such as membrane-filtration processes (Reverse osmosis, electro dialysis, nano-filtration) and various adsorption techniques. The major disadvantage associated with the membrane filtration processes is that they have a limited lifetime, the problem of membrane fouling and the cost of periodic replacement must thus be included in any analysis of their economic viability (Zheng *et al*., 2015). The process of adsorption has an edge over the other methods due to its sludge free clean operation, completely removed dyes, convenience operation and simplicity of design (Elgeundi, 1991). Some physical methods are discussed below.

Membrane separation process is the method that uses the membrane's micropores to filter and makes use of membrane's selective permeability to separate certain substances in wastewater. Membrane separation has high separation efficiency, low energy consumption, easy operation, no pollution and so on. However, this technology is still not large-scale promoted because it has the limitation of requiring special equipment, and having high investment and the problem of membrane fouling (Ghaly et al., 2014). The important membrane separation processes are reverse osmosis and nano-filtration. Reverse Osmosis is a technology that is used to remove a large majority of contaminants from wastewater by pushing the wastewater under pressure through a semi-permeable membrane. Reverse osmosis permits the removal of all mineral salts, hydrolyzed reactive dyes, and chemical auxiliaries (Zheng et al., 2015). Nanofiltration has been applied for the treatment of colored effluents from the textile industry. Nanofiltration membranes retain low molecular weight organic compounds, divalent ions, large monovalent ions, hydrolyzed reactive dyes, and dyeing auxiliaries. The treatment of dyeing wastewater by nanofiltration is also used for the treatment of solutions with highly concentrated and complex solutions (Ghaly, et al., 2014).

2.3.2 Chemical Methods

Chemical methods include coagulation or flocculation combined with flotation and filtration, precipitation–flocculation with Fe (II)/Ca $(OH)_2$, electro flotation, electro kinetic coagulation, conventional oxidation methods by oxidizing agents (ozone), irradiation or electrochemical processes. These chemical methods are often expensive, and although dyes are removed, accumulation of concentrated sludge creates a disposal problem. There is also the possibility that a secondary pollution problem will arise because of excessive chemical use (Maria, 2014).

Recently, other emerging techniques, known as advanced oxidation processes, which are based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been applied with success for pollutant degradation. Although these methods are efficient for the treatment of waters contaminated with pollutants, they are very costly and commercially unattractive. The high electrical energy demand and the consumption of chemical reagents are common problems (Beyene, 2014).

2.3.3. Biological Method

Biological treatment procedures for the removal of contaminations from wastewater are considered highly useful due to their eco-friendly nature, minimum usage of chemicals and energy saving nature. The principle of the biological treatment procedures is the conversion of biodegradable wastes into simpler and harmless species through biological processes by various microorganisms. There are many types of biological treatment methods such as trickling filters, activated sludge process, anaerobic process etc. Biodegradation methods such as microbial degradation, adsorption by living or dead microbial biomass and bioremediation systems are commonly applied to the treatment of industrial effluents (Karthik et al., 2014). Biological process is cheaper than other methods. When compared to chemical methods, for biological process investment cost is 5-20 times less and operating costs are 3-10 times less than chemical methods. However, conventional biological processes are not effective for treating dyestuff wastewater because many commercial dyestuffs are toxic to organism being used and result in the problems of sludge bulking, rising sludge and pin flock, most dyes are designed to resist to microbial attack, require large land area and less flexibility in design and operation (Kharub, 2012). Summary of conventional treatment methods for dye removal shown below on table 1

Treatment methodology	Advantages	Disadvantages
Coagulation	Good removal efficiencies. Elimination of insoluble dyes	Cost of coagulants and chemicals for pH adjustment. Dewatering and sludge handling problems.
Membrane filtration	Removes all dye types. Recovery and reuse of chemicals and water. Wider application for complex wastes.	Concentrated sludge production. Dissolved solids are not separated in this process. High running cost
Ion-exchange	Regeneration with low loss of resins.	Specific application. Not effective for all dyes.
Electrochemical Oxidation	No additional chemicals required and end products are non-hazardous. Capacity of adaptation to different volumes and pollution loads.	Process with high cost. Iron hydroxide sludges.
Adsorption on activated Carbon	Good removal efficiency. Suspended solids and organic substances well reduced.	Regeneration process with high cost. Excessive solid waste generation.
Advanced oxidation Processes	Complete mineralization ensured. Effective pretreatment methodology in integrated systems and enhances biodegradability.	Expensive process.
Ozonation	Effective for azo dye removal. No alteration in volume.	Releases aromatic amines. Short half-life (20 min.).
Photocatalysis	Process carried out at a Inputs are non-toxic and inexpensive.	Effective for small amount of colorants. Expensive process.
Aerobic biodegradation	Color removal is facilitated along with COD removal.	Longer retention times. Less resistant to recalcitrant compounds.
Anaerobic biodegradation	Resistant to wide variety of complex colorants. Bio gas produced is used for electricity and steam generation.	Longer acclimatization phase.
Bacterial, fungal and algal biodegradation	Good removal efficiency for concentrations. Very effective for specific colorant removal.	Culture maintenance is expensive. Cannot cope up with largevolumes of colored effluents.

Table 1: Summary of conventional treatment methods for dye removal (Ghaly et al., 2014; Kharub, 2012).

2.4. Adsorption

Adsorption is the process in which different molecules, ions and atoms of a liquid or gas get attached to the surface. Adsorb ate is attached in the form of a film on the surface of the adsorbent. This process is different from absorption since in absorption, the substrate which is usually in the form of fluid percolates into the absorbent (Ramakrishna, 2013). Thus absorption includes the whole matter whereas adsorption is only effective on surfaces. But both the terms are included in a single term called "sorption", and the reverse of "sorption" is called "desorption". Adsorption is proving to be a better and more efficient method of waste water treatment in recent years. It is the process of formation of a layer of solid or gas on the substrate. Thus in the process of adsorption, the substance gets separated from fluid phase and gets accumulated on the solid phase substrate (Abbas F. S., 2013).

And it is a well known equilibrium separation process and an effective method for water de-contamination application. Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants. Adsorption also does not result in the formation of harmful substances. The process is influenced by many physicochemical factors such as dye/sorbent interaction, sorbent surface area, particle size, temperature, pH, and contact time (Ramakrishna, 2013) as (described in section 2.4.1).

Most of the solid adsorbents of great industrial applications possess a complex porous structure that consists of pores of different sizes and shapes. In terms of the adsorption science, total porosity is usually classified into three groups. According to international union of pure and applied chemistry (IUPAC) recommendation, the micro-pores are defined as pores of a width (<2nm), mesopores are pores of a width (2-50nm), but macro-pores represent pores of a width (>50nm) (Nuriya 2015).

However, the importance of porous structure on adsorption of many contaminants in aqueous solution is not well understood. As to physisorption on porous materials, it's generally accepted that adsorption mechanism and process may be significantly different as a consequence of porous structure. Further, a powder is easily recognized as a mass of small dry particles, but the

precise definition is inevitably somewhat arbitrary. The term fine powder is also used in an imprecise manner, but it seems reasonable to apply it to a material consisting of particles less than about 1μm. The unit mass of a fine powder contains a large number of small particles and exhibits an appreciable surface area (Serin & Selen, 2012).

In addition to the performance, a number of other factors greatly influence the choice and viability of waste materials as adsorbents, for example the cost of processing materials, wastewater selectivity and regeneration of materials. Cost is a very important factor when considering materials for use as adsorbents. It is generally recognized that a material can be deemed low-cost if it requires little processing, is abundant in nature, or is a byproduct or waste material from another industry (Eng-Cheong Khoo, 2011).

2.4.1. Adsorbent for Dye Removal

Adsorbents can be classified into natural adsorbents and synthetic adsorbents. Natural adsorbents include charcoal, clays, zeolites, and ores. These natural materials, in many instances are relatively cheap, abundant in supply and have significant potential for modification and ultimately enhancement of their adsorption capabilities. Synthetic adsorbents are adsorbents prepared from Agricultural products and wastes, household wastes, industrial wastes, sewage sludge and polymeric adsorbents. Each adsorbent has its own characteristics such as porosity, pore structure and nature of its adsorbing surfaces. Many waste materials used include fruit wastes, coconut shell, sawdust, rice husk, fertilizer wastes, bagasse fly ash, clays, red mud, zeolites, sediment and soil, ore minerals etc. The removal of dyes from water and wastewater is generally carried out by adsorption using activated carbon, low cost adsorbents and other types of adsorbents (Azeb, 2016).

2.4.1.1 Activated Carbon

Activated carbon, also called activated charcoal or activated coal, is a form of carbon that has been processed to make it extremely porous and thus have a very large surface area available for adsorption or chemical reactions. Activated carbons are well known for their high surface area (up to 3000 m2 g-1) and great adsorption ability for all kind of pollutants. The excellent adsorption abilities and economic promise of activated carbons can be attributed to their origin

from natural materials such as biomass, lignite and coal, which exhibit high sorption properties (Rafatullah et al., 2010). In aqueous solution, an electric charge is generated on the surface of activated carbon, either due to dissociation of the functional group of the carbon or due to the adsorbed ions which greatly depend on the solution conditions such as surface characteristics and solution pH. Various kinds of atoms or functional groups can be found on the surface of activated carbon which are responsible for adsorption, such as hydroxyl, carboxylic and epoxy, depending on the source of precursor materials (Ahmad et al., 2015).

2.4.1.2. Low Cost Adsorbents

Activated carbon has been popular choice as an adsorbent for the removal of a variety of contaminants from wastewater. In spite of that, there is a major disadvantage of high cost regeneration, associated with it to allow for further use. Therefore, there is a need for the development of low cost and easily available materials, which can be used more economically on large scale. Due to the problems mentioned above, research interest into the production of alternative adsorbents to replace the costly activated carbon has intensified in recent years (Rafatullah et al., 2010). Attention has focused on various natural solid materials, which are able to remove pollutants from the contaminated wastewater at low cost. The cost is actually an important parameter for the comparison and selection of adsorbents. An adsorbent can be considered as low cost if it requires little processing and abundant in nature. It may also be defined as a by-product or waste material from the industry and needs additional disposal cost. Certain waste products from industries and agricultural operations, natural materials and bioadsorbents represent potentially economical alternative adsorbents. Some low cost adsorbents are discussed below.

2.4.1.3. Natural Materials

Clays: The clays are hydrous aluminosilicates broadly defined as those minerals that make up the colloid fraction of soils, sediments, rocks and water and may be composed of mixtures of fine grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate and metal oxides. The clays invariably contain exchangeable ions on their surface and play important role in the environment by acting as a natural scavenger of pollutants by taking up cations and/or anions either through ion exchange or adsorption or both. The prominent ions found on clay

surface are Ca2+, Mg2+, H+, K+, NH4+, Na+, and SO42−, Cl−, PO43−, NO3−. These ions can be exchanged with other ions easily without affecting the structure of clay mineral (Rafatullah et al., 2010).

Zeolites and other siliceous materials: Zeolites are highly porous aluminosilicates with different cavity structures. They consist of a three dimensional framework, having a negatively charged lattice. High ion-exchange capacity and relatively high specific surface areas, and more importantly their relatively cheap prices, make zeolites more attractive adsorbents. The use of natural siliceous adsorbents such as silica, glass fibers and perlite for wastewater is increasing because of their high abundance, easy availability and low cost. Among inorganic materials, amorphous silica deserves particular attention, considering chemical reactivity of their hydrophilic surface, resulting from the presence of silanol groups. Their porous texture, high surface area and mechanical stability also make them attractive as adsorbents for decontamination.

2.4.1.4 Bioadsorbents

The accumulation and concentration of dyes from aqueous solutions by the use of biological materials is termed bioadsorption. Biomass used as an adsorbent in order to remove dye from solutions. The bioadsorbents are often much more selective than traditional ion-exchange resins and commercial activated carbons, and can reduce dye concentration to small levels (Rafatullah et al., 2010).

2.4.1.5. Agriculture and Industry Waste Materials And By-product

Agricultural solid wastes: Agricultural materials are basically composed of cellulose, hemicellulose, lignin, lipid, protein etc. and due to the presence of cellulose most of these materials show good sorption capacity for various pollutants. Agricultural waste materials are preferred due to their unique chemical composition, availability in abundance, renewable nature and low cost (Ramesh, 2013). In addition, with their being economic and eco-friendly are viable options for water and wastewater remediation. Also it is a rich source for activated carbon production due to its low ash content and reasonable hardness, therefore, conversion of

agricultural wastes into low-cost adsorbents is a promising alternative to solve environmental problems and also to reduce the preparation costs (Bhatnagar & Sillanpää, 2010).

Previously, various agricultural wastes have been explored as low-cost adsorbent. Some of them include leaves, fibers, fruits peels, seeds etc. and waste materials from forest industries such as sawdust, rice husk, papaya seeds, bark etc. have been used as adsorbents. These materials are available in large quantities and may be potential adsorbents due to their physico-chemical characteristics and low cost. Industrial solid wastes: Industrial solid wastes such as sludge, bagasse fly ash, red mud etc. are classified as low-cost materials because of their low cost and local availability and can be used as adsorbents for dye removal. (Rafatullah et al., 2010).

2.5. Corncob

Corn cob is the hard cylindrical central core of maize on which are borne the grains or kernels of an ear of corn. Corn cob is the agricultural waste product obtained from maize or corn. As a result of the increase in corn production, large quantity of corn cob thus generated remains unused as cellulosic wastes in fields and factories. This poses a serious environmental problem not only to pollution and storage but also for disposal. Maize is grown twice in a year, between February – May and May – October. This agricultural waste can be utilized as a potential renewable source of energy. The most common routes for conversion of this waste to energy or disposal includes; combustion, gasification, liquefaction and carbonization. In all of these processes, combustion is preferred. However, it has its own problem of air pollution from burning (Akuso. S. Alkali, 2016).

2.5.1. Use of Corncobs Activated Carbon

In last few years the growth of corn crop has increased considerably in the Ethiopia because of the government‘s policy of promoting alternative agricultural practice and there is a huge supply of waste corn cobs. However, after the use of corn for wide variety of applications the corn cobs often leave in the fields as very low economic value agricultural waste. Due to their abundance in the region, they are very inexpensive and easily obtained, hence, resulting in their desirability to be used for this research. The efforts of using the corn cobs as a biomass fuel has not given very promising results primarily because of the low calorific value of corn cobs (Adie et al.,2010). Another alternate route to convert these waste corn cobs to high economic value

product can be to convert them into more commonly called as activated carbon. Hence using them for experimental purposes yields no cost, no adverse environmental effect. The use of various precursors such as saw dust, Coffee husk, and lignite coals for producing activated carbon has been studied in detail by several researchers (Narayanan, L., 2014).

One of the excellent precursors for activated carbon could be corn cob because of its botanical origin similar to coconut shells and olive pits. Since the yield of the activated carbon production is usually very low, the cost and availability of the raw material is a very important factor in the economic production of activated carbon. Coconut shell, wood, lignite coals which are often used for commercial production of activated carbon have high price as compared to agricultural waste such as corn cob. Corn cob is available in abundance and is relatively cheap. Also the chemical compositions of corn cobs suggest that it has less mineral matters, which are often responsible for preferential gasification during the activation process resulting in pore. The elemental analyses of corn cobs which show high promises of its use as precursor of nanoporous carbon production because of its carbon content up to 45%. Because of this reasons corn cobs could be an excellent precursor for the commercial production of activated carbon (Debela. T., 2016)

2.4. Principles of Adsorption

Adsorption is a surface phenomenon in which adsorbate molecules or ions (liquid or gas) are concentrated on the surface of a solid. It is a process of binding molecules or particles onto the external surface of solid or internal surface, if the material is porous in a very thin layer (Kandasamy et al., 2011). The binding to the solid are usually weak and reversible. The substance that accumulates at the interface is called ‘adsorbate’ and the solid on which adsorption occurs is known as ‘adsorbent’ (Bhatnagar & Sillanpää, 2010). Adsorption takes place primarily on the walls of the pores or at specific sites inside the particle. Separation occurs because of differences in molecular weight, shape or polarity, causes some molecules to be held more strongly on the surface than others. In many cases, the adsorbate is held strongly enough to allow complete removal of that component from the fluid. In the adsorption process, dye molecules may be adsorbed on the surface of an adsorbent through several forces such as hydrogen bonding, electrostatic interactions, van der Waals forces, hydrophobic interactions etc.

Generally, adsorption process is classified as physisorption and chemisorption (Kandasamy et al., 2011).

Physisorption is a type of adsorption in which the forces of attraction are intermolecular forces (van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapors, and do not involve a significant change in the electronic orbital patterns of the species involved. The adsorbed molecules are not fixed to a specific site at the surface of adsorbent but are free to undergo translational movement within the interface. It is predominant at low temperature and is characterized by relatively low energy of adsorption. Chemisorption is adsorption in which the forces involved are forces of the same kind as those operating in the formation of chemical compounds. Generally, adsorbents possess porous structures to increase the total exposed surface area and allow fluid to pass through faster (Beyene, 2014).

2.5. Factor Affecting Dye Adsorption

Many physicochemical factors influence the amount of adsorption of a adsorbate (dye) onto an adsorbent and these include: surface area of adsorbent, initial dye concentration, temperature, pH and contact time between adsorbate and adsorbent etc.

2.5.1. Effect of Dye Concentration

The amount of adsorption for dye removal is highly dependent on the initial dye concentration. The effect of initial dye concentration depends on the immediate relation between the concentration of the dye and the available sites on an adsorbent surface. In general, the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. On the other hand, the increase in initial dye concentration will cause an increase in the capacity of the adsorbent and this may be due to the high driving force for mass transfer at a high initial dye concentration (Yagub et al., 2014).

2.5.1. Effect of Adsorbent Dose

Adsorbent dosage is an important process parameter to determine the capacity of an adsorbent for a given amount of the adsorbent at the operating conditions. Generally, removal efficiency

increases with increasing adsorbent dosage, where the quantity of sorption sites at the surface of adsorbent will increase by increasing the amount of the adsorbent. The effect of adsorbent dosage gives an idea for the ability of a dye sorption to be adsorbed with the smallest amount of adsorbent, to recognize the capability of the adsorbent from an economical point of view (Sartape et al., 2014).

2.5.3. Effect of Solution pH

Another important factor affecting the capacity of adsorbent in dye removal is solution pH. The efficiency of adsorption is dependent on the solution pH, since variation in pH leads to the variation in the degree of ionization of the adsorptive molecule and the surface properties of adsorbent (Yagub et al., 2014). pH value of the solution will determine the surface charge of the adsorbent which will affect the interaction between the adsorbate and adsorbent. There are two possible mechanisms for the effect of pH on adsorption of dyes on any adsorbent: electrostatic interaction between the protonated or deprotonated groups of adsorbents with dyes, and the chemical reaction between the adsorbate and the adsorbent. The hydrogen ion and hydroxyl ions are adsorbed quite strongly, and therefore, the adsorption of other ions is affected by the pH of the solution. The change of pH affects the adsorptive process through dissociation of functional groups on the active sites of the adsorbent. This subsequently leads to a shift in reaction kinetics and equilibrium characteristics of the adsorption process. It is a common observation that the surface adsorbs anions favorably at lower pH due to presence of H^+ ions, whereas, the surface is active for the adsorption of cations at higher pH due to the deposition of OH^- ions (Amran et al., 2011).

2.5.4. Effect of Contact Time

The contact time between the pollutant and the adsorbent is of significant importance in the wastewater treatment by adsorption. A rapid uptake of pollutants and establishment of equilibrium in a short period signifies the efficiency of that adsorbent for its use in wastewater treatment. In physical adsorption most of the adsorbate species are adsorbed within a short interval of contact time. However, strong chemical binding of the adsorbate with adsorbent requires a longer contact time for the attainment of equilibrium. Available adsorption studies in literature reveal that the uptake of adsorbate species is fast at the initial stages of the contact

period, and thereafter, it becomes slower near the equilibrium. In between these two stages of the uptake, the rate of adsorption is found to be nearly constant. This is obvious from the fact that a large number of vacant surface sites are available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid and bulk phases (Nuriya J, 2015).

2.5.5. Effect of Temperature

Temperature is also a significant physico-chemical process parameter because temperature will change the adsorption capacity of the adsorbent. If the amount of adsorption increases with increasing temperature, then the adsorption is an endothermic process. This may be due to increasing mobility of the dye molecules and an increase in the number of active sites for the adsorption with increasing temperature. Whereas the decrease of adsorption capacity with increasing temperature indicates that the adsorption is an exothermic process. This may be due to increasing temperature decreases the adsorptive forces between the dye species and the active sites on the adsorbent surface as a result decreasing the amount of adsorption (Yagub et al., 2014).

2.6 Adsorption Isotherms

Adsorption is typically represented through isotherms, that is, the quantity of adsorbate on the adsorbent as a function of its pressure (in case of gas) or concentration (in case of liquid) at a constant temperature. Amount of adsorbate adsorbed is almost continuously normalized by the mass of the adsorbent to permit comparison of various materials. Equilibrium studies on adsorption process provide data on the capacity of the adsorbent. Also, an adsorption isotherm is characterized by particular constant values that exhibit the surface properties and affinity of the adsorbent and can even be used to compare the adsorptive capacities of the adsorbent for various pollutants. The most common model at constant temperature for this sort of adsorption Langmuir or Freundlich model.

2.6.1 Langmuir Isotherm

Assumptions of Langmuir Isotherm are: 1) The surface available of the adsorbent for adsorption is assumed to be uniform, that is, all the sites available for adsorption are equivalent. 2) There is

no interaction between molecules of adsorbed materials. 3) There is same mechanism for all sort of adsorption. 4) Only a monolayer is assumed to be formed at the site of maximum adsorption, i.e. molecules of adsorbate do not deposit on another molecules of adsorbate which are already adsorbed. Instead, they only deposit on the remaining surface available for the adsorption

$$\frac{Ce}{qe} = \frac{1}{kl} . \frac{1}{qm} + \frac{Ce}{qm} \qquad (2.1)$$

Ce-concentration at equilibrium, *q*e- amount of adsorbate adsorbed per gram of adsorbent at equilibrium; qm- Langmuir constants related to adsorption capacity, k*l*- Langmuir constants associated with energy of adsorption, The Langmuir constants qm and k*l* are calculated from the slope and intercept of plot between Ce/qe *vs* Ce (langmuir, 1916).

2.6.2 Freundlich Isotherm

Freundlich isotherm theory describes the quantitative relation i.e. the ratio of the quantity of adsorbate adsorbed onto a given mass of adsorbent to the concentration of the adsorbate in the solution. It is applicable to adsorption on heterogeneous surfaces and can be represented by equation in linear form as:

$$\log \mathrm{Qe} = \log \mathrm{Kf} + \frac{1}{\mathrm{nf}} \log \mathrm{Ce} \qquad (2.2)$$

The plot of Log qe versus Log Ce provides the slope 1/nf and intercept Kf ((mg/g)/ (L/g)n) Kf is the Freundlich constant and nf is the Freundlich exponent. Here, Kf and nf are defined as the constants for the adsorption capacity and intensity of adsorption respectively (freundlich 1916).

2.7 Adsorption Kinetics

Adsorption processes are characterized by their kinetic and equilibrium behaviour. The transport of the adsorbate at the solid-solution interface (adsorbent) and the attachment of the adsorbate onto the adsorbent surface (i.e. the rate of the physiochemical interaction at the surface) determine the uptake rate of the adsorbate and thus the kinetics of the process (Husein, 2012). The degree of purification that may be achieved, the approximate amount of adsorbent required to reach that degree of purification and the sensitivity of the process to the concentration of the solute are predicted by the isotherms. Many mathematical models have been studied in order to

describe the kinetics of adsorption processes. The pseudo first-order equation and pseudo second order equation are the widely used models for the adsorption kinetics of organic compounds (Beyene, 2014). A study of the kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for the efficiency of the process. In addition, the design of an adsorption system for water treatment may be influenced or even controlled by the adsorption kinetics (Muhi Mohammed, 2011). The rate of adsorption may be controlled by mass transfer, intra-particle diffusion, or surface chemical kinetics. Several kinetic models for the liquid phase have been widely used to describe experimental data.These include pseudo first order, pseudo second order, and mass transfer/intra-particle diffusion models. The pseudo first-order model is expressed as follows:

$$\frac{dqt}{dt}=k_1(qe-qt) \qquad (2.3)$$

The pseudo second-order model is expressed as:

$$\frac{dqt}{dt}=k_2(qe-qt)^2 \qquad (2.4)$$

Where, qe and qt are the amounts of adsorbate adsorbed (mgg^{-1}) at equilibrium and at any time t and k1 (min^{-1}), k2 (min^{-1}) are the pseudo first and second-order rate constants respectively.

2.8 Techniques for Analysis

2.8.1 Uv - Visible Spectrometer

Ultraviolet (UV) and visible radiation comprise only a small part of the electromagnetic spectrum, which includes such other forms of radiation as radio, infrared (IR), cosmic, and X rays. The absorption of radiations involves transfer of energy to medium and this is specific phenomenon related to the characteristic molecular structure. For a given excitation process, molecules absorb discrete amount of energy corresponding to only one frequency which should give rise to absorption line.

2.8.3 FTIR Analysis

Fourier Transform Infrared Spectroscopy i.e. FTIR technique has been widely used for the prediction of organic compounds present in the sample by the absorption of low energy light i.e. ultraviolet light of each wavelength. We obtain absorption spectra of the compounds which is a unique reflection of the molecular arrangement of the compound in the sample. This spectrum is a graph which contains percent transmittance along Y axis and frequency or wavelength along X axis. By studying the peak between a particular frequencies i.e. gap or band, type of the functional group present can be predicted with the help of available table.

3. MATERIALS AND METHODS

3.1. Materials

3.1.1. Chemicals and Reagents

All chemicals used in this work are analytical grades and include; phosphoric acid: used as activating agent of corn cob activated carbon production process, hydrochloric acid & sodium hydroxide for pH adjustment, malachite green ($C_{23}H_{25}N_2Cl$) for intial adsorption experiment, sodium thiosulfate, potassium iodate, starch, iodine and potassium iodide for iodine test. The aqueous solutions of varied concentrations of malachite green dye will be prepared by dilution from its stock solution and the study will be done by varying different parameters. All experiments were used distilled water.

3.1.2. Apparatus and Instruments

The major equipments used were UV-Vis spectrophotometer (model-NV 203) :used to measure absorbance of the solution, furnace (model 91e made in England): used for pyrolysis/carbonization of the corn cobs, orbital Shaker (model VRN-480 made in Germany) : was used to agitate the adsorbents with adsorb ate, pH meter (Jenway 430 Model): to measure the pH of the solution, digital balance (model AP210S made in Switzerland): to weigh the samples, Filter paper (Advantec, 45μm): to filter the content of the flasks, oven (model DHG-9030 made in Japan): was used for subsequent moisture removal and drying, and sieving equipment. The laboratory wares used were volumetric flask, aluminum foil, vacuum desiccators, beaker and conical flask: to handle the solutions, pipettes: to transferring the solution into test tube and burette.

3.2. Methods

3.2.1. Adsorbent Preparation

Since corn cob will be the selected adsorbent for the preparation of activated carbon. Corn cobs were collected from Sidama Regional State, Arbegona woreda. They were then repeatedly washed with distilled water to remove dirt particles and were dried at 105 ^{0}C for 24 h. The dried

corn cob was crushed and sieved to the size of 1.5 mm then preserved in clean containers for activated carbon production.

3.2.1.1. Optimization of Activated Carbon Production Parameters

Different process parameters such as acid concentration, impregnation ratio, carbonization temperature and holding time were studied to estimate the effect on porous characteristics of AC.

3.2.1.1.1 Effect of Acid Concentration on Iodine Number Adsorption

The effect of acid concentration studied by varying the acid concentration from 35%−95% and kept other parameters constant (Temperature 400^0C, impregnation ratio 1:1 and time 2hr).

3.2.1.1.2 Effect of Impregnation Ratio on Iodine Number

The effect of impregnation ratio was optimized by taking different ratio of raw material to acid (2:1, 1.5:1,1:1, 1:1.5,1:2) impregnation ratio at the optimum temperature and time of 400^0C and 120 mins respectively. The prepared activated carbon was further characterized by selected physical properties. Consequently, optimum condition was selected as starting precursor for preparation of activated carbon.

3.2.1.1.3 Effect of Activation Temperature on Iodine Number

Using H_3PO_4 as the best activation chemical based on the iodine number, the optimum activation temperature was determined by varying the temperature of activation between 300, 350,400, 450, 500 ^{0}C using the same impregnation ratio of 1:1.5 for 120mins each in a furnace. With this the iodine number was determined.

3.2.1.1.4 Effect of Activation Time on Iodine Number

The effect of activation time on iodine number of activated carbon produced was determined by varying the activation time at the optimum activation temperature of 450^0C and 1:1 impregnation ratio. The time variation were; 60mins, 90mins, 120mins, 150mins and 180mins.

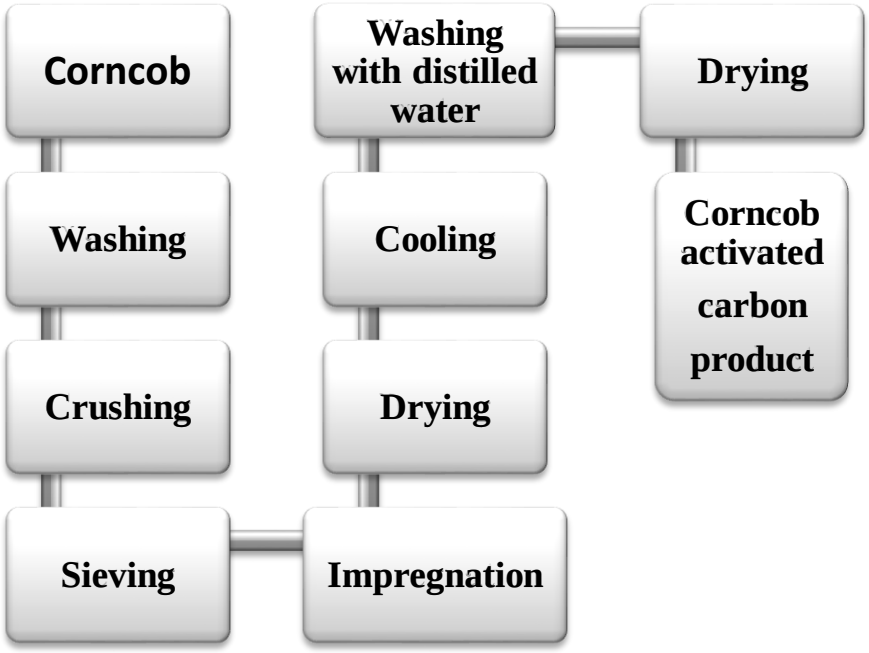


Figure 2: Activated carbon preparation flow diagram

The obtained activated carbon called ACC. The optimized ACC was used in further experiments.

3.2.4. Characterization of Corncobs Activated Carbon

3.2.4.1 Proximate Analysis on Raw Adsorbent

The proximate analysis of a substance is a means of determining the distribution of products obtained when the sample is heated under specified conditions. Proximate analysis (moisture content, ash content, volatile matter and fixed carbon) of the adsorbents were measured using the method of ASTM.

3.2.4.1.1 Moisture Content Determination

The moisture content of ACC was determined by the oven drying method. This was carried out at temperature of 105 $^{\circ}$C in accordance with the ASTM. 1 g of the adsorbent (W_1) was placed into reweighed crucible (W_o) and placed into a hot drying oven at 105 $^{\circ}$C for 1 h. The crucible

was removed, cooled in desiccators and weighed. The process of drying, cooling and weighing was repeated until a constant weight (W_2) was obtained.

$$\text{Moisture content (\%)} = \frac{W1-W2}{W1-W0} \times 100\% \qquad \textbf{(3. 1)}$$

3.2.4.1.2 Ash content determination

Ash content was determined using the ASTM. A crucible was washed and dried in a hot air oven for 30 minutes at a Temperature of 105 °C. After heating, it was then cooled in desiccators for 30 minutes. The crucible was weighed using analytical balance. 1 g of each of the samples was placed into the crucible and its weight was recorded. It was transferred to a muffle furnace maintaining a temperature of 500 °C for 2 hours, for complete de-carbonization to obtain white ash. The crucible and ash was cooled and the weight recorded. The result was expressed as percentage of the weight of ash over the original weight of sample.

$$\text{Ash content (\%)} = \frac{W2-W0}{W1-W0} \times 100\% \qquad \textbf{(3. 2)}$$

Where, W_0 is weight of crucible (gm), W_1 is weight of crucible plus original activated carbon sample (gm) and W_2 is weight of crucible plus ash sample (gm).

3.2.4.1.3 Volatile Matter Determination

Determination of volatile mater for the activated carbon was conducted according to the procedure specified by ASTM for activated carbon. The sample was measured carefully and placed in the crucible which was dry, clean and known weight. And then the crucible was closed and placed in the furnace as it was closed to avoid contact between the air and sample. The sample was ignited in the furnace at 900^0C for 7min. After seven minute the sample was removed from furnace and cooled to room temperature and then weighted by using electronic balance. Then the volatile mater was calculated by using the following equation.

$$\text{Volatile matter (\%)} = \frac{W2-W0}{W1-W0} \times 100\% \qquad \textbf{(3. 3)}$$

Where, W_2 is weight of crucible and ignited sample (gm), W_1 is weight of crucible and original sample (gm) and W_0 is weight of crucible.

3.2.4.1.4. Fixed Carbon Determination

Fixed carbon was calculated as the resultant summation of percentage of all proximate analysis (moisture content, ash content, and volatile matter content) and subtracted from 100. The fixed carbon was determined by using:

$$\text{Fixed carbon (\%)} = 100 - (\text{moisture \%} + \text{ash \%} + \text{volatile matter \%}) \quad \textbf{(3. 4)}$$

3.2.4.2 Iodine Number Determination

The iodine number is determined according to the ASTM D4607-94 method. A stock solution containing 5% by weight of hydrochloric acid (HCl) was prepared by adding 70 mL of concentrated hydrochloric acid to 550 mL of distilled water and mixed well. A stock sodium thiosulfate (0.1N) was prepared by dissolving 24.82 mL Sodium Thiosulfate in approximately 75 mL of freshly boiled distilled water and 0.1 g of sodium carbonate was added to minimize bacterial decomposition of thiosulfate solution. The mixture was transferred to 1 L volumetric flask and diluted up to mark. The solution was standed for 4days before standardizing and stored in an amber bottle. To standardize iodine solution 12.7 g of iodine crystals and 19.1 g of potassium iodide per liter mixed and stired at least for 4hrs and quantitatively transferred to 1 L volumetric flask and diluted to the mark. The prepared stock solution was standardized using a standard solution of sodium thiosulphate. To a 250 mL conical flask, 0.8 g, 0.9 g and 1 g (separately) of the composite activated carbon of ACC and 10 mL of 5 % v/v hydrochloric acid were introduced. Then, 100 mL of the stock iodine solution was added and heated at a heating plate for a period of 30 sec. The mixtures were filtered through one sheet of folded filter paper (Whatman No.42). An aliquot portion (50 mL) was titrated with 0.1 N sodium thiosulphate using 2 mL starch as an indicator and continued the titration until one drop produced a colorless solution. The concentration of iodine adsorbed by ACC carbon at room temperature was calculated as amount of iodine adsorbed in mg.

$$I\ (mg/g) = X/M = [A - (DF)\ (B)\ (S)]/M \quad \textbf{(3. 5)}$$

Where, X/M is iodine absorbed per gram of carbon (mg/g), S is sodium thiosulfate (mL), and M is mass of activated carbon (g). Where, A= N_2 (12693.0), N_2 normality of iodine, dilution factor (DF) = (I +H)/F, B = N1 (126.93), N1 normality of sodium thiosulfate, I volume of iodine (mL), H volume 5 % hydrochloric acid (mL), and F volume of filtrate (mL)

3.4.2.4. Point Zero Charge Determination

The pH value, at which the surface charge is zero, is called the point of zero charge (PZC). Determination of point zero charged: the (Farahani *et al*., 2011) test method was adopted. 500ml of 0.1N KNO_3 in the pH range of 2 to 10 was prepared in 9 different flasks. 45ml of KNO_3 solution was taken from the 500ml of KNO_3 solution and initial pH of solution were adjusted by adding drops of 0.5N NaOH and 0.5N HCl solutions and 1gram of activated carbon samples were added to each flask and shacked for 48hours at room temperature. Finally, the pH was measured and recorded. The total charge adsorbed (Δ pH on activated carbon surface was determined by the difference between pH after 48hr and pH before. The pH values (pH of 2 to 10) are plotted along the x-axis and Δ pH along y-axis, the data obtained from the experiment are plotted and the intersection point is taken as a reference for determining the pH PZC value. The ΔpH value was expressed as follows:

$$\Delta pH = pHf - pHi \qquad \textbf{(3. 6)}$$

3.4.2.5 Surface Functional Group Analysis by Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis was carried out in order to identify the functional groups that might be involved in the binding of dye ions. The functional groups of Adsorbents were determined using FTIR Spectrometer (Spectrum 65 FT-IR, PerkinElmer) at wave number range of 4000-400 cm^{-1}. First, the adsorbents were mixed with KBr particles to make it suitable to infrared analysis. The mixture was then pressed to a small thickness, slightly below 1 mm, required for FTIR analysis. FTIR analysis was done at Addis Ababa University, College of Natural Science, Chemistry Laboratory.

3.4.2.6 X-Ray Diffraction (XRD)

X-ray diffraction spectroscopy (XRD) analysis the prepared adsorbents were carried out at Addis Ababa University in departments of chemistry laboratory, using X-ray diffraction instrument (model miniflex 600 PXRD). X-ray diffraction technique is power full tool to analyze the crystalline nature of the materials. If the material under investigation is crystalline, well- defined peaks were observed while non- crystalline or amorphous systems show a hollow instead of

well- defined peak (Ahmaruzzaman and Bhattacharjee, 2015). The crystallite domain sizes of adsorbents were calculated from the width of the peaks, using Scherrer's formula.

$$\boldsymbol{D = \frac{K\lambda}{\beta Cos\theta}} \qquad (\mathbf{3.7})$$

Where D is the average dimension of the crystallite domain size, K is a non-dimensional shape factor (usually fixed to 0.9), λ is the wavelength of the Cu Kα radiation, β is the full width at half maximum (FWHM) in 2θ value of the diffraction peaks and θ is the diffraction angle. Therefore studying the diffraction of X-ray is used to generate information about the structural properties of any crystalline material.

3.4.3 Analytical Methods

In order to know the maximum wave length absorbency of MG dye, 20mg/L of the dye solution was taken and scanned using UV-vis spectrophotometer and it was found that maximum absorbency (λ max) of the dye is 617nm. To calculate the dye concentration from each batch adsorption experiment, a calibration curve was first prepared by using the standard MG dye solution with known concentrations. Different concentrations were prepared and absorbance values were recorded at λmax of the dye using UV-visible spectrophotometer.

3.4.4. Batch Adsorption Experiment

Batch experiments were conducted in a series of conical flask of 250mL capacity. In all the experiments, solution volume was 50mL and the mixture of solution and the adsorbent was agitated by using rotary incubator shaker at 120 rpm for desired time at (27°C) temperature. Initial pH of the solution was measured using an electronic pH/conductivity meter by adding 0.1M HCl or 0.1M NaOH before adding the adsorbent.

At the end of each adsorption experiment, small amount of the test solutions were withdrawn at predetermined time and the powder was removed by filtration using Whatman number 1 filter paper and concentration of the residual dye was measured using UV-visible spectrophotometer at a λ_{max} corresponding to the maximum adsorption for the dye solution (λ_{max} = 617nm). All

experiments were performed in triplicate and the mean value was presented. The adsorption experimental data were annexed.

To calculate the dye concentration from each batch adsorption experiment, a calibration curve was first prepared by using the standard MG dye solution with known concentrations. Different concentrations were prepared and absorbance values were recorded at λ_{max} of the dye using UV-visible spectrophotometer. Absorbance versus concentration of the standard dye solution was recorded as presented in Table 3 to obtain absorbance-concentration profile. Linear calibration curve of this data was served as the basis for determining the dye concentration variation as a result of the dye adsorption process during the experimental work. The uptake of dye concentration was calculated using equation 3.7, while the dye uptake q (mg dye ion g^{-1} of adsorbent) was calculated from the mass balance of equation 3.8. The adsorbed quantity was calculated using the following equation:

$$\boldsymbol{Q = \frac{(Co - C)}{R}} \qquad \textbf{(3. 7)}$$

and the fading percentage/removal efficiency/adsorption efficiency:

$$\textbf{\% Removal} = \frac{(Co - C)}{Co} \times 100 \qquad \textbf{(3. 8)}$$

Where Q (mg/g) is the adsorbed quantity,C_0 (mg/L) is the initial dye concentration, C (mg/L) is the dye concentration at a time t, and R (g/L) is the mass of adsorbents per liter of solution.

3.4.3.1 Effect of Solution pH

The effects of pH were studied by varying the pH and important parameters for the assessment of practical application of adsorption process.50mL of the 30 mg/L malachite green solution was put in each different conical flask. The pH of each flask was adjusted in the range of 2, 4, 6, 8 and 10 with dilute HCl (0.1M) and NaOH (0.1M) solution by the use of pH meter. An adsorbent dose of (0.2 gm) was put in each flask. Then, all the flasks were kept inside the orbital shaker at 150 rpm for 90 minutes. After that the flasks were withdrawn from the shaker and solutions were filtered immediately through awhat man filter paper and absorbance of the filtrate solutions was measured using UV-visible Spectrophotometer at maximum wavelength of 617 nm. A graph was plotted with percent removal versus initial pH.

3.4.3.2 Effect of Adsorbent Dose

To study the effect of adsorbent dose 50mL of the working solution with 30 mg/L concentration was put in each different conical flask. And adjust the solution with an optimum pH of 8 and 10 for ACC and PCC respectively. Then, the concentration of adsorbent was varied as 0.05g, 0.1g, 0.2g, 0.3g and 0.4g/50mL. The test solutions were shaken at agitation speed 150 rpm for 90 min in order to determine the effective dose for the dye removal.

3.4.3.3 Effect of Initial Concentration

To examine the effect of initial dye concentration, experiments were conducted by varying dye concentrations ranging from 10 to 50 mg/L at constant adsorbent dose of 0. 2 g/L for ACC and 0.3g/L for PCC.

3.4.3.4 Effect of Contact Time

The effect of contact time were studied by taking 50mL of the malachite green solution with the optimum pH, initial concentration and adsorbent dose as obtained from the above studies were put in each flask. Then, all the flasks were put in the orbital shaker at 150 rpm for a predetermined time period ranging from 30 to 150 minutes, on a 30 minutes interval.

3.4.4 Adsorption Isotherm Models and Kinetics

After the selection of the optimum values for the adsorbent dose, initial concentration, pH, and time, isotherms and kinetics of adsorption were studied. Different dye concentration of 10mg/L,20 mg/L,30mg/L,40mg/L and 50mg/L were mixed with 0.3g/50mL for PCC and 0.2g/50mL ACC of adsorbents. The adsorption processes were carried out until equilibrium is achieved. The results obtained from adsorption experiments were analyzed by Langmuir and Freundlich models.

The kinetics of adsorption was determined by analyzing adsorptive uptake of the dye from the aqueous solution at different time intervals. The same adsorption kinetic data were treated with pseudo-first order kinetic model and pseudo-second order kinetic models.

3.5. Method Validation (Percent recovery)

In order to evaluate the analytical applicability of the method, determination of malachite green in water samples. The validity of the optimized parameters was checked by adding the samples with a standard of known concentration of the analyte MG (10 mg/L) in to 25mL of the textile wastewater sample. The recovery test can be calculated by using equation 3.9:

$$\mathbf{R} = \left(\frac{\mathbf{C\ total - C\ found}}{\mathbf{Cadded}}\right) \mathbf{100} \qquad \mathbf{(3.\ 9)}$$

Where C_{total}, C_{found}, and C_{added} are the concentrations of analyte after addition of known amount of standard in the real sample, the concentration of analyte in real sample and the concentration of known amount of standard which was mixed to the real sample, respectively.

4. RESULT AND DISCUSSION

The following chapter provides result of laboratory analysis made for adsorbent preparation and study on some factors affecting dye adsorption such as initial solution pH, adsorbent dose, initial dye concentration and contact time by powdered corncob and activated corncob adsorbents from aqueous solution and findings of other scientific data generated from this study.

4.1 Optimization of Activated Corncob Production

Optimization is the act of achieving best/possible results under given circumstances. Its goal is either to minimize effort or to maximize benefit. The effort or benefit can be expressed as a function of certain variables. Hence, optimization is the process of finding the condition that gives the maximum or the minimum value of a function. In this study optimization focuses on to maximizing the pore size distribution of corncob by activating phosphoric acid on its surface. The production of corncob activated carbon was optimized by using iodine adsorption test. Different process parameters such as acid concentration, impregnation ratio, carbonization temperature and activation time were studied to estimate the effect on porous characteristics of AC. The experimental result of the activated carbon is tabulated under appendix B. (Table I). The effects of acid concentration, activation temperature, activation time and impregnation ratio on some properties of the prepared activated carbons are shown in Figure 3-5.

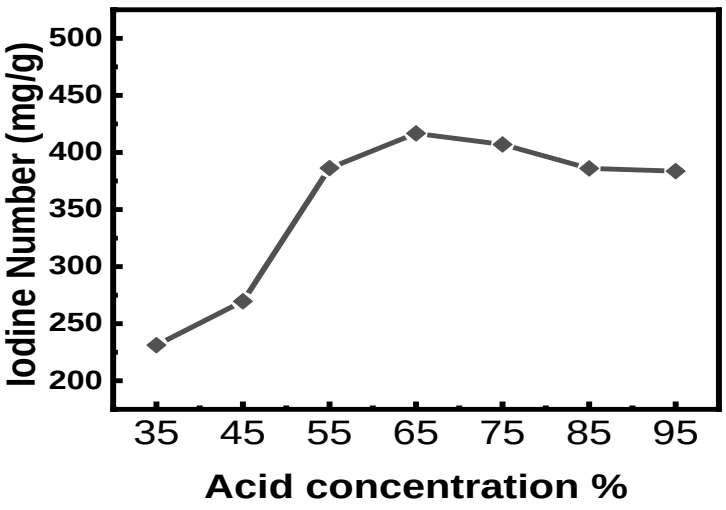


Figure 3: The effect of acid concentration on the iodine number of ACC

Figure 3 shows the iodine values of ACC prepared at a impregnation ratio of 1:1 , activation temperature of 400^0C, activation time 2 hours and the acid percentage was varied from 35% to 95%. It can be seen that iodine values increases continuously with the increasing acid percentage, until reaching a maximum at acid percentage of 65 %. Then, the iodine values decreased with the increasing acid percentage from 65 to 95 %. The highest iodine value was 416.75±65.81787 mg/g developed at acid percentage of 65 %. Thus, keeping the acid concentration at around 65% was better development of the sorbent porosity.

The effect of impregnation ratio on the iodine number of corn cob activated carbon at constant temperature of 400^0C, acid concentration 65% and activation time of 2h showed in Figure 4. The effect of iodine number adsorption on corn cob activated carbon result showed that increase in iodine values is due to development of pores and increased porosity in the carbons, which reached a maximum value at impregnation ratio of 1:1.5 for corncobs activated carbon.

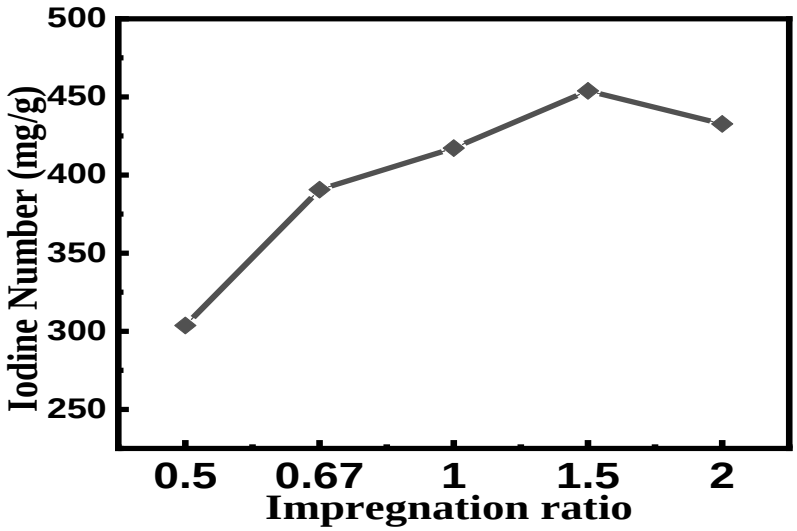


Figure 4: The effect of the impregnation ratio on the iodine number of ACC

At a value more or less than 1.5 the iodine numbers decrease. Therefore, 1.5 is the suitable impregnation ratio value leading to the best iodine number and consequently, to the best development of porous structure**.** Figure 5 shows the iodine adsorption with the increase of activation temperature from 300^0C to 450^0C. It can be seen from Fig. 5 that the increase in activation temperature causes an improvement in value of the iodine numbers up to 523.76333 ± 69.66249 mg/g, thereafter it decreases. Where the increase in temperature from 300^0C to 450^0C

at 1:1.5 and 65 %, increases the iodine number from 412.8833 ± 65.63498 mg/g to a maximum value of 523.76333 ± 69.66249 mg/g, indicating the formation of a greater number of active sites and pores inside and on the surface of the samples. Therefore, 450^0C can be considered as best activation temperature for preparation of activated carbon in this study.

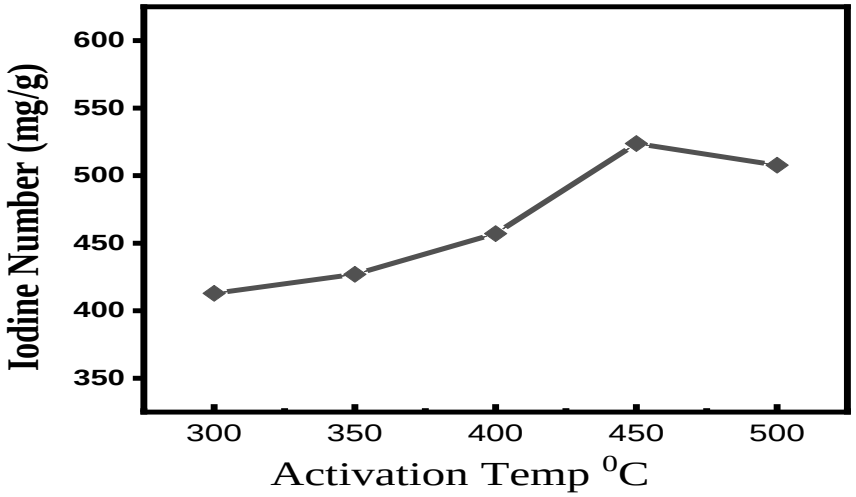


Figure 5: Effect of activation temperature on the iodine number of corn cob activated carbon

Activation time at final carbonization temperature played an important role in the development of porous structure. The ACC samples were prepared at optimum conditions of impregnation ratio and carbonization temperature with different holding times (60 – 180 min). Figure 6, below represents the effect of activation time at final carbonization temperature on iodine number of AC prepared. The effect of activation time on the iodine number of ACC (Figure 6) showed that the iodine number of carbon begin to increase with an increase of the time from 60 min to 120 min, and then decrease when the time exceeds 180 min. Hence, the activation time of 120 min was required and was used in subsequent experiments. Thus, keeping the activation time at around 120 min leads to a better development of the sorbent porosity.

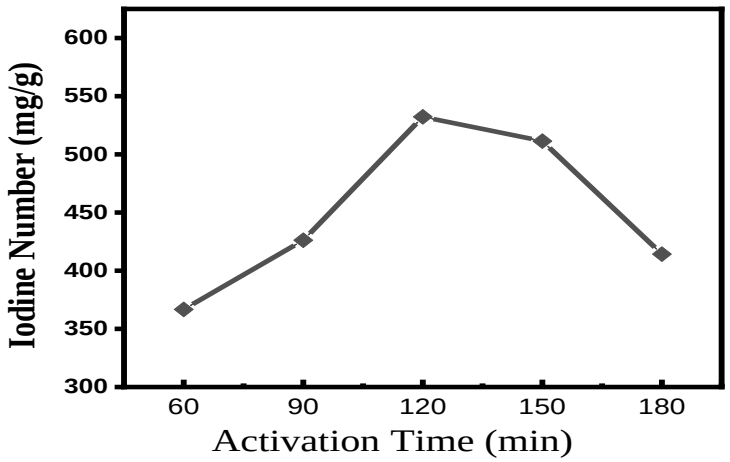


Figure 6: Effect of activation time on the iodine number of corn cob activated carbon.

The results indicated that acid is the best activating agent for corncob activated carbon. The corn cob activated carbon produced chemically using phosphoric acid has the highest iodine number of 532.23667±68.304mg/g. This indicates highly active surfaces present on the activated carbon, with high porosity and surface area. The above results shows that the most efficient corn cobs activated carbon is that obtained under the following optimal conditions: an impregnation ratio of 1.5, activation temperature of 450^0C and activation time 120 min. Finally, the above conditions selected for preparation of Activated carbon.

4.2. Proximate analysis of corncob activated carbon

The results of proximate analysis of adsorbent prepared from corncobs are presented in Table 2. The Corncob activated carbon has the highest fixed carbon content related to the result obtained from cotton stalks (Girgis and Ishak 2010), sugarcane bagasse (Girgis *et al* 2008) and peanut hull (Girgis *et al* 2002). The fixed carbon content value of the corncob activated carbon was 77.5%. This result an indicated in well adsorption of dye. In addition, the physicochemical property of the adsorbents are presented, corncobs activated carbon has the highest iodine number related to the result obtained from banana stalk (Ogunleye *et al.,* 2014) and papaya seed (Mengistu .M, 2018). The iodine value *of* the corncob activated carbon was 532.23667±68.304mg/g. The higher value of the iodine number for the corncob activated carbon shows that it has well developed pore structure. The detailed calculation part is also included under appendix B.

Table 2: proximate analysis of the corncob activated carbon.

Parameter	Moisture content %	Ash content %	Volatile matter %	Fixed carbon content %	Iodine number mg/g
Value	12.4	1.21	20.8	77.5	532.23667±68.304mg/g.

4.2. Point of Zero Charge Determination

The pH points of zero charge determination of the adsorbents ACC and PCC were evaluated from the graph of the change in pH versus initial pH for 1gm of the adsorbent. The outcome is presented in figure 7. The pHs of zero charge of the adsorbents were found to be 5.1and 2.7 for PCC and ACC. This result indicates that the adsorbents acquire a positive charge below a pH of 5.1 and 2.7, respectively, for RMC and AMC. Above these points, there is a net negative charge on the cell surface and the ionic state of functional groups at the surface of the adsorbents such as carboxyl, phosphoryl, sulfhydryl, and hydroxyl.

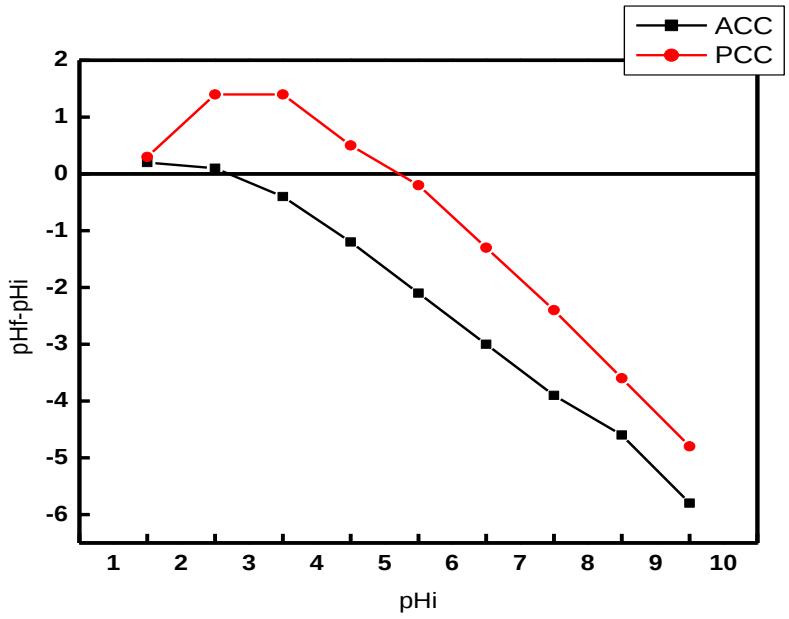
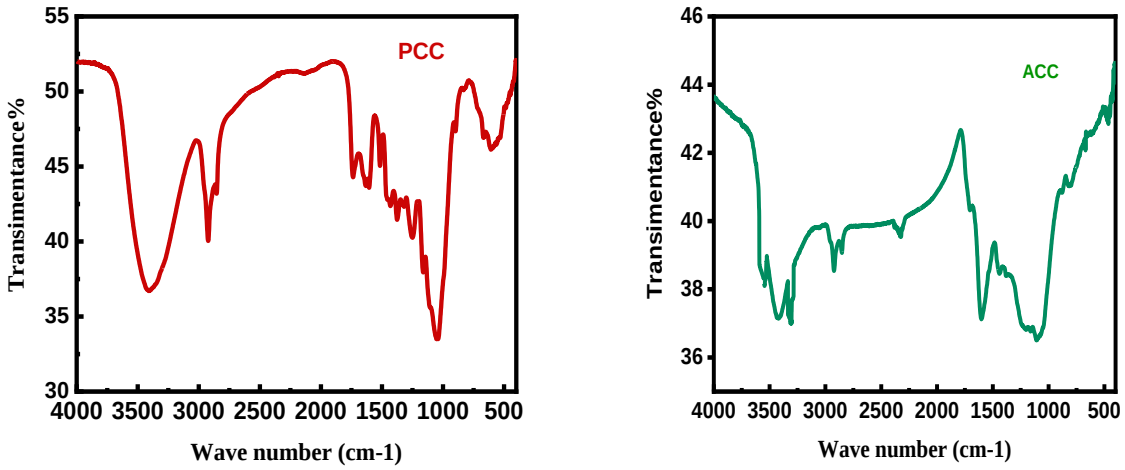


Figure 7: Point of zero charge graphs for PCC and ACC

4.3. FTIR-characterization of the corn cob activated carbon

In this work, spectrum 65 FTIR (PerkinElmer) model in range of 4000−400 cm^{-1} using KBr pellets was used in order to gain better insight into the surface functional groups available on the surface of the investigated adsorbent and the IR spectra were recorded as shown in figure 8. The spectra of the PCC sample shows a broad and strong band present between 3,500 and 3255 cm^{-1}, which can be assigned to the O–H stretching mode of hydroxyl groups and adsorbed water (Yakout & Sharaf El-Deen, 2012). After activation, this band was separated into three more resolute bands; two bands at around 3483 and 3285 cm^{-1} are ascribable to vibrations of hydroxyl groups, whereas the position of the band for non-bonded alcohols, phenols, and carboxylic acids is usually around 3,500 cm^{-1}.The band at 2923 cm^{-1} for the PCC and ACC corresponds to the presence of $–CH_2$ stretching of aliphatic groups. The bands between 1737 and 1605 cm^{-1} for PCC are corresponds to C=C vibrations. The bands become stong narrow in the activated corncob shown at 1602 cm^{-1} are characteristic of C=O stretching vibrations of lactones or carboxyl groups. The bands about 1053cm^{-1} show the C–O–C stretching (alcohols, ethers, or phenols) and O–H deformation (Foo & Hameed, 2011). These bands decreased by activation process as compared to the PCC material.



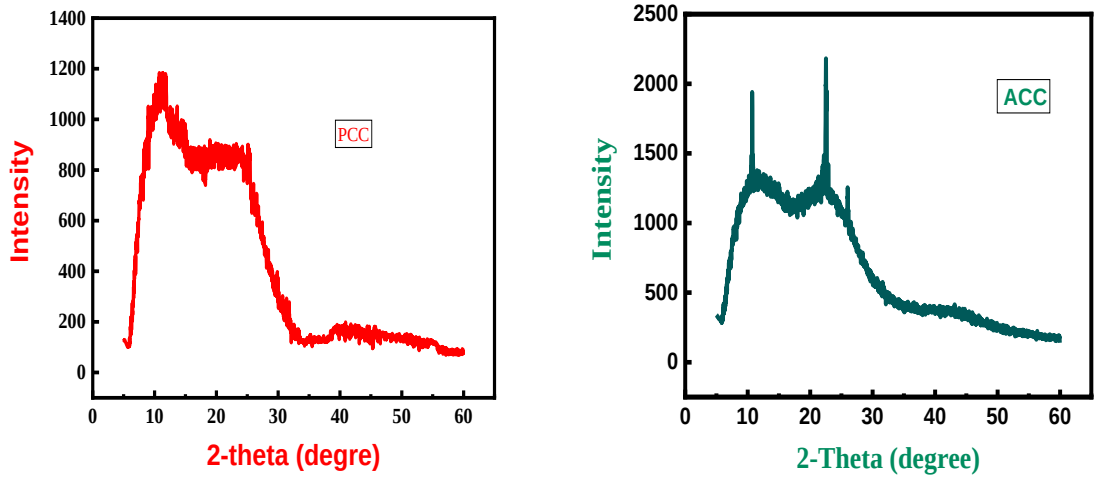
(a) PCC (b) ACC

Figure 8: FT-IR spectra of PCC and ACC adsorbents

4.4. Characterization using X-Ray Diffraction (XRD) analysis

The X-ray diffraction study of adsorbents was carried out using X-ray diffractometer. The amorphous nature and crystal structure of the PCC and ACC were determined by using the intensity of the observed rays with respect to scattering angle (2θ). The XRD spectra of PPC and ACC are shown in Figure 9. Appearance of broad diffraction background and the absence of a sharp peak reveal a predominantly amorphous structure (Abdessalem & mourad benzina, 2012). There are two broad diffraction background corresponding to around 2θ = 11° and 2θ = 23° in the spectrum. The XRD patterns of PCC exhibit broad peaks at 2θ = $11^{0,}$ and 2θ = 23^{0} indicating the amorphous part. In addition the peaks of ACC at 2θ value at 10.7^{0}, 22.5^{0} and 26^{0} mostly shows crystal structure and less amorphousness structure when compared with PCC structure.

The XRD spectra of all the two compounds were analyzed by using Origin 6.0 software. The crystalline size of ACC was determined by taking the full width at half maximum (FWHM) of the most intense peak at 1.4141 using Debye-Scherer's formula. For activated corncob carbon, the calculated grain size for the tallest peak at angle of 2theta which is 22.52° with FHWM 1.4141° is 5.728nm. From the Scherer equation the calculated grain size (mean diameter of the particle) is greater than 2 nm and less than 50 nm, which is the characteristic nature of mesoporous crystalline structure.



(a) PCC (b) ACC

Figure 9: XRD patterns of the synthesized PCC and ACC.

4.5. Calibration Curve for Malachite Green Standard Solution

Calibration curve was produced from five working standard ranging from 10−50 mg/L, which prepared from stock solution by diluting with distilled water. Hence, the instrument was calibrated using five working standards. All determinations were performed in triplicate.

Table 3: Absorbance at 617 nm with different concentration of working standard of MG

	Blank	Measurement(1)	Measurement(2)	Measurement(3)	Measurement(4)	Measurement(5)
Conc.std. soln. (mg/L)	0	10	20	30	40	50
Absorbance	0	0.612	1.254	1.888	2.441	3.011

Calibration graph was plotted absorbance versus concentration. The correlation coefficient of the calibration curve for malachite green standard solution (Figure 10) clearly shows the calibration curves with good correlation coefficient. As listed in Table 3, the results were found to be linear over the concentration range studied. The slope and the regression lines were similarly indicative of similar detector calibration sensitivity for analyte.

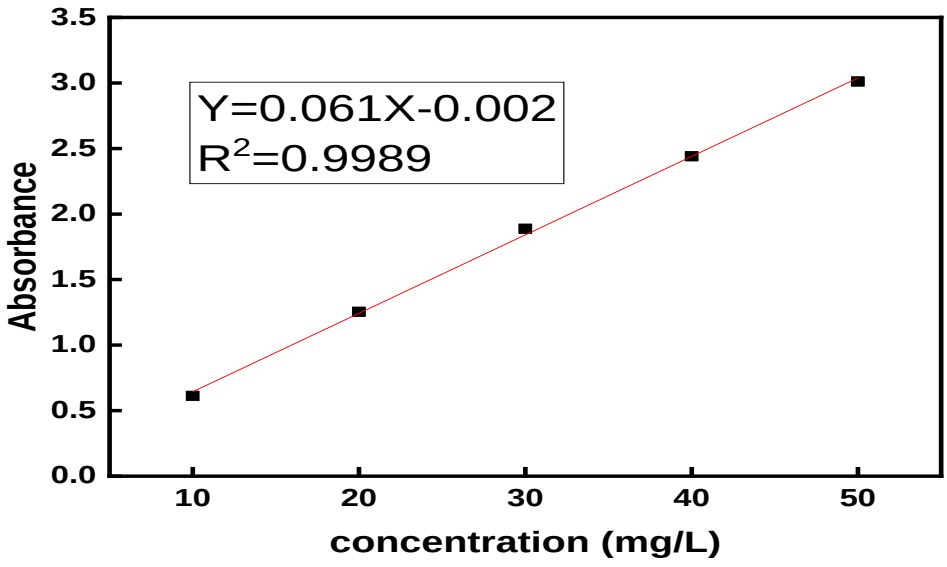


Figure 10: Calibration curve for MG standard solution

4.6. Adsorption Experiments

4.6.1. Effect of pH on the Removal of Malachite Green

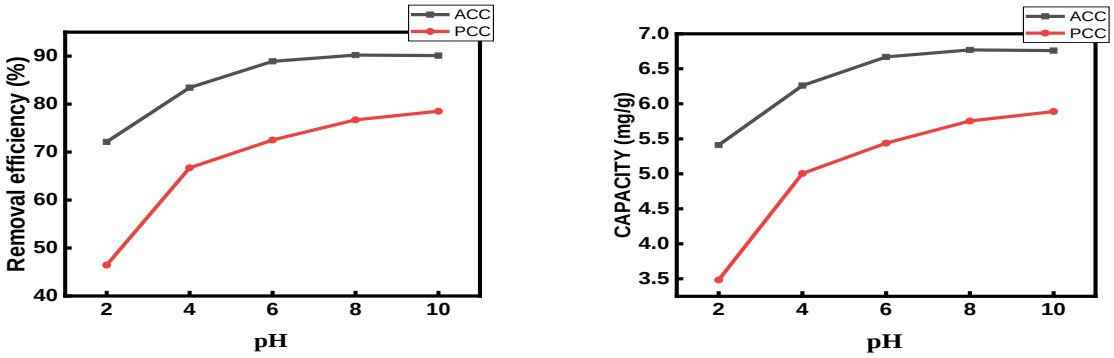
The pH of the system exerts profound influence on the adsorptive uptake of adsorbate molecules most probably due to its influence on the surface properties of the adsorbent and ionization or dissociation of the adsorbate molecule (Santhi & Smitha, 2010). To reveal the effect of solution pH on the adsorption capacity of adsorbents, the adsorption process was carried out at different pH (2 - 10). As shown in Fig. 10, the adsorption capacity increased from 5.41 mg/g to 6.77 mg/g for activated corncob and from 3.48 mg/g to 5.89 mg/g for powdered corn cob adsorbent as the pH increased from 2 to 10. In terms of removal efficiency, a maximum value of 90.22 % was observed for activated corncob and 78.52 % for powdered corncob at adsorbent dose of 0.2-gram, 30mg/L initial concentration after 90 min of contact time. For both adsorbents the maximum adsorption capacity was attained at a pH of 10.

The reason for increasing adsorption capacity with increasing alkalinity may be because of dye is cationic dye and protonated in the acidic medium and deprotonated at higher pH. At lower pH, the number of positively charged adsorbent surface sites increased at the expense of the number of negatively charged surface sites. The carboxylic group of dye was protonated and had high positive charge density at a lower pH (Seey et al., 2012). Consequently, electrostatic repulsion between the positively charged surface and the positively charged dye molecule increased with decreasing solution pH and hence resulting in the decrease of adsorption capacity of dyes to the adsorbent.

The other possible reason is that the point of zero charge of any adsorbent is a very important characteristic that determines the pH at which the surface has net electrical neutrality. It is well-known that for anionic dye adsorption, positively charged groups on the adsorbent are necessary, as discussed elsewhere (Meena Soni & Yadav, 2012).

Changes observed in the adsorption of MG by PCC and ACC as a function of solution pH are presented in Figure 11. The figure indicates that as the pH increases, the adsorption capacities increase. This result may be due to a change in surface charge of the dye molecule and functional groups of adsorbents. The pHs of zero charge (pHPZC) of the adsorbents were found to be 5.7

and 3.5, respectively, for PCC and ACC. The pHPZC values indicate that the adsorbents acquire a positive charge below a pH of 5.7 and 3.5, respectively for PCC and ACC. At pH values above this point, there is a net negative charge on the cell surface and the ionic state of functional groups such as carboxyl, phosphoryl, sulfhydryl, hydroxyl, and amino. Consequently, the adsorbent–adsorbate interactions for the cationic dyes become progressively significant for larger pH values. We can conclude from this result that the negative surface charge of the activated carbon becomes greater with increasing pH.



(a) (b)

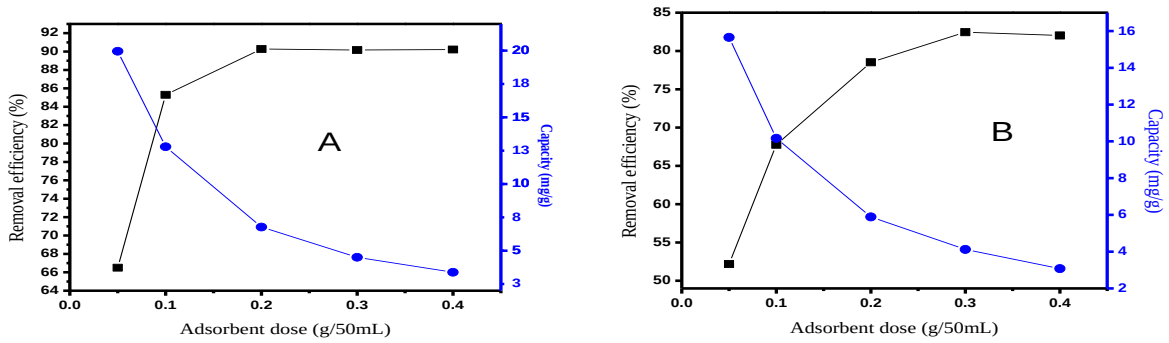
Figure 11: Effect of solution pH on adsorption capacity (a) and efficiency (b) of PCC and ACC (intial conc= 30mg/L, solution contact time = 90min and adsorbent dose 0.2g/50mL)

4.6.2 Effect of adsorbent dose

Adsorbent dose is representing of important parameter due to its strong effect on the capacity of an adsorbent at given initial concentration of adsorbate (Meena Soni & Yadav, 2012). The effect of adsorbent dose on the malachite green dye removal efficiency of powdered corncob and activated corncob were studied by varying mass of adsorbents ranging from 0.05 to 0.4g/50mL at initial concentration of 30 mg/L for minimum contact time 90 min at constant pH 10 (see Table III appendix A) and the results are presented in Fig.12. The figure indicates that the adsorption yield increases with the increase in the adsorbent dosage and stabilizes at high adsorbent dosage. The adsorption efficiency increased from 66.50 to 90.27% for ACC and from 52.19 to 82.437% for PCC when the adsorbent dosage increased from 0.05 to 0.3 g. The observed enhancement in adsorption yield with increasing adsorbent dosage could be due to an increase in the number of possible binding sites and surface area of the adsorbents. A further increase in adsorbent dosage

over 0.2 g for ACC and 0.3 g for PCC did not lead to a significant improvement in the adsorption yield. This may be due to the decrease in driving force for mass transfer at low concentration of dyes in solution (Barka et al. 2011).

On the other hand, the adsorption capacity decreases with increasing dose of the adsorbent. when the adsorbent dosage increase from 0.05 to 0.4 g, the adsorption capacity (qe, mg/g) decreased from 19.951 to 3.383 and 15.656 to 3.046 for ACC and PCC respectively. Similar results were reported (Tehetena, 2017) in removal of reactive red dye from aqueous solution using locally available clay soil as low cost adsorbent. This may be due to the decrease in total adsorption surface area available to dye ion resulting from overlapping or aggregation of adsorption sites. Thus with increasing adsorbent mass, the amount of dye ion adsorbed onto unit mass of adsorbent gets reduced, causing a decrease in qe value with increasing adsorbent mass concentration.



(a) (b)

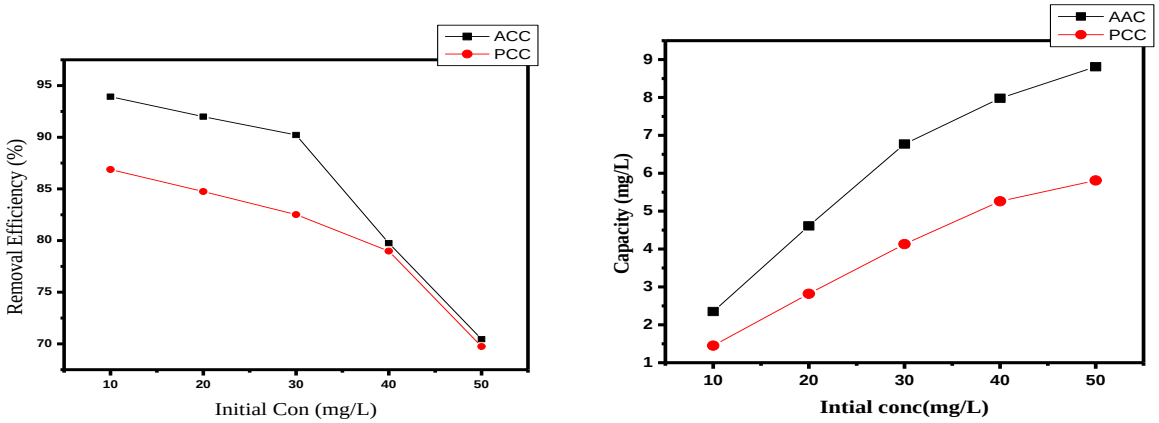
Figure 12: Adsorption capacity and efficiency A) Activated corncob B) powdered corncob (contact time = 90min, solution pH = 10 and [C]o = 30mg/L)

Therefore, 0.2 g of ACC and 0.3 g of PCC doses were taken as an optimum dose for further experiments.

4.6.3 Effect of Initial Dye Concentration

The relationship between initial dye concentrations, percentage removal and the adsorption capacity has been investigated. The adsorption of dye was carried out at different initial dye concentration ranging from 10-50 mg/L (Table III appendix A). The effect of different initial dye

concentration on adsorption of dye presented in Figure 13. The result indicated the percentage of dye removal decreases with an increase in the initial dye concentration, which may be due to the saturation of adsorption sites on the adsorbent surface. This can be explained by the fact that the initial concentration of dye had a restricted effect on dye removal capacity; simultaneously the adsorbent media had a limited number of active sites, which would have become saturated at a certain concentration. This was lead to the increase in the number of dye molecules competing for the available functions groups on the surface of adsorbent material (Abbas F. S., 2013). Since the solution of lower concentration has a small amount of the dye molecules than the solution of higher concentration of it, so the percent removal was decreased with increasing initial concentration of the dye.



(a) (b)

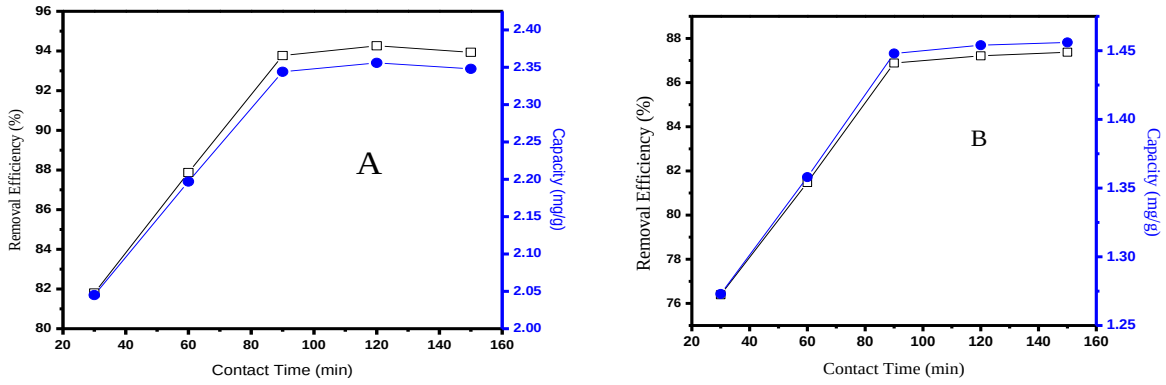
Figure 13: Effect of initial dye concentration on removal efficiency (a) and adsorption capacity (b) of ACC and PCC (initial solution pH = 10, solution contact time = 90min and adsorbent dose 0.2g for ACC and 0.3g for PCC)

On the other hand the increase in initial dye concentration will cause an increase in the capacity of the adsorbent and this may be due to the high driving force for mass transfer at a high initial dye concentration. The increase in the initial dye ions concentration also enhances the interaction between the dye ions in the aqueous phase and the adsorbent surface. This also resulted in higher uptake of dye for the given amount of adsorbent (Salleh MAM, et al., 2011). Thus, effect of initial dye concentration depends on the immediate relation between the concentration of the dye and the available sites on an adsorbent surface. The initial concentration provides an important

driving force to overcome all mass transfer resistance of dye ions between the aqueous and solid phases.

4.6.4 Effect of Contact Time

In general the adsorption capacity and the removal efficiency of dye will increase with increase in contact time. However, in practice it is necessary to optimize the contact time, considering the adsorption process. Figure 14 shows the percentage removal of dye ions and the adsorption capacity as a function of contact time**.** Further increase in contact time did not increase both percentage removal and adsorption capacity. The equilibrium was nearly reached after 120 min. (Tehetena, 2017) Also stated the most of adsorption was found to take place within the first 2hrs of mixing. This is due to the fast adsorption rate before equilibrium may be explained by an increased availability in the number of active binding sites on the adsorbent surface. The adsorption rapidly occurs and normally controlled by the diffusion process from the bulk to the surface. At equilibrium stage the adsorption is likely an attachment controlled process due to less available sorption sites (Sen TK, Afroze S, Ang HM., 2011).



(a) (b)

Figure 14: Effect of contact time on adsorption capacity and efficiency A/ activated corncob and B/powdered corncob (Co = 10mg/L, solution pH = 10 and adsorbent dose 0.2g for AAC and 0.3g for PCC)

4.7. Spectrophotometric Determination of MG in the Real Sample of Textile Waste Water

The concentration of malachite green solution before and after adsorption was determined by measuring absorbance using UV-Visible spectrophotometer at the maximum wavelength of 617nm. The Calibration equation, malachite green concentration before and after adsorption values were calculated from absorbance. The amount of malachite green adsorbed was presented in Table 4, at optimum conditions of (pH = 10, adsorbent dosage = 0.3 g and 0.2 g, contact time = 150 and 120 minutes and initial of MG concentration = 10 mg/L) using PCC and ACC respectively.

Table 4: Data of Spectrophotometric determination for MG in real sample of textile waste water.

Sample	Absorbance Before Adsorp.	Absorbance After Adsorp.	Conc.(mg/L) Before adsorp.(Co)	Conc.(mg/After adsorp.(Ce)
PCC	0.512	0.047	8.426	0.803
ACC	0.512	0.042	8.426	0.721

These result indicated that the adsorption of real sample was reduced compared to the optimized one for the model pollutant. This is may be because of the various type of dye compost ion in the wastewater and its higher concentration.

4.8. Adsorption Isotherm

Adsorption isotherms study can describe how an adsorbate interacts with adsorbent. The isotherm provides an association between the concentration of fluoride in solution, and the amount adsorbed on the solid phase when both phases are in equilibrium. At present study equilibrium adsorption data were analyzed using the Langmuir, and Freundlich isotherm models figures, 16 and 17. Also, analysis of isotherms were used to describe the experimental adsorption

data, and then best results can be obtained when correlation coefficients (R^2) come close to 1, indicate the conformity among experimental data with model isotherm.

4.8.1. Langmuir Isotherm model

Langmuir isotherm model assumes a monolayer adsorption on to a surface containing a finite number adsorption sites that all the adsorption sites have uniform strategies of adsorption for molecules of the adsorbate with no transmigration of adsorbate in the plane of the surface (Langmuir I, 1916). The Langmuir equation is useful for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage expressed by:

$$\mathbf{q_e = \frac{q_m bCe}{1+bCe}} \qquad \textbf{(4. 1)}$$

The linear form of equation 4.1 is given as:

$$\mathbf{\frac{Ce}{qe} = \frac{1}{K_L qm} + \frac{Ce}{qm}} \qquad \textbf{(4. 2)}$$

Where, Ce is the equilibrium concentration of the adsorbate (mg/L), qe is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), qm and K_L are Langmuir constants related to adsorption capacity or the amount of a solute adsorbed per unit mass of the adsorbent for monolayer coverage of the surface and heat of adsorption or the binding strength, respectively. The higher the value of K_L the higher is the affinity of the adsorbent for the adsorbate. The constants can be determined from the slope and intercept of the Ce/qe versus Ce plot of Equation 4.2. The slope of the straight line, gives 1/qm and the constant K_L can be determined from the intercept (intercepts$1/K_L q_m$). The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor RL that is given by equation 4.3

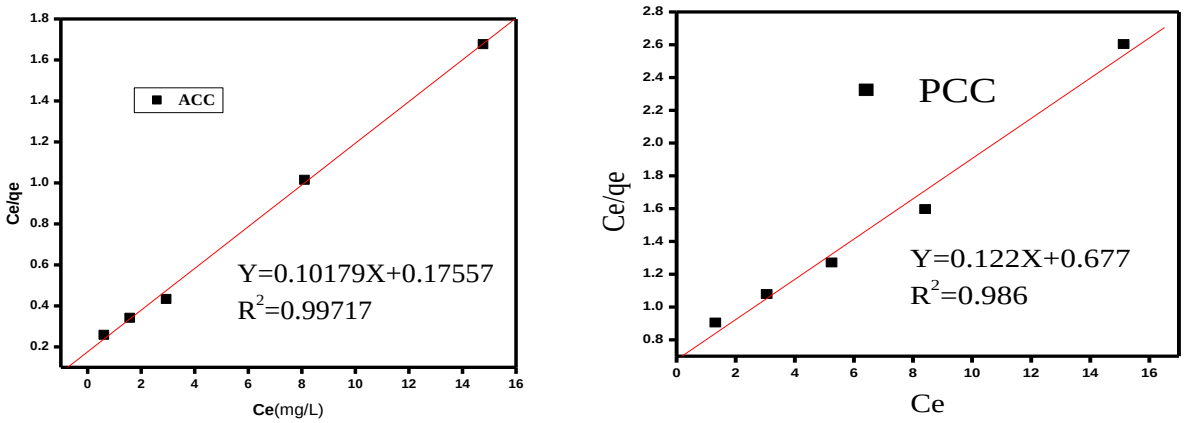
$$\mathbf{R_L = \frac{1}{1+KLCo}} \qquad \textbf{(4. 3)}$$

Where C_O is the highest initial concentration of the adsorbate (mgL^{-1}), and K_L (Lmg^{-1}) is Langmuir constant. The value of RL indicates the shape of the isotherm to be either unfavorable (RL>1), linear (RL=1), favorable (0<RL<1), or irreversible (RL=0).

According to the analysis of the experimental data by Langmuir model (Figure 15), it was found that Dye adsorption by ACC and PCC, have the RL values between 0 and 1 indicate favorable adsorption. Although the value of RL of the Langmuir isotherm for ACC and PCC was

respectively 0.0333 and 0.0999 (Table 5), indicating that the adsorption of Dye by the adsorbents was favored by this model.

Figure 15 shows Langmuir isotherm model fit for the experimental data. The result of the Langmuir isotherm model shows that the experimental data satisfactorily fitted to the model with a correlation coefficient (R_2) about 0.99717 for ACC and 0.9860 for PCC. The maximum sorption capacity corresponding to complete monolayer coverage is found to be 9.824 mg/g for ACC and 8.19672 mg/g for PCC. The constant K_L related to adsorption intensity is 0.5798 for ACC and 0.18021 for PCC.



(a) (b)

Figure 15: Linearized Langmuir isotherm model of ACC (a) and PCC (a), (adsorbent dose of ACC= 0.2 g and PCC = 0.3g equilibrium contact time = 90 min and pH = 10).

4.8.2 Freundlich isotherm model

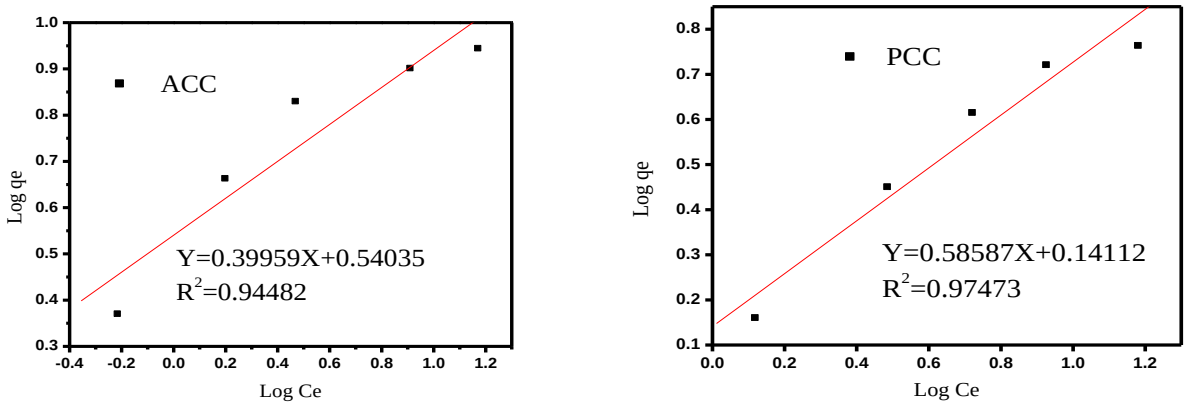
While Langmuir isotherm assumes that enthalpy of adsorption is independent of the amount adsorbed, the empirical Freundlich equation, based on adsorption on heterogeneous surface, can be derived assuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites (Freundlich, 1906). The Freundlich equation is purely empirical based on adsorption on heterogeneous surface and is commonly given by the following non-linear equation:

$$q_e = K_f\, Ce^{1/n} \qquad \textbf{(4. 4)}$$

Rearranging equation 4.4 given linearized Freundlich equation

$$\log qe = \log K_F + \frac{1}{n}\log Ce \qquad (4.5)$$

Where, qe is the amount of the dye adsorbed (mg/g), Ce is the equilibrium concentration of the dye in the solution (mg/L) and Kf and n are Freundlich isotherm constants incorporating all factors affecting the adsorption capacity and intensity of adsorption, respectively. K_F and 1/n can be obtained from the intercept and slope of the linear plot of log qe versus log ce (patil,2014). The applicability of the Freundlich adsorption isotherm was also analyzed, using the same set of experimental data. The Freundlich plots between log qe versus log Ce for the adsorption of malachite green dye were drawn in Fig.16 and Table 5. The favourable adsorption of this model can be characterized; the magnitude of the exponent n gives an indication on the favourability of adsorption. It is generally stated that values of sorption intensity, n in the range 2 to 10 represent good, 1 to 2 moderately difficult, and less than 1 poor adsorption characteristics (S. Anuradha Jabasingh, 2015).



(a) (b)

Figure 16: Linearized Freundlich isotherm model of ACC (a) and PCC (b) (adsorbent dose of ACC = 0.2g and PCC = 0.3g, equilibrium contact time = 90 min and pH = 10).

In this study the calculated values of n (n= 2.50256 for ACC and 1.706863 for PCC) was greater than 1, which indicating that the adsorption process is favorable. It is clearly seen that Langmuir model is better fit in the case of ACC adsorption than Freundlich model since it has the higher

value of correlation coefficient R^2 = 0.99717 in comparison with R^2 = 0.94482. In addition Langmuir model is better fit in the case of PCC adsorption than Freundlich model since it has the higher value of correlation coefficient R^2 = 0.986 in comparison with R^2 = 0.97473 as indicated in (Figure 16) and from the K_F values of ACC better adsorption than PCC this is because high value of K_F shows that high adsorption 3.4702 is greater than 1.38395. The values of the constants and calculated parameters of the isotherms, showed as indicated in the Table 5.

Table 5: Langmuir and Freundlich isotherm for adsorption of MG onto ACC and PCC

ACC			PCC		
Langmuir	Freundlich		Langmuir	Freundlich	
q_m 9.824	K_F 3.4701		q_m 8.19672	K_F 1.38395	
K_L 0.5798	n 2.50256		K_L 0.18021	n 1.706863	
R^2 0.9971	R^2 0.94482		R^2 0.9860	R^2 0.97473	
R_L 0.0333			R_L 0.0999		

4.9. Adsorption Kinetics

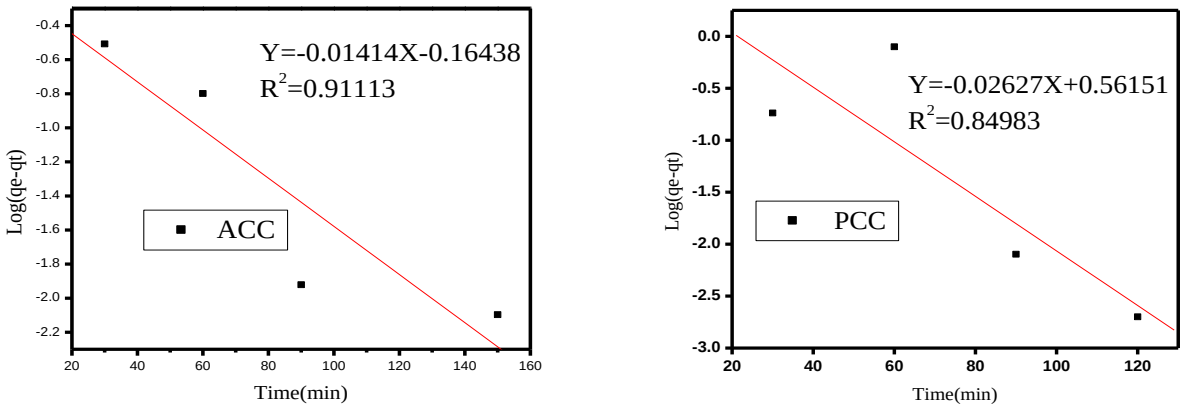
Kinetic models have been used to investigate the mechanism of sorption and potential rate controlling steps, which is helpful for selecting optimum operating conditions for the full-scale batch process. The kinetic parameters, which are helpful for the prediction of adsorption rate, give important information for designing and modeling the adsorption processes (Sivarajasekar & Baskar, 2014). Thus, the kinetics of MG dye adsorption onto ACC and PCC were analyzed using pseudo-first-order and pseudo-second-order kinetic models. The conformity between experimental data and the model-predicted values was expressed by the correlation coefficients. The relatively higher value is the more applicable model to the kinetic of the dye adsorption onto the adsorbent. The pseudo-first-order rate expression based on solid capacity is generally expressed as follows (Meroufel & Zenasn, 2013):

$$\frac{dqt}{dt} = k_1(qe - qt) \qquad (4.6)$$

After integration and applying boundary conditions, t = 0 to t and qt= 0 to qe; the integrated form of equation (18) becomes:

$$\log(qe - qt) = \log qe - \frac{K1\ t}{2.303} \qquad (4.7)$$

Where, qe (mg/g) is the amount of dye adsorbed at equilibrium, qt (mg/g) is the amount of dye adsorbed at time t and k_1 (min^{-1}) is the rate constant of pseudo-first-order adsorption. In order to obtain the rate constants, the values of log (qe − qt) were linearly correlated with *t* from which k1 and predicted qe can be calculated from the slope and intercept of the plot, respectively and the results are presented as in Fig. 17. The variation in rate should be proportional to the first power of concentration for strict surface adsorption (Santhi & Smitha, 2010).



(a) (b)

Figure 17: Pseudo- first- order kinetics on ACC (a) and PCC (b) samples at initial Dye concentration of 10 mg/L, dose of 0.2 g and 0.3g respectively.

For evaluating the kinetics of ACC and PCC interactions, the pseudo-first-order kinetics model was used to fit the experimental data. The pseudo-first-order rate constant k1 and the value of qe were calculated from the plot of log (qe–qt) versus t, and the results are given in Table 6. As clearly seen from Figure 17, the correlation coefficient (R_2) is relatively low for both adsorbents which may be indicative of a bad correlation. In addition, the value of qe determined from the model is not in a good agreement with the experimental value of the qe experimental for ACC.

Therefore, the adsorption of Dye on to ACC is not suitable for the first-order reaction. On the other hand, the value of qe determined from the model is in a good agreement with the experimental value of the qe experimental for PCC even its correlation coefficient (R_2) is lower.

But, the main criterion to fit the kinetics model with the experimental data is its correlation coefficient (Ayanda O, et al., 2012).

Table 6: Summary of the Pseudo – first – order rate constant (K1), correlation coefficient (R2), qe value of experimental and calculated data of both ACC and PCC.

	ACC	PCC
Rate constant (K_1)	-0.03256	-0.0605
Correlation coefficient (R_2),	0.91113	0.8498
Experimental q_e	2.356	1.456
Calculated q_e	0.68489	3.64343

The adsorption kinetic may be described by the pseudo-second order model (Meroufel & Zenasni, 2013). The pseudo-second-order equation based on adsorption equilibrium capacity may be expressed in the form:

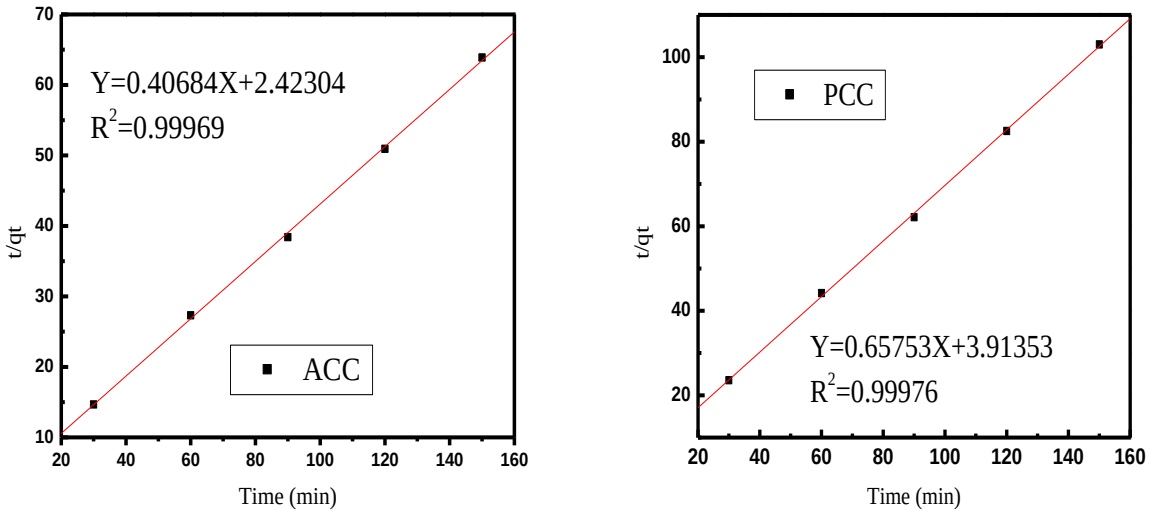
$$\frac{dqt}{dt} = k_2(qe - qt)^2 \qquad (4.\ 8)$$

For the same boundary conditions the integrated form of equation (18) becomes:

$$\frac{t}{qt} = \frac{1}{K2qe^2} + \frac{1}{qe}t \qquad (4.\ 9)$$

Where K_2 (g mg^{-1} $.min^{-1}$) is the equilibrium rate constant of second-order sorption and qe (mg/g) is the amount of dye adsorbed at equilibrium. K_2 can be determined from the intercept and qe from the slop by plotting t/qt versus t, respectively.

To evaluate the kinetics of ACC and PCC interactions, the pseudo−Second − order kinetics model was also used to fit the experimental data. The pseudo−second−order rate constant k_2 and the value of qe were calculated from the plot of t/qt against t and the results are given in Table 7. The correlation coefficients (R_2) were as near to unity for both adsorbents (Figure 18). In addition, the value of qe determined from the model is in a good agreement with the experimental value of qe for ACC and with PCC. It confirmed that the adsorption of Dye ions by the prepared ACC and PCC followed pseudo second order kinetics model.



(a) (b)

Figure 18: Pseudo – Second – order kinetics on ACC (a) and PCC (a) samples at Co = 10mg/L, dose of 0.2 g/50mL and 0.3g/50mL respectively.

The larger the K_2 value, the slower the adsorption rate (Meroufel & Zenasni, 2013) which means ACC has faster rate of adsorption than PCC in pseudo second order model.

Table 7: Summary of the Pseudo-second-order rate constant (K_1), correlation coefficient (R_2), qe value of experimental and calculated data of both ACC and PCC

	ACC	PCC
Rate constant (K2)	0.06831	0.1105
Correlation coefficient (R2),	0.99969	0.99976
Experimental qe	2.356	1.456
Calculated qe	2.45797	1.52084

4.10. Method validation (Percent recovery) Test for MB in the textile wastewater

Method validation is the process of providing that analytical method is acceptable for its intended purpose. The percentage recovery of the analyte was calculated and provided in (Table 8) percentage recoveries for MB in water samples is 99.84%, which are within the acceptable range (100 $\pm$ 10), obeys the Beer-Lambert law. This confirms that, the laboratory performance for the analyte is in control and the optimized procedure is valid. Therefore, the optimized adsorption was valid for water samples and is believed to remove MG from textile wastewater solution. Results of the recovery experiments shows the percentage recoveries for the MG 99.84% is within the acceptable range (100 $\pm$ 10%) verifying the validity of the method for MG analysis.

Table 8: Recovery table of MG in the water sample

Sample	MB found (mg/L) C_F	MB added (mg/L) C_A	Abs total	Total MB found C_T (mg/L)	Recovery $(C_T-C_F / C_A) \times 100$
	8.426	10	1.121	18.401	99.84%

6. CONCLUSIONS AND RECOMMENDATIONS

6.1. CONCLUSIONS

This study has investigated MG adsorption from an aqueous solution by PCC and H_3PO_4 ACC. The sorption characteristic has been examined using various sorption conditions. It was found that maximum adsorption of the dye took place at a basic solution pH. The effective solution (pH = 10, adsorbent dosage = 0.3 g and 0.2g, contact time = 150 and 120 minutes and initial of MG concentration = 10 mg/L) using PCC and ACC respectively. At these experimental conditions, the dye removal efficiency of 94.26% was achieved. Equilibrium and kinetic studies were conducted for the adsorption of the dye from aqueous solution onto adsorbents. The equilibrium data have been analyzed using Langmuir and Freundlich isotherms. The characteristic parameters for each isotherm and related correlation coefficients have been determined. The Langmuir isotherm was demonstrated to provide the best correlation for the adsorption of the dye. This indicates the adsorption capacity to the applicability of monolayer coverage of the dye on to the surface of the adsorbent. Adsorption kinetics was determined using pseudo first order and pseudo second order models and it was found that the adsorption follows pseudo second order model. Finally, these results show that ACC can be used as an efficient and economical adsorbent for the treatment of wastewaters containing synthetic dyes.

6.2. RECOMMENDATION

The following recommendations were made for the further study in the production and application of activated carbon from corncob for the removal of dye from aqueous solution. In this study the adsorbent was modified by using phosphoric acid in order to increase negative surface charge of the adsorbent, so further researches should be investigated by using different types of acid and base to found high removal efficiency. For future research, it is recommended batch kinetic studies at various temperatures and agitation speed may be conducted to determine thermodynamic parameter for Dye adsorption on corncob activated carbon as they were kept constant in this work. This research was conducted only the removals of the MG from wastewater, further work should be conducted on removal of other Dyes by using corncob activated carbon. Investigate the adsorption capacity of the adsorbent from mixed dye effluent.

Investigate the application of the adsorbent to remove other organic and inorganic pollutants from aqueous and actual wastewater.

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8. APPENDICES A AND B

8.1. Appendices A

Table I: Optimization of Initial pH

pH	C_o (mg/L)	Volume (mL)	Time (min)	Mass (g/50ml)	C_e (mg/L)	q_e (mg/g)	Efficiency (%)	Adsorbent
2	30	50	90	0.2	8.361	5.41	72.13	ACC
4	30	50	90	0.2	4.97	6.26	83.44	
6	30	50	90	0.2	3.33	6.668	88.91	
8	30	50	90	0.2	2.97	6.76	90.11	
10	30	50	90	0.2	2.93	6.77	90.22	
2	30	50	90	0.2	16.066	3.483	46.448	PCC
4	30	50	90	0.2	9.989	5.004	66.721	
6	30	50	90	0.2	8.246	5.438	72.513	
8	30	50	90	0.2	6.984	5.754	76.72	
10	30	50	90	0.2	6.443	5.889	78.523	

Table II: Optimization of Adsorbent Dosage

pH	Co (mg/L)	Volume (mL)	Time (min)	Mass (g/50mL)	Ce (mg/L)	qe (mg/g)	Efficiency (%)	Adsorbent
6	30	50	90	0.05	10.049	19.951	66.503	ACC
6	30	50	90	0.1	4.410	12.951	85.301	
6	30	50	90	0.2	2.918	6.770	90.273	
6	30	50	90	0.3	2.915	4.508	90.164	
6	30	50	90	0.4	2.934	3.383	90.218	
8	30	50	90	0.05	14.344	15.656	52.186	PCC
8	30	50	90	0.1	9.672	10.164	67.760	
8	30	50	90	0.2	6.443	5.889	78.523	
8	30	50	90	0.3	5.269	4.123	82.437	
8	30	50	90	0.4	5.611	3.046	81.297	

Table III: Optimization of initial concentration.

pH	Co (mg/L)	Volume (mL)	Time (min)	Mass (g)	Ce (mg/L)	qe (mg/g)	Efficiency (%)	Adsorbent
6	10	50	90	0.2	0.607	2.348	93.934	ACC
6	20	50	90	0.2	1.574	4.606	92.131	
6	30	50	90	0.2	2.934	6.766	90.218	
6	40	50	90	0.2	8.098	7.975	79.754	
6	50	50	90	0.2	14.770	8.807	70.459	
8	10	50	90	0.3	1.311	1.448	86.885	PCC
8	20	50	90	0.3	3.049	2.825	84.754	
8	30	50	90	0.3	5.246	4.126	82.514	
8	40	50	90	0.3	8.410	5.265	78.975	
8	50	50	90	0.3	15.131	5.811	69.738	

Table IV: Optimization of Adsorption Time

pH	Co (mg/L)	Volume (mL)	Time (min)	Mass (g)	Ce (mg/L)	qe (mg/g)	Efficiency (%)	Adsorbent
6	10	50	30	0.2	1.820	2.045	81.803	ACC
6	10	50	60	0.2	1.213	2.197	87.869	
6	10	50	90	0.2	0.623	2.344	93.770	
6	10	50	120	0.2	0.574	2.356	94.262	
6	10	50	150	0.2	0.607	2.348	93.934	
8	10	50	30	0.3	2.361	1.273	76.393	PCC
8	10	50	60	0.3	1.852	1.358	81.475	
8	10	50	90	0.3	1.311	1.448	86.885	
8	10	50	120	0.3	1.279	1.454	87.213	
8	10	50	150	0.3	1.262	1.456	87.377	

Table V: Langmuir and Freundlich Isotherm Model

Co(mg/L)	Ce(mg/L)	Qe(mg/g)	Ce /qe	Log Ce	Log qe	Adsorbent
10	0.607	2.348	0.2585	-0.2168	0.3707	ACC
20	1.574	4.6065	0.3417	0.1970	0.6634	
30	2.934	6.766	0.4336	0.4675	0.8303	
40	8.098	7.975	1.0154	0.9084	0.9017	
50	14.770	8.807	1.6771	1.1694	0.9448	
10	1.311	1.448	0.9054	0.1176	0.1608	PCC
20	3.049	2.825	1.0792	0.4842	0.4510	
30	5.246	4.126	1.2714	0.7198	0.6155	
40	8.410	5.265	1.5973	0.9248	0.7214	
50	15.131	5.811	2.60385	1.1799	0.7642	

Table VI: Pseudo first and Pseudo second order kinetic model

Time (min)	Co(mg/L)	Ce(mg/L)	Qt(mg/g)	Qe –Qt	Log(Qe-Qt)	t/Qt	Adsorbent
30	10	1.820	2.045	0.311	-0.50724	14.6699	ACC
60	10	1.213	2.197	0.159	-0.79860	27.3100	
90	10	0.623	2.344	0.012	-1.92082	38.3959	
120	10	0.574	2.356			50.9338	
150	10	0.607	2.348	0.008	-2.09691	63.8842	
30	10	2.361	1.273	0.183	-0.73754	23.5664	PCC
60	10	1.852	1.358	0.098	-0.10088	44.1826	
90	10	1.311	1.448	0.008	-2.09691	62.1550	
120	10	1.279	1.454	0.002	-2.69897	82.5309	
150	10	1.262	1.456			103.022	

8.1. Appendix B

The One-Way ANOVA test for iodine number optimization

Table B- 1: The effect of acid concentration on the iodine number of ACC

Acid concentration %	Amount of AC used for adsorption	Volume of filtrate (residual Iodine solution)	Volume of Sodium thiosulphate used (average)	Iodine value(mg/g)	X/M mean±standard deviation
35	0.8	50	38.18	253.92	231.2±22.45969
	0.9	50	38.02	230.67	
	1.0	50	37.97	209.01	
45	0.8	50	36.52	311.87	269.61667±39.01024
	0.9	50	37.01	262.01	
	1.0	50	37.01	234.97	
55	0.8	50	32.43	454.63	386.36667±66.22864
	0.9	50	33.14	382.09	
	1.0	50	33.91	322.38	
65	0.8	50	31.64	482.21	416.75±65.81787
	0.9	50	32.00	417.46	
	1.0	50	32.90	350.58	
75	0.8	50	32.00	469.64	407.015±60.2502
	0.9	50	32.50	401.945	
	1.0	50	32.94	349.46	
85	0.8	50	33.01	434.39	386.03±44.26797
	0.9	50	33.33	376.19	
	1.0	50	33.01	347.51	
95	0.8	50	33.21	427.41	383.69333±44.00274
	0.9	50	33.07	384.26	
	1.0	50	33.30	339.41	

Table B- 2: The effect of impregnation ratio on the iodine number of ACC

Impregnation ratio	Amount of AC used for adsorption	Volume of filtrate (residual Iodine solution)	Volume of Sodium thiosulphate used (average)	Iodine value (mg/g)	X/M mean±standard deviation
2:1	0.8	50	35.04	363.52	
	0.9	50	36.11	289.94	303.68333±54.28582
	1.0	50	36.23	257.59	
1.5:1	0.8	50	32.31	458.82	
	0.9	50	33.04	385.19	390.66±65.59628
	1.0	50	33.71	327.97	
1:1	0.8	50	32.08	466.84	
	0.9	50	32.11	414.04	417.28333±48.01722
	1.0	50	32.17	370.97	
1:1.5	0.8	50	30.81	511.18	
	0.9	50	30.92	450.97	453.86667±55.92129
	1.0	50	31.15	399.45	
1:2	0.8	50	31.68	480.81	
	0.9	50	31.52	432.36	432.7±47.9409
	1.0	50	31.67	384.93	

Table B- 3: The effect of activation temperature on the iodine number of ACC

Activation temp ^{0}C	Amount of AC used for adsorption	Volume of filtrate (residual Iodine solution)	Volume of Sodium thiosulphate used (average)	Iodine value (mg/g)	X/M mean±standard deviation
300	0.8	50	31.64	482.21	
	0.9	50	32.41	404.74	412.88333±65.63498
	1.0	50	32.86	351.70	
350	0.8	50	31.12	500.36	
	0.9	50	31.98	418.08	426.96667±69.37818
	1.0	50	32.44	362.46	
400	0.8	50	31.06	502.45	
	0.9	50	30.92	450.97	457.11667±42.59394
	1.0	50	30.52	417.93	
450	0.8	50	28.40	595.30	
	0.9	50	28.71	519.85	523.76333±69.66249
	1.0	50	29.12	456.14	
500	0.8	50	29.03	573.31	
	0.9	50	29.21	504.34	

	1.0	50	29.50	445.52	507.72333±63.96215

Table B - 4: The effect of activation time on the iodine number of ACC

Activation time (min)	Amount of AC used for adsorption	Volume of filtrate (residual Iodine solution)	Volume of Sodium thiosulphate used (average)	Iodine value (mg/g)	X/M mean±standard deviation
60	0.8	50	33.630	412.74	366.75667±44.31218
	0.9	50	33.750	363.20	
	1.0	50	33.84	324.33	
90	0.8	50	31.16	498.96	426.23333±68.63727
	0.9	50	32.01	417.15	
	1.0	50	32.47	362.59	
120	0.8	50	28.33	597.74	532.23667±68.304
	0.9	50	28.13	537.53	
	1.0	50	28.93	461.44	
150	0.8	50	29.01	574.01	511.4±61.88327
	0.9	50	29.02	509.92	
	1.0	50	29.33	450.27	
180	0.8	50	31.91	472.78	414.23667±58.44525
	0.9	50	32.11	414.04	
	1.0	50	32.71	355.89	

Table B- 5: Point zero charge determination

PHi	2	3	4	5	6	7	8	9	10	Adsorbents
PHf	2.2	3.1	3.6	3.8	3.9	4	4.1	4.4	4.2	ACC
ΔpH	0.2	0.1	-0.4	-1.2	-2.1	-3	-3.9	-4.6	-5.8	
PHf	2.3	4.4	5.4	5.5	5.8	5.7	5.6	5.4	5.2	PCC
ΔpH	0.3	1.4	1.4	0.5	-0.2	-1.3	-2.4	-3.6	-4.8	

Proximate Analysis

Moisture content determination

$$\textbf{Moisture content (\%)} = \frac{W1-W2}{W1-W0} \times 100\%$$

Weight of crucible, W_0 =14.003 gm

Weight of crucible + original activated carbon sample, W_1 = 15.003 gm

Weight of crucible plus moisture free sample (after heating), W_2 = 14.879

$$\textbf{Moisture content (\%)} = \frac{15.003-14.879}{15.003-14.003} \times 100\%$$

$$= \underline{\mathbf{12.4}}$$

Ash content determination

$$\textbf{Ash content (\%)} = \frac{W2-W0}{W1-W0} \times 100\%$$

Weight of crucible, W_0 =14.003 gm

Weight of crucible + original activated carbon sample, W_1 = 15.003

Weight of crucible + ash sample, W_2 =14.015

$$\textbf{Ash content (\%)} = \frac{14.015-14.003}{15.003-14.003} \times 100\%$$

$$= \underline{\mathbf{1.21}}$$

Volatile matter determination

$$\textbf{Volatile matter (\%)} = \frac{W2-W0}{W1-W0} \times 100\%$$

Weight of crucible + ignited sample, W_2 = 14.211

Weight of crucible + original sample, W_1 = 15.003

Weight of crucible, W_0 =14.003 gm

$$\textbf{Volatile matter (\%)} = \frac{14.211-14.003}{15.003-14.003} \times 100\%$$

$$= \underline{\mathbf{20.8}}$$

- **Fixed Carbon Determination**

Fixed carbon (%) = 100 – (moisture, % + ash, % + volatile matter, %)

= 100 - (12.4+1.21+20.8) = **77.5**

Table B - 6: Proximate analysis of the corncob activated carbon.

Parameter	Moisture content %	Ash content %	Volatile matter %	Fixed carbon content %	Iodine number mg/g
Value	12.4	1.21	20.8	65.59	532.23667±68.304