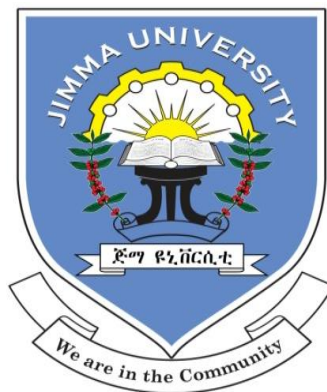


JIMMA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
DEPARTMENT OF CHEMISTRY



THESIS ON
DETERMINATION AND REMOVAL OF PHENOLIC COMPOUNDS
FROM DRINKING WATER OF JIMMA TOWN BY USING AVOCADO
***KERNEL SEED* ADSORBENTS**

OCTOBER, 2014

JIMMA, ETHIOPIA

**DETERMINATION AND REMOVAL OF PHENOLIC COMPOUNDS
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KERNEL SEED ADSORBENTS**

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Abbreviations and Acronyms

FMoH: - Federal Ministry of Health of Ethiopia

2CP:- 2- chlorophenol

2, 4- DCP: - 2, 4-Dichlorophenol

2, 4, 6-TCP: - 2, 4, 6-trichlorophenol

USEPA:-United State Environmental Protection Agency

BIS: - Bureau of Indian Standard

WHO: - World Health Organization

4AAP:- 4-Aminoantipyridine

AC-1: Activated Carbon prepared from avocado kernel seed treated by 43% K_2CO_3 solution

AC-2:- Activated Carbon prepared from Avocado kernel seed treated by 2N HCl

ES: - Specification of Ethiopian standard

UW: - Untreated Water

TW: - Treated Water

SDW: - System Distributed Water

FT-IR: - Fourier Transform Infra Red

NSD: - Normal Standard Deviation

ARE: - Average Relative Error

ABSTRACT

Phenolic compounds are a versatile precursor to a large collection of drugs most notably aspirin, various herbicides and pharmaceuticals. However, these compounds are considered as priority pollutants since they are harmful to organisms' especially human and aquatic life, it is toxic when present in elevated levels and to be carcinogens. Therefore, removing phenols and their derivative from drinking water is an essential task to safe the water. Thus, the objective of this study was to determine the level of phenolic compounds and compare the adsorption capacity of both AC-1 and AC-2 prepared from avocado kernel seeds by adsorption onto drinking water in Jimma town. For adsorption process cleaned and washed avocado kernel seeds(*per sea americana*) were dried at 100 °c in an oven overnight and carbonization was carried out by increasing the furnace temperature at a rate of 5 °C/min to a final temperature of 800 °C for 160 minutes. Then, the activated carbon was sieved, washed with distilled water until the solution pH reached 7.0. Optimization of activated carbon was done through effects of solution pH, contact time; initial phenol concentration and temperature on the adsorption. From the analysis of water using 4-Aminoantipyrine (4-AAP), it was found that treated and system distributed water has more phenolic compounds as compared to untreated water due to the presence of chlorination after disinfection. The kinetic studies for the adsorption process were also carried out by checking various models and the data obtained was best fitted to pseudo-second order kinetic model. The isotherms models were analyzed with Langmuir, Freundlich and Temkin to validate the adsorption process. It was found that Langmuir model was best fitted to the obtained result for both adsorbents. Thermodynamic parameters were calculated for adsorption process and the result showed that the values of ΔG , ΔH , and ΔS are - 13.6 kJ/mol, - 69.36 kJ/mol and - 181.04 J/K at 303 K. Thus, it could be summarized that the adsorption of phenol compounds are spontaneous, chemisorbed, monolayer and exothermic on activated carbon prepared from avocado kernel seeds.

Key words: Chemisorbed, monolayer, carbonization, activated carbon, adsorption, raw water, system distributed water.

1. INTRODUCTION

1.1. Back ground of the study

In the current scenario several acute global issues came up like, global warming, fresh water crisis, environmental pollution, dreadful diseases, etc. However the fresh water crises among all these are crucial since in day to day life we need water for our survival. In Ethiopia, the quality of drinking water is a powerful environmental determinant of health. Water can serves as a medium for disease transmission in countries on all continents which affected from the poorest to the wealthiest. Moreover, millions of people are exposed to unsafe concentration of chemical contaminants in their drinking water, this contamination linked to organic compounds such as phenol which causes carcinogenic (FMoH, 2012). The industrial and domestic activities have polluted the surface water as well as ground water to a greater extent¹. In order to deal with the problem we need to treat the waste water and reuse it instead of leaving that as such. Among the various organic and inorganic pollutants there is a common organic pollutant existed named as Phenol.²

Organic pollution is the term used when large quantities of organic compounds exist in the environment. It originates from domestic sewage, urban run-off, industrial effluents and agriculture wastewater. During the decomposition process of organic pollutants the dissolved oxygen in the receiving water consumed at a greater rate than it can be replenished, causing oxygen depletion and having severe consequences for the stream biota. Wastewater with organic pollutants contains large quantities of suspended solids which reduce the light available to photosynthetic organisms and, on settling out, alter the characteristics of the river bed, rendering it an unsuitable habitat for many invertebrates. These Organic pollutants include pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, greases, pharmaceuticals, proteins and carbohydrates.³⁻⁵

Phenolic compounds which are generated from petroleum and petrochemical, coal conversion and phenol producing industries are common contaminants in wastewater. Phenols and its derivatives are widely used for the commercial production of a wide variety of resins including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives, and polyamide for various applications.^{6,7} Phenols and phenolic compounds are considered as priority pollutants since they are harmful to organisms especially human and also to aquatic life, at low concentrations and can be toxic when present in elevated levels and are known or suspected to be carcinogens.⁸ Phenol decomposition is difficult due to its stability and its solubility in water. It has a strong and unpleasant smell which makes the contaminated water totally unusable.⁹ Phenolic compound finds its way in to the environment through industrial effluents and is found in very high

amounts in several industrial effluents, which makes its removal must. The amount of phenol derivatives present in different sources is mentioned in table 1 as follows.

Table 1: Amount of phenol derivatives present in various industrial effluents.²

Industry	Amount of phenol derivative (ppm)
Refineries	6-500
Coal processing	9-6800
Coking	28-3900
Petrochemical manufacturing	2.8-1220

Among a total of nineteen possible chlorinated phenol existed, only 2-chlorophenol (2CP), 2, 4-dichlorophenol (2, 4-DCP), and 2, 4, 6-trichlorophenol (2, 4, 6-TCP) are found in drinking water as possible by product of disinfection. These chlorophenols generally have very low organoleptic thresholds. The taste threshold in water for 2CP, 2,4DCP and 2, 4, 6-TCP are 0.1, 0.3, and 0.2 µg/liter respectively and Odor thresholds 10, 40, and 300 µg/liter respectively. Increasing concern for public health and environmental quality has led to the establishment of rigid limits on the acceptable environmental levels of particular pollutants. Due to the toxic nature of phenolic compounds several regulatory bodies all over the world like the Ministry of Environment and Forests (MOEF) of Government of India and EPA, USEPA have listed phenol and phenolic compounds on the priority pollutants list and also have proposed maximum permissible limits of phenol derivatives in different categories of water and the detailed values of phenolic compounds in different source of water which is mentioned in table 2. Phenol derivatives are being highly toxic and difficult to degrade biologically, it has led to setting up of rigid limits on the acceptable level of phenol in the environment.

Table 2: Maximum permissible limit of phenolic compounds in water

Agency	Type of water	Maximum permissible limit	Reference
USEPA	Drinking water	0.5 ppm	10
BIS	Drinking water	1.0 ppb	10
WHO	Drinking water	1.0 ppb	10, 11
MOEF	Industrial effluent	1.0 ppm	11, 12
ES*	Drinking water	2 ppb	(FMOH,2012)

ES* =Ethiopian Standard Specification of Toxic Chemicals.

The water solubility of chlorophenols is low, in the presence of chlorine in drinking water; phenols form chlorophenol, which has a medicinal taste that is quite pronounced, and objectionable¹³⁻¹⁵. Chlorine substitution on phenols does not only increase water taste and odor, but also its toxicity effects.¹⁶ Residues of chlorophenol have been found worldwide in soil, water, air sample, food products, human, animal tissues and body fluids. Due to their slow degradation, chlorophenol represent a major threat to ecosystems.¹⁷ Chronic toxic effects due to phenolic compounds reported in humans include vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, fainting and other mental disturbance.¹⁸ The toxicity levels usually range between the concentrations of 10-24 mg/L for human and 9-25 mg/L for fish. In addition to this, the lethal blood concentration of phenol is around 1500 mg/L. Since it is harmful compound there is a necessity for its removal in order to preserve the environmental quality, thus as recent studies shown that biotic and abiotic processes can degrade phenol.¹⁹

Various physical and chemical techniques, like coagulation, chemical oxidation, froth floatation, oxidation or ozonation, membrane separation, solvent extraction and adsorption processes have been used by a number of researchers for the removal of organics as well as inorganic from the wastewater; however, these processes are effective and economic, only in the case where the solute concentrations are relatively high.²⁰ Also, these treatments involve high operational cost and aerobic digestion. For instance, photo-catalytic degradation processes have shown considerable success in the removal of organic dyes from wastewater.²¹ However, there are certain shortcomings. Coagulation process produces large amount of sludge leading to high disposal costs. Ion-exchange process has no loss of adsorbent on regeneration; however, it cannot accommodate wide range of dyes and is expensive. Membrane separation process is also effective in the removal of dyes; however, due to relatively high investment and membrane fouling problem, its application is restricted as there is a wide range in pH of dyes and even the conventional biological methods are not effective to treat dye bearing wastewaters.²²

Adsorption has been found to be a superior technique as compared to other methods of waste treatment in terms of cost, simplicity of design and operation, availability, effectiveness, and their insensitivity to toxic substances^{23, 24}. The more recent methods for the removal of organic pollutants from potable water and wastewater were compiled and reported in the form of review article.²⁵ Adsorption is a physiochemical wastewater treatment in which dissolved molecules are attached to the surface of an adsorbent by physical/chemical forces. Depending on the nature of the interactions ionic species and molecular species carrying different functional groups held to the surface through electrostatic attraction to sites of opposite charge at the surface or physisorbed due to action of van

der Waals forces or chemisorbed involving strong adsorbate–adsorbent bonding. So, it leads to attachment of adsorbate molecules at specific functional group on adsorbent surface. It is true that choice of adsorbent plays a very important role.²⁶ This technique is quite popular due to the availability of a wide range of adsorbents, and it proved to be an effective and attractive process for the removal of non-biodegradable pollutants (including dyes and phenolic compounds) from wastewater.^{27, 28}

Activated carbon is one of the most effective adsorbents for organic compounds because of their extended surface area, high adsorption capacity, micro porous structure and special surface reactivity.²⁹ This occurs in pores slightly larger than the molecules that are being adsorbed, which is why it is very important to match the pore size of the activated carbon with the molecules we are trying to adsorb. Activated carbon is a form of carbon that has been processed with oxygen to create millions of tiny pores between the carbon atoms. This increases the surface area of the substance from 500 to 1500m²/g.³⁰ Traditionally, the activated carbons used in wastewater treatment are obtained from coal or lignite, wood or animal bones but, recently there is growing interest in the use of alternative and low-cost precursors for their production.³¹ Specifically, lignocelluloses wastes are a low cost natural carbon source for the synthesis of several materials including the production of activated carbons. In this context ,it is convenient to remark the natural products play a dominant role in the economic activities and utilization of lignocelluloses wastes for synthesis of valuable commercial products contribute to the economic development and to prevent environment pollution in developing countries.³² Therefore, lignocelluloses' materials are considered as an interesting and important natural resource for production of activated carbons based on the fact that several billion tons of these materials are available.^{31, 32} Actually, these precursors are considered as the most appropriate candidates for a cost-effective preparation of activated carbons.³³ This study, avocado kernel seeds raw material was used in preparing activated carbon to remove phenolic compounds from drinking water using K₂CO₃ and HCl as the activating agents. Recently, activated carbons with large specific surface area are produced by chemical activation using KOH as activation reagent.³⁴ However, in order to get large specific surface area, a large amount of KOH, which is strong reagent, has to be used and the activated carbon is produced under the very severe condition. In order to produce the activated carbon under the safe condition, K₂CO₃ and HCl are used, which are not needed in large quantity as compared to KOH as activation reagent.³⁵ Moreover, KOH activation toward carbon materials produce slightly slower surface area of 917 m²/g than K₂CO₃ activation of carbon material produce a surface area of 1104 m²/g. Therefore, that activation of avocado kernel seeds by K₂CO₃ and HCl was more preferred over activation of KOH due to producing the higher surface area

for adsorption.³⁵ To our best knowledge, there is no research document available that has been done on the removal of phenolic compounds particularly in Jimma town water treatment plant by using Activated carbon prepared from Avocado kernel seeds. Hence, this study was conducted to increase the characteristics adsorption of phenolic compounds from drinking and aqueous solution using both K_2CO_3 and HCl as activating agent and was also compared the adsorption capacity of activated carbons based on solution pH, contact time, initial concentration of adsorbate, adsorbent doses and temperature effect. Finally, adsorption isotherm, kinetics and thermodynamics parameters of phenolic compounds were evaluated.

1.2. Statement of the Problems

Phenols and their derivatives are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been grouped as hazardous pollutants because of their potential to harm human health even in low concentration. They have been discharged into the environment as industrial wastes as mining, textile; petro-chemical, tannery, agro-chemical byproducts and painting among others contaminate natural waters.³⁶ Nowadays to mitigate these toxic organic pollutants researchers' devised different conventional and advanced methods such as chemical precipitation and sludge separation, chemical oxidation or reduction, ion exchange, reverse osmosis, membrane separation, electrochemical treatment and evaporation.³⁷ However, these methods face drawbacks as cost incompatibility, sludge production, removal inefficiency. Thus, the searches for low-cost adsorbents activated carbon prepared from avocado kernel seeds (*Per sea americana*) have been selected due to higher surface area for adsorption capacities were investigated. Agricultural by-products have been widely studied for phenolic compounds removal from drinking water. Therefore, removing phenols and derivative of phenolic compounds from drinking water is an essential task to safe the drinking water. This research has given answers for the following questions.

- How much amount of phenolic compounds in the drinking water at Jimma town and nearby areas could be found?
- What is the efficiency of activated carbon prepared from Avocado kernel seeds to remove phenolic compounds from drinking water?
- What kind of adsorption isotherm, kinetics and thermodynamics responsible for adsorption of phenolic compounds onto activated carbon prepared from avocado kernel seeds?

1.3. Objectives of the Study

1.3.1. General Objectives

- To assess the level of phenolic compounds and evaluate the potential of activated carbon treated by K_2CO_3 and HCl onto avocado kernel seeds and their adsorption on the drinking water of Jimma town.

1.3.2. Specific Objectives

- To determine the level of phenolic compounds from drinking water of Jimma town.
- To prepare activated carbon from avocado kernel seed through chemical activation.
- To determine the appropriate adsorption kinetics and isotherm models.
- To describe the thermodynamics feasibility of adsorption for removal of phenolic compounds from drinking water and aqueous solution.

1.4. Significance of the Study

Phenolic compounds are one of the most common groups of priority contaminants because they are not readily biodegradable and are highly toxic, causing problems with the human respiratory and nervous system. Phenol is a primary reagent used in synthesis of a variety of highly chlorinated phenols and pesticides. Chlorophenols which are commonly found in drinking water as disinfection by products constitute an important family of pollutants of wastewater production by chemical, petrochemical and food processing industries. Phenols and Chlorophenol are considered as toxic and carcinogenic when the amount of it above the limited concentration(2 ppb, according to Ethiopian standard) in tap water.³⁸ Thus, removing phenolic compounds from the drinking water by adsorption through activated carbon from avocado kernel seed is an economically feasible because of their relatively low investment and operational cost and environmentally friendly that is an important prior task to treat wastewater before discharging in to the environment. Moreover, the advantage of this study is to use the unwanted avocado kernel seeds for water treatment in Jimma town.

2. LITERATURE REVIEW

2.1. Phenol

Phenols are the key for production of polycarbonates, epoxies, Bakelite, nylon, detergents and a large collection of drugs, herbicides and pharmaceuticals³⁹. Chemically it is slightly acidic: the phenol molecules have weak tendencies to lose the H⁺ ion from the hydroxyl group, resulting in the highly water-soluble phenolate anion C₆H₅O⁻ (also called phenoxide). Compared to aliphatic alcohols, phenol is about 1 million times more acidic, although it is still considered a weak acid and it reacts completely with aqueous NaOH to lose H⁺, whereas most alcohols react only partially, and also less acidic than carboxylic acid and even carbonic acid³⁹. The major uses of phenol, are consuming two thirds of its production, involve its conversion to plastics or related materials. It is also used as an oral anaesthetic/analgesic, commonly used to temporarily treat pharyngitis. Phenol injections were used as a means of individual execution by the Nazis during the Second World War⁴⁰. The health hazards caused by phenol are given in tabular form as mentioned in table 3, which affected the nasal cavity, eye, mouth and skin of human beings.

Table 3: Health hazards caused by phenolic compounds.⁴⁰

Exposure mode	Effects due to exposure
Inhalation	<ul style="list-style-type: none">• Can irritate the nose, throat, and lungs.• Higher exposures may cause a build-up of fluid in the lungs.
Oral	<ul style="list-style-type: none">• Ingestion of as little as 1 gram can be fatal to humans.
Eyes	<ul style="list-style-type: none">• Can also cause severe eye damage, including blindness
Skin	<ul style="list-style-type: none">• Irritating and corrosive to the skin.• Little or no pain may be felt on initial contact due to its local anesthetic effect.• Skin contact will cause the skin to turn white; later severe burns may develop.• Rapidly absorbed through the skin; toxic or fatal amounts can be absorbed through relatively small areas.
Chronic exposure	<ul style="list-style-type: none">• Repeated or prolonged exposure to phenol or its vapors may cause headache, nausea, dizziness, difficulty swallowing, diarrhea or vomiting.• Can affect the central nervous system, liver and kidneys.

2.2. Adsorption

Adsorption is the phenomenon of concentration or assimilation of gas (or liquid) at the surface of a solid (or liquid) with which it is in close proximity or contact. It arises as a result of the unsaturated and unbalanced molecular forces that are present on every solid surface. Thus, when a solid surface is brought into contact with a liquid or gas, there is an interaction between the fields of forces of the surface and that of the liquid or the gas. The solid surface tends to satisfy these residual forces by attracting and retaining on its surface of the molecules, atoms, or ions of the gas or liquid, adsorption is associated with decrease in residual surface energy. The molecules which are adsorbed are called adsorbates and the surface is called as adsorbent. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. The process of adsorption of gases into the solid surface is called occlusion. Depending upon the nature of the forces involved, the adsorption is of two types: physical adsorption and chemisorption. In the case of physical adsorption, the adsorbate is bound to the surface by relatively weak van der Waals forces, which are similar to the molecular forces of cohesion and are involved in the condensation of vapors into liquids. Chemisorption, on the other hand, involves exchange or sharing of electrons between the adsorbate molecules and the surface of the adsorbent resulting in a chemical reaction. The bond formed between the adsorbate and the adsorbent is essentially a chemical bond and is thus much stronger than in the physisorption. Physisorption and chemisorption again differ from each other due to following two differences namely, magnitude of the enthalpy of adsorption, in physical adsorption the enthalpy of adsorption is of the same order as the heat of liquefaction and does not usually exceed 10 to 20 KJ/mol., whereas in chemisorption the enthalpy change is generally of the order of 40 to 400 kJ/mol. Taking into account specificity physical adsorption is nonspecific and occurs between any adsorbate-adsorbent systems, but chemisorption is specific. Another important point of difference between physisorption and chemisorption is the thickness of the adsorbed phase although it is multi-molecular in physisorption and is uni-molecular in chemisorptions.⁴¹ The reverse process of adsorption is called desorption in which the adsorbed substances are removed from the surface. By nature adsorption is exothermic, the amount of heat evolved when one mole of any molecule is adsorbed on a solid adsorbent surface is called enthalpy (or heat) of adsorption.⁴² In figure 1 the common difference between adsorption and desorption process is mentioned as well.

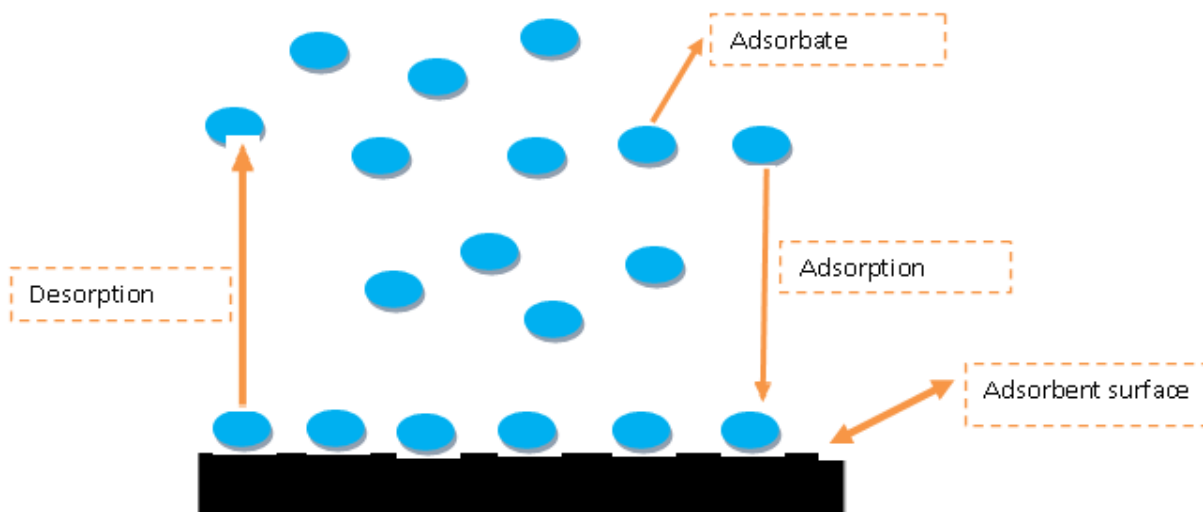


Figure1: Adsorption and Desorption Process

2.3. Activated Carbon

Activated carbon is a porous material which is commercially used for the removal of liquids and gaseous pollutants as well for the gas storage application because of its large surface area. It is carbonaceous adsorbent and has highly amorphous structure³⁹. There have been quite a number of researches that has been done to utilize agricultural waste as activated carbon. Most of the produced activated carbon came from plant and fruit residue, seashell and wood. Furthermore, natural adsorbent from clay mineral has been discovered to be one of the potential adsorbent. Activated carbon with high surface area and pore volume can be prepared with any carbonaceous material such as almond shell⁴³, avocado kernel seeds⁴⁴ bamboo charcoal⁴⁵ and plum stones.⁴⁶ Activated carbons are produced by two methods: physical activation and chemical activation. In physical activation, the raw material is carbonized and subsequently is gasified by CO₂⁴⁷ or steam.⁴⁸ and in chemical⁴⁹ activation, the raw material is impregnated with activation reagent such as H₃PO₄⁵⁰ and ZnCl₂⁵¹ and the impregnated raw material is carbonized. Recently, there has been an increasing trend towards the preparation of activated carbon from agricultural by-products as these materials are high quality and inexpensive sources of activated carbon.⁵² Previous studies have found that the oil palm shell contains high levels of carbon and low levels of ash, making it a good raw material for preparing activated carbon as an adsorbent. In addition to being economical, this use helps reducing environmental wastage.⁵³

A variety of treatments have been used previously to eliminate phenolic compounds from drinking water, including catalytic wet oxidation, photochemical and biological treatment methods. Adsorption

onto activated carbon also shows promising potential as an effective method for removing phenolic compounds.^{54, 55} Activated carbons are used in a number of industrial applications including separation and purification technologies, catalytic processes, biomedical engineering, and energy storage, among others. The extensive application of activated carbon is mainly due to its relatively low-cost with respect to other adsorbents, wide availability, high performance in adsorption processes, surface reactivity and the versatility to modify its physical and chemical properties for synthesizing adsorbents with very specific characteristics.⁵⁶ In particular, the adsorption on activated carbon is the most used method for drinking water treatment because it is considered a low-cost purification process where trace amounts of several pollutants can be effectively removed from drinking water. Recently, the demand of activated carbons has increased significantly as a water-purifying agent to reduce the environmental risks caused by the water pollution worldwide.^{57, 58} Activated carbons have their well-developed porosity and large surface area. Therefore, they are used as not only adsorbent, but also catalyst and catalyst support.⁵⁹

There are several factors on which the effectiveness of adsorption process depends upon these adsorption conditions which may either be the nature of the adsorbent (acidic/ basic) or the characteristics of adsorbent which includes the high surface area, pore size distribution, ash content and hydrophobicity. These characteristics defined the concentration of carbon atoms in the matrix, and the density and type of functional groups present on the surface⁶⁰. On the other hand, adsorption also depends on the nature of the adsorbate, hydrophobicity, polarity, and size of the molecule⁶¹.

There are several agricultural and biomass waste materials such as waste apple pulp, straw, coconut shell, coir pith, saw dust, apricot stone shell, olive stones, sugarcane bagasse peanut hull, water hyacinth roots and many others have been employed to produce activated carbons with high surface area⁶².

2.4. Phenolic compounds Adsorption by Different Adsorbents with the Emphasis on Activated Carbons

Liquid phase adsorption has been shown to be a highly efficient, well-established technique for the removal of organic compounds due to its simplicity, low adsorbent cost, effectiveness and the availability of a wide range of adsorbents. Adsorption by activated carbons (ACs) is one of the most frequently used methods to remove phenolic compounds from water, because ACs possesses perfect adsorption ability for that class of compounds because of their heterogeneous surface. Heterogeneous surface of activated carbon is consequence of both geometrical heterogeneity (porosity) as well as chemical one i.e. due to presence of several functional groups which act as the potential adsorption

sites⁶³. Combined calorimetric and adsorption techniques showed that in the case of phenol adsorption from either dilute or concentrated aqueous solutions, water is always adsorbed preferentially by the oxygen-containing surface groups of the carbon which reduces the surface and/or the micropore (<2 nm diameter) volume accessible to the phenol molecule and quantitatively explains the decrease in the limiting adsorption of phenol on a given carbon after oxidation. On the other hand, for concentrated solutions (15-25% of water), they had observed a process of micropore filling by phenol⁶⁴.

The adsorption capacity was slightly higher at low phenol concentration (≤ 1.6 g/L) than the one of activated carbon (surface area close to 1150 m²/g). Furthermore, siliceous zeolite appeared as an efficient adsorbent which was able to be easily regenerated keeping initial properties intact.⁶⁵

Cardenas and his co-workers had studied the adsorption of phenol and dichlorophenols (2, 5- DCP and 3, 4- DCP) from water by porous clay hetero-structure (PCH). Experiments were carried out for the analysis of adsorption equilibrium capacities using batch equilibrium technique. The Freundlich adsorption model was found to be the best to describe adsorption equilibrium data for dichlorophenols. The adsorption capacities showed by the PCH for both phenol and DCPs from water (48.7 mg/g for 3,4-DCP, 45.5 mg/g for 2,5-DCP and 14.5 mg/g for phenol), suggests that the PCH have both hydrophobic and hydrophilic characteristics due to the presence silanol and siloxane groups formed during the pillaring and preparation of the PCH⁶⁶.

For the adsorption equilibrium study also applied the well known Freundlich, Langmuir and Redlich-Peterson isotherm equations to the adsorption data and evaluated various isotherm parameters. The Langmuir monolayer adsorption capacities were found to be 0.7877 and 0.5936 mmol/g, for phenol and o-cresol respectively. Kinetic studies performed indicate that the sorption processes can be better represented by the pseudo-second order kinetics.⁶⁷

Shawabkeh and Abu-Nameh, had prepared the activated carbon by pre-treating the pecan shell with phosphoric acid followed by surface treatment with sodium dodecyl sulphate (an anionic surfactant) for the removal of phenol and methylene blue. For the phenol surfactant suppress the phenol removal efficiency. While on the other hand the maximum uptake of activated carbon for dye was 98 %. The sorption capacity of 410 mg/g was obtained at pH 9 and for phenol 18 mg/g at pH 11 for initial concentration 35 mg/l. They also have observed that moderate adsorption was obtained for phenol with a capacity of 18 mg/g at pH 11 and the same solution concentration. The increase or decrease in solution pH has a favorable effect on the sorption of both adsorbates⁶⁸.

The adsorption mechanism was discussed based on the experimental results, and the π - π interactions, solvent effects, hydrophobic interactions and molecular dimensions were considered to be important in the adsorption. Kinetic studies showed rapid adsorption kinetics of the phenols, due to the open

pore structure of the ACFs. The kinetics was fitted with the pseudo-first order, pseudo-second-order and intraparticle diffusion models. Steric effects on adsorption kinetics were observed for TCP, 4-NP and DNP, but serious impact on the ultimate uptake was only found for DNP. The relationship between the steric effects and the molecular dimension was also proposed ⁶⁹.

2.5. Adsorption Isotherm

In a solid–liquid system adsorption results in the removal solutes from solution and their accumulation at solid surface. The solute remaining in the solution reaches at a dynamic equilibrium with that adsorbed on the solid phase. The amount of adsorbate that can be taken up by an adsorbent as a function of both temperature and concentration of adsorbate, and the process, at constant temperature, can be described by an adsorption isotherm according to the general Eq. (1): in this study the extent of phenolic compounds adsorption capacity at equilibrium, q_e ($\mu\text{g/g}$), was calculated

$$q_e = \frac{(C_o - C_e) - V}{W} \text{-----(1)}$$

$$q_t = \frac{(C_o - C_t)V}{W} \text{-----(2)}$$

The percentage of phenolic compounds removal was calculated using Eq. (3):

$$\text{Removal}(\%) = \frac{C_o - C_e}{C_o} \times 100 \text{-----(3)}$$

C_o corresponds to the initial concentration of phenolic compounds, and C_e ($\mu\text{g/g}$) corresponds to the concentration of phenolic compounds at equilibrium. V (L) is the volume of the solution, and W (g) is the mass of the dry adsorbent.

2.5.1. Langmuir and Freundlich Isotherm

Taking into account that adsorption process can be more complex, several adsorption isotherms were proposed. Among these the most used models to describe the process in water and wastewater applications were developed by (i) Langmuir, (ii) Freundlich and Temkin isotherm model. In this study were applied the Langmuir, Freundlich and Temkin adsorption model. The Langmuir adsorption model is valid for single-layer adsorption, whereas the BET model represents isotherms showing apparent multilayer adsorption. So, when the limit of adsorption is a monolayer, the BET isotherms reduce to the Langmuir equation. Both equations are limited by the assumption of uniform

energies of adsorption on the surface. Sorption equilibrium provides fundamental physiochemical data for evaluating the applicability of sorption process as a unit operation. In order to facilitate the estimation of the adsorption capacities at various conditions, the Langmuir adsorption isotherm, a typical model for monolayer adsorption was applied. The Langmuir equation was modeled using the equation 4 below and its validity was checked by regression coefficient (R^2), normal standard deviation, (NSD), average relative error (ARE) and the probability of the model with experimental data.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \text{-----(4)}$$

Where C_e is the equilibrium concentration of solute in solution ($\mu\text{g/L}$), q_e is the amount of solute adsorbed at equilibrium ($\mu\text{g/g}$), q_m ($\mu\text{g/g}$) and K_L (L/ mg) are the Langmuir constants, and q_m signifies adsorption capacity and K_L is related to energy of adsorption process. A plot of C_e/q_e against C_e yields a straight line and q_m and K_L are obtained from the slope and intercept respectively.

The experimental equilibrium data was also analyzed using the Freundlich isotherm model and that was adopted to characterize the adsorption intensity of phenol and phenolic compounds by fitting the experimental data. The linearized form of the Freundlich was described by equation 5 as follows.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \text{-----(5)}$$

Where q_e is the adsorption density ($\mu\text{g/g}$), C_e is the concentration of the adsorbate in solution at equilibrium ($\mu\text{g/dm}^3$); K_F and $1/n$ are the Freundlich constants. If a plot of $\log q_e$ versus $\log C_e$ yields a straight line, then the sorption process obeys a Freundlich adsorption isotherm. The K_L and $1/n$ can be obtained from the intercept and slope of the straight line simultaneously.

2.5.2. Temkin Isotherm

The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The heat of sorption of all molecules in the layer would decrease linearly with coverage due to sorbate/sorbent interactions. The Temkin isotherm has generally been applied in the following equation 6⁷⁰ as follows.

$$q_e = \frac{2.303RT}{b_T} \log a_T + \frac{2.303RT}{b_T} \log C_e \text{-----(6)}$$

Where b_T is the Temkin constant related to heat of adsorption (Joules per mole), a_T is the Temkin isotherm constant (liters per gram), R is the gas constant (8.314 J/mol K), and T is the absolute temperature (K).

The validity and applicability of the isotherm models was confirmed by calculating the standard normal deviation (SND) and average relative error factor between the experimental data and the model estimates. These were then used to predict the adsorption behavior of phenol. The mathematical equation of SND and ARE is given below in equation 7 and 8.

$$NSD(\%) = 100 \sqrt{\frac{1}{N-1} \sum_i^n \left[\frac{q_{i, \text{exp}} - q_{i, \text{cal}}}{q_{i, \text{exp}}} \right]^2} \text{-----} (7)$$

$$ARE = \frac{100}{N} \sum_{i=1}^n \left| \frac{q_{i, \text{exp}} - q_{i, \text{cal}}}{q_{i, \text{exp}}} \right| \text{-----} (8)$$

Where $q_{i, \text{exp}}$ and $q_{i, \text{cal}}$ ($\mu\text{g/g}$) are experimental and calculated mass of the phenolic compounds adsorbed by AC-1 and AC-2 at a time t , and N is the number of measurements made. Smaller NSD and ARE values implies more accurate estimations.^{71, 72}

2.6. Adsorption Kinetic Studies

Designing batch adsorption systems is an important method to determine the rate at which equilibrium is established. Consequently, it was important to establish the time dependence of such systems under various process conditions in an attempt to understand the sorption process, various kinetic rate expression models have been applied to the experimental data in this study. The time dependent experimental data in this study was analyzed using three kinetic models namely, pseudo first order, pseudo second order, intra-particle diffusion models.

2.6.1. Pseudo –First Order

The linear form of the pseudo –first order is generally expressed as follows in equation 9:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \text{-----} (9)$$

Where q_e is the amount of phenol and phenolic compounds adsorbed at equilibrium ($\mu\text{g/g}$), q_t is the amount of phenolic compounds adsorbed at time t ($\mu\text{g/g}$), k_1 is the first order rate constant (min^{-1}) and t is time in min). The straight line plot of $\log(q_e - q_t)$ against time t , should give a linear relationship from which the pseudo first order rate constant (k_1) and equilibrium sorption capacity (q_e), can be calculated from the slope and intercept respectively.

2.6.2. Pseudo Second Order

The linear form of the kinetic rate expression for a pseudo second-order model was expressed by applied to the experimental data using (equation 10).⁷³

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{1}{q_e} t \quad \text{----- (10)}$$

Where q_t is the amount of phenolic compounds on the activated carbon surface ($\mu\text{g/g}$) at time t , q_e is the amount ($\mu\text{g/g}$) of phenolic compounds adsorbed at equilibrium, the initial sorption capacity ($\mu\text{g/min}$), h_o , is obtained as shown in equation (11).

$$h_o = k_2 q_e^2 \quad \text{----- (11)}$$

Where k_2 is the Pseudo-second order rate constant ($\text{L}/\mu\text{g}\cdot\text{min}$). The parameters h_o and k_2 are determined experimentally from the slope and intercept of a plot of t/q_t against t . In this case, t/q_t versus time, t was taken to obtain straight lines. From the slopes and intercepts of these plots, the pseudo-second order rate constants k_2 , the equilibrium sorption capacity q_e ($\mu\text{g/g}$) and the initial sorption capacity, h_o ($\mu\text{g/min}$) were computed.

2.6.3. Intra-Particle Diffusion

To investigate intra-particle diffusion was the sorption rate limiting step, intra-particle diffusion model was employed in equation 12 as follows.⁷⁴

$$q_t = k_{id} t^{0.5} + C \quad \text{----- (12)}$$

Where, k_{id} is the intra-particle diffusion rate constant ($\mu\text{g/g}\cdot\text{min}^{1/2}$), q_t ($\mu\text{g/g}$) is a constant and C that gives idea about the thickness of the boundary layer, i.e. the larger the value of C the greater boundary layer effect.⁷⁵ If the plot of q_t versus $t^{1/2}$ give straight line, then the sorption process was controlled by intra-particle diffusion only and slope gives the rate constant k_{id} . However, if the data exhibit multi-linear plots then two or more steps influenced the sorption process.

2.7. Thermodynamic Analysis of Experimental Data

Experimental data derived from the effect of temperature on the sorption process was analyzed using different equations which made it possible to determine some thermodynamic parameters such as Gibb's free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS). The adsorption equilibrium constant K_o was estimated from the expression of equation 13.

$$K_o = \frac{C_o}{C_e} \text{----- (13)}$$

The thermodynamic parameters were determined according to equations (14 and 15) as given below

$$\Delta G^o = -RT \ln K_o \text{----- (14)}$$

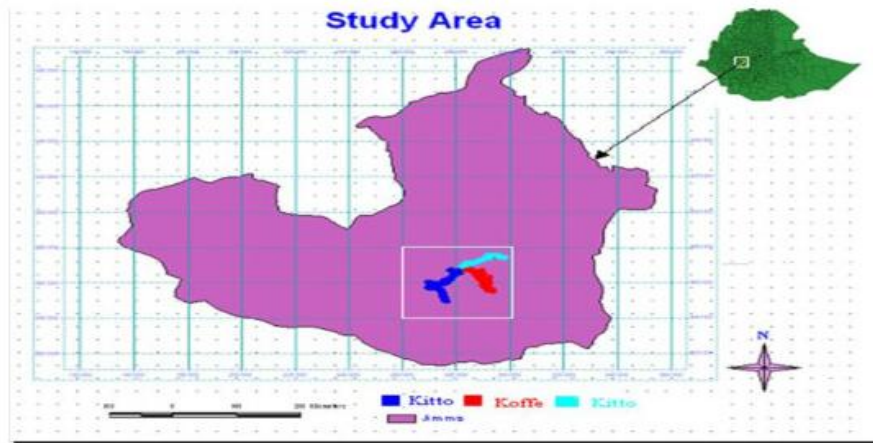
$$\ln K_o = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \text{----- (15)}$$

The values of ΔH and ΔS are calculated from the slope and intercept of the linear plot of $\ln K_o$ against reciprocal of temperature ($1/T$).

3. MATERIALS AND METHODS

3.1. Study Area

The study was conducted at Jimma town, located 350 Km south-west of Addis Ababa. The town's geographical coordinates are 7 ° 41'N latitude and 36 ° 50' longitude. The town is found at an average altitude of about 1780 m above sea level. It lies in the climate zone locally known as “woyna Daga” (1500-2400m above sea level) which is considered as ideal for agriculture as well as human settlement. The town is generally characterized by warm climate with a mean annual maximum temperature of 30 °C and minimum temperature of 14 °c. The annual rainfall ranges from 1138-1690mm.



Source: Alemu *et al*, malaria journal 2011,10:173

Figure2: Study Area of Jimma Town taken from Ethiopia Map

3.2. Sample Collection and Preservation

The study samples of activated carbon and water were collected from Jimma town cafeterias and Jimma town water treatment plant. The number of water samples collected were 28 which were 8 for untreated water, 8 for treated water and 12 samples are for system distributed water. Water samples were preserved and stored by acidifying to pH 4 with H_3PO_4 under cool environment (5 °C) and 1 g $CuSO_4 \cdot 5H_2O/L$ was added for the sample to inhibit biological degradation. The preserved samples were analyzed within 24 hours.

3.3. Apparatus and Instruments

3.3.1. Apparatus

The following materials were used for this study. Crucible, pH meter (HANNA instruments, pH 211), Electronic balance (ADAM AFP-110 g), Volumetric flask, Measuring cylinder, Mortar and pestle, Oven (Model GENLAB WIDNES, England), Thermostatic water bath (Model Grant GLS400, England), Sieve (mesh size, 150 μm), a 1-liter Pyrex distilling apparatus with Graham condenser., Separatory funnels: 500 or 1,000 mL, stainless steel knife, Pipette ,Beakers, test tube, reagent bottle, digital thermometer, conical flasks, Centrifuge(model Ultra-8V,) filter paper (Whatman No 540 Folded of 110 mm).

3.3.2. Instruments

The following instruments were used for this study.

- UV-visible spectrophotometer (double beam model T80+)-For use at 460 to determine the complex concentration during extraction of phenolic compounds from drinking water and using wavelength 272 nm for determination of its concentration at equilibrium and after certain time.
- Electrical furnace (Model Nabertherm ^(R)) used for preparing activated carbon made from avocado kernel seed wastes.
- Fourier transforms infrared [FT-IR] spectrophotometer (Spectrum 65 FT-IR, Perkin Elmer model) used for functional group identification of prepared activated carbon before and after loaded.

3.4. Chemicals and Reagents

The following chemicals were used for this study. Avocado kernel seeds were collected from Jimma town cafeterias, treated and untreated water samples were collected from Jimma town and surrounding areas water treatment plant. Potassium carbonate [K_2CO_3] solution (43% by mass) and hydrochloric acid [HCl] (2 N) aqueous solution used to impregnate the collected avocado kernel seeds by appropriate proportion. Sodium hydroxide [NaOH] (BDH, England) solution (2.5 N) for extraction of phenolic compounds from water and, H_2SO_4 : Concentrated solution, purity 98% used for adjusting the pH of the solution and preservation. Distilled water and deionized water that used to prepare

standard stock solution. 1.0 g C₆H₅OH purity >98% (sigma Aldrich) standard, that used for preparing the standard phenolic compounds for water analysis. Potassium dihydrogen phosphate [KH₂PO₄] and potassium hydrogen phosphate [K₂HPO₄] were used for preparation of buffer solution. 2 g of 4-aminoantipyrine, purity, 98.5%) and 8 g of potassium hexacyanoferrate [K₃Fe (CN) ₆] used for prepare colored complex. Chloroform [CHCl₃] used for extraction of phenolic compounds and hydrated copper sulfate [CuSO₄.5H₂O] for removal of sulfur containing interference compounds and finally, potassium Iodide [KI] solution used for oxidizing chlorine and all chemicals were used in their analytical grade.

3.5. Preparation of Solution

A 1.445 g K₂HPO₄ and 1 g KH₂PO₄ was dissolved in distilled water and dilute to 100 mL, then the pH of this solution was adjusted to 6.8. And 2 g of 4-AAP was dissolved in distilled water and diluted to 100 mL and the solution was prepared .then, 8 g of K₃Fe (CN) ₆ was dissolved in distilled water and diluted to 100 mL distilled water in both case the solution was prepared daily. A 0.5 N ammonium hydroxide was prepared by diluted a 35 mL fresh concentrated NH₄OH with 1000 mL of distilled water. And methyl orange indicator: was prepared by mixing a 0.5 g methyl orange in the one liter distilled water. The 28 mL of conc. H₂SO₄ was diluted to 1 L distilled water and for preparation of 1N Sulphuric acid. 2.5N Sodium hydroxide was prepared by adding 10 g NaOH in 100 mL distilled water for extraction of phenol derivative salts. 1.0 g phenol was dissolved in freshly boiled and cooled distilled water and diluted to 1 liter distilled water for preparation of stock phenol solution. The intermediate phenol solution was prepared by adding 10 mL or appropriate volume of stock phenol solution in 1 litre volumetric flask and diluted to the mark with freshly boiled and cooled distilled water as to get 1 mL = 10 µg phenol. Standard phenol solution was prepared by 50 mL intermediate phenol solution to 500 mL with freshly boiled and cooled distilled water and the solution were prepared within two hours of use that contained 1 mL = 1 mg of phenol.

3.6. Procedures

3.6.1. Chloroform Extraction Method for Real Water Analysis

The steam distillable phenols react with 4-aminoantipyrine at a pH of 7.9 in presence of potassium ferricyanide to form a coloured antipyrine dye. The dye was extracted from aqueous solution with chloroform and the intensity was measured at 460 nm. This method is applicable in the concentration range of 1 µg/L to 250 µg/L with a sensitivity of 1µg/L, the procedures follow the guidelines of EPA method 9065 for drinking water ⁷⁶.

3.6.1.1. Distillation

- A. A 500 mL original sample was measured and 50 mL phenol-free distilled water was added into a beaker then the pH of the solution was lowered to 4.0 with H_3PO_4 solution using methyl orange as an indicator and 5 mL CuSO_4 solution was added. The sample of water was transferred in to a 1L distillation flask and 500 mL distillate was collected using measuring cylinder as receiver.
- B. 500 mL an original sample was taken and acidified with 1 N H_2SO_4 using methyl orange as an indicator then the water sample was transferred into a separating funnel and 150 g NaCl was added. The transferred sample was shaken with five increment of chloroform, using 40 mL in the first increment and 25 mL in each of the following increments. Chloroform layer was transferred to another separatory funnel and shaken with three successive increments of 2.5 N NaOH solutions using 4.0 mL in the first increment and 3.0 mL in each of the next two increments. Finally the alkaline extracts were combined and heated on the water bath until chloroform was removed. The cooled alkaline extracts were diluted by the 500 mL distilled water and proceed for distillation as in (A).

3.6.1.2. Extraction and Color Development

A 500 mL of the distillate, or a suitable portion containing for more than 50 mg phenol was diluted to 500 mL in 1 litre beaker and 500 mL distilled water blank was taken in to a series of 500 mL phenol standard containing 5, 10, 20, 30, 40 and 50 μg phenol, in respective beakers. A 12 mL of 0.5 N NH_4OH solution and the pH was adjusted to 7.9 ± 0.1 with phosphate buffer and transferred to 1 liter separating funnel, then 3.0 mL 4-aminoantipyrine solution was added in each separatory funnel, mixed well and 3.0 mL potassium ferricyanide, was again mixed and the color was developed after waited 15 minutes. 25 mL chloroform was added and shaken at least 10 times in each separatory funnel until chloroform settled again and each of the chloroform extracts were filtered through what-man number 540 containing 5 g layer of anhydrous Na_2SO_4 . The dried and clean cells extracts were collected and the absorbance of sample and standard were measured against the blank at 460 nm. The calibration curve plot was drawn absorbance against μg phenol concentration. Sample phenol content from photometric reading was estimate by using a calibration curve.

3.7. Calculations

Equation 16 was used to determine the exact concentration of phenolic compounds from a given volume of sample water in the presence of 4-aminoantipyrine.

$$\mu g / L, phenol = \left[\left(\frac{A}{B} \right) \times 1000 \right] \text{-----} (16)$$

Where: A = Mass of (μ g) phenol in sample (estimated from calibration curve)

B = Volume (mL) original sample

3.7.1 Precision and Bias

The concentration of phenol varies with types of phenol derivatives within given sample. Since the concentrations of phenolic compounds are based on C₆H₅OH, the method is regarded only as an approximation. Therefore, it is impossible to express accuracy of the method. The blank, standard and samples were treated in the same manner.

3.7.2. Quality Control

All quality control data was maintained and available for easy reference or inspection. A calibration curve was composed of a minimum of a blank and three standards. A calibration curve was made for every hour of continuous sample analysis. More concentrated samples were diluted and the standard was falling on the plateau of a calibration curve. A minimum of one blank per sample batch was employed and determined.

3.8. Preparation of Activated Carbon

Avocado kernel seeds (*persea Americana*) were collected and then the wastes were cut into pieces approximately 2-3 mm size. The impregnation process was performed by mixing 100 g of raw material with a 43% K₂CO₃ solution and hydrochloric acid (2 N) at a ratio of 1:2 (W:V) separately. This mixture was heated in an oven at 50°C for 12 h. The raw material was then sieved, washed with distilled water until the solution pH was reached 7.0 and dried overnight in a 100 °C oven. The sample was then placed in a vertical tubular stainless steel reactor and placed in an electric furnace. The furnace temperature was increased at a rate of 5 °C/min to a final temperature of 800 °C. The temperature then held at 800 °C for 160 min. The product was cooled to room temperature, and then it was washed with distilled water, and then dried in a 100 °C oven for 3 hours. The product was then

washed with distilled water until the solution pH was between 6 and 7 and then it was dried and preserved in desiccators for further analysis.

3.8.1 Characterization of the Adsorbent

Fourier transforms infrared (FT-IR) (Spectrum 65, Perkin Elmer model FT-IR spectrophotometer) spectra of dried unloaded activated carbon and phenol loaded AC-1 and AC-2 was recorded with in wave number range at 4000-400 cm^{-1} to determine the surface functional groups. Proximate analysis of total ash content, moisture content, volatile matter and fixed carbon and organic carbon were also performed.

3.8.1.1. Ash Content Determination

Dry raw material of avocado kernel seeds samples (5.0 g) were placed in to a crucible and transferred into an electric furnace set at a temperature of 800 °C. The furnace was left on for two hour after which the crucible and its content was transferred to desiccators and allowed to cool for 2 hour. The crucible and content was reweighed and the weight lost was recorded as the ash content of the AC sample (W_{ash}). Then the % ash content (dry basis) was calculated by equation 17 as follows.

$$\text{Ash content (\%)} = \frac{W_{ash}}{W_o} \times 100 \quad \text{----- (17)}$$

Where, W_o and W_{ash} is the dry weight of carbon sample before ashing and ash content of the AC sample respectively.

3.8.1.2. Moisture Content Determination

Thermal drying method was used in the determination of moisture content of the samples. 10 g of the dried raw materials of avocado kernel seeds were weighed in triplicates and placed in washed, dried and weighed crucible. The crucibles were placed in an oven and dried at 105 °C to constant weight for 4 hours according to the method of Rengaraj ⁷⁷. The percentage moisture content (%MC) was computed as follows in equation 18.

$$\text{Moisture content (\%)} = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \quad \text{----- (18)}$$

W_1 = Weight of crucible

W_2 = Initial weight of crucible with sample

W_3 = Final weight of crucible with sample

3.8.1.3. Organic Carbon Determination

The determination of loss of mass on ignition was done by weighing 5 g of the adsorbent (avocado kernel seeds) and put inside furnace at constant temperature of 800 °C for 2 hours. After roasting, the sample was removed and put in desiccators for cooling. The residual product is then weighed and the difference in mass represented the mass of organic carbon present in the sample. This operation was done repeated four times and averaged value was recorded.

3.8.1.4. Volatile Matter Determination

Thermal drying method was used in the determination of volatile matter of the samples. 1.0 g of the dried raw materials were weighed in triplicates and placed in washed, dried and weighed crucible. The crucibles were placed in an oven and dried at 105 °C to constant weight for 24 hours. The percentage volatile matter (% VM) was computed in equation 19 as follows:

$$\text{volatile matter(\%)} = \frac{\text{weight of volatile component(g)}}{\text{oven dried weight(g)}} \times 100 \text{----- (19)}$$

$$\% \text{ fixed carbon} = 100 - (\% \text{ ash content} + \% \text{ volatile matter content} + \% \text{ moisture content})$$

3.9. Adsorption Study

Equilibrium studies were carried out by taking 0.3 g powdered activated Carbon with 25 mL phenol solution of different initial concentrations (10, 20, 30, 50, 60,70) for aqueous and 0.829,2.73 and 3.64 µg/L of phenol in sample water from Jimma town in fifteen (250ml) conical flask. The pH of the solutions was adjusted to 6.0 by adding either 0.1 N HCl or 0.1 N NaOH solutions. The suspensions were agitated at 160 rpm on a shaker at room 30 °C for 100 min and 120 min for AC-1 and AC-2 respectively. At the end of the agitation period the samples were filtered through Whatman No 540 filter paper and centrifuged for 5 min and the supernatant phenolic compound's concentrations in the filtrate was analyzed using a UV/Vis spectrophotometer measuring absorbance at the wavelength of maximum absorption for phenolic compounds at (272 nm). Samples were run in triplicate.

3.9.1. Effect of Contact Time

The effect of contact time on the amount of phenol removal was analyzed over the contact time range from 20 to 160 minutes. 0.3 g each of activated carbon was weighed and put in twelve (250 mL) conical flasks. 25 mL of 10 µg/L⁻¹ concentration of phenol solutions was prepared separately in distilled water from the stock solution was added to the biomass. The pH values of these suspensions

were adjusted to 6.0. The flasks were labeled for time interval of 20, 40, 60, 80, 100, 120, 140 and 160 minutes. The flasks were tightly covered with cellophane and shaken at 160 rpm for the appropriate time intervals on an electric shaker at 30°C. The suspensions were filtered through Whatman No 540 filter paper and centrifuged for 5 minutes. The supernatants were analyzed using UV-Visible spectrophotometer. Determinations were run in triplicate.

3.9.2. Effect of pH

0.3g each of powdered activated carbon was weighed and introduced into twelve (250 mL) conical flasks. 25 mL of 10 µgL⁻¹ solutions of phenol was added separately to the activated carbon. The pH value of these suspensions was adjusted to 2.0, 4.0, 6.0, 8.0, 10.0 and 12.0 by adding a solution of either 0.1 N HCl or 0.1 N NaOH. The flasks were tightly covered with cellophane and shaken for 100 min and 120 min at 160 rpm for AC-1 and AC-2 respectively. The suspension was filtered through Whatman No 540 filter paper, centrifuged for 5 minutes and analyzed.

3.9.3. Effect of Initial Phenol Concentration

Equilibrium studies were carried out by contacting 0.3 g activated carbon with 25 mL phenol was prepared in distilled water from the stock solution of different initial concentrations (10, 20, 30, 50, 70 and 100 µg/L) in twelve (250 ml) conical flask. The pH of the solutions was adjusted to 6.0 by adding 0.1N HCl or 0.1 N NaOH solutions. The suspensions were agitated at 160 rpm on a shaker at temperature (30 °C) for 100 min for AC-1 and 120 for AC-2. At the end of the agitation period the samples were centrifuged for 5 min and the supernatant phenol solution, was filtered through filter paper. Phenol concentrations in the filtrate were analyzed using a UV/Vis spectrophotometer measuring absorbance at the wavelength of maximum absorption of (272 nm). Determinations were run in triplicate.

3.9.4. Effect of Adsorbent Dosage

Different masses of activated carbon ranging from 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6 g was accurately weighed and transferred into twelve (250 mL) conical flasks. 25 mL of phenol was added separately to each of the conical flasks. The flasks were tightly covered with cellophane and shaken for 100 min and 120 min at 160 rpm. At the end of time of agitation, the suspension was filtered using Whatman No 540 filter paper, and centrifuged for 5 minutes and the supernatant solution were analyzed by UV-visible spectrophotometer.

3.9.5. Effect of Temperature

A 25 mL of phenol solutions was mixed separately with an initial concentration of 10, 20 and 30 $\mu\text{g L}^{-1}$ was placed in eighteen (250 mL) conical flasks. 0.3 g each of activated carbon was added to these solutions. The conical flasks were labeled at temperatures of 30, 35, and 40 °C respectively. The flasks was agitated at 160 rpm and heated on a thermostat water bath to the appropriate temperatures for respective time for both activated carbons. The suspensions were filtered using Whatman No 540 filter paper, and centrifuged for 5 minutes and the supernatant solution were analyzed by UV-visible spectrophotometer.

4. RESULT AND DISCUSSION

4.1. Part 1 Determination of Phenol in Untreated Water, Treated Water and System Distributed Water

The following results were obtained during analysis of water samples by 4-aminoantipyrine and the phenolic compounds were extracted in the presence of chloroform and the values were measured triplicate and the average values were taken for analysis.

Table 4: Determined concentration of phenol in untreated water, treated water and system distributed water

Samples code	Average concentration Mean \pm SD (μg)	Total phenol derivative con. in water Mean \pm SD (μg)	Determined Conc. of phenol derivative in 350 mL (ppb)
UW-1	0.176 \pm 0.008		
UW-2	0.162 \pm 0.012	0.290 \pm 0.043	0.829
UW-3	0.142 \pm 0.019		
UW-4	0.680 \pm 0.134		
TW-1	0.434 \pm 0.322		
TW-2	0.317 \pm 0.091	0.956 \pm 0.163	2.73
TW-3	0.630 \pm 0.108		
TW-4	2.443 \pm 0.132		
SDW-1	2.471 \pm 0.019		
SDW-2	1.714 \pm 0.005	1.275 \pm 0.007	3.64
SDW-3	0.286 \pm 0.002		
SDW-4	0.629 \pm 0.003		

It can be seen in the table 4 above that the concentration of phenolic compounds found in the untreated water, treated water and system distributed water were calculated based on equation 16 are 0.829, 2.73 and 3.64 $\mu\text{g/L}$ respectively. This result reveals that the amount of phenolic compounds in untreated water is below the permissible limit of 2 ppb . This indicates that before treatment the formation of chlorophenol derivatives were not found due to the absence of chlorine. On the other hand, the water while treating and after treatment, contained the slightly higher concentration of phenolic compounds due to the formation of disinfection by products like 2CP, 2, 4-DCP and 2, 4, 6-

TCP. The amount of chlorine added during disinfection was responsible for the higher concentration in treated and system distributed water. The amounts of phenolic compounds that are permissible in drinking water are different in different environmental protection agencies. According to United State Environmental Protection Agency (EPA), WHO and Ethiopian Standard the allowed value of phenol in the drinking water is 1 ppb, 0.1 ppm and 2 ppb respectively. Therefore, the amount of phenolic compounds in the untreated water of Jimma town water treatment plant was below the permissible level, thus this result is in agreement with in all environmental protection agencies.⁷⁸ Amount of phenolic compounds in the treated and system distributed water was slightly above the permissible range, this shown that the reaction of chlorine with phenolic compound increases after disinfection takes place to form chlorophenol derivatives. It is evident that the presence of chlorine produced some sources of phenolic resin and increase the amount of phenolic compounds in system distributed water samples as well. Therefore, the method of removal was applied to decrease the pollutants by using the low cost avocado kernel seeds activated carbon through adsorption process. Figure 3 shown as the level of phenolic compounds before and after treatment of Jimma town in comparison of the allowed and determined values of phenol and its derivatives.

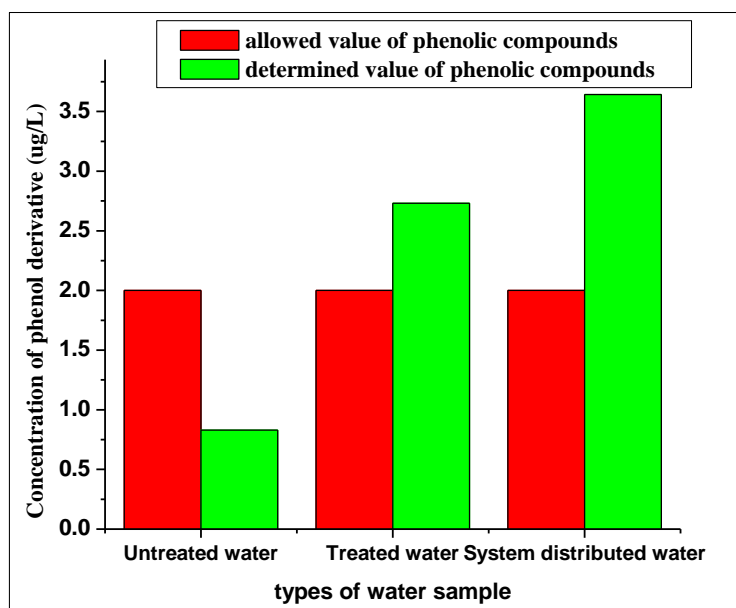


Figure 3: Concentration of Phenolic compounds that Allowed and Determined Values in Untreated, Treated and System Distributed Water at Jimma Town

Determination of Maximum Wave Length on the Adsorption of Phenolic Compounds of Jimma Town

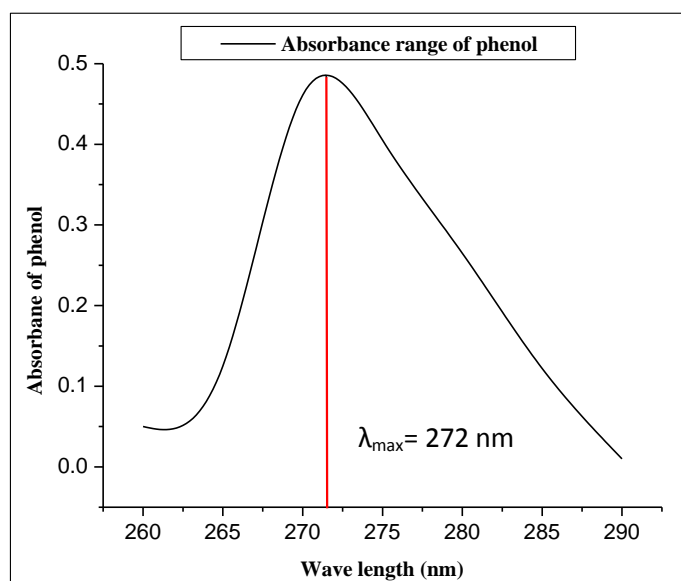


Figure 4: adsorption of phenolic compounds from drinking water at $C_0 = 10 \mu\text{g/L}$, mass of adsorbent = 0.3 g at temp. = 303K, contact time 100 min. and pH=6

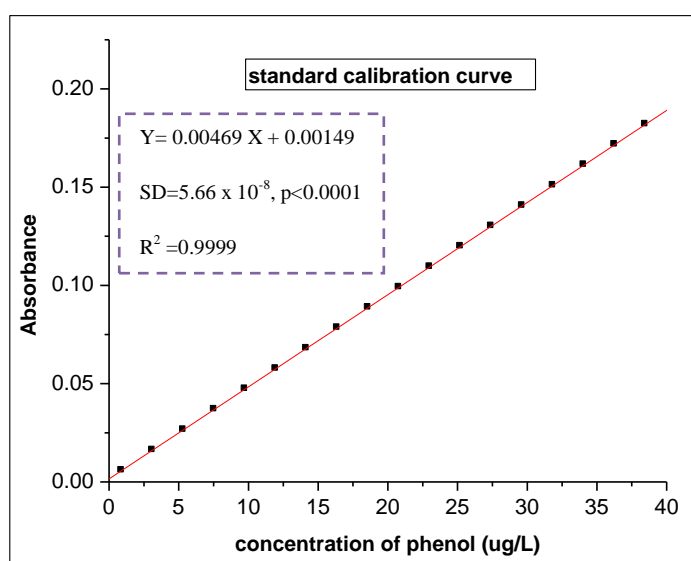


Figure 5: Calibration curve of standard phenolic compound concentration (0.1-50 $\mu\text{g/L}$)

From Figure 4 and Figure 5 the maximum adsorption of phenolic compounds were carried out at wave length of $\lambda_{\max} = 272 \text{ nm}$ and the standard calibration curve was more precise to study the adsorption of phenol in the concentration ranges of 0.1 to 50 $\mu\text{g/L}$. Since the correlation coefficient is nearest to 1(0.9999) and the SD (0.0061) and probability (0.0001) is very small the study of this compound is more valid.

Comparative adsorption of phenolic compound by untreated and treated activated carbon

It can be seen from table 5 and Figure 6 the percentage adsorption of phenolic compounds from raw water, treated water and system distributed water using treated and untreated activated carbons were (87.58%, 84.92%);(94.80%, 93.96%); and (95.25%, 94.37%) respectively. The adsorption capacity of phenolic compounds by treated and untreated activated carbon were also mentioned as (0.061, 0.059); (0.216, 0.214) and (0.289, 0.286) $\mu\text{g/g}$ for both AC-1 and AC-2 respectively. From this study one can conclude that the percentage adsorption and the adsorption capacity of phenolic compounds in all types of water have higher for treated activated carbon than untreated activated carbon. This is due to the fact that in treated activated carbon there is an available site for adsorption of phenol due to increasing the surface area as compared to untreated activated carbon. Generally, the percentage adsorption and adsorption capacity of phenolic compounds in Jimma town untreated water, treated water and system distributed water have higher when treated activated carbon was used in comparison of untreated activated carbons.

Table 5: Percentage adsorption and adsorption capacity of sample water by untreated and treated activated carbon

Types of water	Initial concentration before adsorption($\mu\text{g/L}$)	Types of activated carbon used	Concentration of phenol after adsorption ($\mu\text{g/L}$)	adsorption $(C_0 - C_e)/C_0 \times 100$ (%)	Adsorption capacity $(C_0 - C_e)V/m$ ($\mu\text{g/g}$)
Untreated water	0.829	Treated AC	0.103	87.58	0.061
		Untreated AC	0.125	84.92	0.059
Treated water	2.73	Treated AC	0.142	94.80	0.216
		Untreated AC	0.165	93.96	0.214
System distributed water	3.64	Treated AC	0.173	95.25	0.289
		Untreated AC	0.205	94.37	0.286



Figure 6: Effect of initial concentration on the phenol adsorbed capacity and percentage adsorption of AC-1 and AC-2 at pH =6, contact time of 100 min, mass of adsorbent =0.3 g and temp. 30 °C

4.2. Characterization of the Adsorbent

4.2.1 Physicochemical Characteristics of Adsorbent

Activated carbons are widely used as adsorbents due to their high adsorption capacity, high surface area and micro porous structure. Some important physico-chemical characteristics of avocado kernel seeds are given in Table 6. The activation process of *Per sea americana* by adopting 43% K_2CO_3 and 2N HCl treatment leads to the corrosion of the surface of a carbonaceous material and the appearance of micro-pores, macro-pores and meso-pores.

Moisture content of the carbon has no effect on its adsorptive power; it dilutes the carbon which is necessary to use of additional weight of carbon during the treatment process. The avocado kernel seed samples were determined using standard test method for moisture in AC.⁷⁹ The moisture content (%) was tabulated in table 6, which is 19.56% and 11.75 % for AC-1 and AC-2 respectively. Ash content can affect activated carbon performance that is; it reduces the overall activity of activated carbon. It also reduces the efficiency of reactivation.⁸⁰ Therefore, the lower the ash contents the better the activated carbon for use as adsorbent. Table 6 also describes the ash content of both activated carbon is 30.44% for AC-1 and 4.97% for AC-2, this result was seen with the amount of organic carbon exist in the activated carbon. Thus, the amount of organic carbon in the AC-1 (16.91%) is higher than the AC-2(2.76%). Therefore, the adsorption of phenolic compounds by this activated carbon is dominated

by the amount of organic carbon content, than the ash content which means that AC-1 has higher organic carbon content and has higher percent adsorption and adsorption capacity than AC-2.

The pH value of activated carbon is a measure of whether it is acidic or basic. Activated carbon, when coming out of the kiln tends to be a bit acidic, with a pH of around 6.86 as indicated in table 6. Too high a pH indicates too much contaminant. Too low a pH, especially for acid washed activated carbon, means that the acid has not been properly rinsed away. For most applications, activated carbons are specified for a pH of 6-7. The pH values of the activated carbon samples are therefore within the specified pH range of activated carbons.⁸¹

Table 6 : Physico-chemical characteristics of *Per sea americana* activated carbon treated by 43% K_2CO_3 and 2 N HCl

Parameters	Types of activated carbon	
	AC-1	AC-2
pH	6.86	6.86
Moisture content (%)	19.56	11.75
Volatile content (%)	3.912	5.0
Ash content (%)	30.44	4.97
Mesh size (μm)	150	150
Fixed carbon (%)	46.08	78.28
Organic carbon content (%)	16.91	2.76

4.2.2. FT-IR Analysis

FT-IR spectrum is an essential tool to identify the surface functional groups which contribute significantly to enhance adsorption efficiency of activated carbon by surface complexation. The functional groups on the avocado kernel seed activated carbons (raw, untreated, AC-1 and AC-2) are closely identical to one another. FTIR spectra shown in Figure 7 and table 7 display a number of peaks and indicated a complex nature of the adsorbent.⁸² Bands at 3326-3389 cm^{-1} were assigned to O-H stretch of the phenol functional group.⁸³ The absorption bands observed in this area particularly correspond to the vibration of hydroxyls fixed on the surface of carbon and water chemisorbed on carbon and the presence of N-H bond of amino group of avocado kernel seeds.⁸⁴ 2924 to 2818 cm^{-1} correspond to stretching C-H groups, and they represent aliphatic hydrocarbons. The bands that was observed at 1458 to 1443 was due to aromatic C=C stretch vibration and the bands that have been observed at 1368 to 1353 due to alcoholic C-O-H bending coupled with C-C stretch vibration⁸⁵ and finally the band that was observed at 1093 to 1021 cm^{-1} due the presence of C-O stretching. From Figure 7 and table 7 we observed that the O-H stretching vibration onto both AC-1 and AC-2 before and after loaded was affected due to adsorption of phenolic compounds takes place on the surface of activated carbon and C-O bending vibration was changed on both activated carbon of loaded and unloaded. Generally the change of intensity of both activated carbons on the O-H and C-O vibrations was due to the interaction of H^+ ion with the surface of negatively charged activated carbon in acidic pH, thus the adsorption of phenolic compounds increase up to pH 6 due to dissociation of phenol into H^+ and phenoxide ions. On the other hand, the presence of C=C of aromatic stretching and C-H stretching of alkanes mentioned spectra on the figure 7(a, b) and table 7 are not highly affected by the adsorption of phenol on both activated carbon. Finally, the spectra of raw avocado kernel seeds, untreated and unloaded activated carbons have almost the same. This indicates that the adsorption of phenolic compounds on this carbon materials are lower due to change of functional group intensity during adsorption is very small.

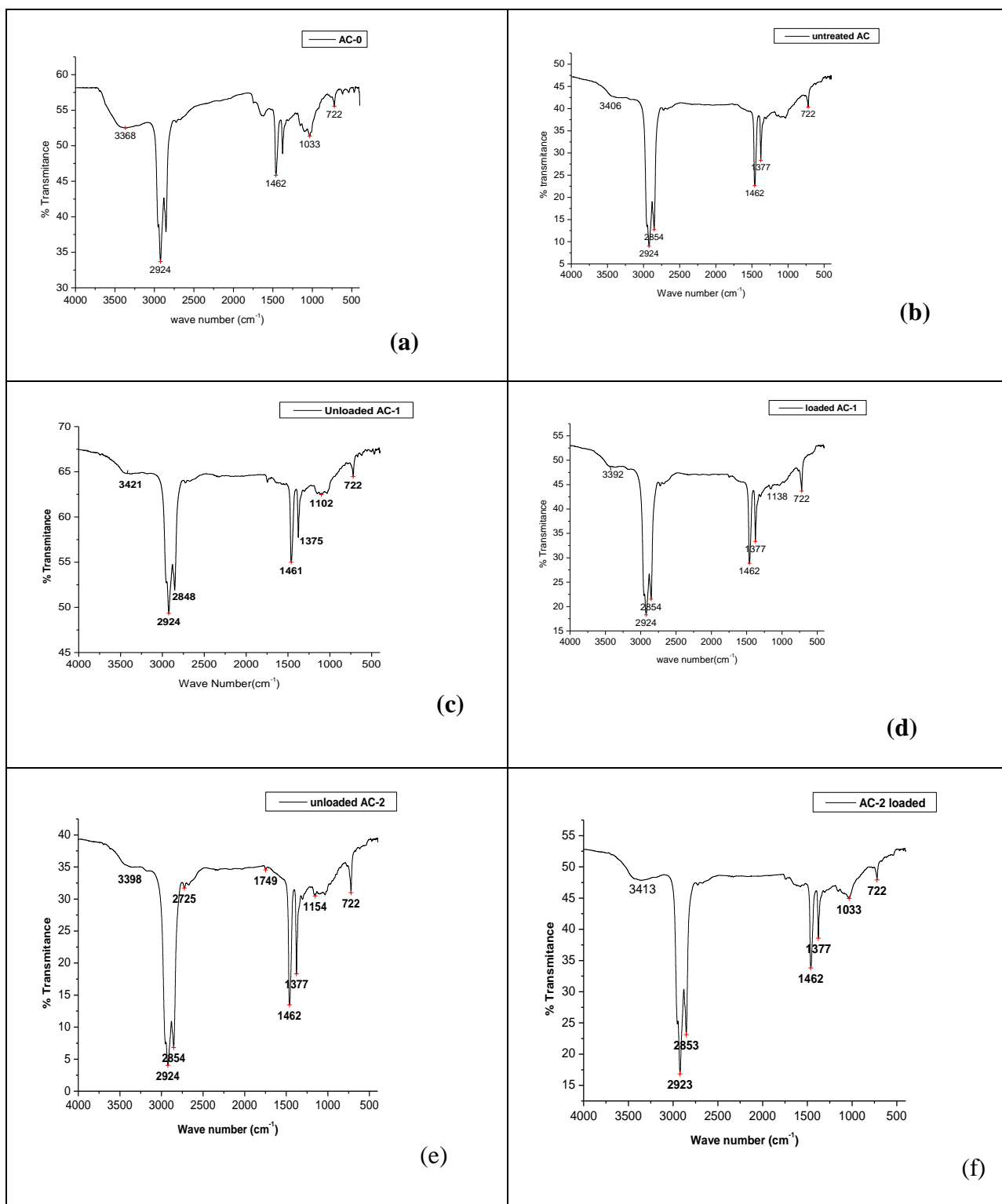


Figure 7: The IR spectra of (a) Raw Material of Avocado Kernel Seeds (b) Untreated Activated Carbon (c) unloaded AC-1 (d) loaded AC-1 (e) Unloaded AC-2 (f) Loaded AC-2

Table 7: The FT-IR Spectral Characteristics of Avocado Kernel Seed (per sea americana) Activated Carbon before and after Adsorption of Phenol

Types of activated carbon	Absorption bands (cm ⁻¹)		Difference	Functional groups Indicated
	Before adsorption	After adsorption		
AC-1	3421	3392	71	O-H hydrogen bonded and N-H stretch
	2924	2924	-	SP ³ C-H stretching vibrations
	2848	2854	6	
	1461	1462	1	Aromatic C=C stretching vibration
	1375	1377	2	C-O-H bending vibration
	1102	1138	36	C-O stretching coupled with C-C stretch vibration
	722	722	-	Long chain aliphatic bands of alkane
AC-2	3398	3413	15	O-H stretch hydrogen bonded
	2924	2923	1	SP ³ C-H stretching vibrations
	2854	2853	1	
	1462	1462	-	Aromatic C=C stretching vibration
	1377	1377	-	C-O-H bending vibration
	1054	1033	21	C-O stretching coupled with C-C stretch vibration
	722	722	-	Long chain aliphatic bands of alkane

4.3. Effect of Different Parameters on Adsorption of Phenol derivative in Aqueous Solution

4.3.1. Effect of Contact Time and initial concentration for Adsorption of Phenolic Compounds onto Activated

Figure 8 presents the plot of phenol removal versus contact time for AC-1 and AC-2 at initial concentrations between 10 and 100 µg/ L at 303 K with a contact time in between 20 and 160 minutes. Increase in contact time increased the percentage removal of phenol in both activated carbons. Rapid removal was noticed initially and reached equilibrium at around 100 min and 120 min for AC-1 and AC-2 respectively. The initial rapid phase is due to availability of more adsorption/vacant sites at the initial stage; as a result, there exists an increased concentration gradient between adsorbate in solution and adsorbate in the adsorbent. This can be explained by strong

attractive forces between phenol molecules and the sorbent and fast diffusion into the inter particle matrix to attain rapid equilibrium.⁸⁶ Phenol removals versus contact time curves are single and continuous leading to saturation, suggesting the possibility of monolayer coverage of phenol on the outer surface of the adsorbent. Moreover, the amount of phenol adsorbed (micrograms per grams) increased with increase in contact time. The increase in adsorption capacity with increasing phenol concentration could be due to higher probability of collision between phenol molecules and adsorbent surface.⁸⁷ On the other hand, the smaller concentration of phenol onto both activated carbons gave higher percentage adsorption. Generally, as initial concentration of phenol increases after equilibrium the percentage adsorption was remain constant due to all active sites of the activated carbon was occupied.

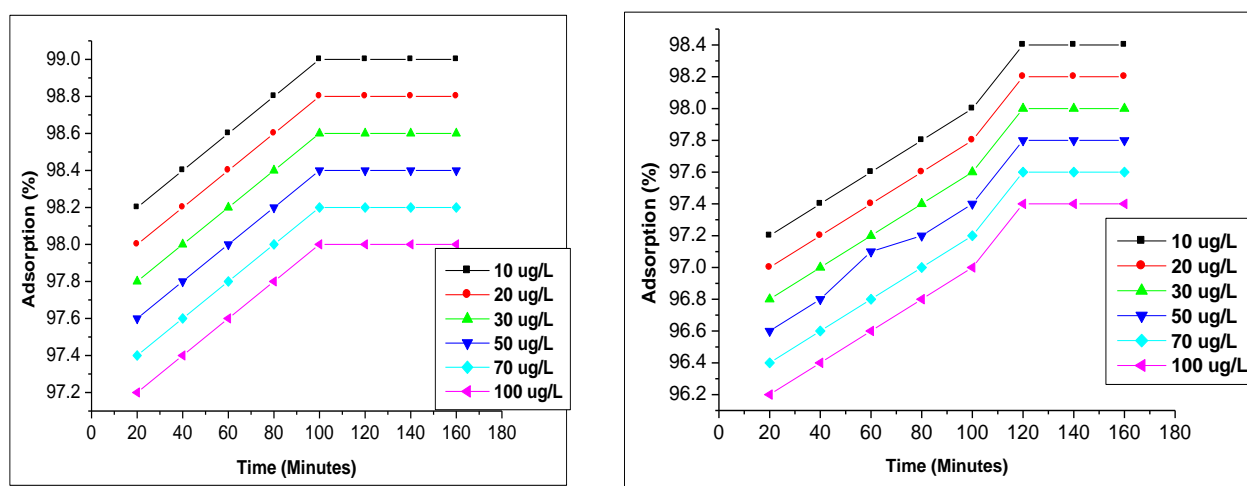


Figure 8: Effect of Contact time on the adsorption of phenolic compounds at different initial concentration on to AC-1 and AC-2 at constant temp. 303K, mass of adsorbent =0.3 g, pH = 6.

4.3.2. Effect of pH on Phenolic Compound Adsorption

It is well known that phenol adsorption onto activated carbon can occur via a complex interplay of electrostatic and dispersion interactions with three possible mechanisms namely, (1) π - π dispersion interaction between the phenol aromatic ring and the delocalized electrons present in the aromatic structure of the graphite layers. (2) Hydrogen bond formation (3) Electron donor-acceptor complex formation at the carbon surface. Although in adsorption process electrostatic attraction exists between phenolate ions ($C_6H_5O^-$) and adsorbent surface plays a very significant role, the oxygen of the surface carbonyl group acts as the electron donor and the phenol aromatic ring as the acceptor. Both aspects are determined by the solution pH. Due to the amphoteric character of a carbon surface, its adsorption properties may be influenced by the pH value of the solution.⁸⁸ The effect of initial pH on the

adsorption of phenol was also evaluated at 30°C, initial concentrations of 10 µg/L for phenol, 100 min. for AC-1 and 120 minutes for AC-2 of contact time, 0.3 g adsorbent dose at different initial pH values in the range of 2–12 for solution adjusted by adding either 0.1M HCl or 0.1M NaOH. The variation of adsorption with different values of pH is shown in Figure10 below,

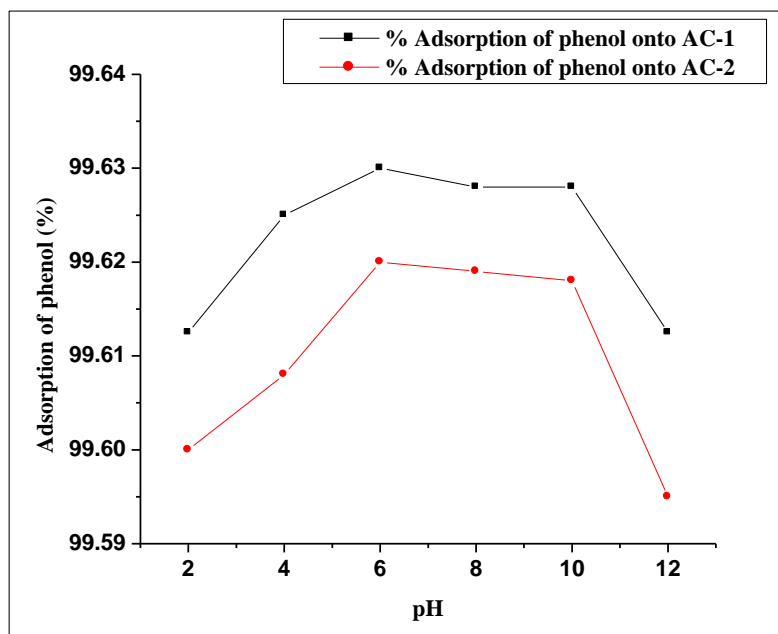


Figure 9: Effect of pH on the Adsorption of Phenolic Compounds by Activated Carbon prepared from Avocado Kernel Seed (AC-1 and AC-2) at constant (t=100 min, 120 min, m=0.3 g, C₀ =10 µg/L, speed =160 rpm and T=30 °C)

Table 8: Effect of pH on the Adsorption Capacity of activated Carbons

pH	Equilibrium Concentration, (q _e)(µg/g)	
	AC-1	AC-2
2	3.3204	3.3200
4	3.3208	3.3203
6	3.3210	3.3207
8	3.3209	3.3206
10	3.3209	3.3206
12	3.3204	3.3198

It is evident from table 8 and Figure10 that the uptake of phenol increases with the increase in pH, and attain to the maximum value at pH 6 (3.321 µg/g) thereafter, the uptake of phenol slightly

decreases with increase in pH up to 10. Further, increase in pH causes again increase in phenol uptake. In this study the amount of phenol adsorbed is highest at pH= 6 followed by 8, next to that the uptake of phenol gradually decreases. The pH also affects the degree of ionization of phenol in adsorption medium. In addition to this, the amount adsorbed of phenol increases at low pH values and decreases at high pH in both activated carbon cases. Since the pKa value of phenol at room temperature is 9.89 was expected to become negatively charged phenolate ion above this pH and repulsion between the surface layer and the anionic phenolate results in reduced adsorption.⁸⁹ In this study, the activated carbon prepared from avocado kernel seeds treated by 43% K₂CO₃ has higher percent of adsorption (99.63%) as compared to activated carbon treated by 2N HCl which has percentage adsorption of 99.62%. The effect of the solution pH on the adsorption capacity of activated carbons AC-1 and AC-2 for phenols studied is shown in Figure10. At acid pH, the amount of phenols adsorbed was slightly increases from pH 2-6 and, at a certain value of pH 8-10, there is a constant in the value of q_e which completely decreases above pH 10. These results indicate that phenol is preferentially adsorbed on the surfaces of the activated carbons in their molecular form, because at acidic pH values phenol is not dissociated. This variation in the surface charge density of the activated carbons affects their adsorption capacity, essentially when the phenol compounds are dissociated, because now the phenolate anions are repelled by the negative charge on the surface of the carbons. The phenol compounds start to dissociate at a pH close to their pKa, (9.89)⁹⁰. However, the amount of phenol adsorbed depends also on the surface charge of the carbon. Thus, in the AC-2 the surface charge is lower than that of carbon AC-1. At pH values higher than 10, both the external and internal surfaces are negatively charged and the phenol is not dissociated. Therefore, the amounts adsorbed above that pH are very low in both activated carbon cases.

4.3.3. Effect of Adsorbent Dosage

The amount of adsorbents in the water is one of the major factors which affect the adsorption capacity. The batch adsorption experiments were carried out using various amounts of AC-1 and AC-2 from 0.1 to 0.6 g while the pH, agitation speed and contact time were fixed at 6-7, 160 rpm and 100 minutes and 120 min, respectively. The results displayed in Figure 11 indicate that the adsorption capacity increases with increase in adsorbent dosage up to 0.3 g, and then remains almost constant for the remaining dosages. For the range below 0.3g, the increase in percentage removal with the increase in dosage rate is expected because of the higher the dose of adsorbents in the solution, the greater the availability of exchangeable sites for ions. However, after certain dosage rate, which is 0.3 g in this study, the dosage rate was found to have no effect on the

percentage removal. This indicates that the phenol removal is an equilibrium reaction and is not limited by number of adsorption sites of the adsorbent within the concentration range investigated in this study.

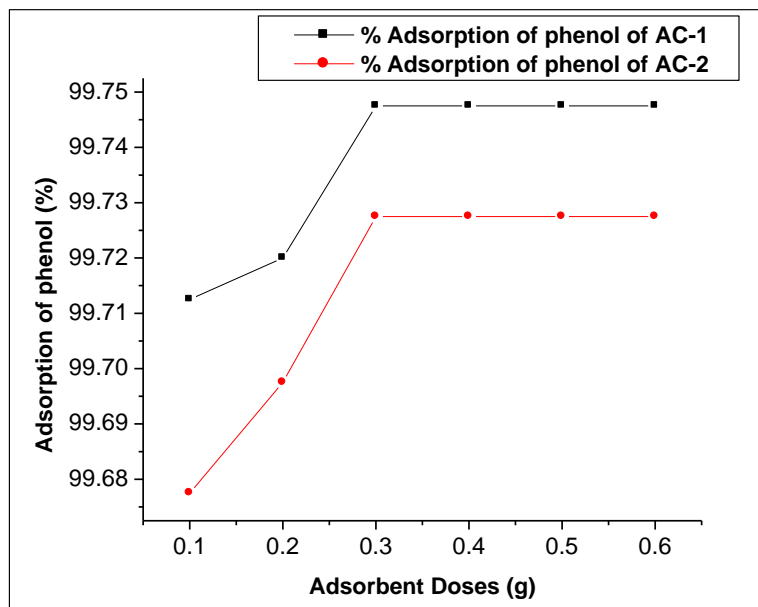
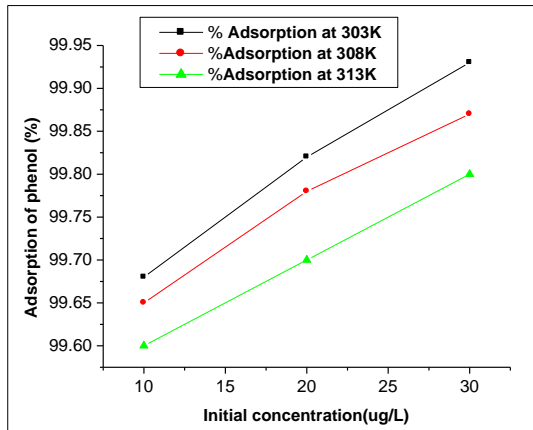


Figure 10: Effect of Adsorbent Dosages on the Percentage Adsorption of Phenolic compounds and on the Adsorption Capacity of Phenol onto Activated Carbon Prepared from Avocado Kernel Seeds (AC-1 and AC-2)

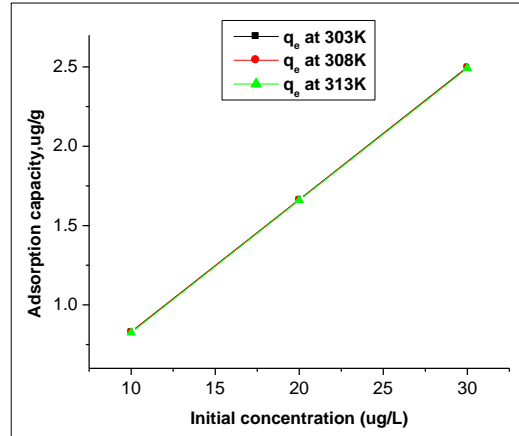
4.3.4. Effect of Temperature on Initial Concentration and Adsorption of Phenolic Compounds

For analyzing the effect of temperature on adsorption, phenol solutions of different concentrations namely, 10, 20, 30 ppb were prepared. All sample solutions were maintained at pH of 6 and 0.3g of activated carbon was added to each solution, then the samples were agitated 100 minutes for AC-1 at different temperatures 30, 35 and 40 °C respectively. A plot of uptake capacity of activated carbon against initial concentrations at different temperatures was plotted shown in Figure12 below.

It is evident from both Figure12 (a & b) that the value of maximum adsorption capacity, q_e decreases with temperature thus suggesting that adsorption of phenol on activated carbon is exothermic in nature. In this study the maximum adsorption was recorded at lower temperature (303 K) and the minimum adsorption was observed at higher temperature (313 K). The increased uptake of phenol with increase in initial concentration indicates that chemisorptions more dominate over Physisorption⁹¹.



(a)



(b)

Figure 11: Effect of temperature on (a) percentage adsorption of phenol onto AC-1 and AC-2 (b) Adsorption capacity of Activated carbon

4.4. Adsorption Isotherm

Adsorption equilibrium provides fundamental physiochemical data for evaluating the applicability of sorption process as a unit operation. The equilibrium study has been conducted based on the commonly used adsorption isotherm models as Langmuir, Freundlich and Temkin. According to the plots of C_e/q_e versus C_e for Langmuir isotherms and $\log q_e$ versus $\log C_e$ for Freundlich, and q_e versus $\log C_e$, for Temkin the experimental data was found to fit better to Langmuir model. The Langmuir adsorption isotherm is the best known of all isotherms describing sorption and it has been successfully applied to many sorption processes.⁹² The Langmuir model been empirically most often used, contained the two parameters q_m and K_L , which reflect the two important characteristics of the sorption systems they are calculated from the intercept and the slope. The Freundlich isotherm was adopted to characterize the adsorption intensity of phenol by fitting the experimental data. The Freundlich isotherm model is based on the assumption that the adsorption occurs on heterogeneous surfaces with interaction between adsorbed molecules and suggests that adsorption energy has a non-uniform distribution over the adsorbent surface.⁹³ The Freundlich equation does not consider all sites on the adsorbent surface to be equal. Furthermore, it is assumed that, once the surface is covered, additional adsorbed species can still be accommodated.

Even though, the Langmuir and Freundlich constant q_m and K_F have different meanings, they led to the same conclusion about the correlation of the experimental data with the sorption model. The basic difference between K_F and q_m is that Langmuir isotherm assumes adsorption-free energy independent of both the surface coverage and the formation of monolayer whereas the solid surface reaches

saturation, while the Freundlich isotherm does not predict saturation of the solid surface by the adsorbate, and thus, the surface covering being mathematically unlimited.⁹⁴

4.4.1. Langmuir Isotherm

The assumption made on the Langmuir adsorption isotherm model is that all adsorption sites have equal affinities for adsorbate molecules at one site which do not affect the adsorption of molecules at an adjacent site. The Langmuir model produced a good fit with a wide variety of experimental data. The Langmuir isotherm is given in equation 4. The theoretical maximum monolayer adsorption capacity q_m (micrograms per gram) is given from the slope. As can be seen from Figure 12 (a) and Table 9, Langmuir model effectively described the sorption data with all R^2 values greater than 0.98 which are 0.994 and 0.985 for AC-1 and AC-2 respectively. The adsorption isotherm of phenol exhibits Langmuir behavior which indicates a monolayer adsorption. The maximum monomolecular capacity is found 3.585 and 3.753 $\mu\text{g/g}$ phenol for both (AC-1 and AC-2) at 303K. According to the b_L (liters per gram), parameter sorption on activated carbon is produced in the following sequence 303>308>313 K. The essential characteristics of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R_L , of Hall et al⁹⁵, which is defined as:

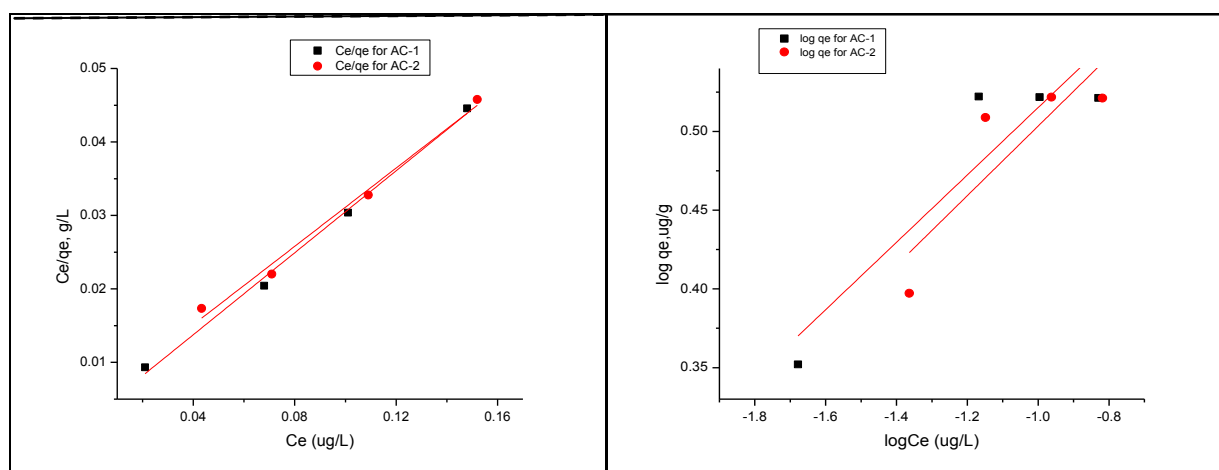
$$R_L = \frac{1}{1 + b_L C_0} \text{-----} (20)$$

Where b_L is the Langmuir constant and C_0 is the initial concentration of the adsorbate in solution. The values of R_L indicates the type of isotherm to be irreversible ($R_L=0$), favorable ($0 < R_L < 1$), linear ($R_L=1$), or unfavorable ($R_L > 1$). The values of R_L were found to be 9.35×10^{-4} , 4.678×10^{-3} , 3.12×10^{-3} , 1.87×10^{-4} , 1.34×10^{-4} , and 9.35804×10^{-05} for the initial concentrations of 10, 20, 30, 50, 70 and 100 $\mu\text{g/L}$, respectively, at 303 K for AC-1. This indicates that adsorption of phenol is favorable on AC-1 and AC-2 because all R_L values are between 0 and 1.

As it can be seen from Table 9, p values vary between 0.002 and 0.005; looking at the variation of p values, it is seen that phenol adsorption mechanism with increasing temperature is more compatible with this model. The least p value is found for adsorption at 313 K. A very low probability value demonstrates a very high significance for the regression model than the other model. Moreover, the values of NSD and ARE for both activated carbon is smaller in the Langmuir isotherm model than the Freundlich and Temkin models. Thus, these smaller values of NSD and ARE imply the experimental data is best fit with Langmuir isotherm model.

4.4.2. Freundlich Isotherm

The Freundlich isotherm is originally empirical in nature but was later interpreted as sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. This assumed that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation. Freundlich isotherm model is represented as in equation 5. The numerical value of $1/n < 1$ indicates that adsorption capacity is only slightly suppressed at lower equilibrium concentrations. This isotherm does not predict any saturation of the sorbent by the sorbate; thus, infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface. The Freundlich sorption isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies and indicates a multilayer sorption of the surface. A greater value of k_F indicates a higher adsorption capacity. It can be stated that at 303 K, adsorption capacity has the maximum value with 5.360 and 5.297 $\mu\text{g/g}$ to AC-1 and AC-2 on phenol adsorption respectively. High k_F and $1/n$ values imply that the binding capacity reaches the highest value, and affinity between the adsorbent and phenol ions was also higher. The magnitude of the exponent n gives an indication on the favorability of adsorption. It is generally stated that values of n in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics.⁹⁶ As can be seen from Table 9 and Figure 12(b), activated carbon is a good adsorbent for phenol adsorption ($4.525 < n < 4.674$). P values vary between 0.075 and 0.135 which is higher than the Langmuir isotherm model and this causes the value of R^2 is smaller. Moreover, NSD and ARE values didn't indicated the significance of the model for this isotherm, so the Freundlich isotherm is not the best isotherm model for the phenol adsorption mechanism.



(a)

(b)

Figure 12: Adsorption of Phenol (a) Langmuir Isotherm Model (b) Freundlich Isotherm model

4.4.3. Temkin Isotherm

The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The heat of sorption of all molecules in the layer would decrease linearly with coverage due to sorbate/sorbent interactions. The Temkin isotherm has generally been applied in the following form⁷⁰ in equation 6.

The parameters of Temkin model as well as the correlation coefficients are given in Figure 13 and Table 9. The R^2 values of activated carbons (0.695 and 0.831) which is smaller than other isotherms and the higher values of NSD and ARE values of the model revealed that the experimental data didn't fit with the Temkin model. The variation of adsorption energy is negative (-37.577 for AC-1 and -56.655 KJ/mol for AC-2 at all the studied temperatures (303,308,313 K) respectively. From adsorption energy one can conclude that the adsorption reaction is exothermic. In addition to this, the Temkin equilibrium binding constants for both ACs are 6.14 and 5.202 L/g and the constant related to heat of sorption ($B=RT/b_T$) of AC-1 and AC-2 are -67.03 and -44.46 J/mol. this value of heat of sorption indicates the adsorption of phenolic compounds onto both ACs physisorption process. Generally, it is evaluated that p values, NSD and ARE values are in a larger intervals for all two-parameter isotherm models; also with increasing temperature, the two-parameter isotherm models are not more suitable with the phenol adsorption mechanism carried out in this study.

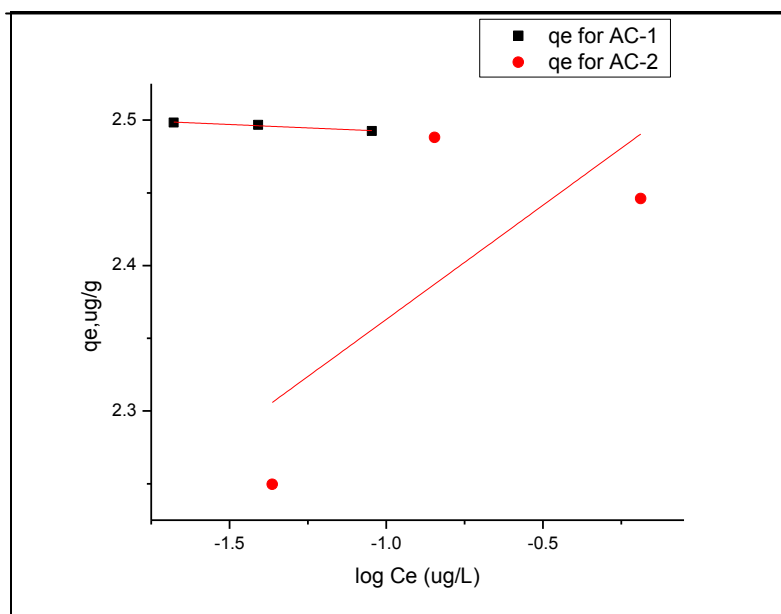


Figure 13 : Temkin isotherm model at 303K of the initial concentration of phenolic Compounds

Table 9 : Isotherm Parameters for Phenolic compounds Adsorption on Activated Carbon at Different Temperatures

Adsorption isotherm & constants	Values	
	AC-1	AC-2
<u>Langmuir</u>		
q_m ($\mu\text{g/g}$)	0.215	0.134
b_L ($\text{L}\cdot\mu\text{g}^{-1}$)	-8.034	-6.032
R^2	0.916	0.976
$R_L \cdot 10^{-5}$ ($100\mu\text{g/L}$)	9.4	16.8
NSD	0.018	0.023
ARE	0.325	1.004
Probabilty	1.4×10^{-4}	0.002
<u>Freundlich</u>		
n	4.673	4.525
K_f	5.360	5.297
R^2	0.784	0.623
NSD	0.062	0.090
ARE	0.003	0.003
Probability	0.075	0.135
<u>Temkin</u>		
b_T (kJ/mol)	-37.577	-36.655
a_T	6.140	5.202
R^2	0.695	0.831
NSD	1.557	1.161
ARE	15.703	20.585
Probability	0.024	0.007

4.5. Adsorption Kinetics Model

For any adsorption system, study of chemical kinetics is very important so as to determine the rate constants for the reaction and to know how quickly or slowly the reaction is proceeding. Adsorption kinetics is used to explain the adsorption mechanism and characteristics. Three kinetic models (pseudo-first order, pseudo-second order, and intra-particle diffusion, were applied to experimental data in order to investigate the kinetics of sorption of phenol on AC-1 and AC-2. Kinetic parameters were determined by the help of origin6 software program. Kinetic model equations used in this study and the calculated kinetic parameters are given in Table 10.

4.5.1. Pseudo First Order Reaction Kinetics

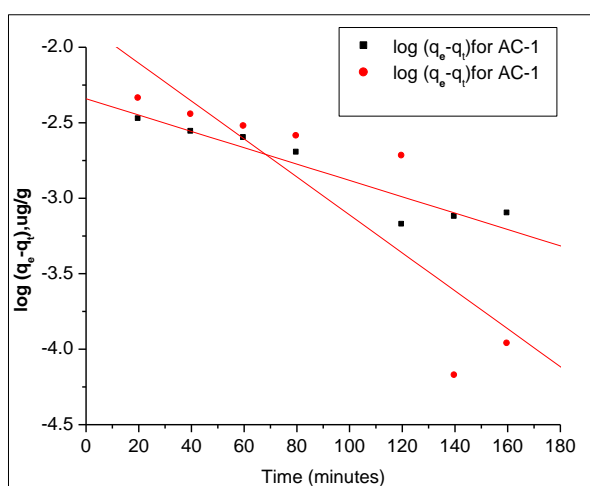
The plots of $\log(q_e - q_t)$ versus t (equation 9) give a linear relationship, and k_1 and q_e values can be determined from the slope and the intercept of the equation. Figure 14 (a) shows the linear plot of the

pseudo-first-order equation and as can be seen from table 10 the correlation coefficients for the pseudo first-order kinetic model obtained at 303K is 0.875 and 0.706 for AC-1 and AC-2 respectively. Thus, this study indicates that the kinetics of adsorption did not governed by pseudo-first order reaction. Also, the calculated q_e (0.005, 0.011) and the experimental q_e (8.323, 8.320) did not close to one another, this indicates that the pseudo-first order model was not fit for the adsorption of phenol by this locally prepared activated carbons.

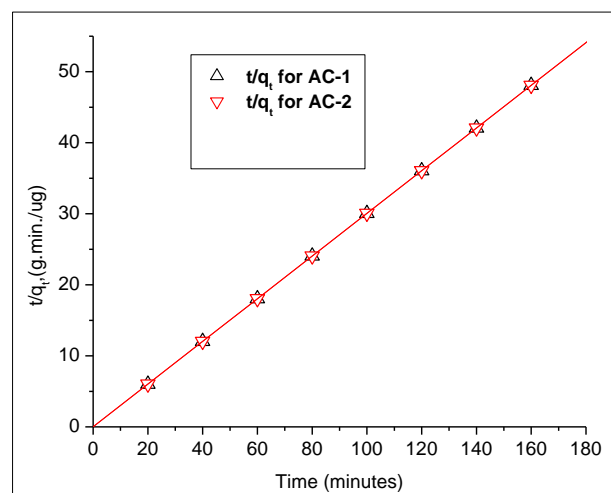
4.5.2. Pseudo Second Order

The pseudo-second-order kinetic equation 10 was first proposed by Blanchard et al.⁹⁷ and since then it has been frequently employed to analyze sorption data obtained from various experiments as reviewed by Ho et al.⁹⁸

The q_e and k_2 values of the pseudo-second-order kinetic model can be determined from the slope and the intercept of the plots of t/q versus t , respectively. Figure 14 (b) gives the results of the linear form of the pseudo-second-order kinetic model. The calculated q_e (3.328, 3.327 $\mu\text{g/g}$) values are same to the experimental data (3.328, 3.327) and the correlation factor as shown in table 10 is higher ($R^2=1.00$) than that of the pseudo-first order kinetics. Therefore, kinetics of the adsorption of phenol approximated more favorably by the pseudo-second-order model⁹⁹ for both AC-1 and AC-2.



(a)



(b)

Figure 14: Kinetics of (a) Pseudo-first order and (b) Pseudo second order kinetics model of AC-1 and AC-2

4.5.3. Intra-Particle Diffusion Model

The adsorbate move from the solution phase to the surface of the adsorbent particles occurs in several steps. The overall adsorption process may be controlled by one or more steps as film or external diffusion, pore-diffusion, surface diffusion, and adsorption on the pore surface or a combination of one or more than one step¹⁰⁰. Intraparticle diffusion model or Weber–Morris equation is given by (equation 12). If the plot of q_t versus $t^{0.5}$ gives a straight line, then the adsorption process is controlled by intra-particle diffusion only. However, if the data exhibit multi-linear plots, then two or more steps influence the sorption process.

Figure 15 gives the plots of q_t versus $t^{0.5}$ for the adsorption of phenol onto AC-1 and AC-2 at different temperatures. It can be seen from the Figure17 that the adsorption data could not fitted by a straight line and the line didn't passed through the origin. Thus, the experimental data do not fit to the intra-particle model data. The graph indicates that the pore diffusion is the only rate-limiting step. Calculated C values are decreased with increasing temperature indicating that the boundary layer effect is higher in low temperatures for the adsorption of phenol onto both activated carbons. The correlation coefficients and the kinetic parameters given in Table 10 are representing that the intra-particle diffusion model shows lower representation of the data than the pseudo-first-order kinetic model. The result of intra-particle diffusion rate constant k_{id} that was higher at a higher temperature is consistent with the fact that the diffusion needs some energy to overcome the mass transfer resistance¹⁰⁰.

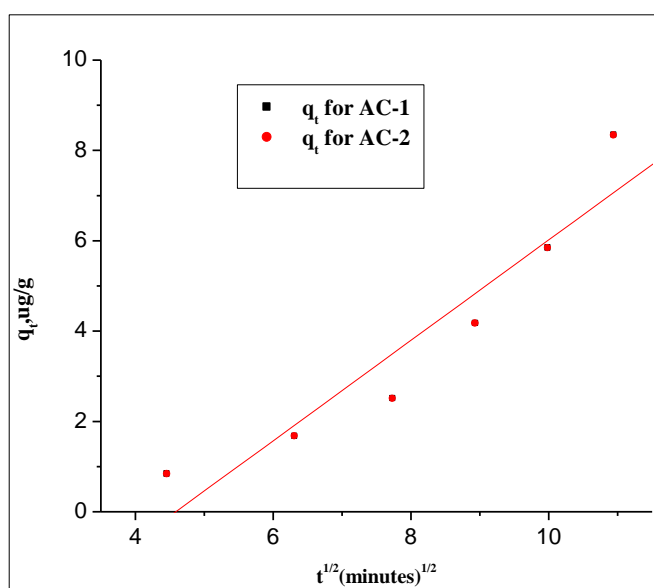


Figure15: Intra-Particle Diffusion Model of Phenolic Compounds onto AC-1 and AC-2

Table 10: Values of Kinetics Parameters on the Adsorption of Phenol on Activated Carbon Prepared from Avocado Kernel Seeds

Kinetic model & constants	Values	
	AC-1	AC-2
q_e (exp)	3.328	3.327
Pseudo-first order		
Q_e (cal)	0.005	0.011
k_1	0.012	0.023
R^2	0.875	0.706
Pseudo-second order		
Q_e (Cal)	3.328	3.328
k_2	9.91	5.055
R^2	1.000	1.000
Intra-particle Diffusion		
K_d	1.112	1.112
C	-5.105	-5.103
R^2	0.872	0.872

4.6. Thermodynamic Studies

Using the K values determined from the adsorption isotherm equations (13-15), the corresponding values of Free energy of adsorption determined at different experimental temperatures. Free energy is the function of change in enthalpy of adsorption (ΔH) as well as change in standard entropy (ΔS): as shown by equation (13, 14, and 15). The values of ΔH and ΔS can be determined from the slope and the intercept of the linear plot of $\ln K_o$ versus $1/T$. The equilibrium constants obtained from the initial concentration of phenol at 303, 308, and 313 K were used to determine the Gibbs free energy.

The van't Hoff plot for the adsorption of the phenol onto both AC -1 and AC-2 is given in the relation of $\ln K_o$ versus $1/T$. The thermodynamic parameters obtained are summarized in Table 11. The exothermic nature of the process onto both AC-1 and AC -2 is well explained by the negative value of the enthalpy change (Table 11). Moreover, the study notice that all of the values of the enthalpy are failed between -40 to -400 kJ/mol (-69.36, -146.011, and -212.40 kJ/mol); consequently, the process of adsorption of the phenol on both activated carbons are chemical, and chemisorptions takes place on the enthalpy values. The negative values of ΔS correspond to a decrease in the degree of freedom of the adsorbed species, suggesting strong interactions between phenol and activated carbons¹⁰¹.

Negative free energy values were observed for all temperatures, indicating that spontaneity of the adsorption process is favored at all concentrations (10 -30 $\mu\text{g/L}$) for the phenol-activated carbon system. The negative value of enthalpy suggests the exothermic nature of the adsorption. ΔH derived from the initial concentration of phenol with AC-1 and AC-2 is larger than 40 kJ/mol for an initial concentration of 10 $\mu\text{g/L}$, which is comparable to those reported for adsorption of phenols on non-ionic polymeric resins ¹⁰². Basically, while the heats of chemisorptions generally falls into a range of 40–400 kJ/mol ¹⁰³. Therefore, it seems that phenol adsorption by AC would be attributed to a type of chemical adsorption rather than a pure physical or chemical adsorption process.

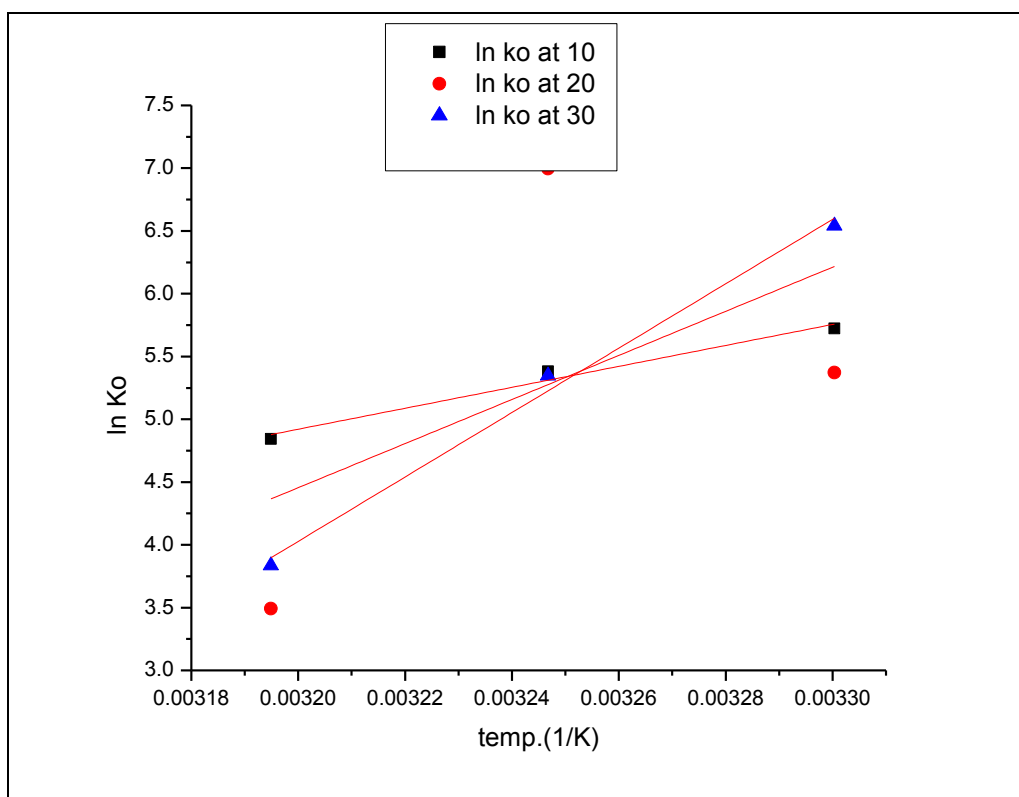


Figure 16: Effect of Temperature on Adsorption of Phenolic Compounds on Initial Concentration of 10, 20, And 30 $\mu\text{g/L}$

Table 11 : Thermodynamic Parameters for The Adsorption of Phenolic Compounds onto Avocado Kernel Seed Activated Carbon at pH 6

Concentration ($\mu\text{g/L}$)		Temp.(K)	$\ln K_o = \ln C_o/C_e$	$\Delta_{\text{ads}}G$ (kJ/mol)	$\Delta_{\text{ads}}H$ (kJ/mol)	$\Delta_{\text{ads}}S$ (J/ K.mol)
C_o	C_e					
	0.033	303.000	5.723	-14.417		
10.000	0.046	308.000	5.382	-13.781	-69.360	-181.040
	0.079	313.000	4.842	-12.600		
20.000	0.093	303.000	5.371	-13.512	-146.011	-430.200
	0.018	308.000	6.997	-17.916		
	0.609	313.000	3.491	-9.085		
30.000	0.043	303.000	6.541	-16.477	-212.400	-648.800
	0.143	308.000	5.348	-13.695		
	0.648	313.000	3.835	-9.979		

Table 12 Comparison of Percent Adsorption and Adsorption Capacity of Different Adsorbents for the Adsorption of Phenol

Types of adsorbent	Time of agitation	Initial phenol concentration	pH	% adsorption /adsorption capacity	references	
Diospyros melanoxydon leaves	7hrs	50 mg/l	6.2	97.88%	104	
Tamarindus indica seeds	7 hrs	50 mg/l	6.2	99.07%		
Dates' stone	3hrs	250 mg/l	7.0	97.1	105	
Rice Bran Ash	240 min.	100 mg/l	5.0	4.63 mg/g		
Indica Biomass	240 min	100 mg/l	7.0	2.14 mg/g	106	
Granular Activated Carbon	240 min.	100 mg/l	7.0	4.85 mg/g		
Coffee residue	Non activated	48 hours	30 mg/l	3.0	42.00 %	107
	-AC 25 %	48 hours	30 mg/l	3.0	67.86 %	
	-AC 50	48 hours	30 mg/l	3.0	59.28 %	
	-AC 75	48 hours	30 mg/l	3.0	57.81 %	
Avocado Kernel Seeds		100 min.	100 $\mu\text{g/l}$	6.0	8.323 $\mu\text{g/g}$	this study
					99.83%	

The percent adsorption and adsorption capacity of phenolic compounds in different carbonaceous materials were different as shown table 12. Even though the agitation time, initial phenol concentration and pH of the solution were the same, the percent adsorption phenol onto one adsorbent

was different. Among the studies carried on the adsorption of phenol the adsorbent that made from avocado kernel seeds has higher percent adsorption and adsorption capacity. This study was preferred from the other studies that carried on the adsorption of phenolic compounds from water due to usage of smaller concentration of the adsorbate and its agitation time. The percent adsorption of phenol onto diospyros melanoxylon leaves, tamarindus indica seeds, dates' stone rice bran ash, Indica biomass, granular activated carbon and coffee residue in different impregnation ratios have lower percent adsorption of phenol and adsorption capacity as compared to adsorbent that made from avocado kernel seeds (99.83%,8.323 $\mu\text{g/g}$).

5. CONCLUSIONS AND RECOMENDATION

Based on the experimental findings of this study the amount of phenolic compound concentration in untreated water is lower than the permissible values whereas the amount of phenol concentration in treated and system distributed water was slightly higher than the permissible values. For the adsorption of phenolic compounds the batch adsorption was applied and the result revealed that the equilibrium adsorption attained at 100 and 120 minutes for AC-1 and AC-2 respectively. Three isotherm models namely, Langmuir, Freundlich and Temkin were used to explain the adsorption of phenolic compounds from drinking water. The result indicated that the Langmuir isotherm model significantly explained the adsorption of these compounds and adsorption is monolayer. The three kinetics studies were investigated namely pseudo-first order, pseudo-second order and intra-particle diffusion models. The result from kinetics study indicated that the pseudo-second order kinetics was best fitted with the adsorption of phenolic compounds from drinking water. The thermodynamics studies were also carried out in determined the values of Gibbs free energy, enthalpy change and entropy changes. Thermodynamic parameters for adsorption such as ΔH , ΔS and ΔG were calculated for adsorption process and the result showed that the free energy, enthalpy and entropy of adsorption were -13.6 kJ/mol, -69.36 kJ/mol and -181.04 J/K at 303 K. That indicates that the adsorptions of phenol compounds are spontaneous, chemisorbed, mono-layered and exothermic on activated carbon prepared from avocado kernel seeds.

Therefore, the findings were helpful to a great extent for treating drinking water from phenol contaminated effluents and the locally prepared avocado kernel seed is environmentally friendly material which employed successfully for separation of phenol in industrial scale. It concluded that activated carbon prepared from avocado kernel seed is a good and cheap adsorbent with high potential for the adsorption of phenolic compounds from contaminated wastewater and could therefore serve as effective and efficient biomass for treating of wastewaters in terms of high adsorption capacity and easy operational methods in developing countries as alternatives of advanced technologies. Further, the study initiates the community to give due attention for treatment of chemicals disposed nearby the water. Finally, nowadays in Ethiopia, different industries are expanded; so that the consequences of these phenolic compounds should have studied before discharging to the environment in order to save the water from organic contaminants like phenol derivatives.

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