



Jimma University

Jimma Institute of Technology

Faculty of Civil and Environmental Engineering

Environmental Engineering Chair

**REMOVAL OF NATURAL ORGANIC MATTER FROM WATER USING
CHEMICALLY ACTIVATED COFFEE HUSK**

By

Dawit Derese

A Thesis submitted to Jimma University, Institute of Technology, Environmental Engineering Chair in Partial Fulfillment of the Requirements for the Degree of Masters of Science in Environmental Engineering

October, 2017

Jimma, Ethiopia

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Main advisor: Dr.-Ing. Fekadu Fufa (PhD)

Co-advisor: Mr. Dida Abera (PhD fellow)

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DECLARATION

I, Dawit Derese, the undersigned, declare that this thesis entitled “REMOVAL OF NATURAL ORGANIC MATTER FROM WATER USING CHEMICALLY ACTIVATED COFFEE HUSK” is my original work, and has not been presented by any other person for an award of a degree in this or any other University.

Name: Dawit Derese Signature: _____ Date _____

Advisors

Dr.-Eng. Fekadu Fufa Signature: _____ Date _____

Mr. Dida Abera Signature: _____ Date _____

Place: Jimma, Ethiopia

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ABSTRACT

Natural organic matters are one of the detrimental parameters to be considered in conventional drinking water treatment processes. The existence of high concentration of natural organic matter in raw and processed water can result in taste, color and odor problem, and facilitate bacterial regrowth in water distribution systems. Moreover, in conventional drinking water treatment systems where chlorine is used as disinfectant, they act as the precursor for the formation of disinfection by products such as trihalomethen, which have carcinogen effect on the health of human being. Hence, they have to be regulated by different treatment mechanisms beyond the conventional drinking water treatment systems. In this study, group of batch adsorption experiments were conducted to examine the HA adsorption capacity of chemically activated coffee husk as the function of contact time, pH of the solution, initial humic acid (as representative of NOM) concentration, adsorbent dose, agitating speed and desorption study parameters. The study revealed that adsorption capacity increased with time until equilibrium time reached 60 min and the maximum adsorption yield was 93.7%. The adsorption of HA was greatly dependent on pH of the solution. Generally, adsorption was remained at a maximum level within PH range 3-6, the optimum pH for maximum HA adsorption was revealed at pH = 3 with maximum adsorption 94.33% and above pH = 6 the HA uptake of the adsorbent dramatically decreased. The amount of HA adsorbed decreased with increasing the dose of adsorbent to 25 g/L. CACH reduced 10mg/L HA to 1.67mg/L which is below the WHO guideline value of 2 mg/L dissolved organic matter in drinking water to prevent formation of dis-infection by product, Hence the 1 g/L CACH was considered as an optimum dose. Also the amount of HA adsorbed increased with increasing the initial HA concentration from 0.5 mg/L to 20 mg/l. The adsorption kinetics data of HA adsorption followed well the pseudo-second order equation with the correlation coefficient $R = 0.997$ and $K_s = 0.078$. The equilibrium adsorption data were better represented by the Langmuir isotherm ($R^2 = 0.998$, $SSE = 0.006$). The desorption experiment done using alkaline solution of 0.1M and 0.2 M of NaOH at pH >11, and the desorption capacity was 70.44 and 90.72% respectively. Thus CACH could be used as a media for HA removal.

Key words: Adsorption isotherm, Adsorption kinetics, CACH, Humic acid, Natural organic matter

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ACRONYMS

AC	Activated Carbon
AOP	Advanced Oxidation Process
CACH	Chemically Activated Coffee Husk
COD	Chemical Oxygen Demand
DBP	Disinfection Byproduct
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
HA	Humic Acid
HAA	Haloacetic Acids
HMW	High Molecular Weight
HPSEC	High Performance Size Exclusion Chromatography
IMW	Intermediate Molecular Weight
LMW	Low Molecular Weight
MWD	Molecular Weight Distribution
NOM	Natural Organic Matter
THM	Trihalomethane
TOC	Total Organic Carbon
USEPA	United State Environmental Protection Agency
WHO	World Health Organization

CHAPTER ONE

1. INTRODUCTION

1.1 Background

Water is very essential to sustain life So: in adequate, safe and accessible supply must be available to all who need water to survive. Improving access to safe drinking-water can result in tangible benefits to health. Every effort should be made to achieve drinking-water quality as safe as possible (WHO, 2006). In order to make water safe for drinking Chlorination is used as disinfectant. The effective disinfection method in water treatment for inactivating microorganisms to safeguard the public health against waterborne diseases. However, reactions of chlorine with natural organic matter (NOM) in water may result in formation of harmful disinfection by-products (DBPs), such as trihalomethane (THMs) and haloacetic acids (HAAs) (Goslan, 2008).

Natural organic matter (NOM) is defined as a complex matrix of organic materials present in all natural waters. As a result of the interactions between the hydrological cycle and the biosphere and geosphere, the water sources used for drinking water purposes generally contain NOM. Thus the amount, character and properties of NOM differ considerably in waters of different origins and depend on the biogeochemical cycles of the surrounding environments (Fabris *et al.*, 2008; Matilainen *et al.*, 2011).

The choice of water treatment process depends on the characteristics of the water and the treatment method costs (Richardson *et al.*, 2007). The NOM can be removed from water by a number of different treatment processes (Jacangelo *et al.*, 1995). An improved understanding of the chemical properties of aquatic NOM is so important on choosing the most appropriate treatment strategies for removing NOM from raw drinking waters (Owen *et al.*, 1985).

A great variety of NOM removal processes have been investigated and employed, such as coagulation (Bell-Ajy *et al.*, 2000; Matilainen *et al.*, 2010), membrane filtration (Siddiqui *et al.*, 2000; Metsämuuronen *et al.*, 2014), advanced oxidation processes (Matilainen and Sillanpää, 2010), and adsorption (Genz *et al.*, 2008).

However, all these methods have their own shortcomings; for example, inorganic coagulants such as aluminum- or iron-based salts remove only a portion of NOM (Chow *et al.*, 2009). NOM with high molecular mass (HMM) is removed effectively from water in the chemical coagulation and flocculation followed by sedimentation/flotation and filtration (Ratnaweera *et al.*, 1999). In the conventional water treatment process, the removal efficiencies of different molecular size fraction of NOM varied significantly. The removal of the HMM matter is sufficient. However, the IMM and the LMM NOM are difficult to remove than the HMM matter (Matilainen *et al.*, 2002). Furthermore, the removal of NOM by conventional treatment process is not always adequate with regard to removal efficiency, chemical and energy consumption, and management of residuals (Genz *et al.*, 2008).

Adsorption is a phase transfer process that is widely used to remove substances from fluid phases (gases or liquids). It can also be observed as natural process in different environmental compartments. In water treatment, adsorption has been proved as an efficient removal process for a multiplicity of solutes (Worch, 2012).

Many adsorbent media have been in use, among which activated carbon (AC) is widely used for adsorption treatment process. By optimizing the preparation conditions or/and adsorption process, it is possible to increase removal efficiency of pollutants onto activated carbon. Agricultural wastes or their modifications are used to produce activated carbon. The maximum adsorption capacities, ease of regeneration and low-cost of adsorbents demonstrated that the adsorbents obtained from agricultural waste have a wide range of applications for organic pollutants removal (Zhou *et al.*, 2015).

Coffee husk used as an adsorbent in this study is one of the agricultural by products or wastes obtained from coffee processing units. Coffee husk is an abundant material on a large scale in many African countries especially in Ethiopia. Ethiopia is home land of coffee & the prominent producer of coffee in Africa, and has many Coffee processing units. The existence of huge amount of coffee production and the increasing number of coffee processing units in the country indicates the likely increase in quantities of coffee husk residue from processing units. Coffee husk is cellulosic and lignocellulosic wastes have long been recognized as raw materials for the preparation of activated carbon (Berhe *et al.*, 2015).

1.2 Statement of the problem

NOM causes problems in the production of drinking water through conventional method. It has an adverse effect on the aesthetic water quality and may result in biofouling of pipelines with negative hygienic consequences (Nordtest, 2003). It has been demonstrated that the NOM is the basis for the production of potentially hazardous disinfection by-products (DBPs), where chlorine is used for disinfection processes (Singer, 1999). Thus, it has to be removed from processed water before chlorination process.

High chlorine dosages are used in some conventional drinking water treatment plants to overcome the deficiencies in the treatment to at least ensure a supply of microbiologically safe water to the population. The reactions of chlorine with NOM found in aquatic environments are becoming a critical concern, due to the formation of chlorination by-products such as trihalomethanes (THMs), which are carcinogenic substances (USEPA, 1998).

In addition, the presence of NOM creates serious problems to drinking water quality and its treatment processes. These problems include: (i) negative effect on water quality due to color, taste, and odor, (ii) increased coagulant and disinfectant dose requirements, which in turn results in increased sludge and potential harmful disinfection byproduct (DBP) production, (iii) promoted biological growth in distribution system, and (iv) increased levels of complexed heavy metals and adsorbed organic pollutants (Jacangelo *et al.*, 1995).

Incomplete removal of NOM in the conventional drinking water treatment has an adverse effect on the water quality. Hence, it is advisable to reduce the concentration of the NOM from drinking water (Matilainen *et al.*, 2002). Thus, CACH is employed to remove HA from drinking water.

Conventional water treatment removes only a portion of natural organic matter (Drikas *et al.*, 2002). Currently different types of technologies are used to remove NOM from drinking water. Some of these are oxidation, reverse osmosis, ion exchange, electro-dialysis, electrolysis, adsorption etc. However, these technologies are expensive, demand large energy and also need skilled manpower and hence not easily applicable in developing countries; except adsorption technology. Adsorption is considered as the best water treatment method due to its universal nature, inexpensiveness and ease of operation. Adsorption can also remove soluble and insoluble organic pollutants (Gupta and Shukla, 2009).

Many adsorbent media have been introduced to be used in water treatment processes. There is a great need of the removal of organic pollutants from water by using low cost adsorbents at pilot and industrial scales (Ambashta and Sillanpää, 2010; Ali *et al.*, 2012). Activated carbon (Karanfil *et al.*, 1994; Daifullah *et al.*, 2004), clays (Johns *et al.*, 1993), Chitosan (Ngah and Musa, 1988), metal modified silica (Moriguchi, *et al.*, 2005), mesoporous silica (Tao *et al.*, 2010), and rice husk ash (Imyim and Prapalimrungsi., 2010) are few to mention. However, yet low cost and locally available adsorbents have to be investigated and employed.

In this study, chemically activated coffee husk (CACH) which is an agricultural waste was used as an adsorbent to remove Natural Organic Matter from aqueous solutions and from drinking water under different experimental conditions. The adsorption isotherm and kinetic studies was carried out to explain nature and rate of adsorption process respectively.

1.3 Research questions

1. What percent of the HA can be removed using CACH?
2. What is the effect of solution pH, contact time, adsorbent dose, agitating speed and concentration of HA in the solution on the adsorption of HA onto CACH?
3. Which adsorption isotherm model best fit to experimental data?
4. Is the exhausted CACH regenerated?

1.4. Objectives

1.4.1. General Objective

- To investigate the removal efficiency of HA from water using CACH under laboratory condition.

1.4.2. Specific Objectives

1. To evaluate the adsorption capacity of the adsorbent
2. To investigate the effect of solution pH, adsorbent dose, contact time, initial concentration of HA and agitating speed on the HA removal efficiency
3. To identify adsorption isotherm model best fit for experimental data
4. To investigate the regeneration of exhausted CACH

1.5. Significance of the study

The finding of this study will redound to the benefit of the society regarding access to improved drinking water quality. The finding indicates that optimizing all the necessary parameters, adsorption using CACH can be used as a means to reduce the concentration of NOM found in our drinking water as a result we can reduce or possibly eliminate the problem related with the existence of NOM like negative effect on water quality due to color, taste and odor, regrowth of biological in the distribution system, consumption of high dose of coagulant and disinfectant. CACH also provide as a means of low-cost adsorbent which is locally available and can be easily prepared from agricultural waste. Also this finding will initiate other scholars to investigate the application of agricultural by-products in water treatment scheme. In addition, it will indicate management option for agricultural by-products like coffee husk waste produced from coffee processing factories.

1.6. limitation of the study

Real sample is not used in the batch experimental analysis because of the lack of direct TOC (Total Organic Carbon) analyzer. In this study we have used spectrophotometer (DR-5000).

CHAPTER TWO

2. LITRATURE REVIEW

2.1 NOM characterization

Natural organic matter (NOM) is a complex mixture of organic compounds present in all fresh water, particularly surface waters. NOM consists of a range of different compounds, from largely aliphatic to highly colored aromatics. Some of this organic matter is negatively charged consisting of a wide variety of chemical compositions and molecular sizes (Thurman, 1985; Swietlik *et al.*, 2004). Thus, NOM present in waters consists of both hydrophobic and hydrophilic components. The hydrophobic part is rich in aromatic carbon, having phenolic structures and conjugated double bonds, while hydrophilic NOM contains a higher proportion of aliphatic carbon and nitrogenous compounds, such as carbohydrates, proteins, sugars and amino acids. Hydrophobic acids constitute the major fraction of aquatic NOM, accounting for more than half of the dissolved organic carbon (DOC) in water (Thurman, 1985; Swietlik *et al.*, 2004). These hydrophobic acids may be described as humic substances.

The NOM in raw water must be characterized to understand its role in water treatment. Ideally, once the various NOM components and fractions of a raw water source have been determined, the treatment processes that will eliminate the most dominant NOM fractions could be selected (Matilainen *et al.*, 2011).

More efficient removal of NOM requires more knowledge of the organic matter present in raw water, and novel methods have been developed for the characterization of these organic compounds. At the same time, existing methods and techniques have been improved. These characterization methods are used to study the composition of NOM prior to treatment and during various stages of the treatment process (Chen *et al.*, 2007; Sarathy and Mohseni, 2007; Liu *et al.*, 2010).

Dissolved organic carbon (DOC), chemical oxygen demand (COD), UV254, pH, turbidity, and color are common water quality parameters assessed by water treatment facilities in their quality control. Assessment of these parameters does not require sophisticated equipment, is simple and fast to perform, and can be automated. Yet, such assessments offer no information about the

characteristics of NOM such as molar mass (MM) or hydrophobicity. Generally, humic substances have been classified into three categories based on their solubility: humic acid (HA), fulvic acid (FA), and humin. This is an operational division, however; the terms do not refer to single compounds but to a wide range of compounds of similar origin (Uyguner-Demirel and Bekbolet, 2011).

NOM characterized by high performance size exclusion chromatography (HPSEC) analysis, which determines the molecular weight distribution (MWD) of NOM (Chow *et al.*, 2008), or by fractionation techniques that use resins to divide the mixture of organic compounds of NOM into hydrophilic and hydrophobic fractions (Sharp *et al.*, 2006). Although these parameters provide useful information regarding the change in organic characteristics during treatment and impact on DBP formation, it has been suggested that their use alone they may not be efficient for predicting DBP formation (Sanly *et al.*, 2007).

Humic substances generally account for over half of the total organic carbon (TOC) content in water (Thurman, 1985). Humic substances can be regarded as natural anionic polyelectrolytes, with an anionic charge at pH values higher than 4. Another way to define hydrophobicity is to determine the specific UV-absorbance (SUVA) value (i.e., UV254 absorbance divided by the TOC concentration). A high SUVA value indicates that the organic matter is largely composed of hydrophobic, high-MM organic material. A low SUVA value indicates that the water contains organic compounds that are mainly hydrophilic, with a low MM and charge density (Edzwald and Tobiason, 1999; Sharp *et al.*, 2006). Due to their diverse properties, different NOM fractions respond differently to treatment by coagulation, coagulant demand, chlorine and ozone reactivity, and disinfection by-product formation potential (DBPFP) (Sharp *et al.*, 2006; Fabris *et al.*, 2008).

2.1.1 NOM composition

NOM is a complex mixture of pedogenic (soil derived) and anthropogenic (water column) material derived from the contact of water with dead and living organic matter in the hydrological cycle (kitis *et al.*, 2002) NOM is spatially and temporally variable and its abundance in natural aquatic environments provides a source of one of the largest active organic carbon reservoirs in the biosphere. Quantity equal to the CO₂ content in the atmosphere. NOM is present in dissolved, particulate and colloidal forms, and has a number of functions in aquatic

systems. These include a carbon source for metabolism of living things, ecological and geochemical functions such as proton binding, influencing biogeochemical processes and photochemical reactions, transportation of inorganic and organic substrates and aggregation and photochemical reactivity. Studies in organic matter characterization have identified its main components as carbohydrates, lipids, protein polymers, humic macromolecules, nucleic acids and phenolic compounds (Parsons *et al.*, 2000).

The components of NOM are traceable to one of two sources within a catchment; autochthonous (within a water body) or allochthonous (within a soil profile). Autochthonous NOM is predominantly produced within the water body itself by algae, bacteria and aquatic plants. Photo degradation of NOM is also a considerable producer of autochthonous NOM in surface waters. Photochemical “weathering” of originally allochthonous organic material can significantly influence the chemical character of NOM, resulting in autochthonous by-products. Catchment based processes such as freezing/thawing and dehydration/rehydration are additional sources of autochthonous NOM. Autochthonous NOM is predominantly phenol and carboxylic in nature, containing amino acids, hydrocarbons, carbohydrates, sterols and low molecular acids. NOM derived from these sources is typically enriched in aliphatic carbon and organic nitrogen. And such type of NOM absorbs less UV light and has fewer aromatic residues (Wang *et al.*, 2013).

Allochthonous NOM is a mixture of acidic organic compounds of medium to high molecular weight, originating from the leaching of decaying terrestrial plant and animal material in a catchment. Humic substances, consisting of humic, fulvic and hydrophilic acids dominate the composition of allochthonous NOM in surface water catchments and are characterized by high aromatic carbon content and low nitrogen content. In the other way the component of NOM was TOC which consists of dissolved organic carbon (DOC) and particulate organic carbon (POC) fraction. Nevertheless, POC only represents a small amount of TOC which indicate that DOC is the main fraction of NOM. In addition, DOC present in natural water was mainly comprised of hydrophobic and hydrophilic components whereas hydrophobic component represents about 50% of DOC while hydrophilic ranging between 25-40%. The remaining fraction is transphilic organic matter (Matilainen, 2007). The hydrophobic and hydrophilic components can be divided into three different classes namely acid, bases, and neutral which have different chemical groups where hydrophobic classes is rich with aromatic carbon,

phenolic structures and conjugated double bonds while hydrophilic classes contains more aliphatic carbon and nitrogenous compounds (Matilainen *et al.*, 2010).

Hydrophobic acid is Humic and fluvic acids whereas hydrophilic acids is carboxylic and polyuronic acids.

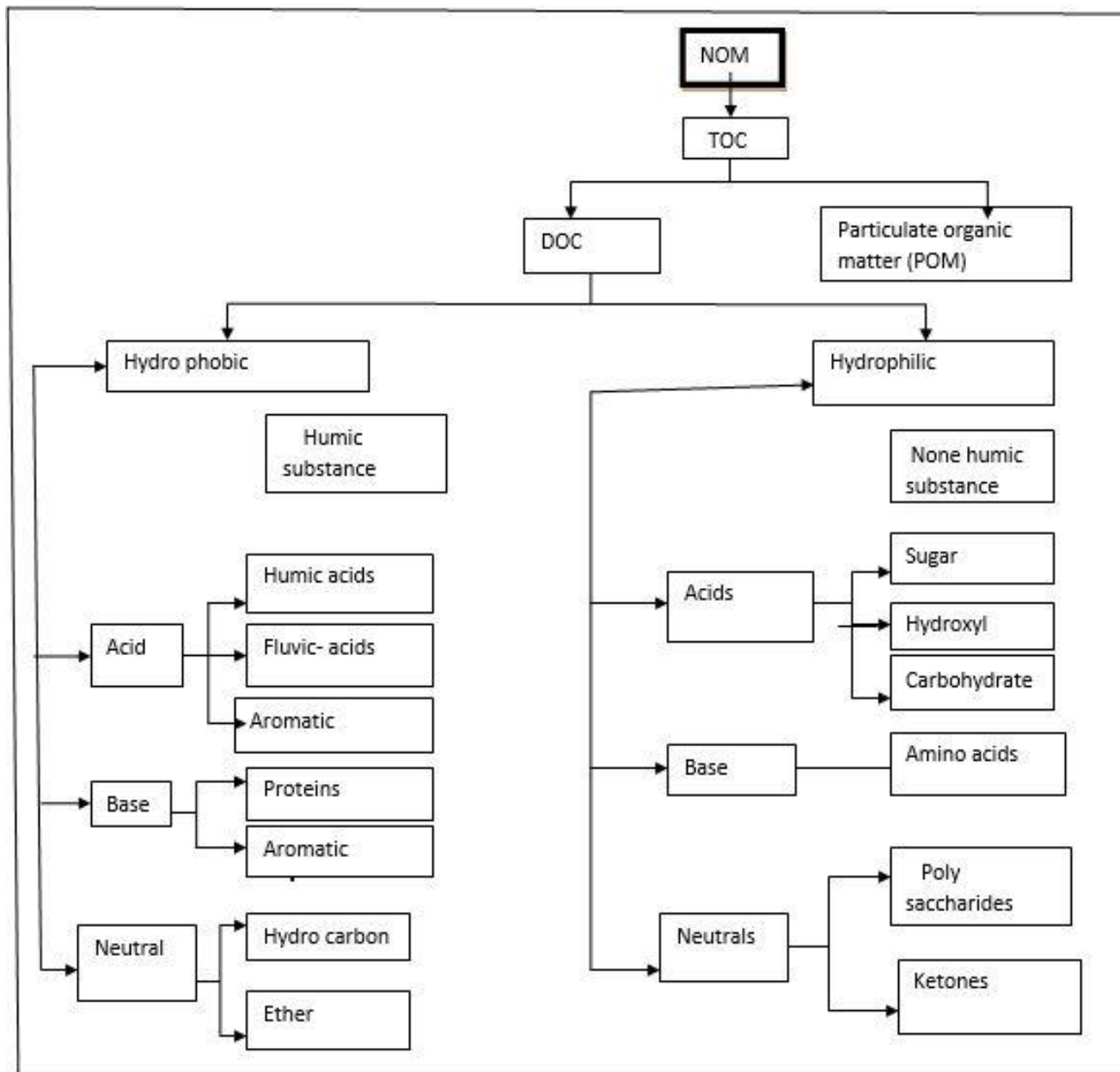


Figure 1: Relationship between NOM fraction and its chemical groups Source: (Matilainen *et al.*, 2010; Ibrahim and Aziz, 2014).

2.1.2 Factors affecting NOM composition

The composition of NOM is more dependent on conditions at which it present, most notably the catchment basin (Sharp *et al.*, 2006). Hydrological pathways, temperature and sunlight and biological predominance help determine relative compositions of NOM in surface waters. Typically, upland and densely vegetated catchments with a higher percentage peat cover have a higher incidence of humic and fulvic like material. This results in increasingly colored and turbid water and is also observed in agricultural catchments where the total soil carbon source has been disturbed. NOM is transported through catchments its composition will be altered by continuous metabolism and photo degradation through fluvial networks (Baker and Spencer, 2004).

2.2 Impact of NOM in drinking water production

NOM has a significant impact on many aspects of water treatment, including the performance of unit processes, necessity for and application of water treatment chemicals, and the biological stability of the water. As a result, NOM affects potable water quality as a carrier of metals and hydrophobic organic chemicals and by contributing to undesirable color, taste, and odor problems. In addition, NOM necessitates the majority of the coagulant and disinfectant used in water treatment. It tends to interfere with the performance of unit operations, such as biofilm growth on media, causing rapid filter clogging and fast saturation of activated carbon beds. NOM is also responsible for the fouling of membranes. NOM contributes to corrosion, is a source of nutrients for heterotrophic bacteria, and acts as a substrate for bacterial growth in distribution systems. NOM also forms stable complexes with metal ions (Jacangelo *et al.*, 1995). Moreover, NOM has been found to be the major contributor to disinfection by-product (DBP) formation (Trang *et al.*, 2012).

NOM does not pose a risk to human health on its own; some NOM compounds are known to react with chlorine and chloramines to produce disinfection by-products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAA) that are thought to be carcinogenic and/or genotoxic (Newfoundland and Labrador, 2011).

The presence of NOM, as already indicated, creates serious problems to drinking water quality and its treatment processes. These problems include: negative effect on water quality due to color, taste, and odor, increased coagulant and disinfectant dose requirements, which in turn results in increased sludge and potential harmful disinfection byproduct (DBP) production, promoted

biological growth in distribution system, and Increased levels of complexed heavy metals and adsorbed organic pollutants (Jacangelo *et al.*, 1995).

2.3 Methods for NOM removal

2.3.1 Coagulation

Coagulation is a physical–chemical process where the repulsive potential of electrical double layer of colloids is reduced in such a way that micro-particles can be produced. These micro-particles collide with each other to form larger structures, called flocs in the flocculation process. The use of coagulants for NOM removal was reviewed a few years ago (Matilainen *et al.*, 2010).

Coagulation, particularly when enhanced or optimized, is a major treatment option to address raised NOM levels. Enhanced coagulation is an especially good option for high-alkalinity waters (Yan *et al.*, 2008).

The aggregation mechanisms through which NOM is removed include a combination of charge neutralization, entrapment, adsorption, and complexation with coagulant metal ions into insoluble particulate aggregates (Jarvis *et al.*, 2008).

NOM removal through coagulation is more effective for organic matter with high molecular weight (HMW), such as humic acid. LMW matter is more difficult to remove than HMW and IMW NOM, which can be easily removed by coagulation. However, the removal of the smallest molecular size fraction can be enhanced by optimizing the water treatment process (Jacangelo *et al.*, 1995; Matilainen *et al.*, 2002; Matilainen *et al.*, 2010).

2.3.2 Advanced oxidation process

AOPs are among the most studied technologies concerning drinking water purification and disinfection, and very promising results have been gained. These processes involve the generation of highly reactive radical intermediates, especially the OH radical. The appeal of AOPs is their ability to achieve complete oxidation or mineralization of organic contaminants at near ambient temperature and pressure (Matilainen and Sillanpää, 2010).

AOPs have not been detected to reach total reduction of NOM in many cases; several studies have shown efficient reduction of NOM and mitigation of DBP formation. However, the circumstances

used in the research studies may not always be economically feasible in full-scale applications (Jarvis *et al.*, 2008)

2.3.3 Adsorption mechanism

Adsorption occurs when one species attaches itself to another through intramolecular forces (i.e., dipole interactions, hydrogen bonds). It is mainly used to transfer a chemical species from a liquid or gaseous phase onto a solid one. The solid species is referred to as the adsorbent and the species that is removed from the gas or liquid phase is called the adsorbate (Dąbrowski, 2001).

The surface of an adsorbent media can be positively or negatively charged, which will impact the types of compounds it can remove. Many NOM fractions are charged at ambient conditions and thus can be removed through adsorption. The hydrophobic acid fraction, which is the most extensively studied, is negatively charged at a neutral pH. Consequently, it is most effectively adsorbed when the media is positively charged. Common adsorbents used for NOM removal include activated carbon, ionic resins, and metal oxides (Newfoundland and Labrador, 2011).

Solution pH and ionic strength can impact the adsorption of NOM by activated carbon. At lower pH NOM molecules are smaller and less charged, which can result in changes in the interactions with the adsorbent. One study found that significantly more NOM was adsorbed onto an activated carbon media at a pH of 3 than at a pH between 7 and 8 (Newcombe, 1999). Increasing ionic strength is associated with more effective adsorption on negatively charged surfaces but less effective adsorption on positively charged surfaces (Summers and Roberts, 1988).

There is a great need of the removal of organic pollutants from water by using low cost adsorbents at pilot and industrial scales (Ambashta and Sillanpää, 2010; Ali *et al.*, 2012). Activated carbon (Karanfil *et al.*, 1994; Daifullah *et al.*, 2004), clays (Johns *et al.*, 1993), Chitosan (Ngah and Musa, 1988), metal modified silica (Moriguchi, *et al.*, 2005), mesoporous silica (Tao *et al.*, 2010), and rice husk ash (Imyim and Prapalimrunsi., 2010) are few to mention. However, yet low cost and locally available adsorbents have to be investigated and employed.

2.3.4 Membrane filtration

Membranes have become increasingly common in water treatment. Membrane filters are now well-established in the water industry as an alternative to traditional media filters. They can be

used in conjunction with coagulation, adsorption, and oxidation processes or combined with one another to produce high quality drinking water without chemical addition. The four main types of membrane processes are:

- ✓ Microfiltration (MF);
- ✓ Ultrafiltration (UF);
- ✓ Nanofiltration (NF); and
- ✓ Reverse osmosis (RO). Which all have different NOM and particle removal potentials (Jacangelo et al., 1995; Zularisam *et al.*, 2006)

Membrane filters can remove much smaller particles than conventional media filters because of the small size of the pores the membrane surface. They also have very small footprints relative to many of the other processes used to remove NOM (Newfoundland and Labrador, 2011).

In developing countries, the approach for new water systems should focus on their own sustainability, the minimal requirements of skilled personnel, low maintenance and operating costs. Besides, the use of local materials to achieve an environment-friendly operation can be a good option instead of synthetic materials, which increase the cost, have a secondary effect on the population health and lead to environmentally negative consequences (García, 2011).

Currently different types of technologies are used to remove NOM from drinking water. Some of these are oxidation, reverse osmosis, ion exchange, electro-dialysis, electrolysis, adsorption etc. However, these technologies are expensive, demand large energy and also need skilled manpower and hence not easily applicable in developing countries; except adsorption technology. Adsorption is considered as the best water treatment method due to its universal nature, inexpensiveness and ease of operation. Adsorption can also remove soluble and insoluble organic pollutants (Gupta and Shukla, 2009).

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Study Design and Period

Laboratory based experimental study was conducted at Jimma University, College of Public Health and Medical Science, Environmental Health science and Technology Department, Environmental Health science and Technology Laboratory from March 2017 to May 2017.

3.2. Study variables

3.2.1. Independent variables: the independent variables are pH, Contact time, Initial HA concentration, Adsorbent dose and Agitating speed.

3.2.2. Dependent variable: the dependent is Adsorption capacity

3.3. Adsorbent Preparation

The solid residue of the coffee husk was obtained from local coffee processing factory. The coffee husk was washed with distilled water, dried at 110 °C for 24 h in a laboratory oven to remove moisture, crushed and sieved to obtain particle size less than 0.3 mm. Then treated with H₃PO₄ acid with 85%(w/w) solution in a 1:1 mass proportion (phosphoric acid: raw material) and activated at 550°C for 2 h in furnace (Nabertherm Muffle Furnace LT 15/11). After the activation, the excess H₃PO₄ was washed with hot distilled water until a neutral pH (\approx 6) was reached (Baquero *et al.*, 2003; Oliveira *et al.*, 2009; Lamine *et al.*, 2014).

3.4 Preparation of Adsorbate Solution

Stock synthetic solution having NOM concentration of 180 mg/L was prepared in distilled water using required 0.5 g of humic acid powder and dilute it to 1 L, in a 1 L volumetric flask. The stock solution prepared by dissolving the HA (Blulux laboratories(P) Ltd. -121001 (Product No. Ho503) in distilled water raised pH \approx 11 with 0.1 M NaOH and stirred in hot plate slowly heating up to 60°C in order to accelerate the dissolution. Then the super-saturated HA suspension was cooled down to room temperature gradually and the pH was adjusted back to pH \approx 6 with 0.1 M HCl (according to analytical method for environmental water quality code 06581) (Analytical Methods

for water environmental water quality, 2014) and filtered through 0.45µm membrane filter (MN 640 d, No. 42, Blauband, Germany) to remove the undissolved HA powder. The stock solution stored in refrigerator at 4-6°C for later use. A series of standard working solutions for adsorption experiment was prepared by diluting the stock solution. The 0.1 M HCl and 0.1 M NaOH was used to adjust solution pH (Joseph *et al.*, 2012).

3.5. Batch adsorption experiments

Sets of batch adsorption experiment was performed in order to investigate the HA adsorption process onto CACH under various experimental conditions. Batch adsorption experiment was carried out by mixing desired amount of adsorbate (NOM containing sample) volume 100 mL with desired amount of adsorbent (CACH) in 250 mL Erlenmeyer flask. Before mixing with the adsorbent, the initial pH was adjusted to 6. The selection of the pH level was due to the fact that the pH of water is almost in the range of 5-7. All experiments were carried out in duplicate at room temperature. Control (only the test substance without adsorbent) and Blank (only the adsorbent without the test substance) experiments had been carried out for each set of experiments. The effects of different parameters such as adsorbate (HA concentration), CACH dose, contact time, mixing speed/agitation time and solution pH was investigated. The HA containing solution was agitated by a horizontal shaker (SM-30, Edmund Buhler GmbH, Germany)) at 200 rpm for a desired contact time. Then each sample was filtered through 0.45µm membrane filter (MN 640 d, No. 42, Blauband, Germany) filter paper and prepared for dissolved organic matter analysis. Finally, HA concentration of solution was determined using DR-5000 spectrophotometer at wavelength of 254 nm (Oliveira *et al.*, 2009; Joseph *et al.*, 2012).

The percentage removal and the amount of NOM adsorbed per unit mass of adsorbent, q_t (mg/g), at any time t (min) are computed respectively using Equ. (1) & (2).

$$HA\ removal(\%) = \frac{(C_0 - C_t)}{C_0} * 100 \dots\dots\dots (1)$$

$$q_t = (C_0 - C_t) * \frac{V}{M} \dots\dots\dots (2)$$

Where: C_0 = initial concentration of HA in aqueous phase (mg/L), C_t = mass concentration of HA in aqueous phase at time t (mg/L), q_t = the amount of HA adsorbed per unit mass of the adsorbent (mg/g), M = dry mass of the adsorbent (g), and V = initial volume of the adsorption test (L).

3.5.1 Effects of contact time, solution pH, adsorbent dose, initial concentration and shaking speed on HA Adsorption onto CACH

The effect of contact time on HA removal investigated by varying the contact time (20-120 min) until equilibrium achieved, while maintain other parameters constant. The pH of a solution is one of the important parameters in adsorption. Solution pH affects the surface charge of the adsorbent. The influence of varying pH on HA removal efficiency of the adsorbents was investigated over pH range 3 to 11, keeping other parameters constant. The effect of adsorbent dose on HA uptake was examined by varying the dose of CACH from 1 to 25g/L. other parameters kept constant. The effect of C_0 was examined varying the concentration of HA (0.5 mg/l to 20 mg/L) while maintaining the solution pH, adsorbent dose, shaking speed, equilibrium contact time. The effect of agitation speed on HA adsorption was carried out with a horizontal shaker at room temperature by varying the agitation speed from 50 to 300 rpm while keeping other parameters to their optimum then optimum agitation speed determined.

3.6 Adsorption Theory

3.6.1 Adsorption kinetics

The pseudo-first order and second order kinetic models are used to study the sorption kinetics of pollutants and to quantify the extent of uptake in sorption kinetics.

To determine kinetic adsorption parameter, the obtained kinetic adsorption data were evaluated by using simple linear Lagergren pseudo-first order equation(Eq.3), pseudo-second equation (Eq. 4) and intra-particle diffusion model (Eq.5)

$$\log(q_e - q_t) = \log q_e - \frac{K_f t}{2.303} \dots\dots\dots (3)$$

Where; k_f is the pseudo-first order rate constant of adsorption (1/min), q_t and q_e (both in mg/g) is the amount of NOM/DOM absorbed at time t and at equilibrium, respectively. Straight line plot of $\log(q_e - q_t)$ versus at different time were plotted to calculate the rate constant and determination coefficient (R^2)

$$\frac{t}{qt} = \frac{1}{Ksqe^2} + \frac{t}{qe} \dots\dots\dots (4)$$

The values of k_s is the pseudo-second order sorption rate constant (mg/min) and q_e (mg/g). It is calculated from the intercept and the slope of the plot of qt versus t , respectively (Hameed *et al.*, 2007; Oliveira *et al.*, 2009; Ahmad and Rahman, 2011).

$$qt = kpt^{0.5} + C \dots\dots\dots (5)$$

Where qt is the amount of HA absorbed (mg/g) at a given time (min); k_p [mg/ (g. min^{0.5})] is the intra-particle diffusion rate constant; C (mg/g) is the intercept of the intra-particle diffusion model. The plot of qt versus $t^{0.5}$ is used to determine the adsorption mechanism (Ahmad, and Rahman, 2011).

3.6.2. Adsorption Isotherms

The adsorption isotherm was used to evaluate the HA sorption capacity of chemically activated carbon of coffee husk, the relationship between the amounts of HA adsorbed at equilibrium per unit mass of the adsorbent and the concentration of HA in the aqueous phase at equilibrium was analyzed by applying adsorption isotherm models. Langmuir and Freundlich models are the most frequently used for describing the adsorption isotherms from experimental data. These models can be used to design and optimize an operating procedure. Both Langmuir and Freundlich models were tested for equilibrium description

3.6.2.1. Langmuir isotherm

It based on a theoretical model, assumes monolayer adsorption over an energetically homogeneous adsorbent surface containing a finite number of adsorption sites. It does not take into account interactions between adsorbed molecules. It can be represented by non-linear equation (Eq.6)

$$\frac{Ce}{qe} = \frac{1}{bQo} + \frac{Ce}{Qo} \dots\dots\dots (6)$$

Where q_e is the amount adsorbed per gram of adsorbent at equilibrium (mg/g), C_e is the solute (HA) concentration (mg/L) in the aqueous solution at equilibrium. The Langmuir constants Q_o (mg/g) represent monolayer adsorption capacity and b (L/mg) relates the heat of adsorption.

In order to evaluate the feasibility of the process, the Langmuir isotherm can be described in terms of the dimensionless constant; separation factor or equilibrium parameter (Eq.7)

$$R_L = \frac{1}{1+bC_o} \dots\dots\dots (7)$$

b (L/mg) is the Langmuir isotherm constant and C_o (mg /L) is the initial concentration of NOM/DOM. The shapes of the isotherm are expressed by R_L. There are four probabilities for the R_L value: For favorable adsorption (0 < R_L< 1), for unfavorable adsorption (R_L> 1), for linear adsorption (R_L = 1) and irreversible adsorption (R_L =0)

3.6.2.2 Freundlich isotherm

Freundlich’s equation is an empirical model based on heterogeneous adsorption over independent sites and is given by non-linear equation (Eq.8)

$$\log qe = \log kf + \frac{1}{n} \log Ce \dots\dots\dots (8)$$

Where K_f (L/g) related with the total adsorption capacity and 1/n dimensionless number is related with the intensity of adsorption

To identify suitable isotherm models for the adsorption of HA onto CACH, the sum of the squares of the errors (SSE) analysis was carried out (Foo and Hameed, 2010). The mathematical statement of the Sum of Square error statistic is given by the Eq. (9).

$$ERRSQ = \sum (q_{e, cal} - q_{e, exp})^2 \dots\dots\dots (9)$$

Where: q_{e,cal} and q_{e,exp} are the theoretical and experimental capacities (mg /g), respectively

3.7. Regeneration of adsorbent

Regeneration of adsorbents is an important process in the water/wastewater treatment to reduce the processing cost, recover adsorbates, and/or explain adsorption mechanism. Different regeneration techniques have been used for desorption study. To investigate the reusability of adsorbent, desorption has been investigated using optimum adsorbent dose to adsorb optimum adsorbate concentration. The adsorbent was separated from the solution by filtration using 0.45µm

membrane filter (MN 640 d, No. 42, Blauband, Germany) filter paper and washed gently with distilled water to remove un-adsorbed HA on adsorbent surface. The HA loaded on AC of coffee husk was dried in an oven at 105°C for 24 hrs and then soaked and shaken in (0.1 - 0.2 M) NaOH solution. Then, the amount of desorbed HA was measured and desorption ratio of HA calculated using Eq. (10).

$$\text{Desorptionratio(\%)} = \frac{\text{Amount desorbed}}{\text{Amount adsorbed}} \times (100) \dots\dots\dots (10)$$

3.8. Data Analysis and Quality

At each set of experiments calibration (standardization) was conducted for analysis. Each batch adsorption experiment was performed in duplicates and the average values were reported to ensure reproducibility and accuracy. Blank and control was used for correction of interference that leached from instruments and adsorbents (Stephenson, *et al.*, 1985). The data was analyzed using originPro8 software using the solver add-in with Microsoft’s Excel spreadsheet 2010. The data presented using graphical and tabular statistical tools.

3.9. Ethical consideration

Each and every of data collection, processing, and analysis followed scientific methods and procedures. Furthermore, all concerned bodies were informed prior to the study get started. Finally, the result of laboratory analysis honestly recorded and interpreted based on scientific procedures.

3.10. Dissemination plan

Based on the findings the data were analyzed, concluded, recommended and then results of the study will be submitted to Faculty of Civil and Environmental Engineering, Jimma Institute of Technology, Jimma University, and the findings will be published on a peer reviewed journal.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1 Characterization of adsorbent

Coffee husk is the solid generated by de-hulling (outer skin, pulp, and parchment). It contains great amount of organic compounds (i.e. fatty acid, lignin, hemi-cellulose and other polysaccharides) (Pujol *et al.*, 2013). Proximate analysis of dry coffee husk includes 6.98 wt% of moisture, 64.94 wt% of volatile, 21.03 wt% fixed carbon and 7.05 wt% ash. The result of ultimate analysis showed that dry coffee husk includes 46.62 wt% of C, 8.87 wt% of H, 23.90 wt% of O, 5.64 wt% of N and 0.94 wt% of S (Chen *et al.*, 2016). Oliveira *et al.*, found that the proximate composition of the coffee husk employed was 10% water, 11% protein, 2% Lipids, 70% carbohydrates and 7% ash (Oliveira *et al.*, 2007). The functional groups at the surface of the husk were predominantly Phenolic (2.24 mol/g), followed by lactonic (1.05 mol/g), Carboxylic (0.60 mol/g) and basic (0.49 mol/g) groups. All the above indicate the differentiation of surface chemistry of coffees which is directly related with the treatment before the adsorptions use (Oliveira *et al.*, 2007).

Untreated coffee husk has rough surface but scraggy with variety of cavities. These cavities can be characterized as channel onto the surface of untreated coffee materials instead of pores, given the small surface area (kyzas *et al.*, 2012). Preparing ACs using activating agent, in our case phosphoric acid has strong influence on the pore volume and structure of ACs. Low impregnation ratios led to essentially microporous ACs, whereas at intermediate ratios, ACs with wider pore size distribution (from microporous to Mesoporous) were obtained. High impregnation ratios yielded essentially mesoporous carbons with a large surface area and pore volume (Baquero, 2003). Preparing the activated carbon by chemical activation of the coffee husk can significantly affect adsorption by creating external surface of the adsorbent to be positively charged (Wang *et al.*, 2016).

4.2 Effect of contact time

The plots of the amount of HA adsorbed versus contact time are given in fig 2. The result showed that HA removal capacity increased from 0.625 to 0.958 mg/g and the removal percent from 62.54% to 93.81% as the contact time increased from 20 to 120 min of agitation speed. From 20

to 60 min of contact time the removal percent and capacity showed high increment, whereas from 60 to 120 min showed increment with insignificant change almost constant. Therefore, 60 min was considered as equilibrium contact time.

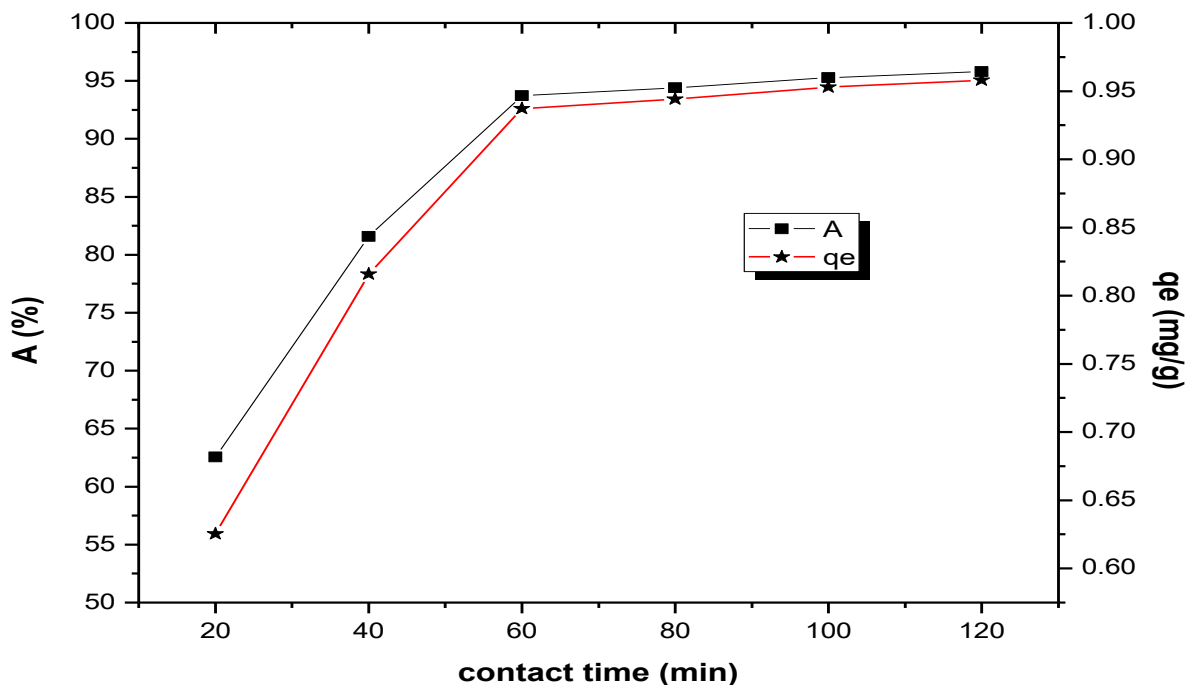


Figure 2: Effect of contact time on adsorption of HA onto CACH (C_0 : 10 mg/L, adsorbent dose: 10 g/L, pH: 6, agitation speed: 200 rpm)

It can be seen that the adsorption of HA is rapid at the initial stage of contact period, but it gradually slowed down until it reached equilibrium. The rapid uptake of HA within the first 20 min agitation time was due to the presence of a large number of free competent active adsorbing sites available on the surface of the adsorbent (Fufa *et al.*, 2014; Berhe *et al.*, 2015). The result shows that the adsorption rate with increasing initial contact time in a given mass of adsorbent is raised and then gradually reaches equilibrium because the adsorbent surface of a given particular mass of adsorbent involve particular site to adsorb HA concentration. So, those site would be occupied by adsorbate within short period of time due to increasing contact time. The study indicated that the highest removal rate of HA occurred at contact time of from 60-120 minutes showing insignificant change within the time interval. However, in the previous studies using similar adsorbents for removal 25-50 mg/L of Remazol Brilliant Orange 3R dye from water by

adsorption, it was found that the equilibrium time needed for it was 5hr (Ahmad and Rahman, 2011).

4.3 Effect of pH

The effect of pH solution of the adsorbent was investigated at initial concentration of 10 mg/L, adsorbent dose 10 g/L with contact time of 60 min and 200 rpm agitation speed. The amount of HA removed was dependent on pH of the solution. The effect of pH on HA removal capacity is shown on Fig 3. HA removal was highly decreased from pH 6 to 11 with the adsorption capacity of 0.8573 to 0.2429 and removal percent of 85.73% to 24.29%. As we have seen from the experiment from pH 3 to 6 achieved high removal. The highest removal obtained at pH 3 with adsorption capacity of 0.9433 and 94.33% removal efficiency.

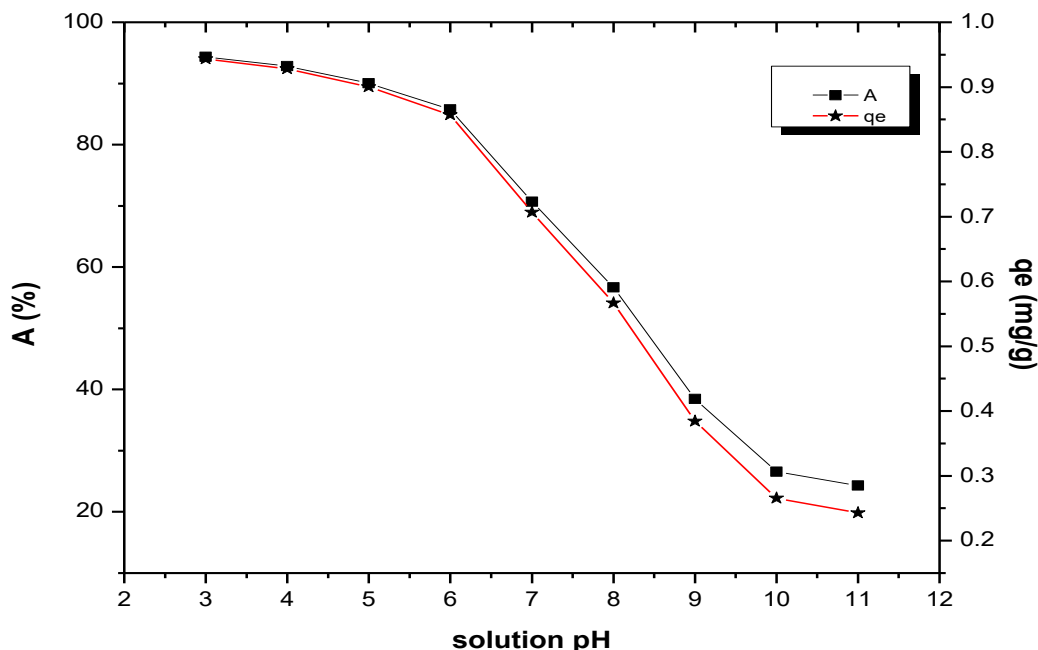


Figure 3: The effect of pH on the adsorption of HA onto CACH (Co:10 mg/L, adsorbent dose: 10 g/L, contact time: 60 min, agitation speed: 200 rpm)

The solution pH plays an important role in controlling the surface charge of the adsorbent. The results showed that the percent removal of humic acid was increased when the pH was decreased. This Increment can be explained as follows humic acid is predominately negatively charged.

Therefore, decreasing the pH renders the adsorbent surface to be positively charged the negatively charged HA molecule attracted toward oppositely charged adsorbent surface. And HA which remain in the solution attract the opposite charged (hydrogen ions in this case) to its surface from the surrounding water and becomes more neutral. A neutral molecule is inherently less soluble in water than a charged molecule (water is highly polar solvent) and, therefore, more adsorbable. In other words, the adsorption process become more favorable as the solution pH decreased. At high pH, the adsorbent surface could be charged negatively, and the electrostatic repulsion between HA molecules and the adsorbent surface, which may reduce the HA adsorption on the adsorbent. It can be concluded that the adsorption of HA is favorable in acidic condition (Newcombe, 1999; Han *et al.*, 2003; Imyim and Prapalimrungsi, 2010; Nsaifabbas, and Saeed, 2014; Wang *et al.*, 2014; Zulfikar *et al.*, 2016). In this study, the initial pH value at 6 of HA solution was selected due to the fact that the pH of water is almost in the range of 5-7.

4.4 Effect of Agitating speed

Adsorption studies were carried out using horizontal shaker at an initial concentration of HA 10 mg/L; CACH (10 g/L) dose with contact time 60 min and pH 6. The agitation speed varied from 50 to 300 rpm adopted from (Berhe *et al.*, 2015). It was observed that the adsorption percentage of HA onto the adsorbents increased with increasing agitation speed reaching maximum of 94.64% at 200 rpm (fig 4). It found that the removal of HA increased with increasing in agitation speed from 50 up to 200 rpm and maximum removal achieved at 200 rpm. This is due to dispersal of the adsorbent particle in the aqueous solution which leads to reduced boundary mass transfer and even then it may increase the velocity of particles, so that it increases the percent removal of HA. Decreased value of HA adsorption on CACH after 200 rpm observed as a result of too vigorous agitation rate which causes more HA molecule to be desorbed from the adsorbed surface (Berhe *et al.*, 2015).

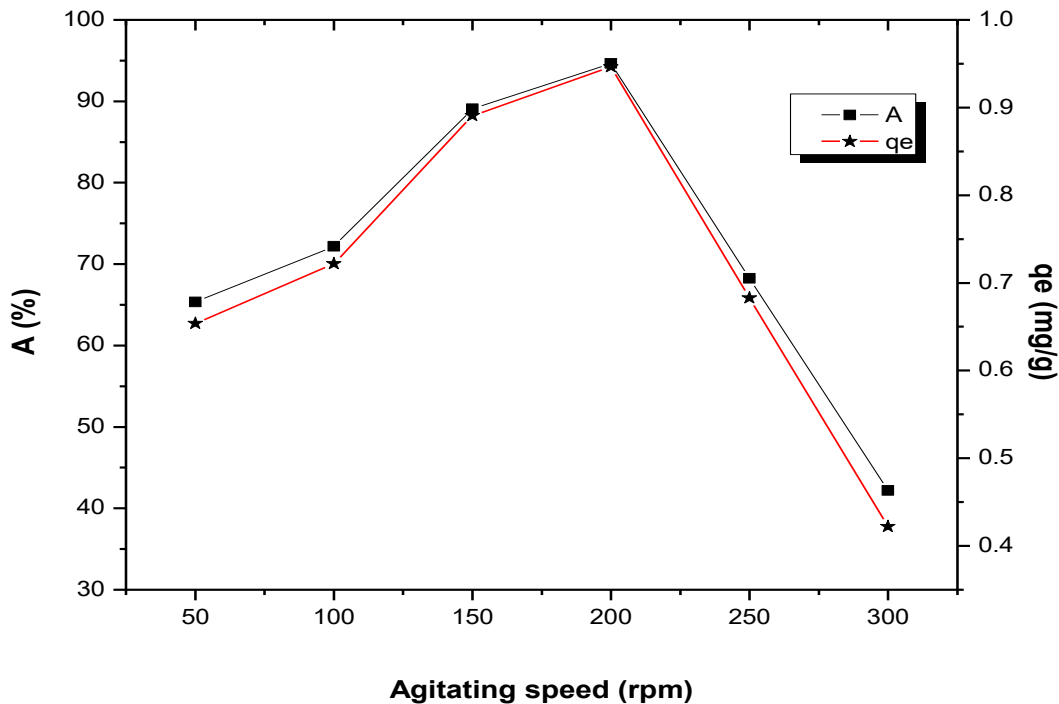


Figure 4: The effect of agitating speed on the adsorption of HA onto CACH (Co: 10 mg/L, adsorbent dose: 10g/L, pH: 6, contact time: 60 min)

4.5 Effect of CACH dosage on adsorption

To determine the optimum dose of adsorbent, CACH powder dosage range (1-25 g/L) were considered as variable and other parameters as constant. The experiment for the adsorbent revealed that the removal efficiency of HA in a fixed contact time of 60 min increase significantly from 83.25% to 98.7%. This observation can be attributed to the increase of the availability of free adsorption site (Banerjee and Chattopadhyaya, 2016). On the contrary, the HA loading capacity (the amount of HA adsorbed per unit mass of CACH) progressively decreased from 8.32 to 0.39 with increasing in the adsorbent dose from 1 to 25 g/L. The progressive decrease in the loading capacity was possibly due to the lower ratio of HA molecules to available active binding sites with the increase in the mass of adsorbent (Berhe, 2009).

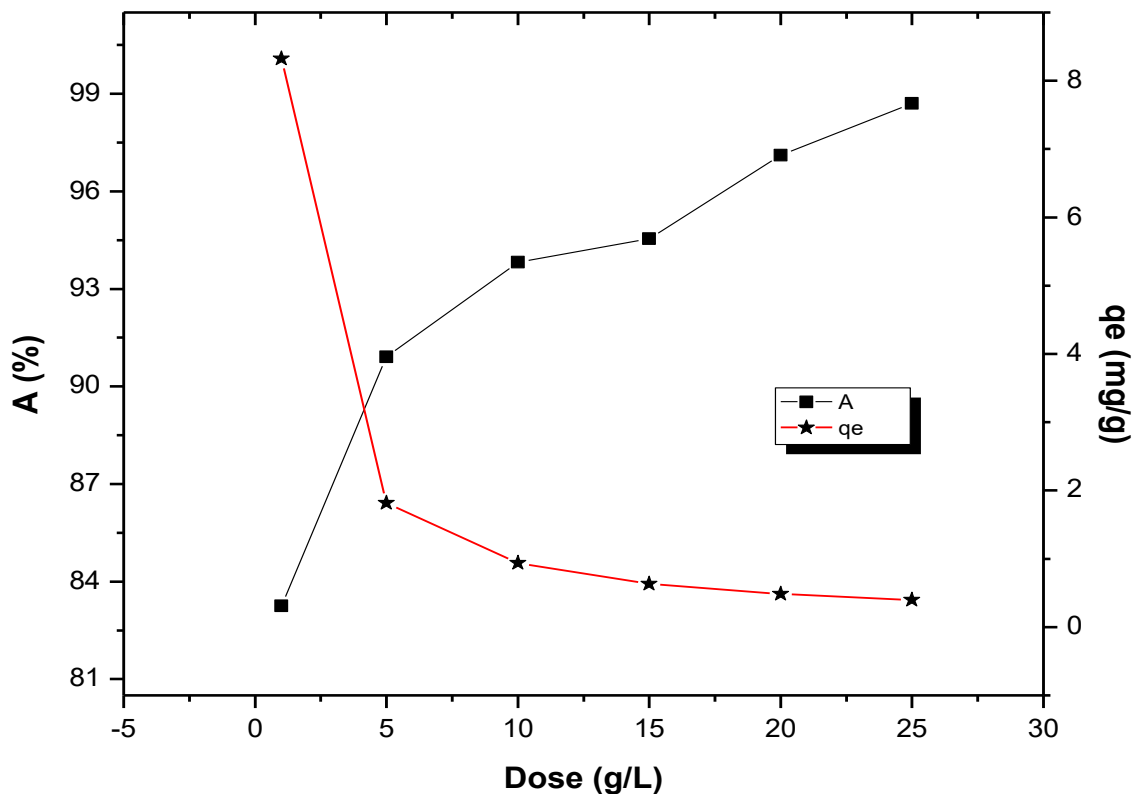


Figure 5: The effect of adsorbent dose on the adsorption of HA onto CACH (Co: 10 mg/L, pH: 6, contact time: 60 min, agitation speed: 200 rpm)

4.6 Effect of initial HA concentration

The effect of initial concentration of HA was investigated by varying the concentration from 0.5 to 20 mg/L at pH 6 using 10 g/L CACH. The equilibrium uptake of HA increased when increasing initial concentration from 0.5 to 20 mg/L, amount of HA per unit mass of adsorbent increased from 0.0487 to 1.394 mg/g, in 100ml solution. This is agreement with the finding from various researcher that suggest the more concentrated solution is better adsorption. (Mohammed and Firas, 2014).

On the contrary, the removal percentage of HA decreased with increasing HA concentration. On changing the initial concentration from 0.5 to 20 mg/l, the removal percentage of HA decreased significantly from 97.34% to 69.7%. this is one of the principles adsorption of adsorption isotherm that is, the site with greater affinity by adsorbate are occupied first followed by other sites with less affinity by adsorbate, until the saturation of the adsorbent (Imyim and Praralimrunsi, 2010; Nsaifabbas and Saeed, 2014).

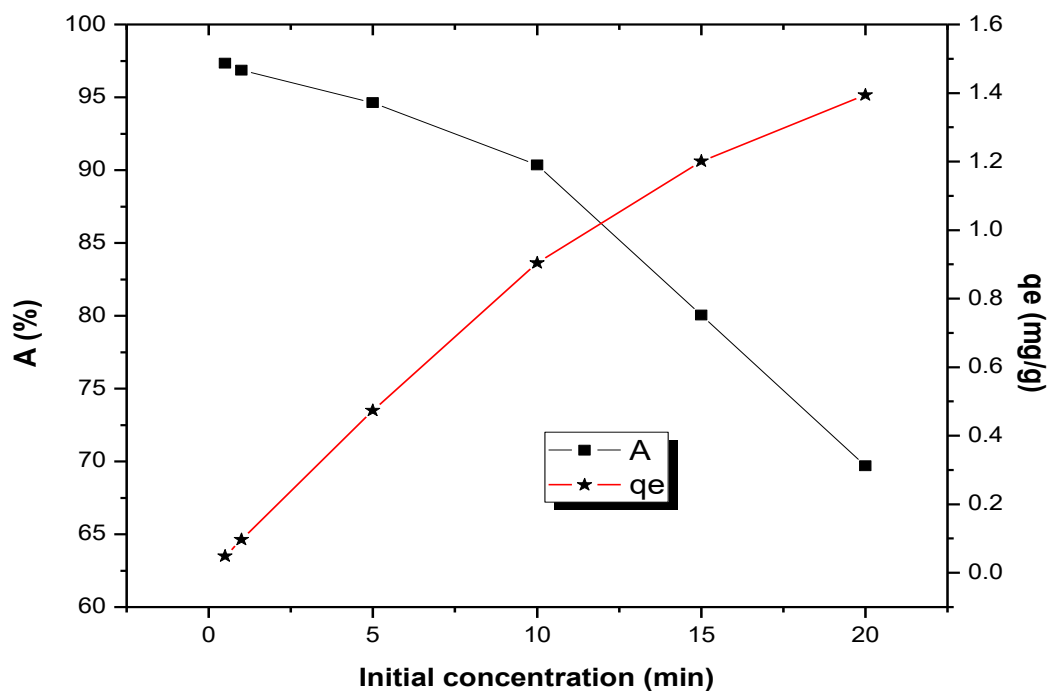


Figure 6: The effect of initial concentration on the adsorption of HA onto CACH (pH: 6, contact time: 60 min, agitation speed: 200 rpm, adsorbent dose: 10 g/ L)

4.7 Equilibrium Isotherm Models

Adsorption isotherms describe the distribution of adsorbate between adsorbent and solution when adsorption process reaches the equilibrium, which are an important data to elucidate the adsorption mechanism. The isotherm plots of the equilibrium adsorption of HA graphically represented in fig 6 and the value of equilibrium constant computed from the isotherm models using non-linear regression using Sum of square error function are given in Table 2. From the evaluation of the fitting criteria, it was clear that the Langmuir isotherm demonstrated higher coefficient of determination, $R^2 > 0.99$, and low SSE ≈ 0.006 . Thus the Langmuir isotherm equation well described the equilibrium isotherm data set of HA adsorption. These facts indicate that the chemical adsorption mechanism may involve in adsorption process of HA on CACH and HA molecules are adsorbed in the form of homogenous coverage on adsorbents' surface. For Langmuir model, the adsorption affinity between adsorbate and adsorbent can be described by the separation factor (R_L). The adsorption process is irreversible if $R_L = 0$, favorable if $0 < R_L < 1$, linear if $R_L=1$ and unfavorable if $R_L > 1$. The calculated value range from 0.032 to 0.570 with decreasing in value at high level of initial concentration indicating that HA adsorption on CACH is favorable.

Table 1: Non-linear isotherm parameters OF HA adsorption onto CACH

Langmuir Isotherm		Freundlich Isotherm	
Parameters	Value	Parameters	Value
Q_{max}	1.495	KF	0.768
B	1.510	1/n	0.365
R^2	0.998	R^2	0.968
SSE	0.006	SSE	0.058

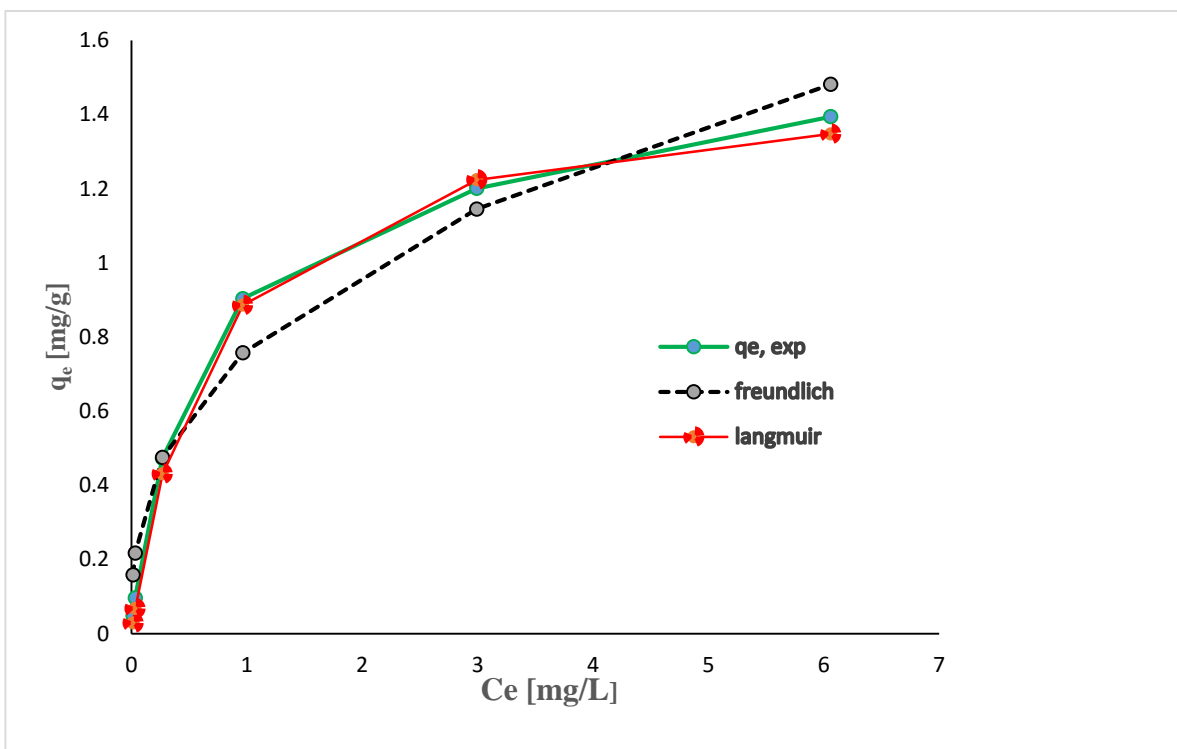


Figure 7: Equilibrium adsorption isotherm of HA on CACH (Co: 10 mg/L, pH: 6, contact time: 60 min, agitation speed: 200 rpm, adsorbent dose: 10 g/L)

4.8 Adsorption Kinetics

The kinetics of HA adsorption on CACH was investigated using 10 mg/L HA concentration and 10 g/L, agitated for 60 min at pH \approx 6. The linear plots of pseudo-first order and pseudo-second order sorption kinetics constant values of K_f , K_s , $q_{e,cal}$ (calculated), and $q_{e,exp}$ (experimental) are reported in Table 2. From the linear plot of pseudo-first order $\log(q_e - qt)$ versus t have coefficient of determination $R^2 > 0.96$ and the modeled equilibrium capacity is $q_{e,cal}$ (0.998). Further in the linear plot of pseudo-second order, the plots of t/qt versus t were straight line with coefficient of determination, $R^2 > 0.99$. In addition, the values of the modeled equilibrium capacity, $q_{e,exp}$ (0.972), was comparable to the experimental equilibrium capacity, $q_{e,exp}$ (0.958) than pseudo-first order kinetics. Thus, the kinetic of HA adsorption on CACH well described by pseudo-second order equation, the pseudo-second order reaction kinetics assumes that chemisorption, involving valence forces by the sharing of electrons between the positive charged surface of CACH and the negative charge of HA, is the rate limiting step. Thus, the overall rate of removal of HA is controlled by chemical adsorption reactions. Similar results are obtained in removal of HA from

aqueous solution (Garcia, 2011; Bouras *et al.*,2015; liu *et al.*, 2015; Wang *et al.*, 2016; An *et al.*, 2016).

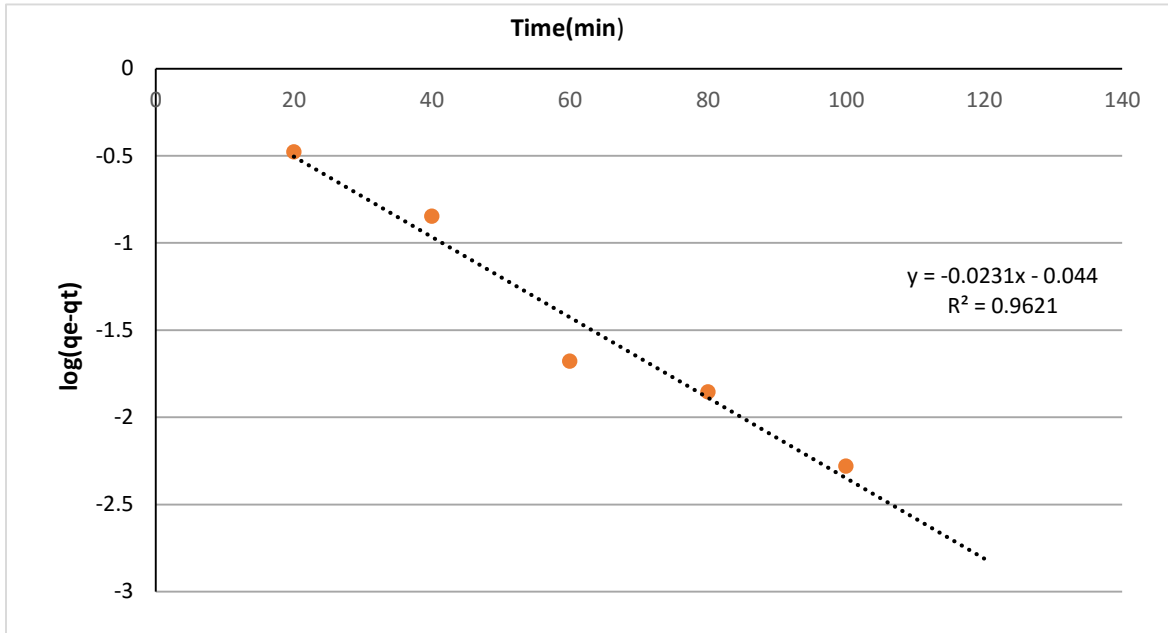


Figure 8: Plot of pseudo-first order kinetics of HA adsorption on CACH (Co: 10 mg/L, adsorbent dose: 10 g/L, pH: 6, contact time: 60 min and agitation speed: 200 rpm).

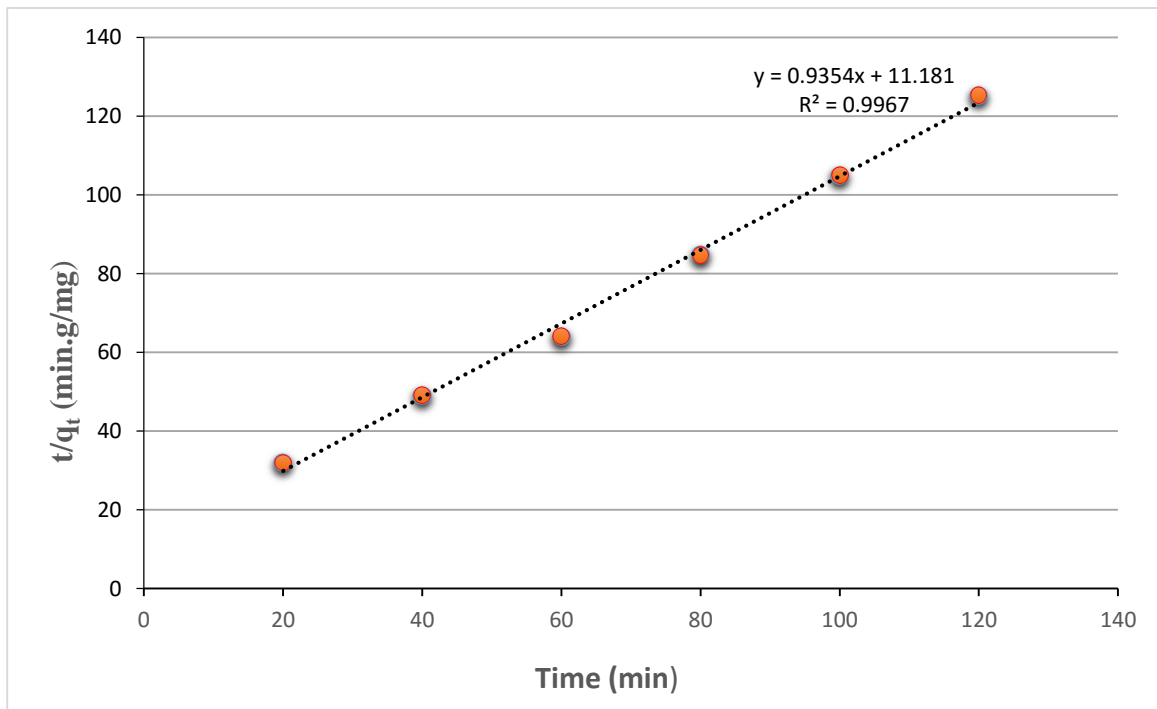


Figure 9: Plot of pseudo-second order kinetics of HA adsorption on CACH (Co: 10 mg/L, adsorbent dose: 10 g/L, pH: 6, contact time: 60 min and agitation speed: 200 rpm).

Besides adsorption on the outer surface of the adsorbent, the HA may also diffuse into the interior of the adsorbent. The intra-particle diffusion model (Eq.5) based on the theory proposed by Weber and Morris (1963) was tested to determine if the intra-particles' diffusion is rate limiting step for the HA adsorption onto CACH. The intra-particle diffusion rate constant (K_p) value estimated from the slope of plot of q_t versus $t^{0.5}$ was found to be 0.0495 and the plot did not pass through the origin. This indicates that the HA adsorption onto CACH is not only controlled by intra-particle diffusion but it is a complex process and this is indicative of that adsorption of HA and its kinetics could be cumulative result of the external diffusion transport of HA, the intra-particle diffusion of the molecules and the adsorption of HA by the active site (Fufa *et al*, 2014; Ncibi, 2008).

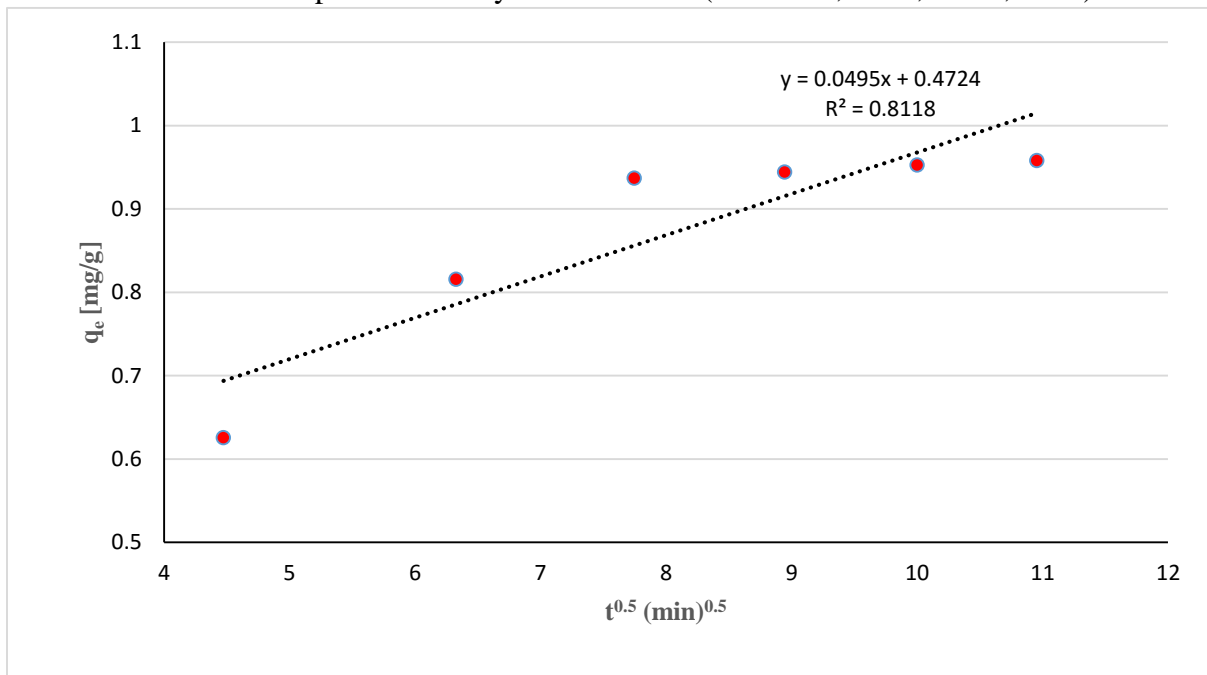


Figure 10: Plot of intra-particle diffusion of HA adsorption on CACH (C_o : 10 mg/L, adsorbent dose: 10 g/L, pH: 6, contact time: 60 min and agitation speed: 200 rpm).

Table 2: The kinetics parameters for adsorption of HA onto CACH

Pseudo-first order		Pseudo-second order		Intra-particle diffusion	
Parameter	Value	Parameter	Value	Parameter	Value
$q_{e,exp} \text{ (mg/g)}$	0.958	$q_{e,exp} \text{ (mg/g)}$	0.958	K_p	0.0495
$q_{e,cal} \text{ (mg/g)}$	0.998	$q_{e,cal} \text{ (mg/g)}$	0.972	C	0.4724
$K_f \text{ [g/(mg.min)]}$	0.055	$K_s \text{ [g/(mg.min)]}$	0.078	R^2	0.812
R^2	0.961	R^2	0.997		

4.9 Desorption Study

Any adsorbent is economically viable for pollutant removal from aqueous environment if the adsorbent can be regenerated and reused. The effect of PH on HA removal by CACH indicated that HA adsorption significantly decrease in $\text{PH} > 11$, so HA desorption from the spent CACH was considered under higher alkaline condition. Based on this, batch desorption of HA adsorbed was carried out identical experimental conditions of the batch adsorption studies using 100 mL of 0.1 and 0.2 M NaOH solution separately (Fufa *et al*, 2014). Fig 8 shows the percentage removal of HA desorbed by different concentration of NaOH solution. The result showed that the percentage of HA desorbed increased from 70.44% to 90.72% as the concentration of NAOH increased from 0.1 to 0.2 in the solution of CACH at $\text{PH} > 11$. The experimental result show that HA loaded CACH could be successfully regenerated. To test the adsorption potential of the regenerated adsorbent, two more cycles of adsorption-desorption studies were conducted by maintaining the same condition. In the second cycle adsorption capacity has shown 76.03%. From the observations these adsorbent have reuse potential for HA removal.

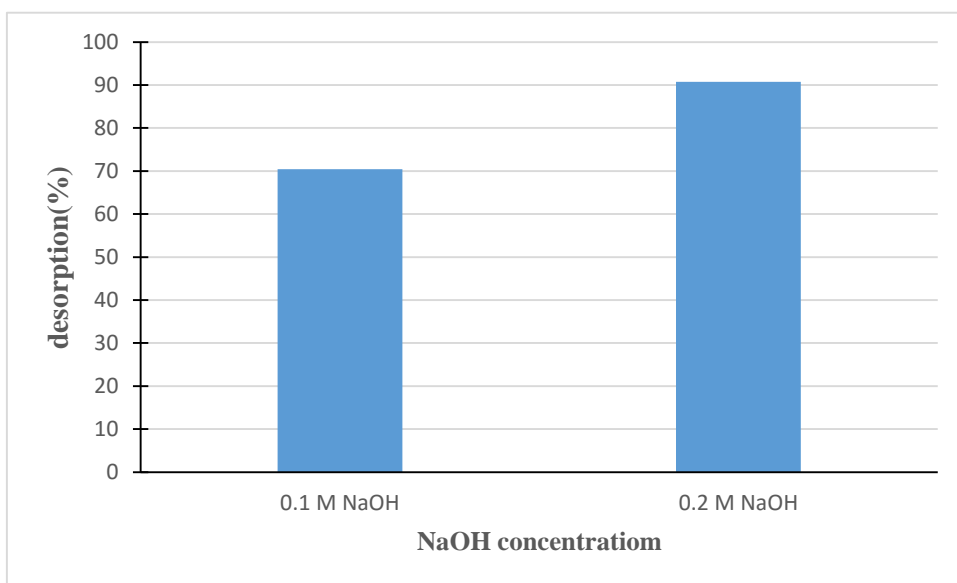


Figure 11: Percentage of HA desorbed from CACH (Co: 10 mg/L, dose: 10 g/L, shaking speed: 200 rpm, $\text{PH} > 11$)

4.10 Comparison among the removal efficiency of untreated coffee, heat treated and chemically activated coffee husk.

To determine which form of the coffee husk as an adsorbent has great removal efficiency we have used untreated coffee husk, thermally treated husk and chemically treated husk. The investigation is done using $C_0 = 10 \text{ mg/L}$, $\text{pH} \approx 6$, dose 0.5 g/100 mL , contact time 60 min , agitating speed 200 rpm . The result showed in fig 10, great removal efficiency variation was observed. From the experiment untreated coffee husk(UCH) achieved removal efficiency of 6.36% , thermally treated coffee husk achieved removal efficiency of 37.83% and the removal efficiency of chemically activated coffee husk was 87.05% . This results clearly show us chemically treated coffee husk has great removal efficiency than the untreated and only thermally/heat treated coffee husk.

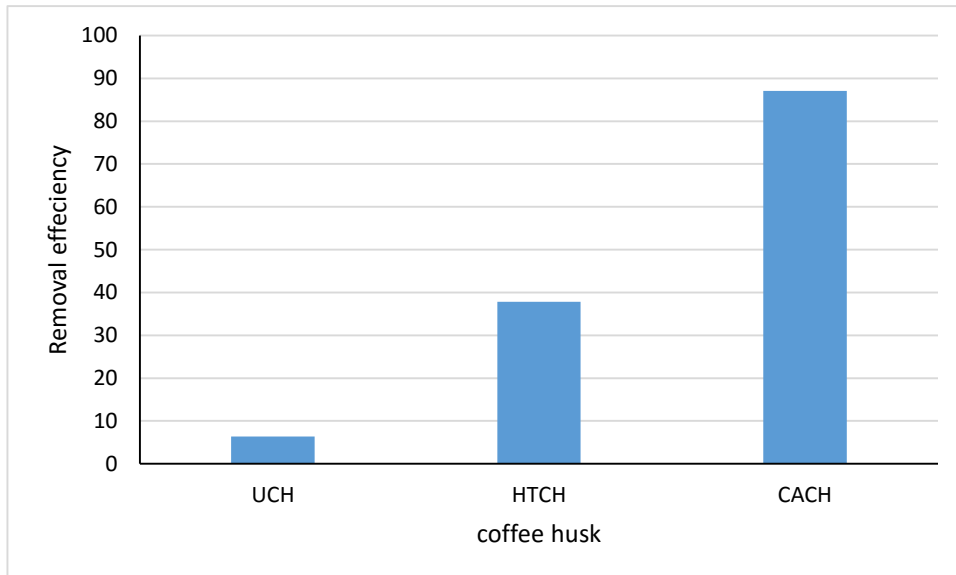


Figure 12: Comparison among the removal efficiency of untreated coffee husk, thermally/heat treated coffee husk and chemically activated coffee husk ($C_0 : 10 \text{ mg/l}$, $\text{PH} : 6$, agitating speed : 200 rpm , contact time : 60 min , dose 5 g/L).

From the result we can understand that the surface of coffee husk is lignocellulose precursor resulted from the presence of cellulose, hemicelluloses and lignin in the raw material without any cracks as a result untreated coffee husk has no active surface sites and pores to be attached. This can be the reason for its lower removal efficiency. In the other hand coffee husk which is treated only with heat has better removal compared to untreated coffee husk. During pyrolysis that is heat treatment at 550°C , the surface of the coffee husk starts to form irregular pores due to the removal

of volatile matter after carbonization this may give the efficiency to remove but it is not satisfactory. Thermal treatment increase carbon content by removing the volatile matter but not capable to make high surface area with pores, to achieve this we need further activation either by physical or chemical activation method. Activation at 550°C with H₃PO₄ resulted in the creation of more pores and a substantial removal of volatile matter. The diffusion of H₃PO₄ molecules into the pores increase the H₃PO₄-carbon reaction via acid hydrolysis process. The glycosidic linkage in hemicellulose and cellulose will be hydrolyzed by H₃PO₄, along with the cleavage of aryl bond in lignin. H₃PO₄ acts as oxidizing and dehydrating agent resulting high active surface area with different pores size micro mesoporous. As a result, chemical activation has high removal efficiency (Wang and (max) Lu, 1998; Hayashi, 2000; Ioannidou and Zabaniotou, 2007; Duman *et al.*, 2009; Mohamad *et al.*, 2013; Goncalves *et al.*, 2016; Shamsuddin *et al.*, 2016).

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

From the experimental result we can conclude that the HA adsorption on the adsorbent is highly dependent on pH and HA adsorption favored at low solution pH. The optimum pH of the solution was achieved at 3 and above pH 6 adsorption capacity and removal efficiency significantly decrease. The effect of adsorbent dosage on the adsorption of HA by chemically activated coffee husk showed that the percentage of HA removed increased with increase in adsorbent dosage due to increased adsorption surface area. Then 1g/100 ml of coffee husk was selected as an optimum dosage through the experiment. With increasing the initial HA molecule concentration, the amount of uptake increase and removal efficiency decrease. Adsorption isotherm of HA on the adsorbent most satisfactorily described by Langmuir isotherm model ($R^2 > 0.99$ and $SSE = 0.006$) than Freundlich model. HA adsorption process follows pseudo-second order kinetics with $R^2 > 0.99$ was suggestive of the dominant chemisorption mechanism of HA adsorption on the adsorbent CACH. The result of the adsorption-desorption-adsorption cycle showed that HA saturated adsorbent can be regenerated using 0.1 M and 0.2 M NaOH solution and the regenerated adsorbent still possessed adsorption capacity for HA in solution. Since coffee husk is widely and locally available, low-cost adsorbent; its utility will be economical and can be viewed as part of a feasible waste management strategy. The present finding highlight that CACH can be used to purify the aqueous HA in drinking water with further investigation.

5.2 Recommendations

- Further investigation is also required to investigate the adsorption capacity of the adsorbent under continuous flow conditions, like column experiment and small-scale for its applicability in large scale.
- Using CACH as adsorbent in Adsorption treatment mechanism is so important in convention water treatment system that use chlorine and other chemical as a means of disinfection mechanism, which result trihalomethane formation reacting with Natural organic matter that has carcinogen effect on human health. So adsorption treatment method is best and low-cost economically

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ANNEXE

ANNEXE I

A. Stock Solution Preparation

Procedure

- 1- Weigh known amount of granular Powdered Humic acid
- 2- Add the measured HA powder into 1L beaker which contain 500 ml distilled water
- 3- Dissolve the HA powder putting stir the solution in the hot plate until the temperature reach 60 °C (temperature and stirring required to facilitate the dissolution process)
- 4- Dry 0.45 μm watchman pore size filter paper in an oven in 105°C for 2 hrs then put for 30 min in desiccator to get constant weight
- 5- Measure the weight of the filter paper register the measured value for further analysis
- 6- Then filter HA containing solution using 0.45micrometer filter paper to get solution with DOC (HA < 0.45 μm)
- 7- Add the filtered solution i.e. HA/DOC containing solution into 1L volumetric flask and fill distilled water until it reaches 1L indicator mark
- 8- Then put the filter paper which contain the filtrate into an oven in 105°C for 2 hrs then put into the desiccator for 30 min to get constant weight
- 9- Measure the weight of the filter paper and the filtrate register the value obtained
- 10- Subtract the difference of weight i.e. (weight of filter paper + filtrate) – (weight of filter paper) to get amount of HA concentration in 1L of our stock solution

Let

- ✓ A – is weight of the dried filter paper before filtering our solution
- ✓ B – is weight of the dried filter paper and filtrate after filtering our solution
- ✓ C – is the weight difference between the weight of filter paper + filtrate and filter paper before filtration

To get the amount of HA concentration in our stock solution

- $B - A = C$ (amount of HA acid found in our stock solution)
- Therefore, our stock solution will have $C[\text{mg}]/\text{L}$ concentration of HA

B. Preparing working solution

Serial Dilutions

Serial dilution is the best method for the preparation of standards. Serial dilution means that an initial standard is diluted, using volumetric glassware, to prepare a second standard solution. The second standard is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.

1. **To prepare a 100 mg/L HA standard** – Pipette 10 mL of the 1000 mg/L standard into a 100 mL volumetric flask. Dilute to the mark with deionized/distilled water and mix well.

2. **To prepare a 10 mg/L standard** – Pipette 10 mL of the 100 mg/L standard into a 100 mL volumetric flask. Dilute to the mark with distilled water and mix well.

3. **To prepare a 1 mg/L standard** – Pipette 10 mL of the 10 mg/L standard into a 100 mL volumetric flask. Dilute to the mark with distilled water and mix well. To prepare standards with a different concentration use the following formula:

$$C1 * V1 = C2 * V2$$

C1 = concentration of original standard

V1 = volume of original standard

C2 = concentration of standard after dilution

V2 = volume of standard after dilution

C. Preparation of Chemically Activated Coffee Husk (CACH)

1. Wash the coffee husk with distilled water to remove impurities, dust and water soluble substance
2. Dry the washed coffee husk at 110 °C for 24 h in a laboratory oven to remove moisture prior to activation
3. Then crush and sieve to obtain desired particle size in our case silt and fine (< 0.3 mm).
4. The resulting product then treated/impregnated with H₃PO₄ solution in a 1:1 mass proportion (phosphoric acid: raw material) for 24 hr

$$\checkmark \text{ Impregnation ratio} = \frac{\text{weight of the H}_3\text{PO}_4}{\text{weight of the coffee husk}}$$

5. The impregnated coffee husk carbonized at 550°C, for 2 h in furnace
6. After the activation, the excess H₃PO₄ is washed with distilled water until a neutral pH is reached then dried at 110°C for 2 hr

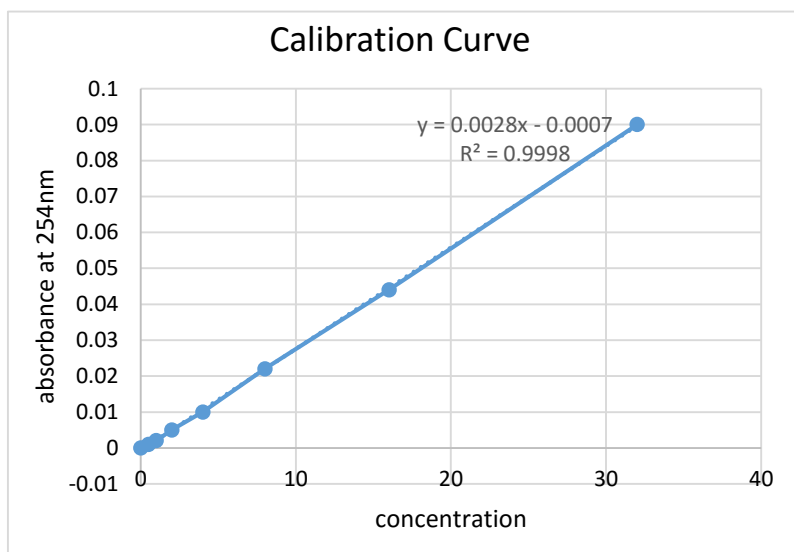
D. Preparation of calibration/standard curve

Standard curves are used to determine the concentration of substances. They are obtained by relating a measured quantity to the concentration of the substance of interest in "known" samples, i.e. Standards of known concentration. These standards provide a reference to determine unknown concentrations. Thus amounts chosen of standards need to span the range of concentrations expected to be found in the "unknown" sample concentration.

Procedure

1. Prepare a HA solution with known concentration (0, 0.5, 1, 2, 4, 8, 16, 32 mg/L) from the stock solution
2. Measure absorbance in the wavelength of 254nm, the wavelength range at which organic matters absorbs
3. Draw the graph concentration vs absorbance.

concentration[mg/L]	absorbance
0	0
0.5	0.001
1	0.002
2	0.005
4	0.01
8	0.022
16	0.044
32	0.09



ANNEXE II

Experimental Result and Laboratory Pictures

I. Experimental Results

1. Contact Time

time(min)	A	B	Av	Co-Ce	A%	q _t
20	3.614	3.877	3.7455	6.2545	62.545	0.62545
40	1.808	1.877	1.8425	8.1575	81.575	0.81575
60	0.638	0.62	0.629	9.371	93.71	0.9371
80	0.538	0.58	0.559	9.441	94.41	0.9441
100	0.467	0.476	0.4715	9.5285	95.285	0.95285
120	0.421	0.417	0.419	9.581	95.81	0.9581

(Co = 10 mg/L, Agitating speed = 200 rpm, CACH dose = 10 g/L, pH = 6)

2. Solution pH

Ph	A	B	Av	Co-Ce	A%	q _e
3	0.611	0.523	0.567	9.433	94.33	0.9433
4	0.748	0.688	0.718	9.282	92.82	0.9282
5	0.971	1.025	0.998	9.002	90.02	0.9002
6	1.421	1.433	1.427	8.573	85.73	0.8573
7	3.309	2.557	2.933	7.067	70.67	0.7067
8	4.864	3.806	4.335	5.665	56.65	0.5665
9	7.207	5.107	6.157	3.843	38.43	0.3843
10	7.361	7.327	7.344	2.656	26.56	0.2656
11	7.607	7.535	7.571	2.429	24.29	0.2429

(Co = 10 mg/L, Agitating speed = 200 rpm, CACH dose = 10 g/L, contact time = 60 min)

3. Agitating Speed

Rpm	A	B	Av	Co-Ce	A%	qe
50	3.456	3.472	3.464	6.536	65.36	0.6536
100	2.825	2.737	2.781	7.219	72.19	0.7219
150	1.131	1.053	1.092	8.908	89.08	0.8908
200	0.533	0.538	0.5355	9.4645	94.645	0.94645
250	3.183	3.164	3.1735	6.8265	68.265	0.68265
300	5.772	5.788	5.78	4.22	42.2	0.422

(Co = 10 mg/L, Contact time = 60 min, CACH dose = 10 g/L, pH = 6)

4. CACH Dose

Dose[g/L]	A	B	Av	Co-Ce	A%	qe
0.1	1.738	1.611	1.6745	8.3255	83.255	8.3255
0.5	0.933	0.886	0.9095	9.0905	90.905	1.8181
1	0.605	0.631	0.618	9.382	93.82	0.9382
1.5	0.583	0.509	0.546	9.454	94.54	0.630267
2	0.284	0.293	0.2885	9.7115	97.115	0.485575
2.5	0.116	0.144	0.13	9.87	98.7	0.3948

(Co = 10 mg/L, Agitating speed = 200 rpm, Contact time = 60 min, pH = 6)

5. Initial Concentration

Co	A	B	Av	Co-Ce	A%	qe
0.5	0.014424	0.012226	0.013325	0.486675	97.335	0.048668
1	0.03147	0.03133	0.0314	0.9686	96.86	0.09686
5	0.25305	0.28345	0.26825	4.73175	94.635	0.473175
10	0.94	0.988	0.964	9.036	90.36	0.9036
15	3.069	2.916	2.9925	12.0075	80.05	1.20075
20	6.154	5.966	6.06	13.94	69.7	1.394

(Contact time = 60 min, Agitating speed = 200 rpm, CACH dose = 1 gm, pH = 6)

6. Equilibrium isotherm model

Experimental	freundlich		Langmuir		Separation factor
q _e	q _e	CF	q _e	CF	R _L
0.048668	0.1589795	0.01216874	0.02948557	0.000367946	0.56975633
0.09686	0.21732433	0.01451165	0.0676711	0.000851992	0.39836312
0.473175	0.47519769	4.0913E-06	0.43094171	0.001783651	0.11694043
0.9036	0.75767579	0.02129388	0.8860564	0.000307778	0.06210129
1.20075	1.14526049	0.00307909	1.22385695	0.000533931	0.04227599
1.394	1.48137478	0.00763435	1.34742855	0.0021689	0.03204568
	SSE	0.0586918	SSE	0.006014198	
	K_f	0.76787521	Q_{max}	1.49465228	
	1/n	0.36470835	B	1.51027254	
	R²	0.96819332	R²	0.9981651	

7. Adsorption kinetics

Experimental		Pseudo-first order		Pseudo-second order		Intra-particle diffusion	
time	q _t	q _t	CF	q _t	CF	t ^{0.5}	
20	0.62545	0.654127	0.000822	0.669535541	0.00194353	4.472136	
40	0.81575	0.880372	0.004176	0.823579553	6.1302E-05	6.324555	
60	0.9371	0.958624	0.000463	0.891987866	0.0020351	7.745967	
80	0.9441	0.985689	0.00173	0.930638289	0.00018122	8.944272	
10	0.95285	0.99505	0.001781	0.955479215	6.9128E-06	10	
120	0.9581	0.998288	0.001615	0.972789917	0.00021579	10.95445	
		SSE	0.010587	SSE	0.00444387	K_p	0.0495
		K_f[g/(mg.min)]	0.055	K_s[g/(mg.min)]	0.078	C	0.4724
		R²	0.961	R²	0.997	R²	0.812

4.8 Desorption of HA from CACH by NaOH solution

cycle	Adsorption (%)	Desorption (%)	
		0.1 N NaOH	0.2 N NaOH
1	98.9	70.44	90.72
2	91.1	65.88	85.56
3	76.03		

(Co = 10 mg/L, Contact time = 60 min, Agitating speed = 200 rpm, CACH dose = 1 gm, pH = 6)

4.9 Efficiency comparison among untreated, only heat treated, CACH

Type of adsorbent	A	B	avg	Co-Ce	A%
UCH	9.407	9.322	9.3645	0.6355	6.355
HTCH	6.329	6.105	6.217	3.783	37.83
CACH	1.225	1.366	1.2955	8.7045	87.045

(Co = 10 mg/L, Contact time = 60 min, Agitating speed = 200 rpm, CACH dose = 1 gm, pH = 6)

II- Pictures taken during Laboratory work



During measuring weight of Humic acid powder and stirring the solution on hot plate to facilitate dissolution



Filtering the HA solution to remove undissolved HA using Pump and 0.45 μ m filter paper. And Final obtained Humic acid stock solution



Coffee Husk obtained from coffee processing factory and during grinding and sieving the husk



untreated coffee husk



only chemically treated



Only thermally treated coffee husk



Finally obtained Chemically Activated Coffee Husk (CACH)



Preparing working solution from the stock solution and Adjusting solution pH



Measuring CACH dose that will be added into the solution and Fixing sample containing Erlenmeyer flask on horizontal shaker.



Filtering the sample and Recording the measurement from spectrophotometer