ADDIS ABABA UNIVERSITY
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SCHOOL OF CHEMICAL AND BIO ENGINEERING

M.Sc. Program in Environmental Engineering

Removal of organic matter and nutrients from grey water using activated carbon of corn cob as an adsorbent in SPA Service Enterprise (Filwoha) Addis Ababa, Ethiopia

A thesis submitted to Addis Ababa Institute of Technology, School of Chemical and Bio engineering in partial fulfillment of the Degree of Master of Science in Environmental Engineering.

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Removal of organic matter and nutrients from grey water using activated carbon

ADDIS ABABA UNIVERSITY

ADDIS ABABA INSITUTE OF TECHNOLOGY SCHOOL

OF CHEMICAL AND BIO ENGINEERING

This is to certify that the thesis prepared by Etsegenet Worku, entitled: "**Removal of organic matter and nutrients from grey water using activated carbon of corn cob as an adsorbent**" and submitted in partial fulfillment of the requirements for the degree of Master of Science in Environmental Engineering complies with the regulations of the university and meets the accepted standard with respect to originality and quality.

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Declaration

I declare that, this thesis for M.Sc. Degree at Addis Ababa University Institute of Technology, hereby submitted by me, is my original work and it hasn't been submitted previously for the degree at this or any other university, and that all resources of materials used in this thesis have been duly acknowledged.

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ABSTRACT

Grey water is one kind of wastewater that is characterized by medium contents of BOD, COD, Tot-N, Tot-P, suspended solids and dissolved solids. It is discharged to the environment without any treatment and significantly affects the environmental media such as soil and water. It also damage microorganism and aquatic life. Therefore, the objective of this study was to reduce the pollutant load of organic and nutrient contents from the grey water to an acceptable level by treating the wastewater using activated carbon of corn cob as an adsorbent. In this study, the effects of adsorbent particle size, adsorbent dosage, pH, adsorption time and agitated speed on the pollutant reduction were investigated in batch experiments. The influent results revealed that the COD, BOD, Tot-N, Tot-P, Turbidity and Conductivity of the grey water were concentration of 1500 mg/L, 152 mg/L, 9.73 mg/L, 15.5 mg/L, 6.64 ms/cm and 200 NTU respectively. On the other hand, the effluent results on the optimum values (pH; 6.5, activated carbon dosage; 0.35 g, time; 60 minutes) showed that the pollutant loads of grey water were reduced to 89 mg/l, 3 mg/l, 0.25 mg/l, 0.4 mg/l, 4.01 NTU and 2.24 ms/cm respectively. Consequently, the experimental results indicated that the agricultural waste corn cob has a potential to be used as an activated carbon for treatment of grey water which is safe and environmentally friendly.

***Key words**; Grey water COD, BOD, Tot-N, Tot-P, conductivity and Turbidity containing SPA Service Enterprise Filwoha, corn cob, activated carbon*

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LIST OF ABBREVIATIONS

AC	Activated Carbon
AOPs	Advanced Oxidation Processes
ASAP	Accelerated Surface Area and Porosimetry System
BET	Brunauer-Emmet-Teller
BJH	Barrett-joyner-Halenda
BOD	Biological oxygen demand
CEC	Cation-Exchange Capacity
COD	Chemical oxygen demand
DFT	Density functional theory
DR	Dubinin-Radushkevich
EC	Electron Conductivity
EPA	Environmental Protection Authority
FTIR	Fourier-Transform Infrared Spectroscopy
IR	Infrared
MB	Methylene Blue
NTU	Number of turbidity unit
pH	potential of Hydrogen
ppm	Part of Per Million
Pzc	Point of zero charge
RSM	Response Surface Method
SI	International System of Units
SPA	Sanus Per Aquam (Latin word, meaning mineral-rich spring water)
TDS	Total Dissolved Solid
Tot-N	Total Nitrogen
Tot-P	Total Phosphorus
UNIDO	United Nation Industrial development Organization
UNWWDR	United Nations World Water Development Report
USEPA	United State Environmental Protection Authority
U.S.	United State
UV	Ultra-Violate

CHAPTER ONE
INTRODUCTION

1.1 Background

An increasing global population coupled with growing urbanization in many already water-scarce regions worldwide has led to increased demands on water supply (USEPA, 2004). In Addis Ababa, Ethiopia, for instance, economic growth and extensive house building are putting water supply under increasing pressure, with the efficient use of water deemed “crucial to successful water resource management over the next 25 years” (Environment Agency, 2001).

Water is a limited natural resource and fundamental for life and health (UNWWDR, 2002). With the growth of mankind, society, science, and technology the world is reaching to new high perspective but the cost which is being paid or will be paid in the near future is surely going to be too high. Among the consequences of this rapid growth, the environmental disorder with a big pollution problem has been translated to a critical aspect (Grover, 2006). Water accumulates the different type of compounds during its use becoming wastewater and unsuitable to be reused. Water pollution with toxic compounds is one of the major concerns for human health as well as for the environmental quality. Discharging different kinds of wastewater and polluted waters such as domestic, industrial and agricultural wastewater into the environment, especially to surface water, produce effluents which are often contaminated with harmful/poisonous substances. There are various methods for the removal of these substances. These broadly fall into three categories: physical, chemical and biological. Any of these treatment processes have their own advantages and disadvantages. The major disadvantage of physicochemical methods has been largely due to the high cost, low efficiency, limited versatility, interference by other wastewater constituents and handling of the waste generated. Biological treatment is a method in which the removal of organic compounds is brought about by biological activity (Metcalf and Eddy, 1991). However, the main disadvantageous of the biological treatment is the low removal yields.

The increasing of wastewater discharge to the environment, it needs solution for selecting proper treatment processes. And also considering economic aspects are important. In addition, employing environmentally-friendly methods for treatment is emphasized much more these days. Application of some waste products that could help in this regard to reuse these waste materials, can be an

advantage. One of the physicochemical treatment is adsorption. It has appeared as one of the promising methods for organic matter, and odor capture, and sequestration due to its low energy consumption, cost-effectiveness, relatively simple technological process and it is applicable over a relatively wide range of temperatures and pressures (Fornwalt H and Hutchins R. 1966, Acharya J, et al., 2009). The development of new and high efficient solid adsorbents is important to the process for the treatment of greywater. The extensive use of activated carbon is widely applied now days, due to its porosity (specific surface area, pore size and pores structure), good adsorbents that are used for capturing COD, BOD_5, Turbidity, odor, total nitrogen and total phosphate from the greywater through adsorption (Sahu J, et al., 2010).

Activated carbon is the most commonly used and most effective adsorbent (Vinod and Imran, 2000). Nevertheless, its application fields are restricted due to its high cost. The use of low-cost waste and agriculture by-product to produce activated carbon has been showed to provide economical solution to this problem (Zabaniotou, 2007). The activated carbon is seems to be black in color and have large microporosity. Activated carbon adsorption also used for treating low concentrations of wastewater streams at extremely low cost. The removal efficiency of Activated carbon is very high for harmful pollutants (Sahu J, et al., 2009).

Filwoha grey water treatment

This study was carried out at Addis Ababa, Ethiopia, in Addis Ababa University. The greywater treatment was carried out through adsorption process using corn cob activated carbon as an adsorbent. The treated water can be used as an alternative water resource for the SPA Service Enterprise (Filwoha), for the purposes of toilet flushing, floor cleaning, car washing, gardening, construction, and irrigation. Toilet flushing can be done by direct pumping treated grey water from treatment tank to piping lines that connected to each toilets. In addition this study explores the organic and nutrient content of greywater and investigates organic nutrient removal through the treatment of adsorption processes.

Greywater is commonly defined as wastewater generated from bathroom, laundry, and kitchen. However, grey water can contain organic matter, nutrients, bacteria fecal matter and quickly develop disease-inducing pathogens if stored in a warm climate.

Greywater used to further sustainable development and resource conservation compromising to public health and environmental quality. And also the treatment and reuse can minimize stress on water resources (Ledin et al., 2001). Under most conditions possible to reuse treated grey water indicates that cost-effective alternative source of water. Domestic wastewater (combined grey water and black-water) is also treated at high cost and then used for limited irrigation. Grey water is separated from black- water, likely benefits will include water savings, reduce treatment costs, reduce groundwater pollution and provides positive environmental and economic benefits.

1.2 Statement of the problem

The wastewater resulting from caustic cleaners contains high amount of organic matter and nutrients washed down the drain, they are likely to kill beneficial treatment bacteria in soils if grey water is reused for onsite garden irrigation (Marshall, 1996). Grey water may contain micro-organisms that can transfer diseases cases of public health and environmental risks (Eriksson et al., 2002). In addition the known content of the community grey water resulting from kitchen, shower and laundry activities included food particles, cooking oil and grease, various biodegradable soaps, urine, pathogen (bacteria that mean easily develop in hot weather) and other nutrients content subsequently causes both surface and ground water pollution and soil contamination (Bulnes, 2009).

In Ethiopia, there is no proper grey water treatment system. More specifically, SPA Service Enterprise (Filwoha) discharged grey water directly to rivers characterized by medium contents of organic and nutrient pollutants (particularly COD, BOD T-N, T- P and turbidity), which had an adverse environmental as well as human health impact. Particularly, it affects surface water, ground water and soil contamination. Besides, the grey water is used by a lot of people for agriculture and washing purpose due to this it might create possibility of contamination and enter to food chain that affects human health and aquatic life (Eriksson *et al.,* 2002). Generally, several reports have shown that the values of grey water has considerably higher than the safe limits prescribed by international standards (Filwoha Spa service Report, 2000). Therefore, the grey water has to be treated before discharging to the rivers streams or sewerage systems for which adequate inexpensive treatment technology is required, and to minimize surface water, ground water pollution and soil contamination. Thus, this research is necessary to use agricultural waste corn cob as activated carbon to treat the grey water and reduce the environmental pollution.

1.3 Objectives

1.3.1 General Objective

The general objective is to reduce the pollutant load of organic matter and nutrients from SPA Service Enterprise (Filwoha) grey water to an acceptable level by treating the wastewater using corn cob activated carbon as an adsorbent.

1.3.2 Specific Objectives

- To investigate the effect of treatment process parameters such as adsorbent dosage, contact time and pH;
- To characterize the grey water before and after treatment (Turbidity, COD, BOD, conductivity, T-N and T-P) ;
- To determine efficiency of activated carbon on pollutant removal;

1.4 Significance of the Study

The significance of this study to treat the grey water using corn cob activated carbon as an adsorbent for the removal pollutant load. In addition to developing a system for reused wastewater discharge as a resource for flash the toilets, vegetation, car-washing and cleaning houses was ensure a constant supply of water and saving fresh water for better consumption. This wastewater need to treat and uphold sanitation standards has encouraged critical thinking to come up with solutions.

These uses to reduce water pollution, and to encourage reusing treated grey water in order to protect human health, aquatic life and utilized proper economical use of wastewater as a resource. In addition to treat and safely reusing grey water aids to avoid any conflict that may arise due to discharge limits.

In general grey water treatment has been continuously developed and various benefits have been raised about reuse of treated water includes:

- To reuse treated grey water in order to sustain the resources.
- To treat the grey water in order to replace freshwater that toilet flashing, irrigation and cleaning purposes.
- To prevent pollution of soil, groundwater, surface water, marine environment (use detergent that are friendly to environment and should not discharge into storm drainage system)

1.5 Scope of the study

This study deals mainly with treating organic matter and nutrient containing grey water to remove pollutant loads particularly COD, BOD, T-N, T-P and conductivity in order to reduce the burden on water pollution to used low cost agriculture waste of corn cob activated carbon which is easily available of row material, environmentally friendly and safe to reuse for the purpose of toilet flushing, floor cleaning, gardening and car washing.

CHAPTER TWO

LITERATURE REVIEW

Increasing of industrial and human activities results environmental pollution that causes harm or discomfort to humans, other living organisms, or that damage surroundings. The world "pollution" has been taken from the Latin word "pollution" meaning to make dirty. Pollution can be in the form of chemical substance or energies that considered as contaminants when it existed overload of the natural levels. It is mainly connected with human activities, discharge of domestic, industrial and agricultural wastes, application of pesticides by farmers, leaks of radioactive materials, gas emissions into the atmosphere etc. (Goel, 2006).

For decades back, water was considered to be pure and unpolluted if it was odorless, colorless and tasteless. However, nowadays the consciousness of water pollution has been reflected on. Even if the water is clear, it may be polluted, it may contain dissolved impurities like toxic metals, organic pollutants, radioactive nuclides, emerging contaminants etc. (Davis, 2008).

2.1 Water pollution and water pollutants

Any undesirable change in the physical, chemical, or biological characteristics of water, which can harmfully affect the health, survival, or activities of human or other living organisms, is as the consequence of water pollution.

There are two types of water pollutant sources: - point source and non-point source (Agrawal, 2009). Pollution occur when harmful substances are emitted directly into a body of water is point sources. Its include factories, wastewater treatment facilities, septic systems, and other sources that are clearly discharging pollutants into water sources. Pollution that delivers from unlimited source through the environment is non-point source. An example of this type of water pollution is when fertilizer from a field is carried into a stream by rain, in the form of run-off which in turn affects aquatic life. Non point sources pollutants are much more difficult to control. Pollution take place from nonpoint sources accounts for a majority of the contaminants in streams and lake (EPA, 2006). The major sources of water pollution can be classified as municipal, industrial and agricultural. Municipal water pollution consists of wastewater from homes and commercial

establishments. The characteristics of industrial wastewater depend on the type of industry and the manufacturing process in question (Haas and Vamos, 1995).

The impact of municipal discharges depends not only on their collective characteristics, such as biochemical oxygen demand and the amount of suspended solids, but also on their content of chemical oxygen demand and nutrients.

The most common water pollutions are nutrients, organic matter, heavy metals, microbial contaminants, toxic organic compounds (oil, pesticides, and other industrial chemicals), salts, acids, sediments and suspended solids, and high temperature (Revenga and Mock, 2001). One of pollutant its grey water discharge plume may remain on the surface of aquatic environments and accumulate pollutants (particularly nutrients) that contribute to the growth of algae, which is known to cause growth problems for aquatic living organism, particularly fish's. For example, water used from the river is often only filtered for use in the kitchen sink, in many cases the water used for washing and showers was taken directly from the river may contain pathogens and other pollutants released by direct discharge of grey water (Environment Protection (Water Quality) Policy 2015).

2.1.1 Filwoha Grey Water

Filwoha Spa service enterprise is located in the center of Addis Ababa, which is the capital city of Ethiopia. In order to establish the exact period, when the Addis Ababa Filwoha/ hot spring/ was originally discovered and the ways in which the people in the district used to benefit from the natural resource in the old days. A foreign visitor named T. Lifetree Visited the spot in 1832 and was an eye witness to the " Miraculous spring" He wrote a book entitled " Voyage in Abyssinia" during the reign of king Haileselassie.

In a book entitled " Les origins Addis Ababa'' the writer mentions the catholic priest Tawlinkahegne, who in 1867 became a Bishop and his name changed to Aba Jacob. This priest came from a town called kelitche to a place, previously known as Finfine (Filwoha Spa service Report, 2000).

According to the story, Aba Jacob stated that when Menelik II had established the city in 1875, originally at Entoto and Later at Addis Ababa. The Emperor and Empress Taitu together with their dignitaries visited the hot spring frequently. The existence of the hot spring contributed to the establishment of the Addis Ababa city in its present location.

This spring hot water was much appreciated and desired by the Emperors and dignitaries. As a result a two-room bath-house was built around 1904. It started rendering service to the public.

In view of the gradual increase in the population of the town, it was no longer able to manage with the public demand. In order to satisfy the public demand, His Imperial majesty Haile Selassie I crown prince of Ethiopia, at the time, commanded Azaj workinch to construct additional baths. It resulted in the building of additional baths in the thermal spring, in 1964 to meet the needs of the public (Filwoha Spa service Report, 2000).

At present the enterprise has a total of 229 different classes of bathrooms known as First class, Second class, Third class, Fourth class, Shower and Family bathrooms. It has also a physiotherapy and sauna service. The main types of the enterprise services are, shower service and Sauna bath.

Since Filwoha is a profit making public enterprise, the management of the spa service responsible to the board of directors that composed of members appointed by PPESA. Filwoha enterprise conducted a study of process and implementing BPR. Currently the enterprise has about 485 permanent workers and 145 contract employees. The total number of employees are about 630 workers. The employees consists of professionals, semi-professionals, and skilled/laborers workers (Filwoha Spa Service, 2012).

The average of customer service consists of five thousand per day. And also as Filwoha Spa service Report, 2000 indicated that the discharge of the Filwoha grey water can be estimated about 251/s and Flowing in the south west discharge direction (along Addis Ababa Stadium).

2.2 Wastewater treatment technologies

2.2.1 Overview

Wastewater treatment technologies can be divided into three categories: chemical, physical and biological methods. Chemical methods rely upon the chemical interactions that either aid in the separation of contaminants from water or assist in the destruction or neutralization of harmful effects associated with contaminants (Cheremisinoff, 2002). Physical treatment methods include sedimentation, flotation, filtering, stripping, ion exchange, adsorption and other processes that accomplish removal of dissolved and undissolved substances without necessarily changing their chemical structures. Biological methods are those that involve living organisms using organic, or

in some instances, inorganic, substances for food, completely changing their chemical and physical characteristics (Woodard, 2001). Each technique provides a different and unique approach is perhaps provides certain advantages over others for particle situation. All three of these technology groups can be combined in water treatment, or they may be used in selected combinations depending upon the objectives of water treatment. Among each of the general technology classes, there is a range of both hardware and individual technologies that one may select from. The selection of the optimum combinations depends on factors such as: how depurated the final water effluent from our plant must be, the quantities and nature of the influent water we need to treat, the physical and chemical properties of the pollutants of that we need to remove or render neutral in the effluent water, the physical, chemical, and thermodynamic properties of the solid wastes generated from treating water and the cost of treating water, including the cost of treating, processing and disposal of the solid wastes.

2.3 Techniques for the treatment of the considered pollutants

2.3.1 Methods to remove organic pollutants

Wastewater often contains a mixture of organic and inorganic compounds, in addition to solid or soluble material. As the result of this the treatment is needed to the effluents polluted with organic compounds. Biological oxidation method is for the removal organic pollutants is the cheapest, but the presence of toxic or biorefractory molecules may hinder this approach (Panizza and Cerisola, 2009). For this reason, a diverse range of physico-chemical methods as filtration, coagulation, adsorption, flocculation, chemical oxidation with use of chlorine, ozone, hydrogen peroxide, and advanced oxidation processes (AOPs) as Fenton's reaction, ozone/UV etc. are currently used to treatment of the wastewater, depending on the specific needs. However, these methods are either economically unfavorable or technically complicated, which make them difficult to be used in practice. For example, filtration is not always sufficient to achieve the discharge limits; adsorption using commercial adsorbents is expensive, coagulation and flotation generates large amounts of sludge; transportation and storage of hazardous chemicals and advanced oxidation processes usually require high investment cost (Panizza and Cerisola, 2009).

Considering all the mentioned above, adsorption on a low cost activated carbon prepared from an agricultural waste, as a general treatment using corn cob were considered in this study for the treatment of the mentioned pollutants.

2.3.2 Total nitrogen (N-total) and Total phosphorous (P-total)

The impact of nutrient pollution has been identified as one of the most widespread, costly, and challenging environmental problems in the 21st century. Nutrient pollution causes excess algae growth (i.e., algal blooms) over large bodies of water, which has impact on the environment, human health and the economy. Algal blooms consume significant amounts of oxygen and thus deprive fish, shellfish and other aquatic organisms of the oxygen needed to survive. In addition, algae can have a negative impact on human health by emitting toxins that can cause stomach aches, rashes and more serious health issues (Piotrowski J. and Wagner, 2011).

Although inorganic nitrate and phosphate can be determined directly in natural waters, this does not provide the wider environmental significance of the organic nitrogen and phosphorus fractions that contribute to the total nutrient loading in bodies of water. In water, nitrogen exists as inorganic and organic species. Inorganic nitrogen is present in the oxidized form (e.g., nitrite and nitrate) and reduced form (e.g., ammonia/ammonium and dinitrogen gas). Organic nitrogen is available in a variety of complex forms such as amino acids, proteins, humic acids and urea. However, before being used as a nutrient, the organic nitrogen must first be converted to ammonia. Total nitrogen (Tot-N) is the sum of all forms of nitrogen in the water sample (Piotrowski J. and Wagner, 2011). Phosphorus exists as inorganic orthophosphate, polyphosphate and organic phosphate. Particulate phosphorus found in suspension or sediment consists of plants, animals, phosphorus in minerals, and phosphate adsorbed on an iron oxyhydroxide mineral surface. Total phosphorus (Tot-P) is a measure of all forms of phosphorus found in water (Marshall R. 2008).

2.3.3 Total thermotolerant coliforms

Coliform bacteria are commonly used bacterial indicator for sanitary quality of water (Laurin, P. 2002). They are defined as members of genera or species within the family Entero-bacteriace capable of growth at 37º C (total coliforms) or 44º - 45º C (thermotolerant coliforms) that possess β- galactosidase (Allen M.J. 2000). Coliform bacteria are abundant in the feces of warm-blooded animals but can also be found in soil, aquatic environments and vegetation. Unlike other coliform

bacteria, Escherichia coli are almost exclusively of fecal origin and can be detected in elevated densities in human and animal feces, sewage and water subjected to recent fecal pollution. It is therefore considered the best fecal indicator microorganism (Allen M.J. 2000 and World Health Organization. 2004).

Fecal bacteria have been used as an indicator to the possible presence of pathogens in surface waters and the risk of disease based on epidemiological evidence of waterborne diseases. Consequently, because of the difficulties to detect the many possible pathogens (such as Salmonella sp, Shigella sp, diarrheogenic E. coli, Giardia lamblia, Cryptosporidium parvum and enteric viruses) concentrations of fecal bacteria including thermotolerant coliforms, enterococci and E. coli, are used as the primary indicators of fecal contamination (Allen M.J. 2000).

2.3.4 Conductivity

Conductivity is a measure of water's capability to pass electrical flow. This ability is directly related to the concentration of ions in the water. These conductive ions come from dissolved salts and inorganic materials such as alkalis, chlorides, sulfides and carbonate compounds. Compounds that dissolve into ions are also known as electrolytes. The more ions that are present, the higher the conductivity of water (Gelhaus and Lacourse, 2004). Electrical conductivity depends mainly on the concentration of dissolved electrolytes and gases. With respect to the dissociated ions in particular, EC is a function of their mobility, determined by charge, dissolved radius, the solution's viscosity and temperature (Coury, 1999). Its units are Siemens per meter [S/m] in SI and millimhos per centimeter [mmho/cm] in U.S. customary units. Its symbol is k or s.

In water and ionic materials or fluids a net motion of charged ions can occur. This phenomenon produce an electric current and is called ionic conduction.

2.3.4.1 Water conductivity

Pure water is not a good conductor of electricity. Ordinary distilled water in equilibrium with carbon dioxide of the air has a conductivity of about 10 x 10-6 W-1*m-1 (20 dS/m). Because the electrical current is transported by the ions in solution, the conductivity increases as the concentration of ions increases.

Thus conductivity increases as water dissolved ionic species (Gelhaus and Lacourse, 2004).

Typical conductivity of waters:

Ultra-pure water 5.5 · 10-6 S/m

Drinking water 0.005 – 0.05 S/m

Sea water 5 S/m

2.3.4.2 Electrical Conductivity (EC) and TDS

Total Dissolved Solid (TDS) is a measure of the total ions in solution. EC is actually a measure of the ionic activity of a solution in term of its capacity to transmit current. In dilute solution, TDS and EC are reasonably comparable. The TDS of the water sample based on the measured EC value can be calculated using the following equation:

TDS (mg/l) = 0.5 x EC (dS/m or mmho/cm) or = 0.5 * 1000 x EC (mS/cm) (1)

As the solution becomes more concentrated (TDS > 1000 mg/l, EC > 2000 ms/cm), the proximity of the solution ions to each other depresses their activity and consequently their ability to transmit current, although the physical amount of dissolved solids is not affected. At high TDS values, the ratio TDS/EC increases and the relationship tends toward TDS = 0.9 x EC. (2)

In these cases the above-mentioned relationship should not be used and each sample should be characterized separately.

Water that used for agricultural and irrigation purpose the values of EC and TDS are related to each other and can be converted with an accuracy of about 10% using the following equation:

TDS (mg/l) = 640 x EC (ds/m or mmho/cm). (3)

2.4 Adsorption on activated carbon

The term adsorption was introduced by Kayser in 1881, to describe the condensation of gases on free surfaces (Gregg & Sing, 1982). Atoms, ions and molecules present in a gasses or a liquid bulk adhere on the surface of a solid and this process is called adsorption. The solid used is called an adsorbent. The material in the adsorbed state is called adsorbate. The substance to be adsorbed (before it is on the surface) is called the adsorptive (Butt et al., 2003).

Adsorption process has prominent method of treating aqueous effluent in wastewater treatment processes for a variety of separation and purification purposes. Wastewater treatment by adsorption is a preferred technique due to its cost, simplicity of design, ease of operation and insensitivity to toxic substances (Ugurlu et al., 2007). Besides, adsorption on activated carbon is

very widely used for achieving high water purification (Dabrowski et al, 2005; Fierro et al., 2008). Activated carbon adsorption has been cited by the US Environmental Protection Agency as one of the best available control technologies (Derbyshire et al., 2001). However, activated carbon is a preferred sorbent, its widespread use is restricted due to the use of non-renewable and relatively high-cost starting material such as coal, which is unjustified in pollution control application. In order to decrease the cost of treatment and expand its use in wastewater treatment, attempts have been made to find low-cost adsorbents, namely by using waste material for that purpose (Dias et al., 2007).

Thermo-chemical processes such as pyrolysis or gasification have been widely applied to biomass, gain due to its energy content. Pyrolysis is one form of energy recovery process, which has the potential to generate char, oil and gas product (Putun et al., 2005). Because of the thermal treatment, which removes the moisture and the volatile matter contents of the biomass, the remaining solid char shows different properties than the parent biomass materials. The remarkable differences are mainly in porosity, surface area, pore structures (Micropores, Mesopores and Micropores) and physicochemical properties such as elemental analysis and ash content (Yaman S. et al., 2005). These changes in the properties usually lead to high reactivity hence, an alternative usage of char as an adsorbent material becomes possible (Putun et al., 2005). Thus, the char becomes an attractive by-product, with applications including production of activated carbons (ACs), which is useful as a sorbent for air pollution control as well as for wastewater treatment (Marshall W. et al., 2004). Activated carbons are carbons of highly microporous form with both high internal surface area and porosity and commercially the most common adsorbents used for the removal of organic compounds from air and water streams. That also often serve as catalysts and catalyst supports.

The process parameters, which have the largest influence on the products of pyrolysis, are the particle size, temperature and heating rate. The process conditions can be optimized to maximize the production of the pyrolytic char, oil or gas, all of which have potential uses as fuels. Any cheap material, with a high carbon content and low in organics, can be used as a raw material for the production of activated carbon (Tsai WT. et al., 1997). For example agricultural by-products have proved to be promising raw materials for the production of activated carbons because of their availability at a low price. The row material could be used for the production of activated carbon

with a high adsorption capacity, considerable mechanical strength, and low ash content (Savova D. et al., 2001). Literature survey indicates that there have been many attempts to obtain low-cost activated carbon or adsorbent from agricultural wastes such as wheat, corn straw (Lanzetta M. et al., 1998), olive stones, bagasse, birch wood (Minkova et al., 2001), sunflower shell, pinecone, rapeseed, cotton residues, olive residues (Yaman S. et al., 2005), sugar cane bagasse (Cetin et al., 2004), almond shells, peach stones, grape seeds, straw, oat hulls, corn stover, apricot stones, cotton stalk, cherry stones, peanut hull, nut shells, rice hulls, corn cob, corn hulls, hazelnut shells, pecan shells, rice husks and rice straw (Marshall WE. et al., 2000).

2.4.1 Definition of Activated Carbon

Activated carbons are defined as a wide range of amorphous-based materials, is "a material prepared to exhibit a high degree of porosity and an extended inter-particulate surface area" (Bansal et al., 1988). Which are very effective adsorbents due to their highly developed porosity, large surface area, variable characteristics of surface chemistry, and high degree of surface (Dias et al., 2007). These unique characteristics make activated carbon very versatile material, which have been studied not only as adsorbents, in addition used as catalysts and catalyst supports and can be produced from carbonaceous material in order to provide adsorptive properties (Derbyshire et al., 2010).

2.4.1.1 Surface area and Porous structure

The surface area of char is important because, like other physico-chemical characteristics, it may strongly affect the reactivity and combustion behavior of the char. The chars from pyrolysis above 400 ^{0}C had a surface area and a high surface area formed (Putun E. et al., 2005). In the study of Tsai et al. (Tsai WT. et al., 1997) surface areas were observed to decrease at higher pyrolysis temperature and soaking time. The higher surface areas are probably due to the opening of the restricted pores. The percentage of micropore followed the increase of pyrolysis temperature, but this rate of increase was not as fast as the rate of declination in surface areas. The surface areas which calculated in the research of Tsai et al. (Tsai WT. et al., 1997) were observed to increase at higher activation temperature and the maximum rate of increase in surface area occurred between 650 and 700 ^{0}C. The molecular and crystalline structure of activated carbon is necessary to discuss the surface chemistry of the material. The basic structural unit of activated carbon is closely

approximated by the structure of pure graphite. The graphite crystal is composed of layers of fused hexagons held by weak Van der Waals forces. The layers are held by carbon-carbon bonds. Activated carbon is a disorganized form of graphite, due to impurities and the method of preparation (activation process).

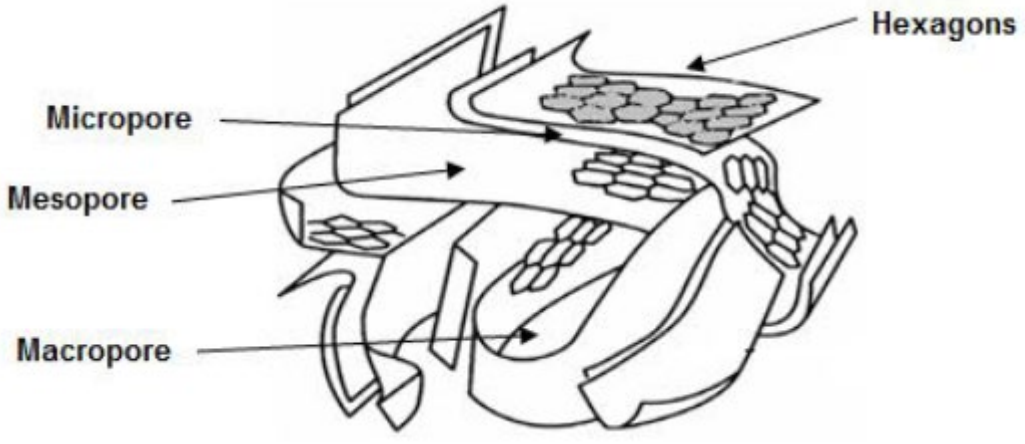


Figure 2.1: Schematic structure of an activated carbon

The structure of granular activated carbon is highly heterogeneous and porous. Difference in pore size affects the adsorption capacity for molecules of different shapes and sizes, and thus is one of the criteria by which carbons are selected for a specific application. Porosity is classified by IUPAC into three different groups of pore sizes micro, meso, and macropores (above figure).

Typical ranges are given in Table, but by special procedures it is possible to prepare activated carbons with even higher porosity, surface area and adsorptive capacity (ASTTE 2006).

Table 2.1 Different types of pores size of typical activated carbons (ASTTE 2006)

	Diameter (nm)	**Pore Volume (cm^3/g)**	**Surface area (m^2/g)**
Macropores	> 50	0.20 – 0.80	0.5 – 2
Mesopores	2-50	0.02	20 – 70
Micropores	< 2	0.10	600 -1900

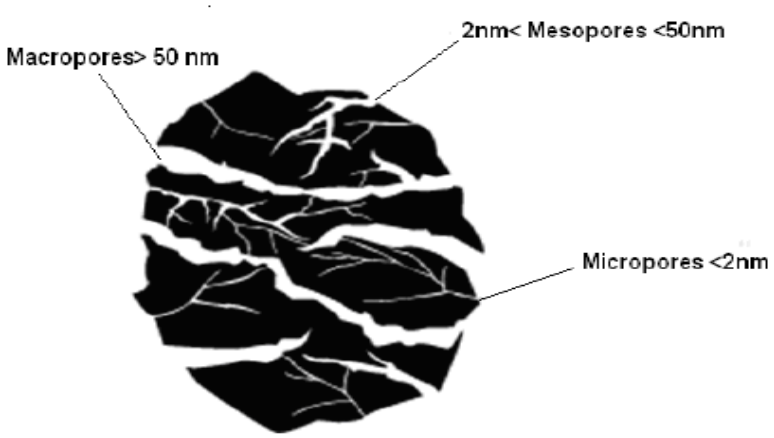


Figure 2.2 Schematic activated carbon model

Activated carbons are highly developed internal surface area and porosity, sometimes described as solid sponges. The large surface area results in a high capacity for adsorbing chemicals from gases or liquids. The most widely used commercial active carbons have a specific surface area of the order of 800-1500 m^2g^{-1}, which is determined typically by nitrogen gas adsorption. Difference in pore size affects the adsorption capacity for molecules of different shapes and sizes, and thus is one of the criteria by which carbons are selected for a specific application.

2.4.1.2 Chemical structure

Activated carbons are mainly built of graphite layers with a slit-shaped porous structure. As well the carbonaceous matrix contains heteroatoms such as; oxygen, nitrogen, hydrogen, sulfur or phosphorus. Those heteroatoms are present in functional groups analogous to well-known groups studied in organic chemistry. Heteroatoms have a key role on the chemical character of carbon surface, acidic or basic, and on its hydrophobicity (Diaz et al., 2005).

2.5 Preparation of activated carbon

Agricultural residues are produced in huge amounts worldwide, their proximate and ultimate analyses are determined for the production of the activated carbons. Pyrolysis temperature has the most significant effect-followed by pyrolysis heating rate, the nitrogen flow rate and then finally the pyrolysis residence time. Generally, increasing pyrolysis temperature reduces yields of both chars and activated carbons. According to Putun et al., increased temperature leads to a decreased yield of solid and an increased yield of liquid and gases. As the temperature is raised, there is a

rise in ash and fixed carbon percentage and there is a decrease in volatile matter. Consequently, higher temperature yields charcoals of greater quality. The decrease in the char yield with increasing temperature could either be due to greater primary decomposition of biomass at higher temperatures or through secondary decomposition of char residue. The secondary decomposition of the char at higher temperatures may also give some non-condensable gaseous products, which also contributes to the increase in gas yield. Indeed, as the temperatures of primary degradation are increased or the residence times of primary vapors inside the cracked particle has to stay shorter, the char yields decrease (Putun 2005). Temperature also studied of Tsai et al. for preparation of ACs with chemical activation ($ZnCl_2$), where it was noticed that char yield decreases with temperature, while soaking time has no effect on the char yield.

2.5.1 Activation

Basically, there are two main steps for the preparation of activated carbon (Putun 2005) the carbonization of the carbonaceous raw material below 800 ^{0}C, in the absence of oxygen, and the activation of the carbonized product (char), which is either physical or chemical (Yaman S. et al., 2005).

There is also an additional one-step treatment route, denoted as steam-pyrolysis as reported (Marshall W. et al., 2004) where the raw agricultural residue is either heated at moderate temperatures (500–700 ^{0}C) under a flow of pure steam, or heated at 700–800 ^{0}C under a flow of just steam. The residues studied with this method were olive, straw, birch, bagasse, apricot stones, cherry stones, grape seeds, nutshells, almond shells, oat hulls, corn stover, and peanut hulls. The samples in the study of Minkova et al. (Minkova V. et al., 2001) were heated with a heating rate of 10 ^{0}C/min to a final temperature of 700 ^{0}C, 750 ^{0}C or 800 ^{0}C and kept 1 or 2 hr. at this temperature in the flow of steam, while the final carbonization temperature in the study of Savova et al. (Savova D. et al., 2001) was 800 ^{0}C for 1 hr. For the preparation and characterization of activated carbon derived from oat hulls or corn stover (Marshall W. et al., 2004) char was heated at 800 ^{0}C for 30, 60, 90 and 120 min. The activated carbons, which had a high pore volume, was weighed to determine activation burn-off or mass loss due to activation.

The yield and the characteristics of the prepared activated carbon depend on the process of preparation used. Thus, applying the two processes on lignocellulosic materials, Rodriguez-Reinso and Molina-Sabio (1992) showed that the yield of activated carbon is higher in the case of

chemical activation with $ZnCl_2$ than when using physical activation with CO_2. Moreover, Laine and Younes (1992) reported that the physical activation with CO_2 leads to an activated carbon with a porous structure which consists mainly of narrow micropores and macroporess, while a broad structure with micropores and a larger high mesoporosity was obtained in the case of chemical activation with phosphoric acid.

i) Physical activation process

Physical activation process is usually carried out in two stages. The first stage is the carbonization stage followed by an activation stage (Haimour and Emeish, 2006). The step of carbonization in carried out in an inert atmosphere (pyrolysis) for 5-6 hours at a temperature ranging from 400 to 850 ^{0}C and can sometimes reaches 1000 ^{0}C. The objective of this step is to remove organic compounds (CO, H_2, CH_4 and other hydrocarbons) to produce a solid residue with high carbon content. Thus, an initial porosity corresponding to a specific surface area of around 5-10 m^2g^{-1} is created. Finally, to further develop the porosity, an activation step at 800-1000 ^{0}C is performed in the presence of steam, carbon dioxide, air or their mixtures (Diao et al., 2002 Ioannidou and Zabaniotou, 2007) for 24 to 72 hours. As a consequence of the activation step, a certain mass of the carbonized material is lost due to the formation of gaseous carbon (Ould-Idriss et al., 2011).

ii) Chemical activation process

This process involve only single step of carbonization process. The activation agent must be used before carbonization takes place. The most activated agents used are zinc chloride, sulphuric acid, potassium hydroxide and phosphoric acid. Howevere, zinc chloride is preferred because of efficient chemical recoverable and environmental friendly rather than other activated agents (Gomez et al., 2005). The chemical activation process is most popular because only required single heating and the temperature used is usually lower than that of physical activation. (Stavropoulos and Zabaniotou 2005).

In the chemical activation process the two steps are carrieed out simultaneously, with the precursor being mixed with chemical activating agents, as dehydrating agents and oxidants at very low temperatures. This agent can increase the surface area and reduce the ash content of final carbonized products. The chemical incorporated to the interior of the precursor particle reacts with the products resulting from the thermal decomposition of the precursor, reducing the evolution of

volatile matter and inhibiting the shrinking of the particle; hence the conversion of the precursor to carbon is high, and once the chemical is eliminated after the heat treatment, a large amount of porosity is formed (Rodriguez-Reinoso and Molina-Sabio, 1992). Chemical activationveral offers several advantages since it is carried out in a single step, combining carbonization and activation, performed at lower temperatures and therefore resulting in the development of a better porous structure, although the environmental concerns of using chemical agents for activation could be developed.

2.6 Methylene blue Adsorption (MB)

The determination of adsorption efficiency of activated carbon is quantified by a methylene blue adsorption process to quantify the quality of the activated carbon as adsorbents. Adsorption of MB has been studied on carbons from various biomasses such as bamboo, straw, coconut husk, corn cob, etc. (Rafatullah et al., 2010). Concentrations of 1.0 to 20 mg/L of methylene blue (MB) (supplied from Sugar Milling Research Institute, Durban) were made up and their absorbance values were measured at 630 nm with a Cary IE Varian UV-Visible spectrophotometer. The maximum absorbance of MB was obtained at 630 nm. Firstly calibration curves of absorbance against concentration of MB were drawn. The calibration curve is an indication of the Beer-Lambert law which shows a linear relationship between the concentration of a solution and the absorbance value at a constant wavelength. Calibration curves were drawn for each newly prepared stock solution.

The absorbance values were converted into concentrations by the calibration equations. From the determined concentrations, the percentage of removal (%) and the amount of MB solution removed per gram biochar (q) were calculated.

$$q\left(\frac{mg}{g}\right) = \frac{Co-C}{m} * V \quad (4)$$

$$\%\, Removal = \frac{Co-C}{Co} * 100 \quad (5)$$

Where Co is initial concentration (mg/L), C is the concentration at t (min), V is the volume of the solution (L) and m is the mass of the activated carbon used in gram. The effect of contact time and adsorption time are determined by a plot of q (mg/g) versus t (min) for all concentrations.

CHAPTER THREE
MATERIALS AND METHODS

3.1 Raw Materials

3.1.1 Sample collection

The grey water was collected from Addis Ababa SPA Service Enterprise (Filwoha) (from bath, shower, laundry and hand basin). Filwoha SPA Service Enterprise is located in the center of Addis Ababa, which is the capital city of Ethiopia. The grey water collection first round in January 20/2018 for the raw sample analysis and the second round February 10/2018.

The wastewater and treated water characterized for the following properties: BOD_5, COD, turbidity, electric conductivity, Phosphorus (Tot-P), nitrogen (Tot-N) and pathogen indicators (total thermotolerant coliforms). The treatment was focused on the removal of organic matter and nutrients in the effect of adsorbent dosage, contact time, and pH in batch studies. All the analysis was carried out as described in Standard Methods (WHO, 2002).

3.1.1.1 Corn cob collection and pre-treatment

The activated carbon were prepared from corn cob. The raw corn cob was collected from farm processing around “Dukem” and “Zeway” located at Oromia region. The corn cob was washing with deionized water for removal of dust adhere to it and dried in the oven at 105^0C for 24 hours in order to remove of moisture. Then cut into smaller pieces for uniform size distribution.

3.1.2 Chemicals

Chemicals zinc chloride ($ZnCl_2$), sodium hydroxide, sodium chloride, BOD_5 reagent, COD reagent, potassium chloride, hydrochloric acid, phenolphthalein indicator, potassium hydroxide standard solution were used the investigation of the laboratory works. Zinc chloride ($ZnCl_2$), BOD_5 reagent, COD reagent, were bought from Charkos market center, but all other listed chemicals were available and used in the Environmental laboratory, School of Chemical and Biochemical engineering, Addis Ababa Institute of Technology, Addis Ababa university.

3.1.3 Apparatus

Apparatus Turbidometer, Desiccator, Crucible, Oven dryer, Muffle Furnace, Analytical Balance, pH Meter, BOD_5 incubator, biker, Erlenmeyer flask, graduated cylinder, Pyrex, magnetic stirrer, mesh, jaw crasher, orbital shaker, conductive meter, whatman filter paper, vacuum pump, aluminum foil, were used during laboratory work. Whatman filter paper and aluminum foil were bought from the market, but all other listed apparatus were available and used in the laboratory, School of Chemical and Biochemical engineering, Addis Ababa Institute of Technology, Addis Ababa University.

Table 3.1 chemicals and their function

CHEMICALS	FUNCTION
zinc chloride	As activated agent
sodium hydroxide	For Bohem's titration method of cation exchange capacity determination
sodium chloride	For pH at the point of zero charge determination
BOD_5 reagent	Reagent used for BOD determination, nitrification bacteria inhibitor
COD reagent	Reagent used for oxidation of organic and inorganic matter determination
potassium chloride	The solution for calibration of conductivity meter
hydrochloric acid	For pH at the point of zero charge determination and pH adjustment of sample for BOD_5 determination
BOD_5 incubator	To determine the BOD of the sample
phenolphthalein indicator	24 Indicator used for Bohem's titration method of cation exchange capacity determination
Potassium hydroxide standard solution	The solution used in the BOD determination, for trap of carbon dioxide, in respiration of nitrification bacteria in gasket of BOD bottle

Table 3.2 Apparatus and their function

APPARATUS	FUNCTION
Turbidometer (2100 NTU)	To measure turbidity of treated water and waste water sample
Desiccator	To control moisture content of the raw sample, for 10 min until measurement weight of activated carbon sample
Crucible	Used as to put the raw sample in the Desiccator
Oven dryer (DAS42000)	To dry soaked sample of corn cob
Muffle Furnace (LHT407GN)	To use for burn raw sample or for preparation of activated carbon
Analytical Balance (CP324S)	To measure the mass of the sample
pH Meter (HANNA,HI11310)	To determine the pH of the sample
BOD5 incubator (TS 606/4-I)	To determine the BOD of the sample
Erlenmeyer flask	To obtain activated carbon
Pyrex	To cook the corn cob sample
Magnetic stirrer	To mix the sample
Mesh	To sieve crashed corn cob
Jaw crasher (55743 IDAR-Oberstein)	To reduce the size of corn cob
Orbital shaker (EXCELLA E24R)	To distribute the activated carbon and facilitate adsorption
Conductive meter (CTS-406)	To measure the waste water and treated water of capability to pass electrical flow
Whatman filter paper	To isolate the activated carbon from distilled water
Vacuum pump	To trap the distilled water from the activated carbon
Aluminum foil	To tie the cylindrical shape of muffle furnace for controlling air, and to protect the contamination of soaked corn cob

3.1.4 Methods

3.1.4.1 Experimental setup

Figure 3.1 Activated carbon preparation processes in laboratory

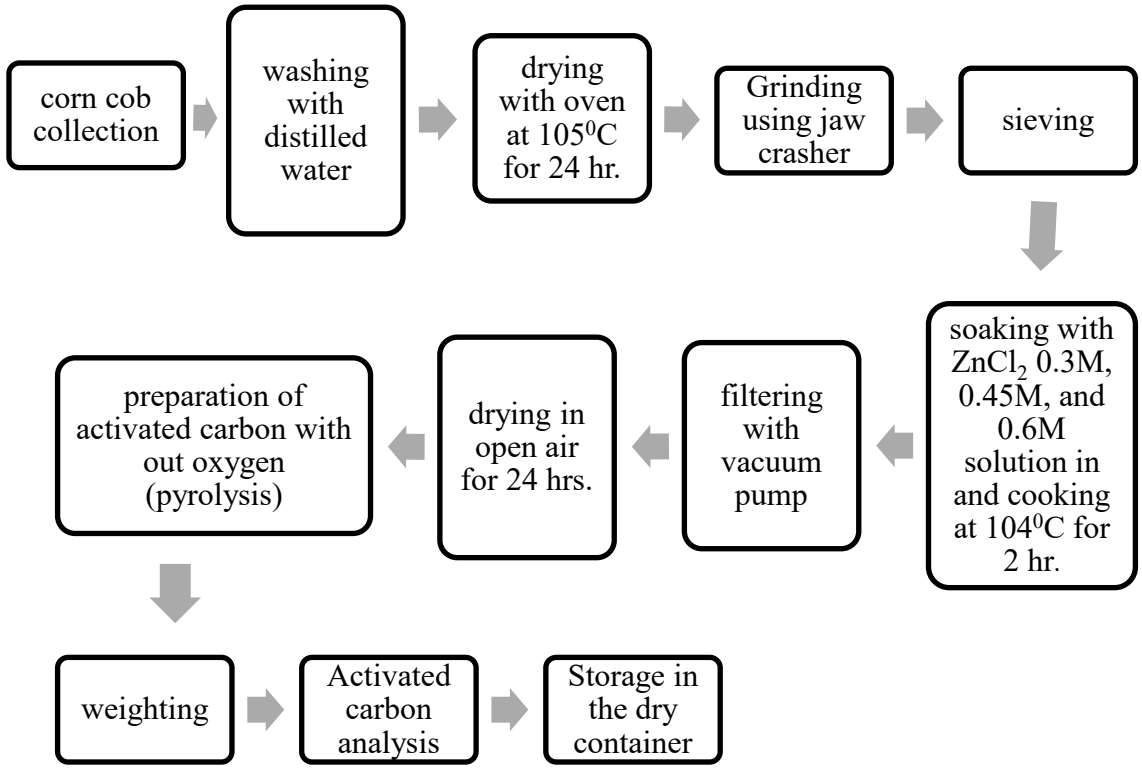
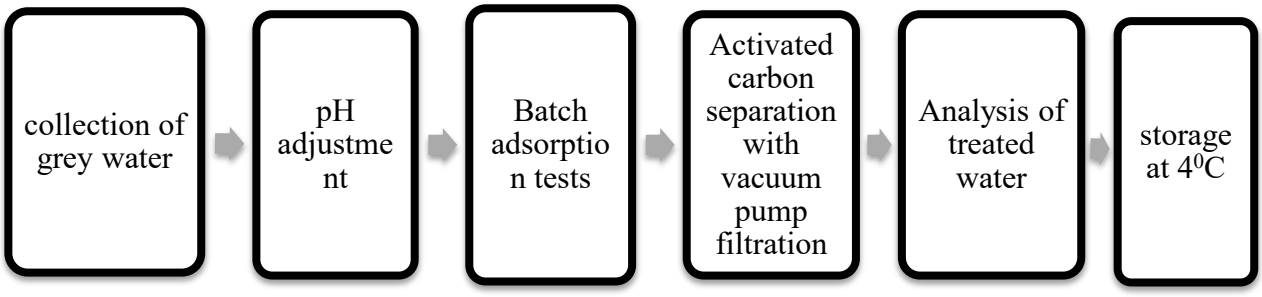


Figure 3.2 Grey water treatment through adsorption processes in laboratory



3.2 Preparation of activated carbon

The activated carbon preparation was within a chemical activation by zinc chloride ($ZnCl_2$) as a dehydrating agent. Chemical activation offers several advantages in that it is carried out in a single step combining carbonization and activation, performed at lower temperatures and therefore resulting in the development of a better porous structure. Besides, part of the added chemicals can be easily recovered. And also physical characterization of activated carbon was analyzed in terms of surface area, total pore volume and pore size distribution.

Dried corn cob was crushed with a jaw crusher and sieved to 1-2 mm size range in order to get a uniform size distribution. Chemical activation of the sieved raw materials was soaked with $ZnCl_2$ to make the Impregnation Ratio (Activating agent/raw material) *100% (40 gm of dried raw material was well mixed with 300 ml of different concentration of $ZnCl_2$ solution). Then sieved sample was properly mixed with $ZnCl_2$ solution and kept at 104^0C temperature in order to the chemical incorporated to the interior with the raw material for the resulted of to increase the surface area, reduce the ash content of final carbonized products, while soaking time is maintained for 2 hours with magnetic stirrer to proper soaking of solution on its surface.

The preparation test in detail was conducted as follows: 40g of the crushed sample to the mesh size of 1-2 mm and dried raw material with $ZnCl_2$ solutions having different concentrations: 40, 50, 60,70 and 80, (98% $ZnCl_2$ pure) was mixed in a glass flask with about 300 ml. The impregnation ratio, defined by the weight ratio of impregnant ($ZnCl_2$) to raw material is 1; 1.25; 1.5; 1.75 and 2. The impregnation is carried out in a stirred Pyrex reactor equipped with a reflux condenser. Stirring is used to ensure the access of the $ZnCl_2$ to the interior of the corn cob waste particles. The temperature and the soaking time are 104 ^{0}C and 2 hours, respectively. Agitation and heating are ensured by a heating magnetic stirrer with connected temperature regulator probe made of Teflon. Then soak corn cob was dry in open air for 24 hr. within stainless steel plat in order to removal moisture.

The pyrolysis of the impregnated material is conducted in a cylindrical stainless steel reactor, inserted into a tubular regulated furnace under continuous nitrogen flow (1.5 barmin^{-1}). The impregnated sample was carbonized at temperatures of 400 and 450 ^{0}C, while time is maintained for 2 hours. The product was then kept in a desiccator until cooled and measured a mass within analytical balance for the determination of yield. The product yield was calculated by:

$$Yield\ (\%) = \frac{M1}{M0} * 100 \qquad (1)$$

Where:

M0: mass of raw material used (dry)

M1: mass of product obtained (dry)

The obtained activated carbon was primarily washed using hot distilled water in order to remove different residual organic mineral matter and salt, then continuously washed using cold distilled water until get neutral pH. After this, washed product was dried at 105 ^{0}C overnight. Finally dried activated carbon was packed in an air tight container for further experiment.

In this experiment, $ZnCl_2$ used because has low cost and recoverable rather than others activating agent. In addition its act as dehydration reagent that lowers the carbonization temperature during chemical activation. This used to increase the surface area, reduce the ash content of final carbonized products, the chemical incorporated to the interior with the products resulting from the thermal decomposition of raw material and inhibiting the shrinking of the particle.

The pyrolysis used to reducing the volatile matter. Through these process the conversion of raw material to activated carbon is high and once the chemical is eliminated after the heat treatment a large amount of porosity is formed (Yorgun S. et al., 2009; Hayashi JI. et al., 2000).

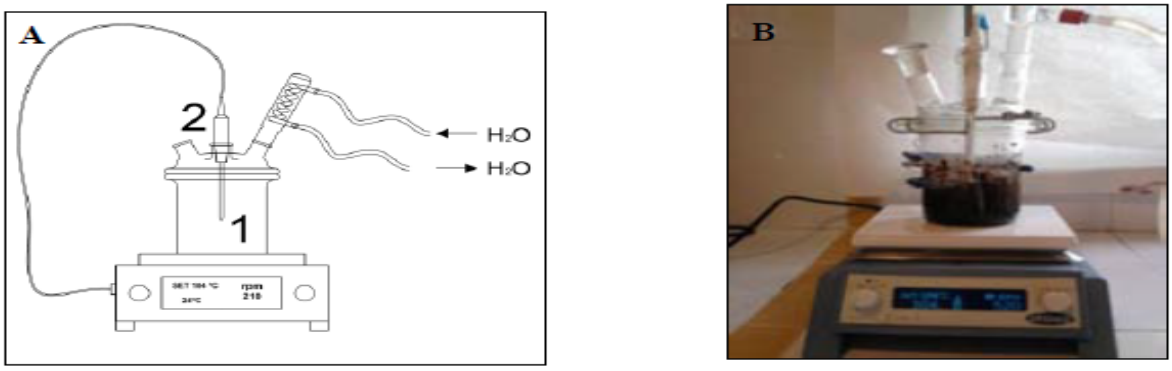


Figure 3.3: - schematic representation (A) and photography (B) of the reactor used for impregnation step

1: Pyrex reactor 2: Probe

3.2.1 Characterization of the prepared adsorbents

3.2.1.1 Determination of ash content

1.0 g of sample was weighed with analytical balance and transferred into crucible, then ignited until completely burned using muffle furnace at 500 ^{0}C for 4 hr. Then put in to desiccators for 10 min in order to cooled and remove moisture. Then measured the ash sample within analytical balance. Finally the ash content was calculated by using equation as follows (Joseph CG. and Frankie Y. 2008):

$$\% \text{ of ash content} = \frac{\text{Weight of sample after ash process}}{\text{Weight of sample before ash process}} * 100\% \quad (2)$$

3.2.1.2 The activated carbon pH measurement

The pH of activated carbon sample was measured primarily, weighting 0.1 g of activated carbon with analytical balance and added in to 100 ml Erlenmeyer flask. Then added 100 ml of distilled water in to Erlenmeyer flask and shaken for 24 hr. maintain agitated speed 200 rpm at temperature of 25^{0}C. Finally separate the activated carbon with vacuum pump filtration and pH was measured by Hana pH meter in order to determine basic, acid or neutral nature. Preliminary calibration of pH meter was carried out using buffer solutions.

3.2.1.3 Determination of pore volume

3.2.1.3.1 Physical characterization: Bulk density of the prepared activated carbon was done by placed in a graduated cylinder, tapped several times until constant volume to its volume and the mass measured. The bulk density is calculated as the ratio of the weight to its volume and expressed in g cm-3 (ECCMF, 1986). Particle density was determined using pycnometer measures volume (V); a balance is used to determine mass (m).

Bulk density (g/cm^3) = Dry sample weight (g) / sample volume (cm^3) (4)

Particle density: The mass of a particle divided by its apparent (particle) volume (5)

Pore space = Bulk density/ Particle density (6)

Textural characteristics were determined by nitrogen adsorption at 77.35 K with an automatic adsorption instruments (ASAP 2010, Micrometrics) in this case the samples are out gassed at

300°C under the flow nitrogen for 6.5 hours before measurement. The surface area of the activated carbon samples were calculated by Brunauer-Emmet-Teller (BET) method in the relative pressure (P/ P°) range of 0.05-0.40. The adsorption isotherms were analyzed and BET method (Teller E. et al., 1938) for determination of surface area. The pore size distribution was determined by using Barrett-joyner-Halenda (BJH) model (Halenda PP. et al., 1951) and t-plot for determining volume of the micropore (Lippens B. and De Boer J. 1965). The cross sectional area of nitrogen molecule is equal to 0.162 nm^2. The micropore volume corresponds to volume adsorbed in the pore less than 2 nm. Mesopores corresponds to volume adsorbed in pores between 2 and 50 nm. The mesopore surface area was calculated by subtraction of BET surface area and micropore surface area (Yorgun S. et al., 2009). The Dubinin-Radushkevich (DR) method is used to calculate the micropore volume. The micropore size distribution calculated by Density functional theory (DFT). The total volume was calculated by converting the amount of Nitrogen gas adsorbed at a relative pressure of 0.95 to the equivalent liquid volume of the adsorbent. The mesopore volume is calculated by subtracting the micropore volume to the total volume.

3.2.1.3.2 Chemical characterization: Elemental analysis was carried out using CHNS/O analyzer to determine the polarity of activated carbon. Proximate analysis was carried out to determine the ash content. The surface organic functional groups and structure were studied by using FTIR spectroscopy (NEXUS 65) to determine the adsorbent efficiency of activated carbon. The FTIR spectra of activated carbon and amine impregnate activated carbon were recorded between 400 and 4000 cm^{-1}. KBr is one of the most widely used transparent media for FTIR analysis of carbonaceous materials. Activated carbon sample were dried in an oven overnight. Samples were mixed with spectrograde KBr at the ratio of 1:200 (wt/wt), which allows preparing pellets which are transparent enough to absorb beam light. In the FTIR analysis Solid powder sample was first mixed with solid KBr powder in mortar pestle and a thin pellet is made using a hydraulic press. Such pellet can be placed in the IR beam for analysis.

3.2.1.4 Cation-exchange capacity

In studies on activated carbons, Bohem's titration is widely used to determine the cation-exchange capacity (CEC) of sorbents in order to analyze the surface oxygen functional groups on activated carbon (EL sheikh et al., 2004). A weighted amount of adsorbent (0.1 g) is placed into 250 ml an

Erlenmeyer flask. A volume of 20 ml of 0.1 M NaOH solution is added. To attain equilibrium, the suspension is shaken for 24 hours. After filtration, the residual NaOH concentration is determined by titration with 0.1M hydrochloric acid solution, using phenolphthalein as indicator. The quantity of NaOH consumed is converted to CEC and expressed in meq g^{-1} (Puziy et al., 2002).

3.2.1.5 Point of zero charge (pzc)

The point of zero charge, pH_{pzc} is defined as the pH of the aqueous solution in which the solid presents a neutral electric potential, pH at which the initial value is the same as the final value. It allows quantifying the acidic or basic character of the carbon. Depending on the raw material and the preparation mode (chemical or physical), activated carbons can have an acidic, basic or neutral nature. The activated carbon surface is positively charged at pH < pHpzc and negatively charged at pH > PHpzc. In addition pHpzc has been determined according to the method described by Furlan et al. (2010). It is noted that pHpzc is considered as the pH at which the electric charge density of a given surface equals zero. This parameter was obtained though mixtures of 0.1 g of activated carbon with 50 ml of 0.01 M NaCl standard solution in six Erlenmeyer flasks to which appropriate quantities of HCl and NaOH were added to obtain the following pH values: 5.0; 6.5; 7.25; 7.5; 8.0 and 9.0. The mixtures were then mixed for 48 hr. with a temperature of 25 ^{0}C using shaker incubator. Then the final pH of each mixture was measured. The pHpzc is the point where the curve pH_{final} versus $pH_{initial}$ intersects the line $pH_{initial} = pH_{final}$. A high precision pH meter (Hanna, model HI11310) equipped with a combined glass electrode (Hanna) was used.

3.2.1.5 Methylene blue Adsorption (MB)

Batch adsorption experiments were conducted in order to determine the maximum adsorption capacity of adsorbent. First, three different model methylene blue concentrations (50 ppm, 100ppm and 150ppm) are prepared in 100ml Erlenmeyer flasks from 1000ppm stock solution. These solutions were placed in a shaker and for each flasks 0.1 gram of activated carbon was added and also one additional blank solution (solution without the adsorbent) was also included in the shaker as a control sample then samples were shaken at 200 rpm for 24 hrs. After the adsorbent and adsorbate are contacted long enough, an equilibrium will be established between the amount of adsorbate adsorbed and the amount of adsorbate in solution. Then the sample was centrifuged at

5000 rpm for 25 minutes and then the supernatant was separated and the concentration was measured using UV-VIS (UVD-3200) photo spectroscopy at (650 nm).

The adsorption performance of the prepared activated carbons was calculated using the given formula as follow:

$$\% MB\ removal = \frac{Co-C1}{Co} * 100 \quad (7)$$

Where:

Co: is initial concentration of methylene blue before adsorption (ppm)

C1: is remaining concentration of methylene blue after adsorption (ppm)

The adsorption capacity, qe, was calculated as follows:

$$qe = \frac{Co-Ce}{m} * V \quad (8)$$

Where: Co and Ce are the initial and equilibrium methylene blue concentrations in (mg/L), respectively, V is a known volume of methylene blue solution (L), and m is a known mass of dry activated carbon (gram).

3.3 Grey water treatment through adsorption

The adsorption tests were carried out in batch system by adding various amounts of adsorbent in to seventeen 250mL Erlenmeyer flasks filled in each with 200 ml grey wastewater. The flasks were shaken at 250 rpm the time maintained for 24 hours until the concentration of the adsorbent became constant (equilibrium). Then each solution was separated from the sorbent by centrifugation at 13000 rpm for 5 min.

3.3.1 Physico-Chemical Test

3.3.1.1 pH measurements

The pH of the sample was measured by using pH meter in order to determine basic, acid or neutral nature. Preliminary standardization was systematically carried out using suitable buffer solutions.

3.3.1.2 Conductivity

The electrical conductivity is determined with an electronic conductivity meter, equipped with an immersion probe. The determination of the cell constant is first performed through a standard solution of KCl 0.1M. Then the conductivity of the grey water was measured before and after

treatment in order to determine the concentration of ions such as dissolved salts and inorganic materials like alkalis, chlorides, sulfides and carbonate compounds (Gelhaus and Lacourse, 2004).

3.3.1.3 Turbidity

Turbidity is the reduction of transparency of a liquid due to the presence of undissolved matter (suspended particulate matter). The apparatus used is equipped with an infrared lamp for making measurements at wavelengths above 800nm, which avoids inference from the colored substances. The Turbidometer was calibrated by using commercial standard: - >0.1, 20, 400, and 1000NTU (Nephelometric Turbidity Unit). Then the turbidity of grey water was measured before and after treatment in order to determine suspended particulate matter by using Turbidometer (2100 NTU).

3.3.1.4 Biological oxygen demand (BOD)

The most widely used parameters of organic pollution applied to both wastewater and surface water is the 5-day BOD (BOD_5). It corresponds to the measurement of the dissolved oxygen used by microorganisms in the biochemical oxidation of organic matter at 20 ^{0}C in dark. BOD_5 is measured by the monomeric method, using a digital respirometer (TS 606/4-i).

3.3.1.5 Chemical Oxygen Demand (COD)

The COD test is used to measure the content of organic and inorganic matter of both wastewater and natural waters. The COD digester was preheated for 30 min at 105^{0}C then 2 ml of grey water sample was added in to standard reagent and digested for 2 hrs. Finally cooled for 15 min (until the sample attain room temperature) and read the COD value with spectrophotometer (NAOCOLOR ® 400).

3.3.1.6 Total organic carbon TOC

Total organic carbon (the organic matter present in the water) is the TOC test, which is especially applicable to measure small concentrations of organic matter. TOC value was directly measured by using the instrument DR/870 colorimeter.

3.3.2 Determination of total nitrogen (N-total) and Total phosphorous (P-total)

Total nitrogen (TN) is the sum of all forms of nitrogen in the water sample (Piotrowski, J.; Wagner, 2011). Total phosphorus (TP) is a measure of all forms of phosphorus found in water (Marshall,

R. 2008). Total nitrogen (TN) and Total phosphorus (TP) values were directly measured by using the instrument DR/870 colorimeter.

3.3.3 Total thermotolerant coliforms

Coliform bacteria are the commonly used bacterial indicator for sanitary quality of water (Rompré A. et al., 2002). From grey water and treated water sample (5 mL) volume was taken. The grey water sample was diluted before analysis. First dilutions of 1 mL were filtered in 4.5 cm diameter, 0.45 µm pore-size, gridded, mixed ester membrane filters, in order to achieve a range of 20 to 60 countable TtC (Thermotolerant Coliforms) Colony Forming Units (CFU). The filters containing different volumes of the samples were transferred to the surface of the mFC (membrane fecal coliform) or mTEC (membrane Thermotolerant Escherichia coli) plates. mFC plates were incubated at 44.5 ± 0.2° C for 20 ± 2 hr. Modified mTEC plates were pre-incubated at 35 ± 0.5° C for 2 hr and then incubated at 44.5 ± 0.2° C for 22 hr. Blue colonies on mFC were counted as TtC. for verification or differentiation of colonies in the membrane filtration technique, typical blue coliform colonies on mFC medium were randomly selected from membrane filter for each tested sample.

3.3.4 Experimental design and data analysis.

In this study the optimization approach provided by the Box–Behnken design (BBD), which is a response surface methodology (RSM) was used. For applying the approach, Design-Expert software (Version 6.0.8) was used. RSM quantifies the relationship between the variable input parameters and the corresponding output parameters. RSM designs allow us to estimate interaction and even the quadratic effects and hence, give us an idea of the shape of the response surface were investigating. And also the Box-Behnken design has a maximum efficiency for an experiment involving three factors and three levels; further, the number of experiments conducted for this is much lesser.

Therefore, to determine the effect of the three operating factors for the grey water treatment, response surface methodology (RSM) was used. The operating factors were time, activated carbon dosage and pH and the response variables were COD, BOD, Turbidity and Conductivity.

Box-Behnken design was used to characterize the process parameters of adsorption using the three factors of grey water treatment. 3D response surfaces and contour plot were plotted to represent

the results. This representation showed the relative effects of the three factors. For this factors designs α = 1 and all factors are run at the three levels, which are -1, 0 and 1 in terms of the coded values. Three level, three factors and three times replication at box-behnken was used and total of 17 experiments were done. The independent factors were time, activated carbon dosage and pH, these factors were selected to investigate the quality of treated wastewater determined.

The data required to optimize the process condition for adsorption of grey water treatment was found by conducting the seventeen experimental runs; and was analyzed by the Design Expert software 6.0.8. And in order to minimize errors the experimental work was randomized.

The significant effect of treatment was judged with the help of 'F' (Variance Ratio). Calculated 'F' value was compared with the table value of F at 5% level of significance. If calculated value exceed the table value the effect will be considered to the significance. The significance of the study was tested at 5% level.

Tale 3.3 selected factors, corresponding symbols and labels.

Factors	Symbol	Labels		
		-1	0	1
Time (min)	A	45	52.5	60
Dosage (g)	B	0.1	0.35	0.5
Ph	C	6.5	7.25	8

The table 3.3 (selected factors) in this study the factors were selected according to the standard methods for Examination of water and wastewater analysis (APHA, 1998). The reason of selection was each were the following: - time is to generate favorable contact duration of activated carbon adsorption on the surface, to get optimum adsorption capacity and to get a good quality (better removal efficiency) of treated water to select 45, 52.5 and 60 min. And also to select the range of activated carbon dosage between 0.1, 0.35 and 0.5 in order to minimize the amount of sludge, after treatment process of wastewater. The pH selection it depends on point of zero charge.

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Percentage of yield

Table 4.1 shows the results of different parameters measured. It shows that the concentration of $ZnCl_2$ played a major role in the evaluation of prepared AC. Based on the data as shown in Table 4.1, percentage of yield increases from 41.2 to 83 %. The highest percentage yield represented by AC1 is 83 % at concentration of $ZnCl_2$ 0.3M while AC5 showed the lowest percentage yield of 41.2 % at concentration of $ZnCl_2$ 0.6M. It also shows that percentage of yield decreases as the concentration of $ZnCl_2$ increases. This is because the chemical activator, $ZnCl_2$, acts as a skin chloride which can be used to protect the internal carbon structure and prevents the product from excessive burn-off. There is a big percentage yield difference between the concentrations of $ZnCl_2$ activation AC which can be observed from Table 4.1 Tsai WT, Chang CY and Lee SL, have done the similar research using $ZnCl_2$ as dehydrating agent in preparation of AC from corn cob. The reason for high percentage yield in chemical AC was due to the $ZnCl_2$ activation, which caused more potential sites to penetrate and occupy the activating agent. This enhances the pore opening and widening.

According to the research of Marshall W. the preparation and characterization of activated carbon derived from oat hulls or corn stover (Marshall W. et al., 2004) char was heated at 400 to 450 ^{0}C for 30, 60, 90 or 120 min. The activated carbons, which had a high pore volume, was weighed to determine activation burn-off or mass loss due to activation. The yield and the characteristics of the prepared activated carbon depend on the process of preparation used. Thus, applying the two processes on lignocellulosic materials, Rodriguez- Reinso and Molina-Sabio (1992) showed that the yield of activated carbon is higher in the case of chemical activation with $ZnCl_2$.

Table 4.1:- Percentage of yield, ash content and its parameter

Sample	*$ZnCl_2$ Concentration*	*Activation Temperature and time*	*Percentage of yield (%)*	*Ash content (%)*
Ac1	0.3 M	400 ^{0}C, 2 hr.	83	0.252
Ac2	0.3 M	450 ^{0}C, 2 hr.	73	0.267
Ac3	0.45 M	400 ^{0}C, 2 hr.	44.8	2.01
Ac4	0.45 M	450 ^{0}C, 2 hr.	43.4	2.21
Ac5	0.6 M	450 ^{0}C, 2 hr.	41.2	2.23

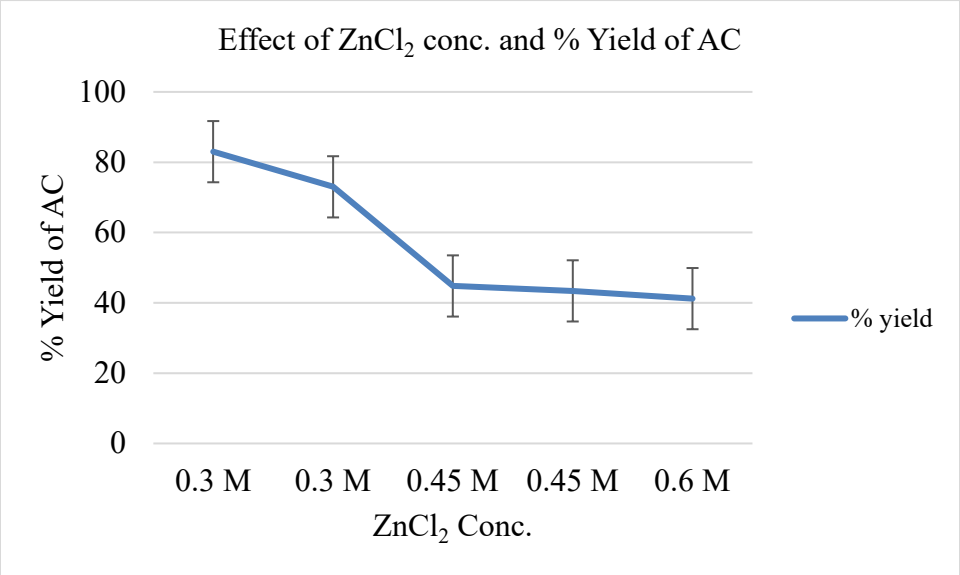


Figure 4.1:- Effect of $ZnCl_2$ concentration and % yield of AC

4.2 Ash content

Normally, the ash content of the activated carbon is dependent on the ash content of the raw material. The ash is a non-carbon material, which is usually mineral additive that is not attached to the surface of the carbon. It can influence the adsorptive capacity of the prepared activated carbon as it is linked directly to the pore structure of the activated carbon. In other words, when

the value of the ash content decreases, the efficiency and adsorptive capacity of the prepared activated carbon increase. Based on the experimental results as shown in Table 4.1, the impregnated carbon with $ZnCl_2$ had less ash content compared to raw corn cob. The raw material contained 2.232 % ash and the rest of the chemical activated carbon had decreasing trend of ash content in the range of 0.252 %. By altering $ZnCl_2$ concentration, this could bring about very significant changes in the ash content of the prepared activated carbon.

4.3 The activated carbon pH measurement

Prepared activated carbon samples after agitated for 24 hr. process, pH was obtained 6.9. Depend on zero point of charge these pH value is accepted for adsorption process. Generally, pH of the activated carbon influenced the surface chemistry and adsorption of various adsorbate that are sensitive to the pH changes. In this study, the pH of the final product was controlled during the washing process to ensure almost neutral pH value.

4.5 Fourier transform infrared spectroscopy analysis (Spectrum 65 FTIR (PerkinElmer) in the range 4000-400 cm-1 using KBr pellets.)

Pore structure of the AC is very important in determining adsorption properties of the sorbent. However, the importance of the surface chemistry of AC should not be ignored. In this work FTIR spectroscopy was used to obtain information about the chemical structure and functional groups of the raw material and the prepared activated carbon (Zawandzki, 1989, Jagtoyen et al., 1992, Pastor-Villegas et al., 1993, Vinke et al., 1994, Solum et al., 1995, Gomez-Serrano et al., 1996). The surface chemistry of an AC was determined by the type, quality and bonding of functional group. Figure 4.2 shows the spectra of the raw corn cob, and figure 4.3 show the spectra of activated carbon with chemical activation concentration with 0.3 M. A broad band located around 3,300–3,800 cm^{-1} is typically attributed to the presence of hydroxyl group either aliphatic alcohol or phenol or even adsorbed water molecule. The band around 1,600–1,800 cm^{-1} is possibly caused by the stretching vibration C=O in carboxyl, ketone, aldehyde and lactone group. Stretching vibration at 1,400–1,600 cm^{-1} corresponds to the aromatic ring or C=C bonding. Presence of this functional group indicates the formation of carbonyl-containing group and aromatization of the raw material. While the band around 1,200 cm^{-1} is typically represented by the C–O group. In chemical activation involving the $ZnCl_2$, the chemical activator promotes

depolymerization, dehydration and redistribution of constituent biopolymer which causes the decomposition of the lignocellulose material when it underwent pyrolysis. Depend on the most of researcher, at low temperature the conversion of aliphatic to aromatic compound can be enhanced. For the spectrum of chemically prepared AC, the band in the region 600–1,400 cm^{-1} could be caused by the C- O groups.

Significant changes in the spectra of activated carbon, 2356 cm, and activated products are observed which, in particular, concern the bands located in the two regions between 2361 and 2356 cm where a sharp decrease in the bands intensities is noticed in these two regions for all the carbon products. These results suggested that under carbonization and activation conditions many strong bonds disappeared. At the same time, the C≡C bonds, in the new aromatic structures, were involved in the formation of the oxygen functional groups with C–O bonds. This significant decrease occurring in the bands intensities was found to be dependent on the activating agent.

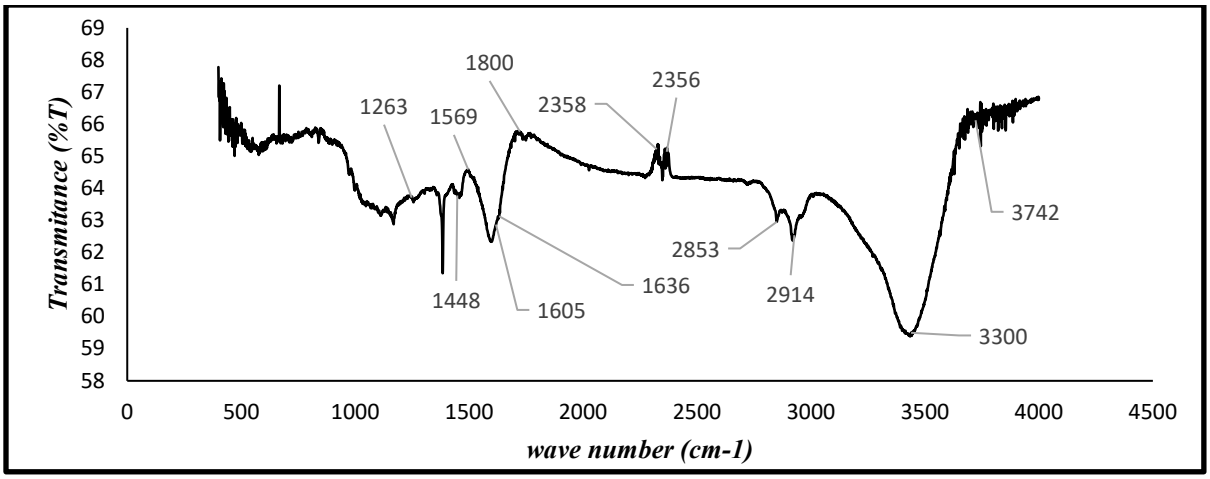


Figure 4.2:- FTIR spectra of raw corn cob

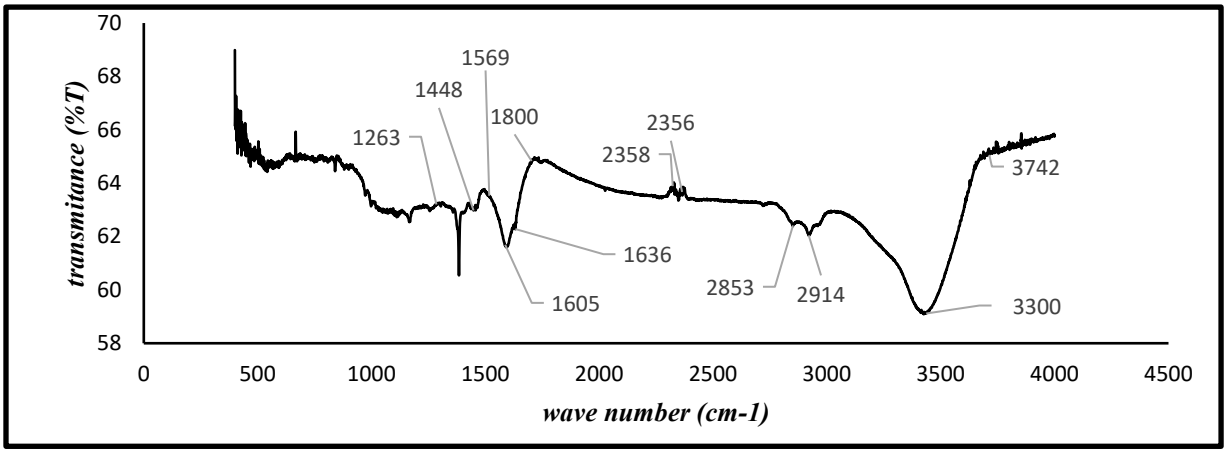


Figure 4.3:- FTIR spectra of chemical AC (0.3 M)

Table 4.2:- peak frequencies in the spectra and possible assignment of the band (Gomez-Serrano et al., 1996)

Band position (cm^{-1})	Possible assignment
3800, 3788, 3742, 3713, 3300	O- H stretching
2361, 2358, 2356	C≡C stretching vibration
1800, 1656, 1636, 1600	C=O stretching vibration
1600, 1569, 1462, 1447, 1400	C=C stretching vibration
1400, 1280, 1273, 1272, 1263, 1200, 600	C- O stretching vibration

Table 4.3 UV-VIS Absorbance measurement of MB (temperature at 400^0C AC)

Concentration of methylene blue	Absorbance before treatment	Absorbance after treatment	% MB removal	q (mg/g) (adsorption capacity)
50 PPM	1.529	0.722	54.84	13.71
100 PPM	2.318	1.486	30.55	15.275
150 PPM	2.290	2.082	29.33	21.995

Table 4.3 shows that, the adsorption capacity and methylene blue removal efficiency of the activated carbon used in this work (at 50 MB concentration were 13.71 mg/g and 54.84), and its favorable capacity prepared from agricultural waste.

Table 4.4 Physical properties and cation exchange capacity (CEC) analysis of activated carbons

Sample name	Activation agent	CEC (meq/g)	S_{BET} m^2/g	Bulk Density g/cm^3
Activated carbon	$ZnCl_2$	2.33	3.814e+00	1.43

From the above table 4.4 indicated that, the chemical activation process was used to prepared activated carbon from agricultural waste corn cob with $ZnCl_2$ activation agent in this study. Under the experimental conditions investigated, the resulting activated carbon is essentially mesoporous material. From the table 4.4 and annex 3 shows that has high surface area carbon (i.e. 3.814e+00 m^2/g).

Table 4.5 Elemental composition of raw corn cob and its activated carbon

Sample	C (%)	H (%)	N (%)	S (%)	O (%)
Raw corn cob	43.135	9.213	4.08	28.35	15.222
Activated carbon	82.85	1.562	1.023	-	2.565

The above table 4.5 shows that, the results of elemental analysis of raw corn con and its activated carbon in the experimental work, the resulting activated carbon contain 82.85 % of carbon. On the other hand, the non-carbon elements (hydrogen, oxygen, traces of nitrogen and sulfur) were mostly removed in a gaseous from during the chemical activation, resulting in low analysis values

for these elements. The commercial activated carbon product contain 90 % of carbon specifications (Tsai and Chang, 1994b). Based on these the carbon contain is feasible on this study work.

4.6 Point of zero charge (pzc)

The point of zero charge, pH_{pzc} is defined as the pH of the aqueous solution in which the solid presents a neutral electric potential, pH at which the initial value is the same as the final value. $pH_{initial} < pH_{final}$ shows the effect is positive charge, $pH_{initial} > pH_{final}$ shows negative charge and $pH_{initial} = pH_{final}$ shows zero charge. In this experiment the values for pH tests at different conditions were: - at pH 5= 5, at pH 6.5= 7.5, at pH 7.25= 6.9, at pH 8= 8.5 and at pH 9= 9. The results of the values at pH 6.5 and 8 were the $pH_{initial}$ value less than pH_{final}, and pH 7.25 and pH 7.5 the $pH_{initial} > pH_{final}$, for both cases the result indicated that the activated carbon surface is positively charged and negative charge respectively. The values have been acceptable since the positive charge and negative charge means the liquid has no pipe scaling and corrosion effect. In addition, the structure of electrolyte at the electrode surface can also depend on the surface charge, on a grey water electrode, water molecules have been reported to be weakly hydrogen-bonded with "oxygen-up" orientation on negatively charged surfaces, and strongly hydrogen-bonded with nearly flat orientation at positively charged surface (Furlan et al, 2010).

At pH 5 and pH 9 the result shows that $pH_{initial} = pH_{final,}$ the potential of the same electrode when the surface charge is zero and the colloidal system exhibits zero potential. For this case the value has been rejected in the absence of specific adsorption other than that of the solvent, against the reference electrode as used. And also the point of zero has salt effect, which causes the liquid has been scale form and corrosion effect on the pipe (Furlan et al, 2010).

Table 4.6 pH zero charge effect of activated carbon

No.	**$pH_{initial}$**	**pH_{final}**	**Result**
1	5	5	pzc
2	6.5	7.5	Positive charge
3	7.25	6.9	Negative charge
4	7.5	7	Negative charge
5	8	8.5	Positive charge
6	9	9	pzc

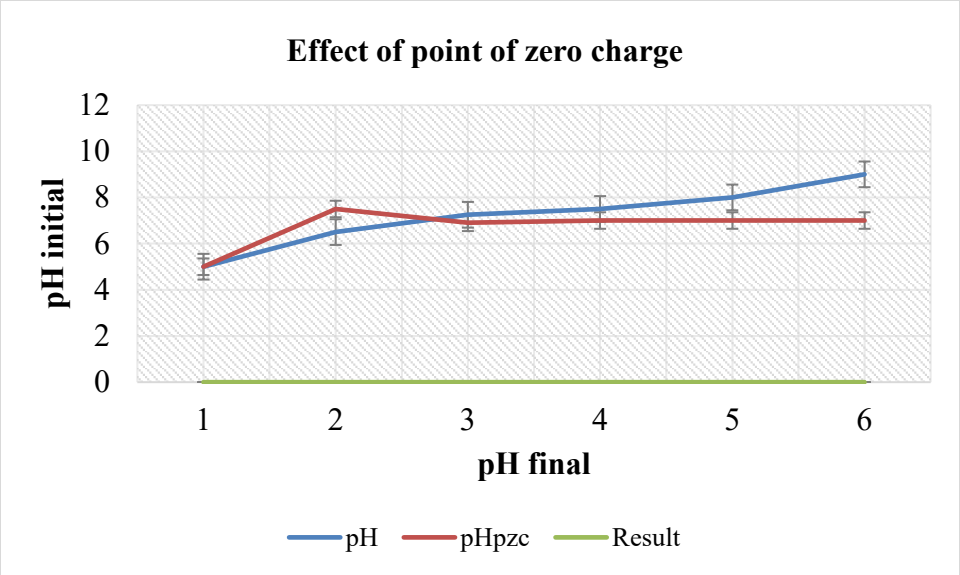


Figure 4.4 effect of point of zero charge

4.7 Treatment water and wastewater analysis

Table 4.7 Raw grey water analysis result

No.	Name of the Analysis	Result
1.	COD (mg/L)	1500
2.	BOD (mg/L)	152
3.	pH	8.96
4.	Conductivity (ms/cm)	6.64
5.	Turbidity (NTU)	200
6.	TDS (mg/L)	4.25
7.	TSS (mg/L)	155
8.	TOC (mg/L)	0
9.	Tot-P (mg/L)	15.5
10	Tot-N(mg/L)	9.73
11	Total coliform (mg/L)	0
12	Zinc (Zn, mg/L)	0.62

4.7.1 Analysis of treated water

The experimental design selected for analysis of variance was surface methodology (RSM). Under response surface methodology, Box–Behnken design (BBD), in which the alpha value is face centered (α=1). The response of the analysis were COD, BOD, Turbidity and Conductivity.

The model assumed for analysis of variance was response surface quadratic model and ANOVA was performed using partial sum of squares methods. Model A: time, B: activated carbon dosage and C: pH and, quadratic model factors; pure quadratic terms (A^2, B^2, C^2 and interaction quadratic terms (AB, AC, BC) depending on the F and P values.

4.7.2 Development model equation

Response surface methodology (RSM) is a collection of mathematical and statistical techniques that are useful for the modeling and analysis of problems in which a response of interest is influenced by several variables. The application of RSM offers an empirical relationship between the response function and the independent variables. The mathematical relationship between the response and the independent variables time (A), dosage (B) and pH(C) in terms of coded and actual factors can be determined by Design Expert software. The model equation that correlates the response (COD, BOD, Turbidity and Conductivity) to the treatment process variables in terms of coded factors after excluding the insignificant terms was given in equation.

Table 4.8 Statistical analysis of treated water

Std	Run	Factor 1 A: pH	Factor 2 B:Time (min)	Factor 3 C:Dosage (g)	Response 1 COD (mg/l)	Response 2 BOD (mg/l)	Response 3 Turbidity (NTU)	Response 4 Conductivity (ms)
1	3	6.5	45	0.35	97	2.01	8.31	3.34
2	2	8	45	0.35	200	15	175	3.14
3	15	6.5	60	0.35	89	3	4.01	2.24
4	11	8	60	0.35	165	24	170	3.66
5	16	6.5	52.5	0.1	66	3.1	3.31	2.07
6	13	8	52.5	0.1	185	23	173	3.71
7	9	6.5	52.5	0.5	90	2	3.01	3.87
8	10	8	52.5	0.5	152	20	168	3.62
9	6	7.25	45	0.1	173	3.6	66	3.34
10	12	7.25	45	0.5	166	4	63	3.4
11	14	6.5	52.5	0.35	93	2.3	8.22	3.86
12	1	7.5	60	0.5	160	2	55	3.31
13	17	6.5	60	0.1	65	2.8	4.52	3.1
14	5	7.5	52.5	0.35	92	2.2	65	3.33
15	7	7.25	45	0.35	144	3.5	65	3.41
16	8	7.5	52.5	0.1	174	2.02	40	3.35
17	4	7.25	60	0.35	142	3.1	60	2.5

Table 4.9 Optimum data of treated water

No.	Name of the Analysis	Raw grey water analysis	Treated water analysis
1.	Tot-N (mg/L)	9.73	0.25
2.	Tot-P (mg/L)	15.5	0.4
3.	TOC (mg/L)	0	0
4.	TSS (mg/L)	155	0
5.	TDS (mg/L)	4.25	2
6.	Total coliform (mg/L)	0	0
7.	COD (mg/L)	1500	89
8.	BOD (mg/L)	152	3
9.	Turbidity (NTU)	200	4.01
10.	Conductivity (ms)	6.64	2.24
11.	Zinc (Zn, mg/L)	0.62	0

Table 4.8 shows that the effect of adsorption capacity through grey water treatment at the optimum condition further analysis (factors at pH 6.5, contact time 60 min and activated carbon dosage 0.35 g).

Effect of pH, Time and AC Dosage on efficiency on removal of pollutant load (COD, BOD, Turbidity and Conductivity)

The pH of a solution is the organic matter containing grey water, expressed as a negative logarithm. It reflects the acidity or alkalinity of a solution, Water with a pH of 7 is neutral; pH lower than 7 levels indicate increasing acidity, while pH levels higher than 7 indicate increasingly alkaline solutions. It is important to consider the effects of pH on efficiency of adsorbent of activated carbon. In this case, the pH varied as (6.5, 7.25, 7.5 and 8).

The contact time is the duration of time for adsorption of grey water, expressed as minutes. It is important to consider the effects of contact time on efficiency of removal of activated carbon. For this part, the contact time varied as (45, 52.5 and 60) minute.

The activated carbon dosage is the amount of activated carbon for adsorption of grey water, expressed as gram. It is important to consider the effects of activated carbon dosage on efficiency of adsorbent of activated carbon. In this case, the activated carbon dosage varied as (0.1, 0.35 and 0.5) gram.

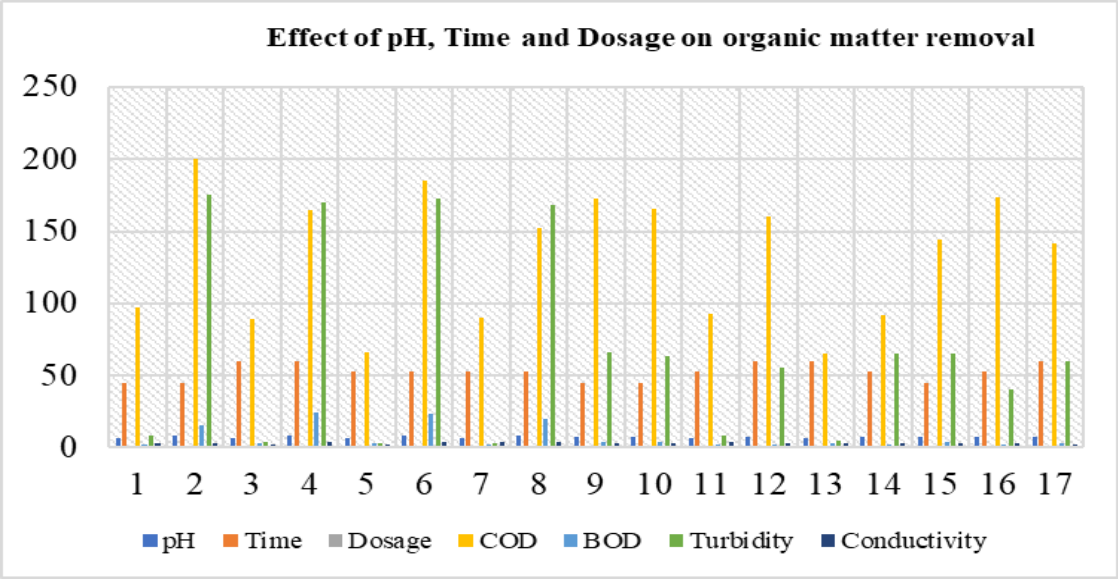


Figure 4.5 Effects of pH, Time and AC dosage on efficiency on removal of pollutant load (COD, BOD, Turbidity and Conductivity)

Figure 4.5 Shows that as the pH, time and AC dosage value increase from 6.5 to 7.5; 45 to 60 minute; and 0.1 to 0.5 gram percentage of pollutants load (COD, BOD and Turbidity) removal also increases, while the maximum removal observed at pH 6.5 then as the pH value increase, beyond time and dosage also 60 minute and 0.35 gram the percentage of removal of pollutants load (COD, BOD and Turbidity) starts increases. Generally, the above figure indicated that the pH, time and dosage value was highly efficient to remove pollutants load (COD, BOD and Turbidity) at 6.5, 60 min and 0.35 g that can be the optimum values. Removal efficiency of activated carbon was highly dependent on pH values figure 4.5 indicates that when the basic nature of the waste solution decreases, the COD, BOD and Turbidity removal efficiency of activated carbon was increases. Lower removal efficiency at low pH is apparently due to the presence of a higher concentration of OH^- in the solution, which competes with metal ions for the adsorption sites of the activated carbon (El-Hendyawy, et al., 2001).

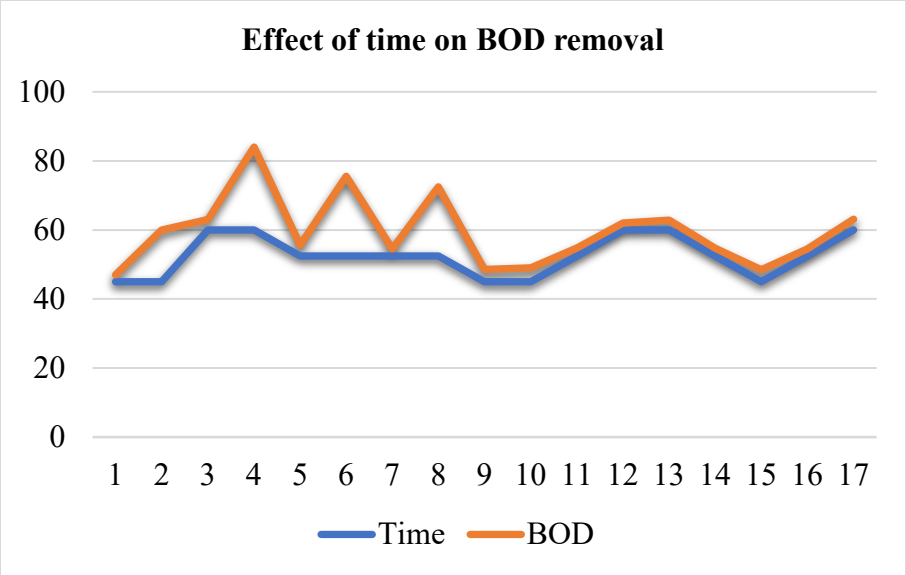


Figure 4.6 Effects of time on efficiency on removal of BOD

Figure 4.6 Shows that as contact time increase from 45 minutes to 60 minutes percentage of pollutants load (BOD) removal also increases while the maximum removal observed at the contact time 60 minutes then as the contact time increase beyond 60 minutes the percentage of removal pollutants load (BOD) starts increases. Generally, the above figure indicated that the contact time was highly efficient to remove pollutant loads (BOD) at 60 minutes that can be the optimum contact time. Removal of efficiency of activated carbon showed slight change as the contact time was changed. As the contact time changed from 45 minutes to 60 minutes the percent removal showed slight increase and started to show a bit decline after 52.5 minutes (figure 4.6).

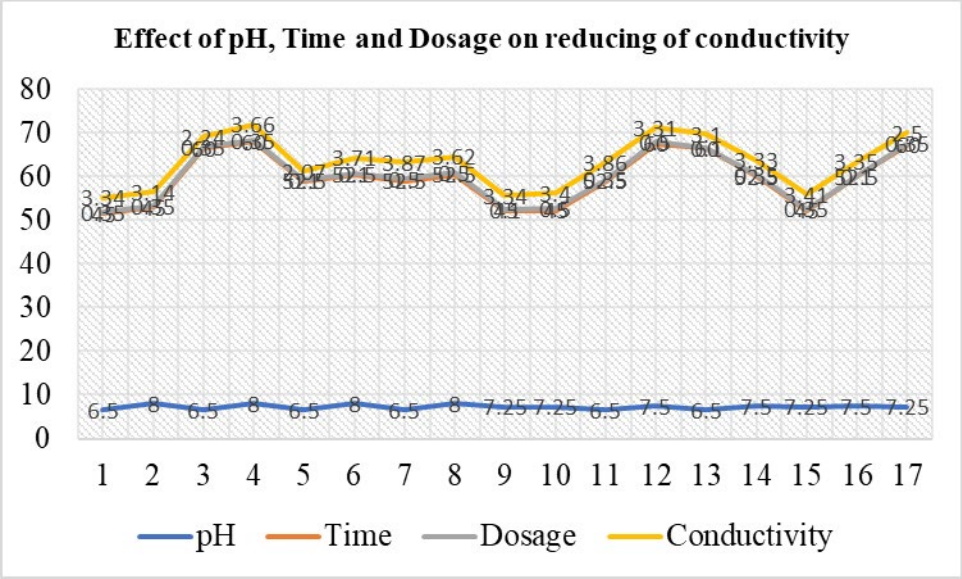


Figure 4.7 Effects of pH, Time and AC dosage on efficiency on removal of Conductivity

Figure 4.7 Shows that as contact time and AC dosage increase from 6.5 to 7.5; 45 minute to 60 minute; and 0.1 g to 0.35 g percentage of pollutants load (Conductivity) also reduced while the maximum reducing observed at the contact time 60 minutes and dosage 0.35 g, then as the contact time and dosage increase beyond the percentage of pollutants load (Conductivity) starts reduced. Generally, the above figure indicated that the contact time and AC dosage was highly efficient to pollutant loads reducing (Conductivity) at 60 minute and 0.35 g that can be the optimum values. Removal of efficiency of activated carbon showed slight change as the contact time and AC dosage was changed.

4.7.3 Response Surface and Contour plot on the Experimental Variables

In order to analyze the regression equation of the model, three-dimensional surface and 2D contour plots were obtained by plotting the response COD, BOD and turbidity on the Z axis against any two variables while keeping the other variable at zero level. These plots are created to analyze the change in the response surface. Conical shape response surface plot indicates optimum conditions. The response optimized value for the removal of COD, BOD and turbidity of grey water was based on the three process variables (pH, activated carbon dosage and time) described on the response surface plot. The effect of the independent variables and their mutual interaction on the efficiency of removal COD, BOD and turbidity can be seen in (Figures 4.4, 4.5 and 4.6) below respectively.

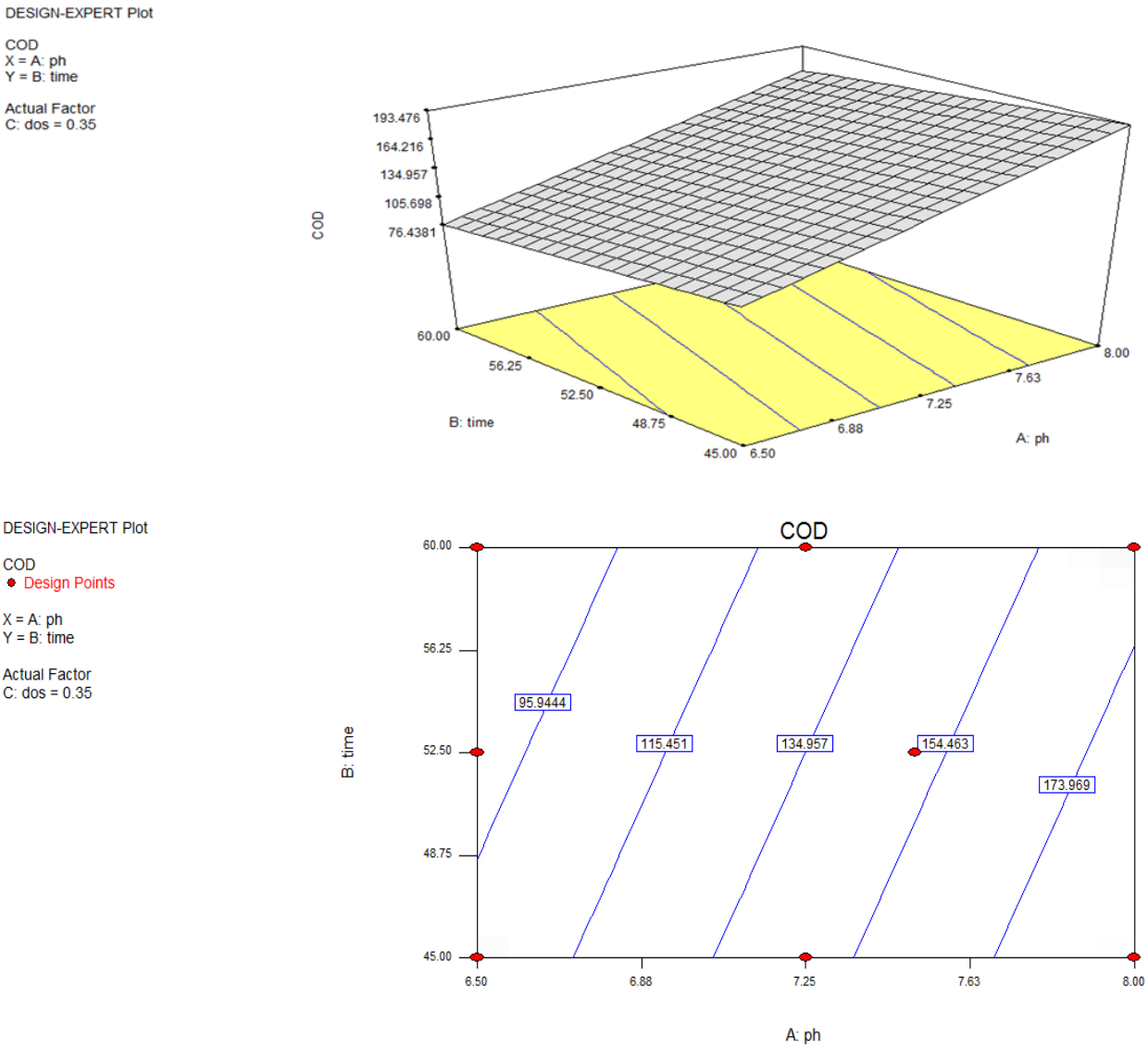


Figure 4.8 3D Response surface and contour plots of the effect of pH and time on the removal of COD.

The above surface plot shows that the highest COD value is obtained when time levels are low and pH levels are high.

Annex 3.1 indicated that the Values of "Prob > F" less than 0.0500 indicate model terms are significant. The coefficient for the linear effect of particle size was highly significant, and it was also observed that there is an interaction effect between pH activated carbon dosage and time. The regression coefficients and the corresponding 95% CI (Confidence Interval) if zero were in the range High and Low 95% confidence interval, the factors have no effect. From the 95% CI High

and Low values of each model term, it could be concluded that the regression coefficients of pH and the interaction terms of pH and time have highly significant effect in COD removal.

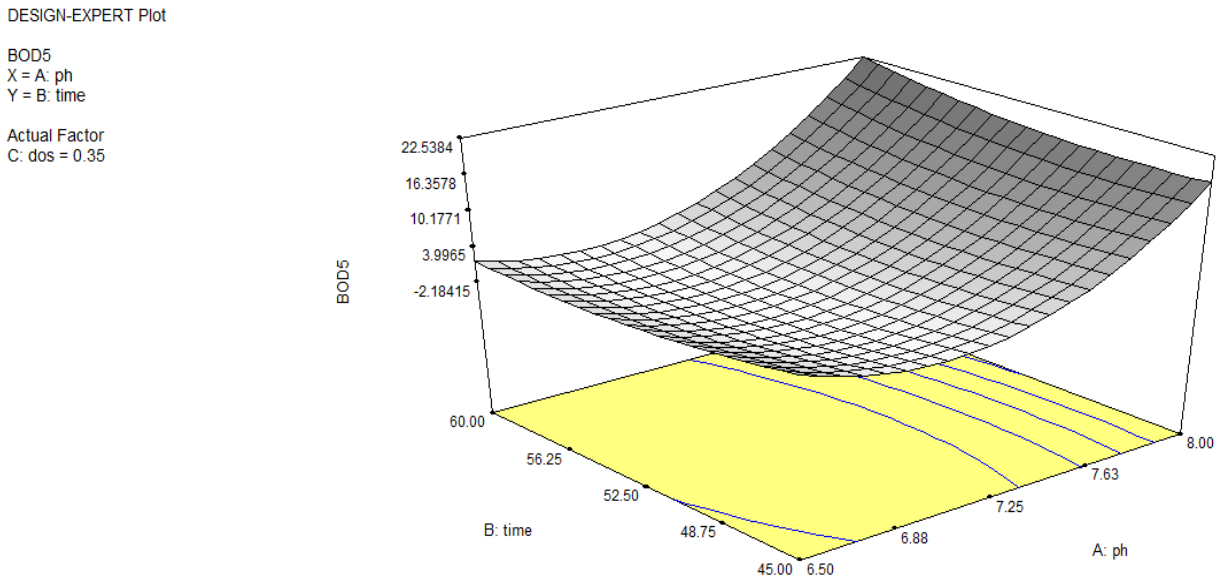
Final Equation in Terms of Coded Factors:

COD = +134.96 + 45.66 * A - 12.86* B - 1.01 * C

Final Equation in Terms of Actual Factors:

COD = -214.09528 + 60.88406* pH - 1.71411* time - 6.76188 * dosage

From the above regression model shows equation in terms of coded factors and actual factors, the response yield was affected by linear terms pH (A), time (B) and dosage (C). On the basis of the coefficients in equations, it was evident that the percentage of response yield increase with the pH (A) but the other two factors (time (B) and dosage (C)) response yield decrease. pH has more weighty positive linear effect on the response yield but time and dosage negative (lower) linear effect on the response yield.



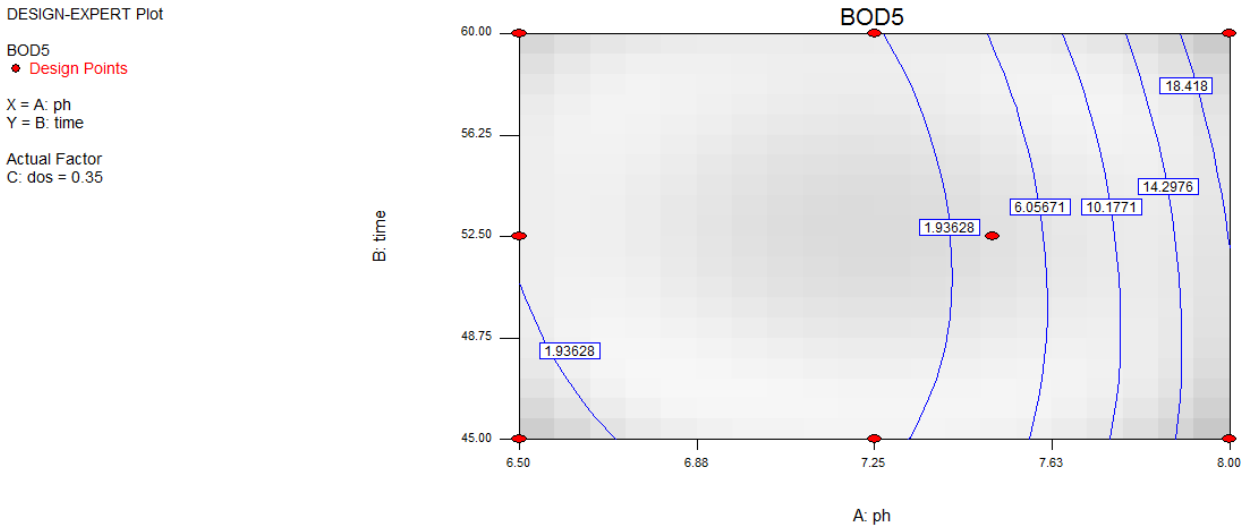


Figure 4.9 3D Response surface and contour plots of the effect of pH and time on the removal of BOD.

The above surface plot shows that the highest BOD value is obtained when time levels are low and pH levels are high.

Annex 3.2 indicated that the Values of "Prob > F" less than 0.0500 indicate model terms are significant. The coefficient for the linear effect of particle size was highly significant, and it was also observed that there is an interaction effect between pH activated carbon dosage and time. The regression coefficients and the corresponding 95% CI (Confidence Interval) if zero were in the range High and Low 95% confidence interval, the factors have no effect. From the 95% CI High and Low values of each model term, it could be concluded that the regression coefficients of pH and the interaction terms of pH and time have highly significant effect in BOD removal.

Final Equation in Terms of Coded Factors:

$$BOD_5 = -0.39 + 8.55 * A + 0.23 * B - 0.29 * C + 10.37 * A^2 + 1.82 * B^2 + 0.47 * C^2 + 1.96 * A * B - 0.59 * A * C - 0.89 * B * C$$

Final Equation in Terms of Actual Factors:

$$BOD_5 = +1081.58792 - 272.40690 * pH - 5.61289 * time + 63.24108 * dosage + 18.43584 * pH^2 + 0.032267 * time^2 + 20.72992 * dosage^2 + 0.34915 * pH * time - 5.27724 * pH * dosage - 0.78878 * time * dosage$$

From the above regression model shows equation in terms of coded factors and the actual factors, the response yield was affected by linear terms pH (A), time (B) and dosage (C) and, quadratic terms pure quadratics terms (A^2, B^2, C^2) and interaction quadratic terms (AB, AC, BC). On the basis of the coefficients in equations, it was evident that the percentage of response yield increase with the pH (A), time (B) and dosage (C). pH, time and dosage have positive linear effect on adsorption process but pH has more weighty positive linear effect on yield as compared to adsorption time and dosage. Pure quadratic (A^2, B^2 and C^2) also has positive effect on the response yield. Interaction of pH and time (AB) has positive quadratic effect on response yield. Interaction of pH and dosage (AC) and interaction of time and dosage (BC) have negative quadratic effect on the response yield.

Final Equation in Terms of Coded Factors:

$$\text{Trbudity} = +37.84 + 80.80 * A - 8.14 * B - 0.79 * C + 45.25 * A^2 + 12.57 * B^2 - 1.57 * C^2 - 1.19 * A * B - 0.30 * A * C - 0.79 * B * C$$

Final Equation in Terms of Actual Factors:

$$\text{Trbudity} = +4051.54782 - 1046.80087 * \text{pH} - 22.76541 * \text{time} + 99.54707 * \text{dosage} + 80.45104 * \text{pH}^2 + 0.22338 * \text{time}^2 - 69.95899 * \text{dosage}^2 - 0.21108 * \text{pH} * \text{time} - 2.63233 * \text{pH} * \text{dosage} - 0.70013 * \text{time} * \text{dosage}$$

From the above regression model shows equation in terms of coded factors and the actual factors, the response yield was affected by linear terms pH (A), time (B) and dosage (C) and, quadratic terms pure quadratics terms (A^2, B^2, C^2) and interaction quadratic terms (AB, AC, BC). On the basis of the coefficients in equations, it was evident that the percentage of response yield increase with the pH (A), but time (B) and dosage (C) of the response yield were decrease. pH (A) has positive linear effect on adsorption process and has more weighty positive linear effect on yield as compared to adsorption time and dosage. Pure quadratic (A^2 and B^2) also has positive effect on the response yield but (C^2) negative effect on the response yield. Interaction of pH and time (AB), interaction of pH and dosage (AC) and interaction of time and dosage (BC) have negative quadratic effect on the response yield.

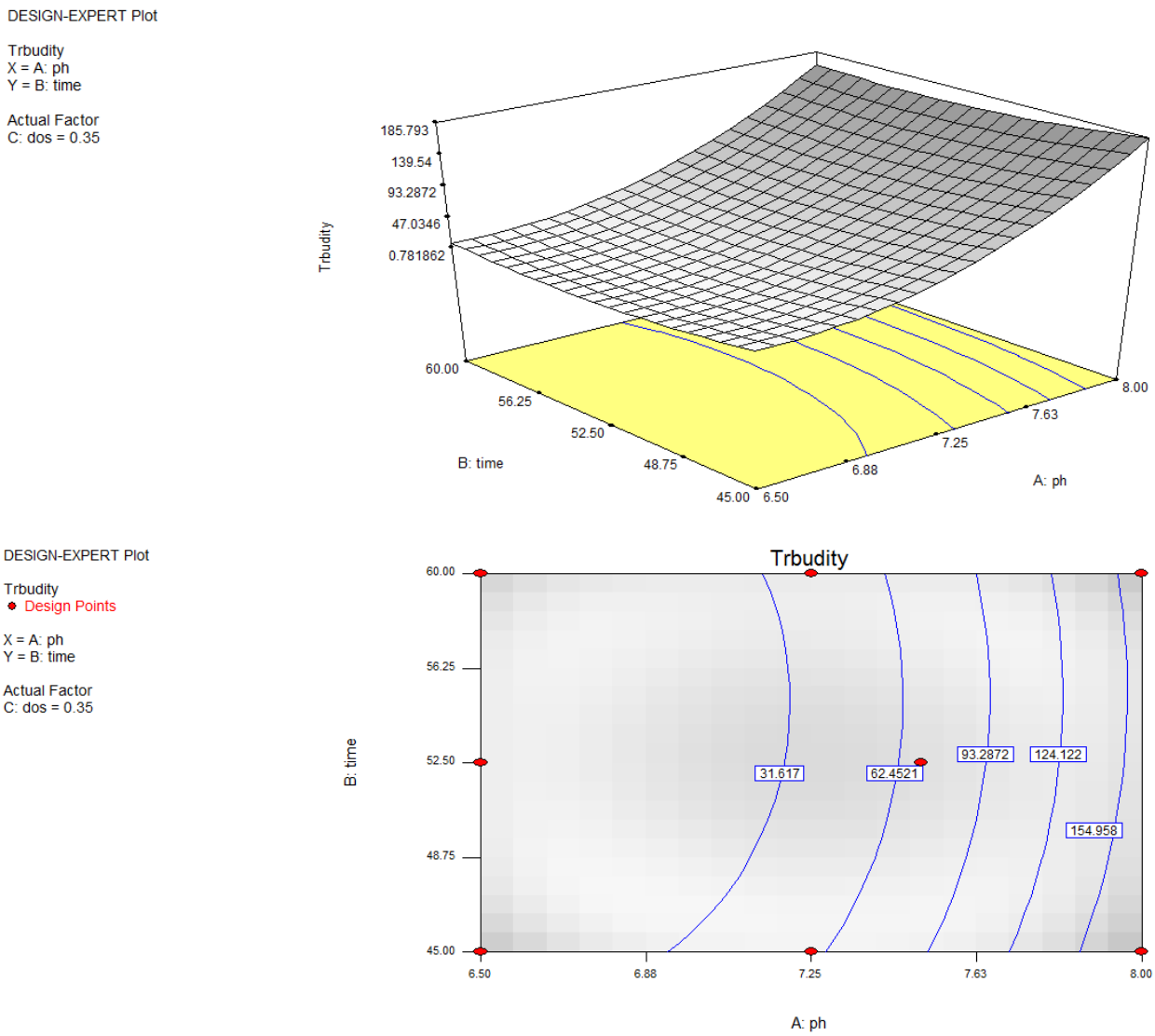


Figure 4.10 3D Response surface and contour plots of the effect of pH and time on the removal of turbidity.

- The surface plot shows that the highest Turbidity value is obtained when time levels are low and pH levels are high.

Annex 3.3 indicated that the Values of "Prob > F" less than 0.0500 indicate model terms are significant. The coefficient for the linear effect of particle size was highly significant, and it was also observed that there is an interaction effect between pH activated carbon dosage and time. The regression coefficients and the corresponding 95% CI (Confidence Interval) if zero were in the range High and Low 95% confidence interval, the factors have no effect. From the 95% CI High and Low values of each model term, it could be concluded that the regression coefficients of pH and the interaction terms of pH and time have highly significant effect in turbidity removal.

CHAPTER FIVE
CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The experimental result indicated that the optimum conditions for reduction of pollutants load were obtained as pH 6.5, time 60 min and activated carbon dosage 0.35 g. In this conditions the efficiency activated carbon and activated agent ($ZnCl_2$ in the concentration of 0.3M) on the removal of pollutants load in particular for (COD, BOD, Tot-N, Tot-P and turbidity) were obtained as (94.067 %, 98.026 %, 98.39 %, 95.89 % and 97.995 %) respectively.

In SPA Service Enterprise (Filwoha) provides shower services. In addition, uses both ground water and surface water for washing, laundry, toilet flushing and other utility purposes. For this purpose, uses 820. 8 m^3 per hour. According to this, it can be concluded that treated grey water used as alternative water resource for toilet flushing and other utility purposes.

In addition, according to the results of statistical analysis it can be concluded that the parameters pH is more significant on removal of COD, BOD, Tot-N, Tot-P and turbidity from COD, BOD, Tot-N, Tot-P and turbidity containing grey water.

From activated carbon preparation of experiment (Pyrolysis process conditions temperature and time) affect the yields of the products. The experimental result indicated effect of activation agent of zinc chloride, the optimum yield of activated carbon was found 83% at the temperature of 400^0C (zinc chloride concentration 0.3M). According to this result, it can be concluded that for activated carbon preparation that an increase temperature the yield is decrease. The characteristics activated carbon (surface area, porosity, cation exchange capacity and surface chemistry) determine the effects of adsorption on grey water.

In general from an environmental point of view, activated carbon is a potential product that could help to overcome the issues such as pollution, uses agricultural waste due to its significant physico-chemical properties, it is cost effective, locally available, environmentally friendly and safe to treat.

5.2 Recommendations

Based on the result of this study the following recommendations are forwarded:-

- There should be governmental or nongovernmental organizations that can support and encourage the improvement of grey water treatment through adsorption and reused system in SPA Service Enterprise (Filwoha) and other grey water discharge in Ethiopia.
- Currently there is no environmental discharge standard set by Ethiopian EPA for grey wastes disposal system while some of the grey water contain COD, BOD, Tot-N, Tot-P and Turbidity. Therefore, SPA Service Enterprise (Filwoha) grey water discharge standard should be prepared and grey water should be dispose their wastewater according to this standard.
- SPA Service Enterprise (Filwoha) grey water and other grey water in Ethiopia should improve their water resource by treatment system using with low cost of agricultural waste activated carbons.
- During the experimental analysis, factors were pH, time and activated carbon dosage in the treatment process with different amount respectively. But time and activated carbon dosage has less effect in adsorption process. For better effect of adsorption (reducing pollutant load) activity, future studies should focus on pH effect of adsorption process.
- Corn cob can also use as energy source, in order to that future studies should focus on determination of its energy source.

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ANNEXES

Annex *1.* Sample picture of raw corn cob, activated carbon and adsorption test experiment in laboratory scale.



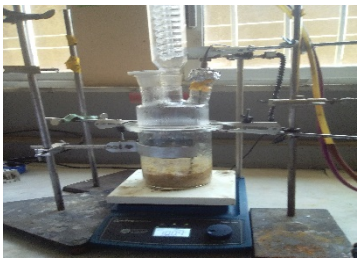
Corn cob collection



Washing with distilled water



Size Reduction



Soaking with $ZnCl_2$ 0.3M, 0.45M, and 0.6M solution in and cooking at 104^0C for 2 hr.



Drying in open air for 24 hr.

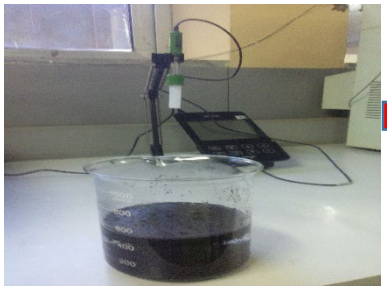


Preparation of activated carbon without oxygen (pyrolysis)





Washing



Checking pH





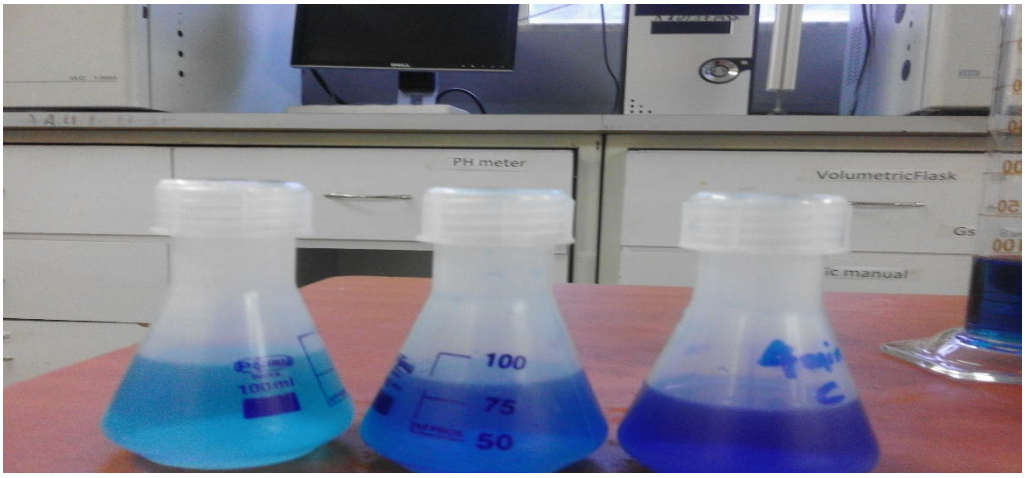
Drying





Annex *2.* UV-VIS Absorbance picture and measurement

Concentration of methylene blue	Absorbance before treatment	K * abs	Absorbance After treatment	K * abs
50 PPM	1.529	15.295	0.722	7.216
100 PPM	2.318	23.183	1.486	14.865
150 PPM	2.290	22.895	2.082	20.818



Percentage Removal and Adsorption Capacity Calculations

$\%\ MB\ removal = \frac{Co-C1}{Co} * 100$, removal efficacy

$\%$ MB removal of 50 ppm $= \frac{1.529-0.722}{1.529} * 100$

= 52.77 %

% MB removal of 100 ppm = 35.89 %

% MB removal of 150 ppm = 9.08 %

$qe = \frac{Co-Ce}{m} * V$, adsorption capacity (V = 100 ml and m = 0.1g)

qe at 50 ppm = $\frac{1.529-0.729}{0.1} * 100$

qe at 50 ppm = 800 ppm

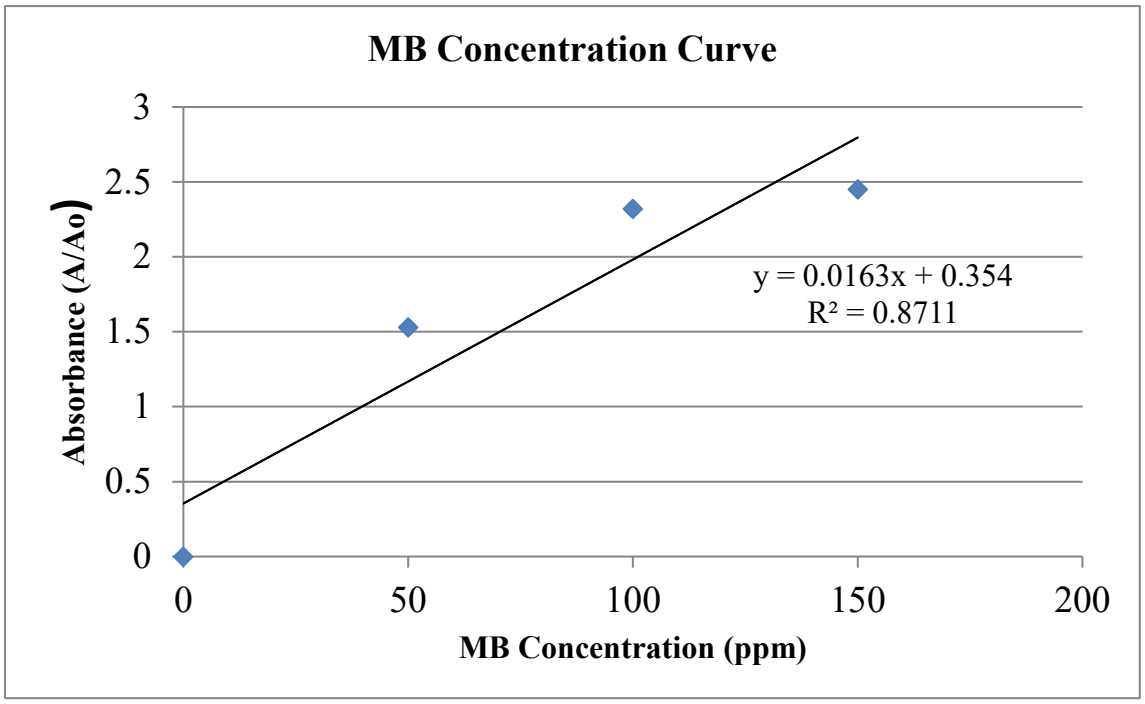
qe at 100 ppm = $\frac{2.318-1.486}{0.1} * 100$

qe at 100 ppm = 832 ppm

qe at 150 ppm = $\frac{2.290-2.082}{0.1} * 100$

qe at 150 ppm = 208 ppm

Calibration curve



50 MB concentration

% MB removal of = $\frac{50-22.58}{50} * 100$

= 54.84 %

q (mg/g) = $\frac{50 - 22.58}{0.1\ g} * 0.05L$

= 13.71 mg/g

100 MB concentration

% MB removal of = $\frac{100 - 69.45}{100} * 100$

= 30.55 %

q (mg/g) = $\frac{100 - 69.45}{0.1\ g} * 0.05L$

= 15.275 mg/g

150 MB concentration

% MB removal of = $\frac{150 - 106.01}{150} * 100$

% MB removal of = 29.33 %

q (mg/g) = $\frac{150 - 106.01}{0.1\ g} * 0.05\ L$

= 21.995 mg/g

Annex 3. BET result of activated corn cob for particle size of 1-2mm diameter

Quantachrome Novawin - Data Acquisition and Reduction
for NOVA instruments
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version 11.0

Analysis Report
Operator: 16512251783 Date:2018/09/17 Operator :16512251783 Date :07/01/2011
Sample ID: 08 Filename: c:\QCdata\physisorb\Etsegenet.qps
Sample Desc: Corn cob activated carbon ps(1-2 mm) Comment:
Sample weight: 0.087 g Sample volume: 0cc
Outgas Time: 6.5 hrs Outgas Temp: 300 ^{0} C
Analysis gas: Nitrogen Batch Temp: 77.35 K
Press. Tolerance:0.100/0.100 (ads/des) Equil time: 60/60 sec (ads/des) Equil timeout: 240/240 sec (ads/des)
Analysis Time: 54.7 min End of run: 2018/09/17 09:37:38 Instrument: Nova station
Cell ID: 0 F/w version: 0.00
Adsorbate Nitrogen Temperature 77. 350K
MoIec. wt.: 28.013 g Cross section: 16.200 A^2 Liquid Density: 0.808 g/cc

Surface Area Data

Multipoint BET	3.312e+00 m^2/g
Langmuir surface area	3.814e+00 m^2/g

Pore volume Data

SF method cumulative pore volume	1.757e-03 cc/g

Pore size Data

HK method pore Radius (Mode)	7.162e+00 Å
SF method pore Radius (Mode)	1.255e+01 Å

Annex *4.* Analysis of variance Tables (Effects of pH, activated carbon dosage and time)

Annex 4-1

Response: COD

ANOVA for Response Surface Linear Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	23766.03	3	7922.01	13.58	0.0003	significant
A	*21155.06*	*1*	*21155.06*	*36.26*	*< 0.0001*	
B	*1645.51*	*1*	*1645.51*	*2.82*	*0.1169*	
C	*17.12*	*1*	*17.12*	*0.029*	*0.8666*	
Residual	7584.21	13	583.40			
Cor Total	31350.24	16				

The Model F-value of 13.58 implies the model is significant. There is only a 0.03% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Annex 4.2

Response: BOD5

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	945.37	9	105.04	9.91	0.0032	significant
A	*650.02*	*1*	*650.02*	*61.31*	*0.0001*	
B	*0.48*	*1*	*0.48*	*0.046*	*0.8370*	
C	*0.61*	*1*	*0.61*	*0.058*	*0.8167*	
A^2	*318.49*	*1*	*318.49*	*30.04*	*0.0009*	
B^2	*10.34*	*1*	*10.34*	*0.98*	*0.3563*	
C^2	*2.08*	*1*	*2.08*	*0.20*	*0.6715*	
AB	*16.39*	*1*	*16.39*	*1.55*	*0.2538*	
AC	*2.93*	*1*	*2.93*	*0.28*	*0.6151*	
BC	*4.63*	*1*	*4.63*	*0.44*	*0.5298*	
Residual	74.22	7	10.60			
Cor Total	1019.59	16				

The Model F-value of 9.91 implies the model is significant. There is only a 0.32% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, A^2 are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Annex 4.3

Response: Trbudity

ANOVA for Response Surface Quadratic Model

Analysis of variance table [Partial sum of squares]

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	65484.47	9	7276.05	24.35	0.0002	significant
A	*58095.35*	*1*	*58095.35*	*194.45*	*< 0.0001*	
B	*617.63*	*1*	*617.63*	*2.07*	*0.1936*	
C	*4.63*	*1*	*4.63*	*0.015*	*0.9045*	
A^2	*6065.13*	*1*	*6065.13*	*20.30*	*0.0028*	
B^2	*495.60*	*1*	*495.60*	*1.66*	*0.2387*	
C^2	*23.64*	*1*	*23.64*	*0.079*	*0.7866*	
AB	*5.99*	*1*	*5.99*	*0.020*	*0.8914*	
AC	*0.73*	*1*	*0.73*	*2.443E-003*	*0.9620*	
BC	*3.65*	*1*	*3.65*	*0.012*	*0.9151*	
Residual	2091.35	7	298.76			
Cor Total	67575.82	16				

The Model F-value of 24.35 implies the model is significant. There is only a 0.02% chance that a "Model F-Value" this large could occur due to noise.

Values of "Prob > F" less than 0.0500 indicate model terms are significant.
In this case A, A^2 are significant model terms.
Values greater than 0.1000 indicate the model terms are not significant.
If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model.

Appendix 5. Different standard tables of treated grey water for reuse purpose

Table 5.1 FAO guidelines for interpretation of water quality for irrigation

Potential irrigation problem	**Units**	**Degree of restriction on use**		
		None	Slight to moderate	Severe
Salinity (affects crop water availability) EC (or)	ds/m	<0.7	0.7-3.0	>3.0
TDS	mg/L	<450	450-2000	>2000

Sources: Food and Agriculture Organization. Water quality for agriculture. Irrigation and Draina ge Paper 29 Rev. 1, 1985. Adapted from University of California Committee of Consultants 197 4.

Table 5.2 the permitted limit for greywater reuse according to the use type

Test	Permitted limit		
	(A) Irrigation of ornamental fruit trees and fodder corps	**(B) Irrigation of vegetables likely to be eaten uncooked**	**(C) Toilet flushing**
BOD_5 (mg/l)	≤ 240	≤ 20	≤ 10
Sample number	Sample/month	Two samples/momth	Sample/week
TSS (mg/l)	≤ 140	≤ 20	≤ 10
Sample number	Sample/month	Two samples/month	Sample/week
Thermotolerant coliforms (cfu/100 ml)	≤ 1000	≤ 200	≤ 10
Sample number	Two samples/month	Sample/two weeks	Sample/week

Source: Report on the WHO/AFESD regional consultation to review national priorities and actio n plans for wastewater reuse and management (WHO-EM/CEH/106/E).

Table 5.3 Jordanian standard (JS: 893/2002) for discharge to streams, storage

Parameter	***Unit***	***Discharge to streams, wadis and water storage areas***	***Ground water recharge***
BOD5	mg/l	60.0	15.0
COD	mg/l	150	50
DO	mg/l	>1.0	>2.0
TSS	mg/l	60.0	50.0
pH	unit	6.0-9.0	6.0-9.0
Turbidity	NTU	-	2.0
NO3	mg/l	45.0	30.0
NH3	mg/l	-	5.0
T-N	mg/l	70.0	45.0
E.coli	MPN/100 ml	1000.0	< 2.2
Intestinal helminth eggs	egg/l	≤ 1.0	≤ 1.0
FOG	mg/l	8.0	-

Table 5.4 Treated wastewater criteria for reuse in Kuwait

Parameter	Maximum allowable
pH	6.5-8.5
BOD (5 day, at 20^0C)	20
COD	100
TSS	15
TDS	1500
Total PO_4	30
NH_3-N	15
Total Kjeldahl nitrogen	35
F	25
S	0.1
Cl_2	0.5-1.0

Source: Decree No. (210), 2001.

Table 5.5 Further tests of raw grey water and treated water (at factors of pH 6.5, time 60 min and activated carbon dosage 0.35 g) in mg/L.

No.	Test types	symbols	Treated water	Raw grey water
1.	Aluminum	$Al(Al_2O_3)$	0.017	0.879
2.	Boron	$B(H_3BO_3)$	0	1.18
3.	Bromine	Br_2	0.07	2.38
4.	Chlorine Dioxide	ClO_2	0	2.38
5.	Chlorine Total	Cl_2	0	1.10
6.	Color	Pt Co	3	550
7.	Cyanide	CN	0	0.097
8.	Cyanuric Acid	CYACD	0	30
9.	Detergents	LAS	0	0.121
10	Hardness, Calcium	$CaCO_3$ (Ca)	0.07	3.96
11	Hardness, Magnesium	$CaCO_3$ (Mg,$MgCO_3$)	0	1.88
12	Hydrazine	N_2H_4	17	539
13	Immunoassay, TPH in water	-	0.017	0.780
14	Iron total, TPTZ	Fe	0	0.61
15	Manganese	Mn (MnO_4, $KMnO_4$)	0	8.3
16	Ozone	O_3	0	0.84
17	Silica	SiO_2	0.9	22
18	Sulfate	SO_4	1	36
19	Sulfide	S	0	0.44
20	Triazole, Benzotriazole	BENZO (TOLY)	0	17.6
21	Tannin and lignin	Tanic	0	3.8
22	Toxicity	Toxic	0.004	0.415 (at ƛ=610nm)
23	Volatile Acids	HOAc	0	1877