

**REMOVAL OF PHENOL, HYDROQUINONE AND 2-NAPHTHOL FROM  
AQUEOUS SOLUTIONS USING TERTIARY AMINE MODULATED  
CORNSTARCH**

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**A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of  
Master of Science in Chemistry of Murang'a University of Technology**

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## DECLARATION

I hereby declare that this thesis is my original work and to the best of my knowledge has not been presented for a degree award in this or any other university.

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AS401/5067/2018

## APPROVAL

The undersigned certify that they have read and hereby recommend for acceptance of Murang'a University of Technology a thesis entitled "**Removal of Phenol, Hydroquinone and 2-Naphthol from Aqueous Solutions Using Tertiary Amine Modulated Cornstarch.**"

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## **DEDICATION**

I dedicate this thesis to my grandparents, although they are no longer of this world, my wife Beatrice, my parent Emily K., my uncles Stanley T. and Wesley T., who instilled in me the hard work value, our sons Ramsey and Theophilus, my brother and sisters, whose uplifting words and push for determination to continue with this work ring in my mind. Your support, hope and love for me knew no bounds. God bless you all.

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## ABSTRACT

Phenolics are a family of chemical compounds with at least one hydroxyl group attached directly to aromatic group. The sources of phenolics pollutants in water are mainly chemical industries and pharmaceutical. They are harmful and toxic even at modest concentrations. Some of their health effects are irreversible and it is prudent to remove phenolics from water to overcome them. The method that has attracted more attention is adsorption. Major strides have been made over years to search for highly selective and efficient bio-adsorbent for water remediation. Despite substantial achievements, there is need to search for bio-adsorbent which is ecofriendly and efficient. The objectives of the study were to modify cornstarch using triethanolamine and to characterize unmodified and modified cornstarch using Fourier Transform Infrared (FT-IR), to optimize selected adsorption parameters for the removal of phenol, hydroquinone and 2-naphthol in water using aminated cornstarch (ACS) and to determine the adsorption capacity of dried raw cornstarch (RCS) and ACS in removal of phenolic compounds (PCs). Pseudo first and second order kinetic models were used to determine mechanisms involved in both chemisorption and physisorption processes. The Langmuir and Freundlich isotherms were used to determine adsorption capacity of the ACS and whether it was monolayer or multilayer. The modulation of cornstarch was in two steps; chlorination of cornstarch using acetyl chloride reflux in aniline at 70 °C and 120 rpm for 5 hours, and amination using triethanolamine refluxed at 40 °C and 120 rpm for 3.5 hours. The FT-IR spectrum of the ACS showed strong broad band with increased intensity at  $3295.44\text{cm}^{-1}$  which confirmed C-N stretch of amine group and N-H stretch of amine salt were anchored. The efficiency of modified cornstarch in phenolics removal at different pH levels, contact time, initial phenolics concentration and dosage of ACS in aqueous media at constant temperature ( $25\pm 1$  °C) were investigated. Batch studies revealed that maximum removal of PCs was realized at a contact time of 10 mins, pH of 5.0-6.0 and constant temperature of  $25\pm 1$  °C for the phenol, hydroquinone and 2-naphthol compounds. The uptake increased with increase in the dosage of ACS and initial concentration of phenolics. The rate of adsorption process was best described by the pseudo – second order kinetic model, indicating that the rate mechanism was chemisorption. The maximum uptake of PCs occurred at initial concentration of 10ppm and then plateaued. The batch experimental data obtained best fitted into the Langmuir isotherm with regression coefficient,  $R^2=0.9998, 0.9999, 1.000$  and monolayer adsorption capacities of 4.297, 4.585 and 5.048 mg/g for phenol, hydroquinone and 2-naphthol respectively. The adsorption process was monolayer and homogenous in nature. These adsorption capacities were relatively higher than many reported processes, thus indicating that the ACS an effective adsorbent for removal of PCs from aqueous media. The findings from this study provides an alternative biopolymer that may be used for the removal of phenolic compounds from water.

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## **ACRONYMS AND ABBREVIATIONS**

<b>ACS</b>	Aminated cornstarch
<b>CCS</b>	Chlorinated Cornstarch
<b>CS</b>	Cornstarch
<b>DMF</b>	Dimethyl formamide
<b>EPA</b>	Environmental Protection Agency
<b>FT-IR</b>	Fourier Transform Infrared Spectroscopy (FT-IR)
<b>NCD</b>	Non – communicable Diseases
<b>PCs</b>	Phenolic Compounds
<b>RB</b>	Regenerated biomaterial
<b>RCS</b>	Raw cornstarch
<b>UNEP</b>	United Nations Environment Programme
<b>UNICEF</b>	United Nations International Children Emergency Fund
<b>UV-Vis</b>	Ultraviolet–Visible spectroscopy
<b>WHO</b>	World Health Organization

## **DEFINITION OF OPERATIONAL TERMS**

**Adsorption:** It is the adhesion of chemical species onto the surface of particles /adsorbents.

**Amination:** It is the chemical process by which an amine group is introduced into a starch unit or an organic molecule.

**Bioadsorbent:** It is substance/ microbial biomass/biological material able to remove /bind contaminants from aqueous solution

**Modulation:** It is the exertion of a modifying or controlling influence on a biomass. Modulation of starch is the process of varying one or more properties of bioadsorbent starch.

**Phenolic compounds:** They are organic compounds or secondary metabolites containing benzene ring (s) with one or more hydroxyl substituents ranging from simple molecules to highly polymerized compounds.

**Starch:** An odourless, tasteless white substance occurring widely in plant tissue and obtained from cereals and potatoes.

**Cornstarch:** It is finely ground maize flour used as bioadsorbent.

## CHAPTER ONE

### INTRODUCTION

#### 1.1 Background of the Study

Water is extremely salient for human being, animals and growth of plants. The world's 1.14 billion people have shortage of water free from toxic contaminants and 2.5 billion have inadequate access to proper sanitation system, especially in developing countries (Jabeen *et al.*, 2015; Gude, 2017; Guppy and Anderson, 2017). Globally, women and school going girls use approximately 200 million hours hauling water daily altering their way of life and living standards, children miss 1863 million days of school attendance affecting their quality of education and more than one of every 9 persons have inadequate access to clean water (Guppy and Anderson, 2017; Mbugua, 2020).

According to Lancet Planetary Health Journal, (2022) reported that one in every six deaths are caused by pollution, in which water pollution attributes to 1.36 million deaths annually. In addition, this has resulted into 66% increase in deaths since year 2000 from modern pollutants viz agrochemicals, heavy metals and fossil fuels. People's health in the planet is facing vital problems due to deteriorating quality of drinkable water. These epidemics lower or decreases human capital in lower-middle-income countries (Mbugua, 2020). Untreated and poorly treated wastewater or grey water is put in use for agricultural activities in a number of developing countries (Grangier, *et al.*, 2012). In these countries they have shown that children (8-13 years) have about 74% prevalence proportion for stomach flu (gastroenteritis) contrary to 12% in countries or areas utilizing freshwater (Grangier *et al.*, 2012). This has attributed to high health cost per child in areas utilizing wastewater.

Natural processes and increasing anthropogenic activities such as mining, agribusiness, manufacturing, and population growth have led to pollution and contamination of water by toxic inorganic and organic pollutants (Kumar *et al.*, 2014; Mbugua, 2020). Pollution of water is a serious worldwide challenge and is one of the leading global causes of diseases and death (West, 2006; Guppy and Anderson, 2017). Pollution of water is among the risk factors for non-communicable diseases (NCD) globally and is responsible for an approximate 17% of all NCD deaths, and these NCDs account for 73% of all mortalities globally and the number is increasing periodically (Fuller *et al.*, 2018). Water pollution caused the deaths of 1.8 million people in 2015 about 3.7 percent of disability-adjusted life years (DALYS) worldwide (Jabeen *et al.*, 2015; Kelland, 2017). Modern society is perplexed with water pollution and contamination in rural and urban areas.

High-income nations such as USA, UK, Germany, Canada and France, have many ways of water pollutions such as heavy use of chemicals and industrial discharge (Landrigan *et al.*, 2018; Fuller *et al.*, 2018). In upper-middle-income countries, like China, South Africa, Mexico and Argentina water pollutions is as a result of release of municipal and industrial waste water with inadequate treatment to the environment as well as heavy use of chemicals in various plants (Fuller *et al.*, 2018; Landrigan *et al.*, 2018;). In these countries water availability is decreasing and competition for access to this scarce resource is increasing. Finally, in rapidly developing low-middle-income countries such as India, Peru, Kenya and Senegal, water pollution is the main risk factor for mortalities from NCDs, water is heavily polluted with harmful ions and only 28% of municipal and industrial wastewater are treated. (Guppy and Anderson,

2017; WWAP, 2017; Landrigan *et al.*, 2018; Fuller *et al.*, 2018). Water pollution globally account for an estimated 9.1 million premature loss of life per annum.

Pollutions caused by phenolic compounds have been associated with a lot of health risks and poor organoleptic properties of water and fish. Phenolics are essential industrial substances of ambient concern because they are used in a large number of industries such as coke, pesticides, cosmetic products, dyes, resin manufacturers, herbicides, plastics polymers, refineries, explosives and pharmaceuticals, and also can be found in their wastewater (El-Ashtoukhy *et al.*, 2013). Some of phenolics are used in chemical synthesis and as solvent, like phenols, in large quantities. Therefore, it is very prudent to remove these compounds from wastewater before being used or released into the ecosystem as they are disintegrated into toxic simple moieties i.e., ecotoxins and others are badly biodegraded and are carcinogenic (Mwangi *et al.*, 2014).

Phenolic compounds are major toxic compounds in water of great concern to researchers on account of their poor biodegradability, high toxicity levels and environmental aspects (Nayak, *et al.*, 2020). Search for appropriate approaches to solve the challenge of phenolics contamination in drinking and domestic water is necessary.

Methods that have been utilized for removal of PCs from water are adsorption, polymerization, ozonation, photocatalytic degradation, electrocoagulation, electroFenton, electrolysis, extraction, biological methods, membrane - based separation and ion exchange (William *et al.*, 2017). Some methods are linked with high capital, poor efficiency, maintenance and operational costs, they include, ultra-

filtration, nano-filtration and reverse osmosis. Adsorption method is the most preferred because of its additional benefits of effectiveness, eco-friendly, user-friendly and availability of various bioadsorbents. Any agricultural product has cellulose/ biopolymers that show potentials for adsorption of hazardous/ toxic organic and inorganic contaminants in aqueous media (Sud Dhiraj *et al.*, 2008).

The pre-eminent constituents discovered in agricultural products and wastes that are responsible for adsorption of toxic substances in water include hemicellulose, simple sugars, proteins, lignin, phenolic, acetamido, carbonyl, sulphhydryl groups, starch and lipids having a variety of functional groups (Bailey *et al.*, 1999; Haskem *et al.*, 2005; Sud Dhiraj *et al.*, 2008). These constituents have high attraction for both organic and inorganic compounds in aqueous media to yield complexes and other organic moieties (Sud Dhiraj *et al.*, 2008). The increasing use of natural adsorbents in sorption for the removal of toxic and hazardous contaminants has been predominantly used because of their prolific availability, low-cost, reusability, easy desorption, biodegradability, requirement of minimum processing and the many active groups they have which are needed for nucleophilic abstraction (Köhler *et al.*, 2007; Bhatnagar *et al.*, 2015).

Starch is a polymeric biomolecule derived from plants which is affordable, available in large quantities and has numerous applications in various industries (Muhammad *et al.*, 2016). Bio adsorbents obtained from readily available starch are effective, efficient and have high sorption capacity for uptake of phenolic compounds from aqueous solution (Franck *et al.*, 2003). Starch can be modified by numerous methods such as physical, genetic and chemical. The most common being chemical modulation. Modulation of starch improves its important properties (e.g., adsorption) and reduces



its undesirable properties (Kaur *et al.*, 2012; Muhammad *et al.*, 2016). Therefore, this study focused on chemical modulation of starch using tertiary amine (triethanolamine) for adsorptive removal of phenolics from aqueous solution. The study brought insight to the environmental studies on remediation of water pollution, green chemistry and treatment of organic wastes/ anionic contaminants.

## **1.2 Statement of the Problem**

Water pollution is a greatest challenge in the modern society due to industrialization and population growth. Phenolic free water is becoming hard to find, a situation made worse by insufficient treated water supply and rapid population growth in the society. When industrial effluents contaminated with phenolics come into contact with clean or drinking water, it makes water unfit for human use. Many techniques have been investigated for removal of toxic phenolics from wastewater and drinking with some limitations such as high capital, high maintenance cost, poor biodegradability, introduction of secondary pollutants, operation cost and less effective adsorbents biomass. This study, therefore, focused on use of biopolymers derived from cornstarch which was first chlorinated using acetyl chloride, secondly amination with triethanolamines and then followed by successive application on the adsorption of phenolics from aqueous solution. The optimization of adsorption parameters was carried out and determination of adsorption capacities and mechanism were done using isotherms and kinetic models.

## **1.3 The Objectives**

### **1.3.1 General Objective**

To investigate the potential of modulated aminated cornstarch with tertiary amine as a bioadsorbent for removal of phenol, hydroquinone and 2-naphthol from aqueous solutions.

### **1.3.2 Specific Objectives**

- i. To modify cornstarch using triethanolamine and characterize both unmodified and modified cornstarch using FT-IR.
- ii. To optimize adsorption parameters of modified cornstarch; pH (3-9), initial concentration (0-40 ppm), contact time (0-120 minutes) and bioadsorbent dosage (0.2-1.2 g) for the removal of phenol, hydroquinone and 2-naphthol in aqueous solution.
- iii. To determine the adsorption capacity of the raw and modified bioadsorbents in removal of PCs from aqueous solutions.

## **1.4 Null Hypothesis**

- i. Chlorination and amination do not modify the functional groups in cornstarch.
- ii. The efficiency of modulated cornstarch in removal of phenol, hydroquinone and 2-naphthol from aqueous solution is not affected by solution pH, initial concentration, contact time and adsorbent dose at the constant temperature.
- iii. Modulated cornstarch does not have adsorption capacity on the adsorption of phenol, hydroquinone and 2-naphthol from aqueous media.

## **1.6 Significance of the Study**

The findings from this research will be used to design a cost effective natural, eco-friendly and available biopolymers resins for removal of toxic phenolic compounds in

water which have been associated or linked to some health emerging problems in the society. Use of natural adsorbents will provide water treatment remedy and recycling of wastewater for domestic purposes. It also enhancing agricultural produce free from harmful phenolics, hence improving food security pursuant to the country's Big four agenda, principles of green chemistry, eliminating health risks impose by phenolics bioaccumulation and vision 2030. Use of modified cornstarch in this study was regenerated for reuse making it ecofriendly and economical resins.

### **1.7 Justification of the Study**

Industrialization has contributed to introduction of toxic organic and inorganic pollutants in the ecosystem and scarce natural resource water. Globally one in every six people and about 17 million persons have inadequate access to clean water (Mbugua, 2020). The existence of phenolic compounds and its derivatives in the environment is majorly created by anthropogenic activities and natural processes. The anthropogenic sources of water pollution with phenolic compounds include: municipal wastes, agricultural activities, domestic wastes and industrial wastes.

In Kenya major source of phenolic compounds in water are excessive application of pesticides, insecticides, herbicides, slimicides and medical or pharmaceutical products (Mwangi, *et al.*, 2014) Phenolics are detrimental ecotoxins. These compounds and their derivatives have carcinogenic, mutagenic, teratogenic and cytotoxic properties. In addition, phenolics and their derivatives change activity of enzymes and the metabolism of cell upon entry into the living organism (Bożena and Sylwia, 2003; Haq *et al.*, 2019). There is need to search for ecofriendly effective adsorbent for removal of phenolic compounds from water for reuse. This has led to far – reaching

intervention and methods for removal of phenolics contaminant in water and wastewater using natural or synthetic materials such as clay, membranes, activated carbon, nanomaterials, zeolites, carbon nanotubes etc. (Haq *et al.*, 2019, Antonio and Cosimino, 2020). Natural sorbents like coconut shells, macadamia nutshells, corn tassels, mango kernels, activated carbon, cornstarch etc. have been used for water remedy due to their effectiveness, biodegradability and adsorption properties (Hossain *et al.*, 2012, Haq *et al.*, 2019).

Moreover, cornstarch was used in this research as opposed to other adsorbents due to its availability, low-cost, biodegradability, biocompatibility, reusability and ease to modulate chemically (Haq *et al.*, 2019, Antonio and Cosimino, 2020). The modulation of biopolymers, like starch, is done to enhance the useful properties and to reduce their unwanted traits. The native cornstarch has some drawbacks such as viscosity, solubility in water and other basic applications. So therefore, to curb these drawbacks and to increase its applications, cornstarch needs to be modulated; chemically modulated (Haq *et al.*, 2019, Antonio and Cosimino, 2020). This study focused on removal of phenolics in water and wastewater using a novel modulated cornstarch anchored with tertiary amines group (triethanolamine).

### **1.8 Scope and Limitations**

This study involved chemical modification of cornstarch for removal of selected phenolics from water as one of the remedies of water pollution. The biopolymer was characterized with FT-IR spectrophotometer and then subsequently applied in PCs removal from the model solutions and environmental contaminated water. UV/Vis was used in determination of phenolics concentrations after adsorption process. The

adsorption variables including pH level, initial concentration, contact time and adsorbent dose was evaluated at room temperature ( $25\pm 1$  °C) to determine their outcome on phenolics removal. Cornstarch was selected without any considerations from local market. Because there are many contaminants and other organic compounds that get into water in addition to phenolics, this study focused only on selected phenolic compounds in water due to the given timeframe for the research.

### **1.9 Contribution of the Study**

The contributions made by this study are highlighted below:

- i. The cornstarch was successfully modified using acetyl chloride as a chlorinating agent in aniline followed by amination of the chlorinated cornstarch using triethanolamine by and this was confirmed by the FT-IR analysis. This gives alternative method of amination of biomass.
- ii. The quantity of PCs adsorbed by the modulated bioadsorbent were influenced by the following adsorption parameters viz dosage of adsorbent, contact time, solution pH and initial concentration of adsorbate. The dose of aminated cornstarch and initial concentration increases with the increase in removal of phenolic compounds. Therefore, the adsorption parameters influenced the uptake of PCs from aqueous solution.
- iii. The modified cornstarch has higher adsorption capacity than the raw cornstarch. The data obtained fitted well into the Langmuir isotherm. These adsorption capacities were relatively higher than some reported processes, thus making the aminated cornstarch (ACS) an alternative adsorbent for removal of phenolic compounds from aqueous

media. The adsorption process was best described by the pseudo-second order kinetic model.

- iv. A paper containing the results of the study has been published.

## **1.10 Organization of the Thesis**

The content of this research is organized into five chapters as highlighted below:

Chapter One is the Introduction. It discusses The Background of The Study, the Statement of the Problem, Justification of the study, the Objectives, Null Hypothesis, Significance of the Study, Scope and Limitation of the Study and the Contribution of the Study.

The next chapter is Chapter Two which is Literature Review. It involves the discussion of the scarcity of water, effects of phenolic compounds, adsorption process, modulation of the cornstarch, factors affecting adsorption of phenolics, analytical techniques, isotherms and kinetic models.

The Chapter that follows is Chapter Three which involves the discussions of the materials used and the methods to be followed in order to achieve the specific objectives of the study. It includes the research design, instrumentation, modulation of cornstarch, characterization of cornstarch, adsorption batch experiments and data analysis methods.

In Chapter Four involves discussion of results and interpretation of data. This includes effects of pH, contact time, initial concentration and dosage of the ACS. Batch experiment showed that high removal of PCs was noted at a contact time of 10 mins, pH of 5.0-6.0 and constant temperature of  $25\pm 1$  °C and agitation speed of 120 rpm for the three compounds selected. The dose of aminated cornstarch and initial concentration increases with the increase in removal of phenolic compounds. The

maximum adsorption of PCs happened at initial concentration of 10ppm and then flatten.

Chapter Five includes the Conclusion of the study based on the objectives, followed by recommendation from the study and for further research.



## CHAPTER TWO

### LITERATURE REVIEW

#### 2.1 Introduction

This chapter involves comprehensive discussion of reported literature related to the study. It involves the discussion of the scarcity of water, phenolic compounds and their effects, adsorption process, modulation of the cornstarch, factors affecting adsorption of phenolics, analytical techniques, isotherms and kinetic models.

#### 2.2 Clean Water Scarcity

The saline water is about 97% of the total water on Earth and only 2.5% is fresh water (Oki and Kanae, 2006; Guppy and Anderson, 2017), and the only available fresh water faces profound water pollution. Water an essential commodity among the natural resources, it is basic of life and it's of greatest importance to the livelihood of all living organisms including human, agricultural production and development of economic (Gude, 2017; Mbugua, 2020). Today, majority of the nations are facing drinking water challenges and conditions of accessibility, and clean water shortages are extremely serious especially in developing countries (Joshua *et al*, 2015; Guppy and Anderson, 2017). This scarce natural resource will require to support an estimated 9.7 billion population in 2050 globally (Guppy and Anderson, 2017).

The world is facing horrifying problems in satisfying increasing demands for clean water (Gude, 2017; Mbugua, 2020). The quality of water is influenced by natural and anthropogenic activities. The available supplies of freshwater are diminishing due to a number of factors viz; more stringent health-based regulations, increasing population, extended droughts and competing demands from a diverse user. Drinkable

water (i.e., water that is free of pathogens and toxic chemicals) is crucial to human health (WHO, 1996; Mbugua, 2020).

Water scarcity meant water per capita supplies of <math>1000\text{m}^3</math> per year (ICA, 2012). Scarcity of clean water is one of the main challenges affecting more than 1.1 billion persons worldwide; this implies that one in every six persons has no access to safe drinking water, (UNICEF/WHO, 2012; Landrigan *et al.*, 2018). The insufficient water supply of acceptable levels of quality and quantity to satisfy the needs of the environment systems and the human population can be aggravated by the water pollution and droughts (Guppy and Anderson, 2017; Fuller *et al.*, 2018). For instance, droughts brought about losses valued at an average US\$7 billion in agriculture in the United State yearly, and in China, droughts have caused in a year loss worth 27 million tons or more of grain production right through the two decades (Zhang *et al.*, 2015; Guppy and Anderson, 2017). Moreover, in Bangladesh about 45 million population drink water that are contaminated with organic and arsenic concentrations above the level WHO standards allow, notwithstanding the progress that has been made for supply of safe drinking water (Guppy and Anderson, 2017).

In rapidly developing and middle- and low- income countries like Kenya, India, Peru, Nigeria etc. water insecurity has worsened because of rapid population growth, many forms of water pollution, climatic conditions and industrialization and about 844 million people lack accessed to safe, reliable and quality drinking water (Guppy and Anderson, 2017; Fuller *et al.*, 2018). In addition, about 1000 children die every day because of preventable water and sanitation- related diseases, and only 28% of industrial and municipal wastewater are treated before release to the environment,

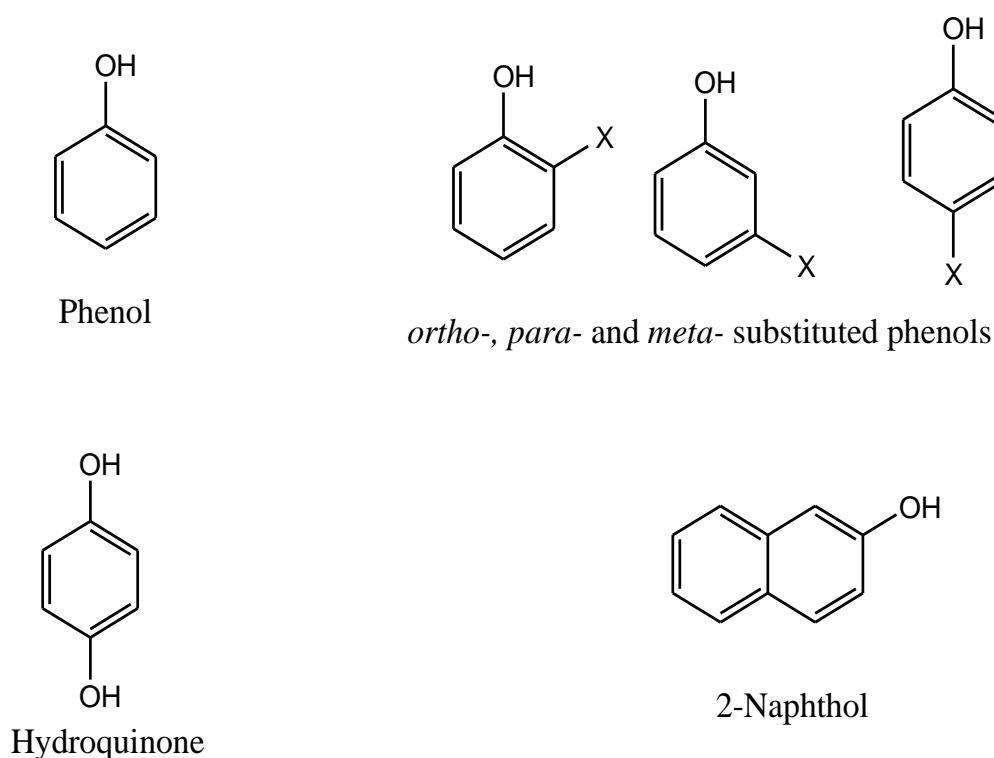
about 72% are discharge without adequate treatment (Guppy and Anderson, 2017; Landrigan *et al.*, 2018). Clean water scarcity in the African region affects one in every three people and is becoming worse with population growth, urbanization and increase in industrial uses and household, (WHO, Africa, 2019).

In Kenya around 17 million persons have inadequate access to clean water (Mbugua, 2020). Because of rapid growth of population, it has been approximated that by 2030 Kenya's per capita water accessibility will be 235 m<sup>3</sup> averages for every person annually, which is two thirds below the current 650 m<sup>3</sup> per annual, (Samantha, 2011). Shortage of clean water in Kenya has been a serious issue activated by periodic drought, mismanagement of water supply, poor collection and storage of rainwater and contamination of accessible water because of rapid population growth (Guppy and Anderson, 2017). Only just 42 % of rural population in Kenya has ingressed to water as opposed to urban population where 88 % of population has ingressed to clean water (Mulei, 2012; Mbugua, 2020).

### **2.3 Phenolic Compounds as Water Contaminants**

Contamination is the presence of a constituent, impurity, pollutant or poison, or some other undesirable element that makes unfit, soils, corrupts, infects, or makes inferior natural environment. Pollution of water is the water reservoirs contamination (like oceans, rivers, seas, lakes, groundwater and aquifers) normally as a result of anthropogenic activities due to lack of proper water treatment and management systems (Landrigan *et al.*, 2018).

Phenolic contaminants consist of phenols and its derivatives in ecosystem due to anthropogenic activities and natural processes, and they are considered as ecotoxins (Bożena and Sylwia, 2003; Haq *et al.*, 2019). Phenol and its moieties are detrimental for living organism especially those in water ecosystem. Most phenolics are soluble in water and those insoluble interact with water to form soluble derivatives. Hence, the solubility and reactivity of phenolics rely on the functional groups attached to the aromatic ring as shown in Figure 2.1 which can stabilize or destabilize delocalized electrons clouds in the ring (William *et al.*, 2017).



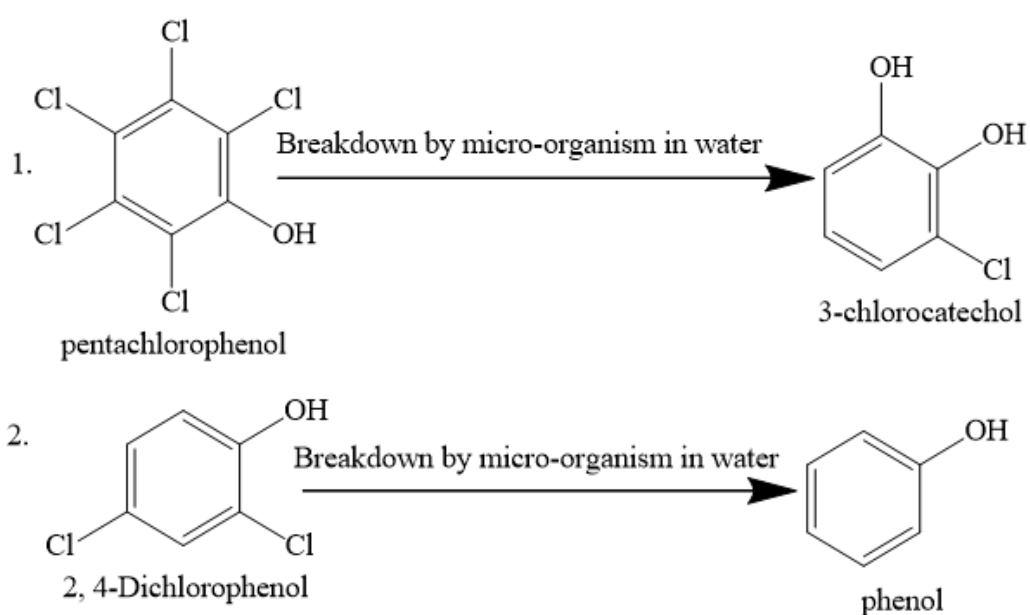
**Figure 2.1 Structures of Simple Phenolics**

The source of phenolic compounds pollution is mainly in the pharmaceutical and chemical industries (Md, *et al.*, 2018). Seemingly, these compounds are encountered in day-to-day situations. According to the US Environmental Protection Agency (EPA), some phenolics have been classified as problematic priority contaminants in water. Phenolic compounds are put through specific regulations and limits, because of their high degree of toxicity, undesirable odor and taste in water. The EPA has set allowable limit of 0.1 mg/L of phenol in wastewater whereas WHO sets a 0.001 mg/L as the limit of phenol concentration in portable water (Nayak *et al.*, 2020). The permissible concentration limit of phenol and chlorophenols in water should be at most 1-2 µg/L, and phenolic compounds can affect the organoleptic properties of water and aquatic animals even at the low concentration levels (WHO, 1996). The world health organization (WHO) set a maximum permissible concentration of 1µg/L of overall phenolic compounds in drinking water (Bentaleb *et al.*, 2017; Ibrahim *et al.*, 2020).

Phenolic moieties are produced in the breakdown of some pesticides in water, e.g., breakdown of pentachlorophenol give rise to chloropyrocatechols (chlorocatechols) (Ibrahim *et al.*, 2020). Breakdown of 2, 4-dichlorophenol with involvement of micro-organisms in water and plants result in generation of phenol as shown in Scheme 1 (Róžański, 1998; Bożena and Sylwia, 2003; Ibrahim *et al.*, 2020). 2, 4-Dichlorophenoxyacetic acid (phenoxy herbicides) in water are degraded under the influence of physical (like UV light), biological or chemical conditions to form metabolites, majorly chloro- and cresols. Chlorophenols in aqueous media are biotransformed/ biosynthesized by many immense fungi species, and phenol-decomposing bacteria species (Swarts *et al.*, 1998; Verhagen *et al.*, 1998). Cresols are constituents of natural oils and coal tar. The phenolic compounds found in the smoked

foodstuff products end up in grey water which have harmful effect on both the natural ecosystem and human (Kjällstrand and Peterson, 2001).

In Kenya the major sources of phenolic compounds in water are agricultural wastes like heavy use of insecticides, pesticides which has major components of PCs, industrial wastes, medical or pharmaceutical products regularly used (Mwangi, *et al.*, 2014). Natural processes introduce the PCs into the soil when decomposition of organic matter takes place. The surface run-off from land then washes these compounds into adjacent water bodies (Muhammad *et al.*, 2016).



**Scheme 1.** Breakdown of some phenolics by micro-organism in water (Rózański, 1998;

Swarts *et al.*, 1998; Muhammad *et al.*, 2016)

## 2.4 Health Effects of Phenolics

Studies have shown some health problems linked to use of water containing phenolic contaminants. Upon consumption of phenolic, lethal side effects are noticed such as diarrhea, stomatitis, impaired vision and excretion of dark urine (Kulkarni *et al.*, 2013; Haq *et al.*, 2019). Phenolics are carcinogenic, mutagenic, teratogenic, cytotoxic and harmful even at trace concentration levels present in the ecosystem (Azizi *et al.*, 2017). Severe exposure to compounds of phenol can have damage on genes and harmful effects on the following organs; eye, liver, lungs, heart, brain, gastrointestinal tracts, and tissues under skin (Saha *et al.*, 2013; Girish and Murty, 2014).

Phenolic compounds (phenol, hydroquinone and catechol) exhibit effect of mutagens by the DNA helix unbinding, aneuploidy formations, DNA synthesis inhibition in the human *HeLa* cells, aberrations of chromosome and gene mutations induction (Tsutsui *et al.*, 1997). Phenol, 1,2-dihydroxybenzene (catechol), 2-naphthol and 2-chlorophenol have been found to give rise to changes of conformational in the growth of human hormones, lung cancer, skin cancer while 2,4-dimethylphenol, 2,4,5-trichlorophenol and 2,4-dichlorophenol cause high levels of lipids peroxidation that is oxidative degradation of lipids in blood erythrocytes (Tsutsui *et al.*, 1997; Bożena and Sylwia, 2003; Liouna, *et al.*, 2022). The phenolics removal from wastewater using effective low-cost methods is of great concern, because of their persistence, bio-accumulation toxicological effects on human well-being and ecosystem (Ibrahim *et al.*, 2020).

## 2.5 Conventional Methods for Phenolics Removal Methods from Water

Different standard techniques have been developed for getting rid of toxic and hazardous organic pollutants in water to make water clean and reusable. Some of the strategies include; solvent extraction, filtration, chemical oxidation, ion exchange, coagulation, foam flotation, sedimentation, solvent extraction, adsorption, electrolysis, disinfection and chemical precipitation (Hossain *et al.*, 2012; Bentaleb, *et al.*, 2017; Haq *et al.*, 2019; Ibrahim *et al.*, 2020). Several methods have been employed for removal of phenolics from aqueous media such as adsorption, polymerization, ozonation, photocatalytic degradation, electro-coagulation, electroFenton, electrolysis, extraction, biological methods (like Enzymatic approach) and ion exchange and membrane-based separation, as well as the latest technique nanomaterials such as graphene, carbon nanotubes (William *et al.*, 2017; Haq *et al.*, 2019; Ibrahim *et al.*, 2020). Some methods which are linked to high capital, high energy, maintenance and operational costs include; ultra-filtration, nano-filtration, and reverse osmosis (Miretzky *et al.*, 2006; Liouna, *et al.*, 2022).

Conventional methods for phenolics removal from water are classified into three major classes; chemical, biological and physical processes. Chemical process is the treatment of phenolics-containing water through ozonation, Fenton reaction, titanium oxide (TiO<sub>2</sub>) and electrolysis. Chemical process has many limitations such as lengthy start-up, high cost for chemicals to be used, slow rate of removal, formation of secondary compounds/pollutants, etc (Antonio and Cosimino, 2020).

Biological methods are recognized as a cheap method to treat water containing phenolics due to the availability of micro-organisms, aerobic bacteria, capable of



breaking down organic compounds, since aerobic bacteria make use of aromatic compounds as the only source of carbon and energy (Marrot *et al.*, 2006). The limitations of this method are microbial growth inhibition, microbial aberrations, slow rate of degradation and long start-up.

Physical methods use the principle of adsorption onto the surface of adsorbent based on the functional groups present mainly carbonyl, hydroxyl in micro pores (Ibrahim *et al.*, 2020). Carbonaceous material, such as activated carbon, is one of the common reliable, fruitful and majorly used material in remediation of low and high concentrations / quantities of phenolics in water (Tan *et al.*, 2009; Chiong *et al.*, 2014; Ibrahim *et al.*, 2020). Many studies have been made in generating inexpensive bioadsorbent obtained from farm waste products such as rice husk ash, palm seed coat, starch, wood charcoal, bagasse ash and oil palm shell and they show high adsorption capacities results (Chiong *et al.*, 2014). The regeneration and disposal of adsorbents can be achieved easily.

The studies have put more attention to physical method adsorption, because of limitations linked to other conventional methods, it is effective, user-friendly, eco-friendly, affordable, availability of biomaterial and can be regenerated (Haq *et al.*, 2019). Adsorption strategy for phenolic removal from water has attracted attention of many researchers (Roostaei and Tezel, 2004). Many adsorbents reported in the various literature shows high maximum phenolics removal from water when undergoes modification/modulation or activated as opposed to unmodified materials (Haq *et al.*, 2019). In this study cornstarch was modulated chemically and used as a novel effective bioadsorbent. Therefore, this study focused on application of modulated

cornstarch as a facile adsorbent in phenolics removal from aqueous media/contaminated water utilizing adsorption technique (Haq *et al.*, 2019).

## **2.6 Adsorption Process and Bio-Sorption**

Adsorption process is the adhesion of chemical species onto the surface of particles /adsorbents (Ferreira *et al.*, 2012). Ferreira *et al.*, (2012) hold that it involves the pile up of the adsorbate (contaminants) on the adsorbent's surface (usually solid material). Adsorption operations are based on ionic interactions, chemisorption, complexation, chelation and the formation of cross - linked compounds between ions and functional groups found on adsorbent's surface (Feng and Guo, 2012).

The adsorption process is controlled by the adsorbent's traits, chemistry of solution and the adsorbate nature (Liouna, *et al.*, 2022). Contaminants in wastewater such as phenolics can be remove by adsorption on solid matrices, such as activated carbon, oxides of metals, starch, zeolites material and agricultural biomass, all of which have been investigated by a number of researchers as adsorbents for phenolic compounds removal from aqueous media (Ibrahim *et al.*, 2020). Some of adsorbents studied includes bagasse ash, activated carbon (William *et al.*, 2017), rice straw (Sarker and Fakhruddin, 2017), wood charcoal, rice husk (Chiong *et al.*, 2014), maize tassels (Mwangi *et al.*, 2014), chemical modification of starches & its use as adsorbents (Haq *et al.*, 2019). Etc.

Bio-sorption is the physiochemical process which permits the natural plants biomass to adsorb particles/ molecules onto their cellulosic surface (Biglari *et al.*, 2016). Bio-sorption is considered in phenolics removal from wastewater using agricultural biomass. Bio-sorption is an attribute of a particular kinds of inactive, lifeless,

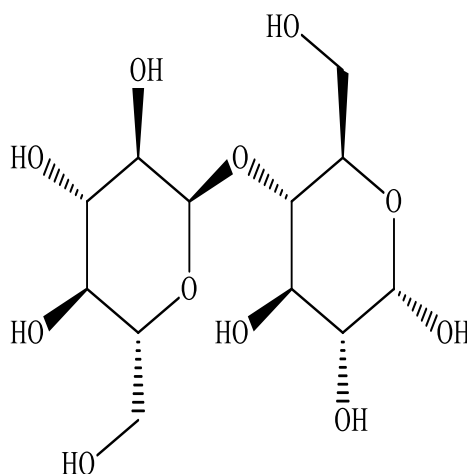
microbial biomass to attach and concentrate contaminants from even extremely dilute solutions (Nthiga, 2016). Biomass works as a chemical material, as a chelant of biological origination and an ion exchanger.

The bio-sorption operation is derived from the interaction of ions at an interface in a biomass surface / aqueous solution (Ferreira *et al.*, 2012). Use of biomaterials as bioadsorbent for contaminants removal are considered the most effective because of formation of hydrogen bonding, ligand exchange, ion exchange, Van der Waals attractions or facile chemical modulation on the adsorbents' surface (Muhammad *et al.*, 2016; Haq *et al.*, 2019).

## **2.7 Modulation of Cornstarch**

Modulation is the exertion of a modifying or controlling influence on a biomass. Modulation of starch is the process of varying one or more properties of bioadsorbent starch. Starch or amyllum is a biopolymeric carbohydrate comprising of so many glucose units  $(C_6H_{10}O_5)_n$  joined by glycosidic bonds as shown in Figure 2.2. Starch is a polymeric biomolecule consists of amylopectin and amylose derived from plants which is inexpensive and available in large quantities and has numerous industrial applications (Muhammad *et al.*, 2016; Haq *et al.*, 2019). Starches are biodegradable, available, biocompatible, nontoxic and renewable (Haq *et al.*, 2019). However, unmodified native starch has limited applications and show very low adsorption capacities, starch is modulated physically, chemically or genetically in order to enhance its uses and adsorption capacities (Haq *et al.*, 2019). In the previously reported studies, starch has been chemically modulated in some many methods where the hydroxyl group in it is replaced with a suitable different group(s), as illustrated in Scheme 2. Biomaterials derived from cheap readily available starch-enriched flour are

effective and have good sorption capacity for the PCs removal from aqueous media; the presences of amino groups enhance the sorption properties of adsorbent for phenolics (Franck *et al.*, 2003). It is practicable to modulate starches through various techniques.

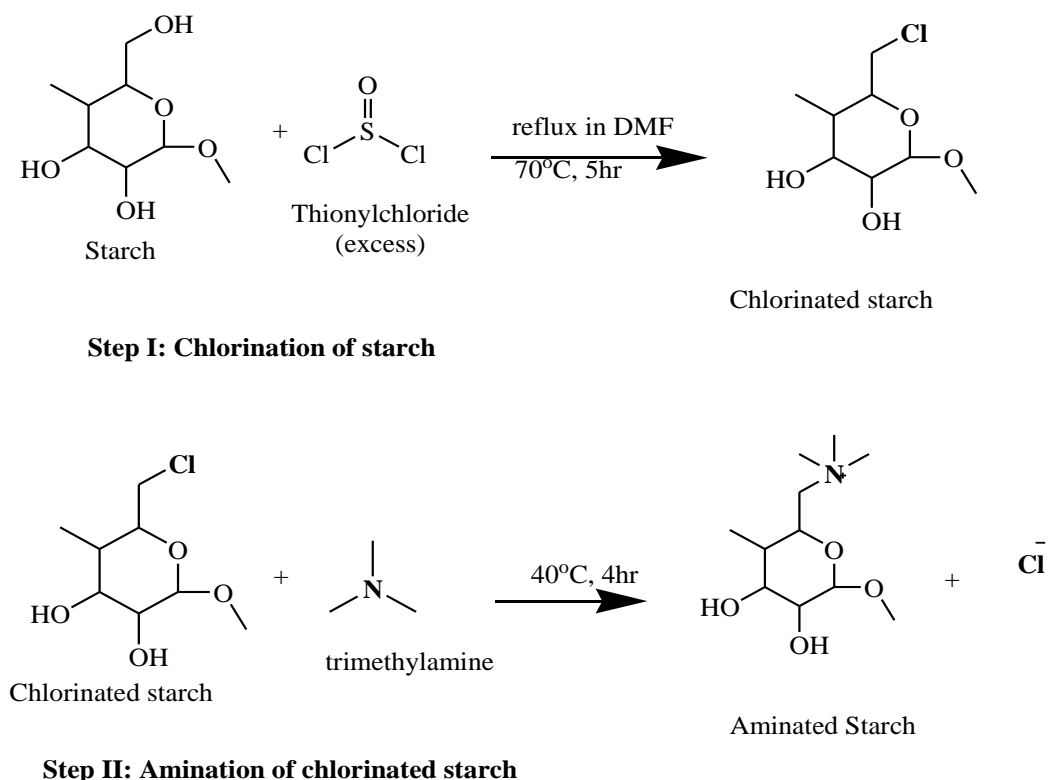


(2R,3S,4S,5R,6R)-2-(hydroxymethyl)-6-[(2R,3S,4R,5R,6S)-4,5,6-trihydroxy-2-(hydroxymethyl)oxan-3-yl]oxyoxane-3,4,5-triol

**Figure 2.2: The Structure of Starch Simple Unit.**

Techniques used to modify starch are physical, biological/genetic and chemical modifications, but the major one is the chemical modulation. The purpose of modulation of cornstarch is to improve the vital traits (e.g., adsorption) of it and to get rid of its unwanted traits (Kaur *et al.*, 2012; Muhammad *et al.*, 2016). Thus, the amination of starch is done by first chlorinating the cornstarch using thionyl chloride  $\text{SOCl}_2$  refluxed in DMF to form an intermediate chloroamyllum as alkyl halide. Other chlorinating agents that can be used is acetyl chloride in aniline or pyridine. Subsequently the intermediate alkyl halides i.e., chlorinated starch is reacted with tertiary amines, chlorine atom is replaced by the nitrogen from the trimethylamine to give an aminated cornstarch adsorbent, the reaction is regioselective and commonly

takes place at carbon-6 of glucose unit of starch as shown in Scheme 2, (Muhammad *et al.*, 2016; Mwangi *et al.*, 2016).

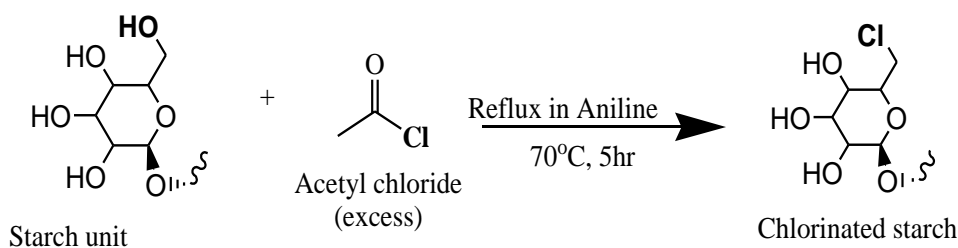


**Scheme 2.** The Chemical Modulation of Starch (Mwangi *et al.*, 2016)

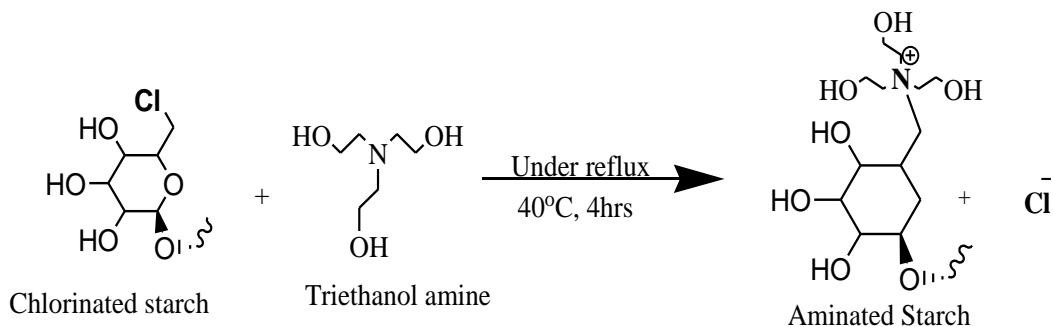
Studies have been done on vast organic matters as affordable, user-friendly, effective and eco-friendly potential biomaterial for adsorptive removal of phenolics in water. For instance, Sarker and Fakhruddin, (2017), studied the effectiveness of raw rice stalks and modified rice stalks as bioadsorbent material for uptake of phenol in solution. The findings obtained revealed that modulated (thermally treated) rice straw has enhanced phenolics removal from water/ aqueous media. Biglari *et al.*, (2016) researched on the modification of activated carbon of Miswak's root with potassium manganate (VII), as an eco-friendly, highly efficient, low-cost and novel bioadsorbent for the uptake of phenols from aqueous media. The findings show that the activated carbon from roots of Miswak treated with potassium manganate (VII) solution has high capacity to adsorb and remove high percent of phenol.

Mwangi *et al.*, (2014) investigated the adsorptive withdrawal of phenolic compounds from water using chemically modulated corn tassels with a quaternary ammonium compound. The study shows that a novel quaternized corn tassels was highly effective biomaterial for the phenolics removal from water and also has high application potential in treatment of wastewater. Girish and Murty, (2014) studied modulation on carbon from *lantana* barks forest by-product as bioadsorbent for the phenol withdrawal from aqueous media. The study revealed that forest waste as among the best precursors for the biomaterial making as sorbent for phenolics removal from water.

Therefore, this study focused on the amination of starch by first chlorinating the dried cornstarch refluxed in acetyl chloride to form an intermediate alkyl halide, as illustrated in Scheme 3. Then, the intermediate alkyl halides i.e., chlorinated cornstarch was reacted with triethanolamine at room temperature, chlorine atom is replaced by the nitrogen from the triethanolamine to give a facile aminated cornstarch adsorbent, as shown in Scheme 3



**Step I: Chlorination of starch**



**Step II: Amination of chlorinated starch refluxed in Triethanol amine**

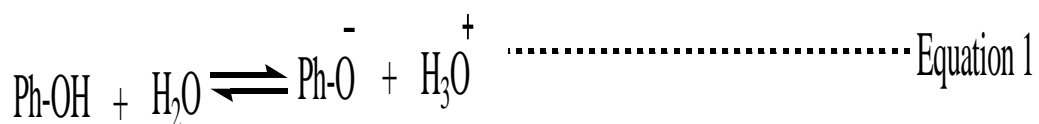
**Scheme 3:** The steps involved in Amination of dried cornstarch using triethanolamine (Mwangi, *et al.*, 2014).

**2.8 Factors Affecting the Rate of Phenolics Removal**

Many factors affect the sorption capacity efficiency of bioadsorbents used. Current studies have deduced that the effectiveness of whichever adsorbent is affected by the following properties viz nature of the solutions, pH levels, original concentration, contact time/agitation time and bioadsorbent dosage (Nayak *et al.*, 2020). Several adsorption studies have published the correlation of these adsorption factors (Nawal *et al.*, 2013). In this study the temperature of solution was kept constant. Moreover, when one factor/parameter was varied the rest were fixed during the optimization of adsorption parameters. These parameters are briefly discussed in the following sub-units;

### 2.8.1 The Effects of pH on Adsorption of Phenolics

The adsorption pH is the most vital parameter in the effectiveness of surface adsorption of phenolics contaminants. The pH of solution determines the charge of the surface of the bioadsorbent influencing adsorption capacity. The adsorbate and the adsorbent have protonation / deprotonation relying on solution's pH, thus the negative effect of raising pH on phenolics adsorption is likely due to the charge properties of both adsorbent and adsorbate (Kaman, *et al.*, 2016). The maximum phenol removal adsorption capacity (95%) and minimum phenol removal adsorption capacity (46%) are attained at pH 5 and 12, respectively (Biglari *et al.*, 2016). The study shows that phenol pKa is around 9.89 and that dissociation of phenol molecules to give ions, as shown in Equation 1, that competes with negative ions (-OH) to occupy surface of sorbent in the system which has high level of pH, lowers the adsorption power of the adsorbent. At low pH (3-5) gives more hydrogen ions as only positive ions resulting to increase in adsorption capacity since a rise in pH results in a buildup of negative charge or loss of positive charge since the surface-active groups are partially /wholly deprotonated (Kaman *et al.*, 2016).



### 2.8.2 The Effect of Initial Concentration on Adsorption of Phenolics

The concentration of phenolics is the key adsorption parameters for high effective uptake of phenolics from aqueous environment. The effect of initial concentration on removal of phenolics is carried out at optimized pH, adsorbent dosage and contact time by varying phenolics initial concentration (Nthiga, 2016). The surface area on the biomaterial decreases greatly with rise in the concentration of the phenolics in aqueous media. This is because the surface areas for a constant number of biopolymers



are reduced and gets concentrated at increased phenolics initial concentration (Mwangi *et al.*, 2016). At higher concentration the available active sites become fewer, leading to decrease in adsorption capacity. Similar studies were done using maize tassels (Mwangi, *et al.*, 2014), sawdust (Nayak *et al.*, 2020), activated carbon of miswak's root with 94.7% maximum adsorption (Biglari *et al.*, 2016).

### **2.8.3 The Effect of Adsorbent Resin Dosage on Adsorption of Phenolics**

The biopolymer resin dosage is one of the adsorption variables that affect the removal of PCs /contaminants from aqueous media. The rise in the sorbent dosage raises the capacity of adsorption due to high surface areas and increase of functional groups sites micro pores on the adsorbent (Nthiga, 2016). Furthermore, the density of adsorption decreases because of unsaturated binding sites and interaction of particle influenced by high adsorbent dosage (Mbugua, 2020). Similar studies were done using sawdust (Nayak *et al.*, 2020), rice straws (Sarker & Fakhruddin, 2017), tamarind seeds (Md, *et al.*, 2018).

### **2.8.4 The Effect of Contact Time on Adsorption of Phenolics**

The effect of the agitation time between the bioadsorbent and the adsorbate on adsorption capacity is a major factor for removal of contaminants from water. Several studies have shown that phenolics adsorption efficiency rises with the increase of the agitation time or time of contact with biomaterial (Biglari *et al.*, 2016). Studies have reported that the maximum equilibrium contact time is after 120-180 minutes (Nawal *et al.*, 2013). This indicates that modulated bioadsorbent requires less residence time for total removal of phenolics (Kaman, *et al.*, 2016). The shorter the equilibrium time for efficient removal of phenolics signifies efficacy. Thus, it is vital to establish the best possible contact time for maximum adsorption of phenolic. Study done using

tamarind seed reports a contact time of 60 minutes for maximum of 72.4 % adsorption (Md, *et al.*, 2018).

## **2.9. Analytical Techniques**

### **2.9.1 Fourier Transform Infrared (FT-IR)**

Infrared (IR) spectroscopy measures the atoms vibrations in a molecule, and because of this it is possible to determine the functional groups in a particular compound. The range of IR spectrum is  $4000\text{ cm}^{-1} - 1500\text{ cm}^{-1}$ , lying next to the microwave region and contains a dozen of peaks used to distinguish between compounds (Skoog *et al.*, 2007). In the adsorption process, those frequencies of IR radiation which match the natural vibrational frequencies of the molecules sample are absorbed, the energy absorbed serves to increase the amplitude of the vibrational motions of the bonds in the molecules (Griffiths and Hasseth, 2007).

The most modern infrared spectrometer is Fourier Transform Infrared (FT-IR). The advantage of an FT-IR spectrometer is that it receives the interferogram in not more than a second, and thus it is practicable to obtain a number of interferograms of the same sample (Skoog *et al.*, 2007). The modern FT-IR spectrometer consists of a sample compartment, interferometer, source, amplifier, detector, *AID* convertor and a computer. FT-IR is the method used to obtain IR absorption spectrum, emission, Raman scattering or photoconductivity of a liquid, solid or gas (Griffiths and Hasseth, 2007). FT-IR analysis method uses IR light to scan tested samples and show chemical properties. The spectrum produces a sample profile, a distinctive molecular fingerprint that can be used to scan and screen samples for several different components. The frequency region of the spectra which consists of the radiation from  $4000\text{ cm}^{-1}$  to about  $1250\text{ cm}^{-1}$  is used in determination of functional groups (Skoog *et al.*, 2007). The

process of detection requires passing a radiation of infrared on a sample to get a spectrum which is then compared with a spectrum of a pure compound. FT-IR is an effectual analytical instrument for detecting functional groups and characterizing covalent bonding information.

The FT-IR technique was utilized in this study for characterization of functional groups in dried cornstarch, chlorinated and aminated cornstarch. This helps in determination changes of structure of bioadsorbent before and after modification, to establish the functional groups responsible for reaction (Nthiga, 2016; Mbugua, 2020).

### **2.9.2 Ultraviolet–Visible Spectroscopy**

Ultraviolet–visible spectroscopy or ultraviolet–visible spectrophotometry or (UV-Vis or UV/Vis) is a molecular spectroscopy that involves study of the interaction of UV-visible radiation with molecules. When a molecule takes in light of a suitable wavelength and an electron is promoted to a higher energy molecular orbital, the molecule is then in excited state. The wavelength of light taken in gives the information on the energy gap which is related to functional group (Griffiths and Hasseth, 2007).

The absorption in the visible region directly influences the discerned colour of the chemicals involved. In this region of the electromagnetic spectrum, molecules and atoms undergo electronic transitions (Skoog *et al.*, 2007). Molecules or chemical species having bonding and non-bonding electrons (n-electrons) can take in energy in the form of visible light to promote these electrons to higher anti-bonding molecular orbitals. UV-Vis spectroscopy is normally used in analytical chemistry for the quantitative determination of various kinds of analytes, like biological

macromolecules, highly conjugated organic compounds (Skoog *et al.*, 2007). Organic compounds highly conjugated absorb light in the UV or visible regions of the electromagnetic spectrum. The solvents for this analysis are often water for water-soluble species or ethanol for organic-soluble species.

The Beer–Lambert law states that absorbance of a solution is directly proportional to the concentration of the absorbing species in the aqueous solution and the path length (Skoog *et al.*, 2007). Thus, for a constant path length, UV/Vis spectroscopy is used to determine the concentration of the absorber in a solution.

In this study, UV/Vis spectroscopy was used in determination of the concentration of phenolics in the aqueous media (filtrate) after adsorption, as shown in Appendix IV. The UV sorption intensity for each solution / filtrate was done in triplicates, in order to minimize experimental errors. The UV/Vis have been used in similar studies using maize tassels (Mwangi, *et al.*, 2014), rice straws (Sarker & Fakhruddin, 2017), tamarind seeds (Md, *et al.*, 2018), sawdust (Nayak, *et al.*, 2020).

## **2.10 Adsorptions Models/ Isotherms**

Adsorption models are very helpful for determining the maximum adsorption capacity, the nature of complexation and the kind of adsorbent-adsorbate synergy/interaction (Mbugua, 2020). In this study, Langmuir and Freundlich models were involved to determine the effectiveness of biomaterial based on data obtained, the maximum sorption capacity of modulated cornstarch on removal of phenolics. The models were used to establish whether the adsorption of phenolics on modulated

cornstarch adsorbent was monolayer or multilayer (Mbugua, 2020). The two isotherms are discussed in the following sub-units.

### 2.10.1 Langmuir Model

The Langmuir model deals with adsorption at monolayer homogeneous on the adsorbent surface (Hossain *et al.*, 2012; Nuhu *et al.*, 2017). The model based on assumption that binding sites on the adsorbent have the same affinity for adsorption of monomolecular layer, and once the active sites have been used up, no more adsorption can occur (Tan *et al.*, 2009). As for solid–liquid interactions results, the Langmuir model is expressed in the linear equation as shown in Equation 2.2;

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C_e \text{-----Equation 2.2}$$

where,  $C_e$  is the phenolics concentration remaining in the solution at equilibrium in mg/L,  $K_L$  is the equilibrium constant (Langmuir constant), apparent energy of sorption,  $q_e$  is the amount of phenolic absorbed at equilibrium (mg/g) and  $q_{max}$  is the complexation capacity.  $q_{max}$  and  $K$  parameters are determined by plotting a graph of  $C_e/q_e$  against  $C_e$ , and give a straight line of intercept  $1/K_L q_{max}$  and slope  $1/q_{max}$ . Langmuir model accounts for the adsorbent’s surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium) (Barrera, 2020).

### 2.10.2 Freundlich Model

The Freundlich model describes a multilayer nature of complexation which takes place on a heterogeneous system (Hossain *et al.*, 2012; Nuhu *et al.*, 2017). The model based on assumption that adsorption occurs in a heterogeneity surface at different active sites and energy. It also assumes a multilayer adsorption of sorbate (Nuhu *et al.*, 2017; Antonio and Cosimino, 2020). The Freundlich model used in this study is expressed as non-linear and linear as shown in the Equation 2.3 and Equation 2.4 respectively.

$$q_e = K_f (C_e)^{1/n} \dots\dots\dots \text{Equation 2.3}$$

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \dots\dots\dots \text{Equation 2.4}$$

Where,  $q_e$  is the maximum uptake amount of adsorption (mg/g),  $K_f$  is the Freundlich constant representing uptake capacity adsorption, and  $1/n$  is the heterogeneity factor of sorption (complexation intensity). When  $1/n$  is less than one it shows a normal adsorption, the degree of nonlinearity between the phenolics concentration and adsorption (Antonio and Cosimino, 2020). If  $1/n$  is tending to zero it shows that the system is homogeneous.  $n$  and  $K_f$  are determined by plotting a graph of  $\log q_e$  versus  $\log C_e$ , where the slope is  $1/n$  and the intercept is  $K_f$  (Hossain *et al.*, 2012; Nuhu *et al.*, 2017).

### 2.11 Kinetic Studies

Adsorption chemical kinetics explains how fast the reaction rate occurs, and are vital in understanding reactions and their application (Edet and Ifelebuegu, 2020). The kinetics was investigated in this study in order to determine the rate controlling reaction mechanism which includes the process/ pathway of chemical reaction and mass transfer rate (Suresh *et al.*, 2012). To determine the rate-limiting step / controlling mechanism that guides the affinity of PCs on aminated cornstarch, the data obtained were analyzed using the pseudo-first order ( $K_1$ ) model and pseudo- second order ( $K_2$ ) model (Edet and Ifelebuegu, 2020).

The pseudo-first-order kinetic model was first proposed by Lagergren (Lagergren, 1898; Suresh *et al.*, 2012). It also known as Lagergren kinetic rate law. This model considers the rate on how adsorption active sites are occupied to be proportional to the

number of unoccupied sites (Suresh *et al.*, 2012). The Lagergren linear law is given by Equation 2.5.

$$\text{Log } (q_e - q_t) = \text{log } q_e - K_1 t \dots\dots\dots \text{Equation 2.5}$$

where  $q_e$  (mg/g) is the equilibrium concentration of PCs on the adsorbent (ACS),  $q_t$  (mg/ g) is the quantity of PCs adsorbed at time  $t$  and  $K_1$  (g/mg.min<sup>-1</sup>) is the pseudo – first order rate constant. A graph of  $\text{log } (q_e - q_t)$  against time  $t$  gives a line, where the gradient and the  $y$  – intercept are the values of  $K_1$  and  $\text{log } q_e$  respectively.

The pseudo-second order kinetic ( $K_2$ ) model was proposed by Ho & McKay (1999). The Ho’s pseudo – second order law considers that each phenolate ion is attracted onto two binding sites which allows formation of binuclear bond which is stable (Suresh *et al.*, 2012; Edet and Ifelebuegu, 2020). The linearized form of Ho’s equation is expressed as in Equation 2.6.

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \dots\dots\dots \text{Equation 2.6.}$$

where  $q_e$  and  $q_t$  are the concentration of PCs adsorbed at optimum conditions and at time  $t$  (mins) respectively, and  $K_2$  is the Ho’s constant (pseudo-second-order rate constant) (g/mgmin<sup>-1</sup>). The graph of the  $\frac{t}{qt}$  against time,  $t$  (min) results to a straight line which is used to calculate  $q_e$  and  $K_2$  from the slope and the intercept respectively (Barrera, 2020).

## **2.12 Chapter Summary**

The chapter extensively discussed about the water scarcity globally and locally, phenolic compounds in water, health effects of PCs, methods of removal of PCs from water, adsorption and biosorption process, modulation of cornstarch, parameters influencing adsorption of PCs, instrumentation used and finally adsorptions isotherms and kinetic models.



## **CHAPTER THREE**

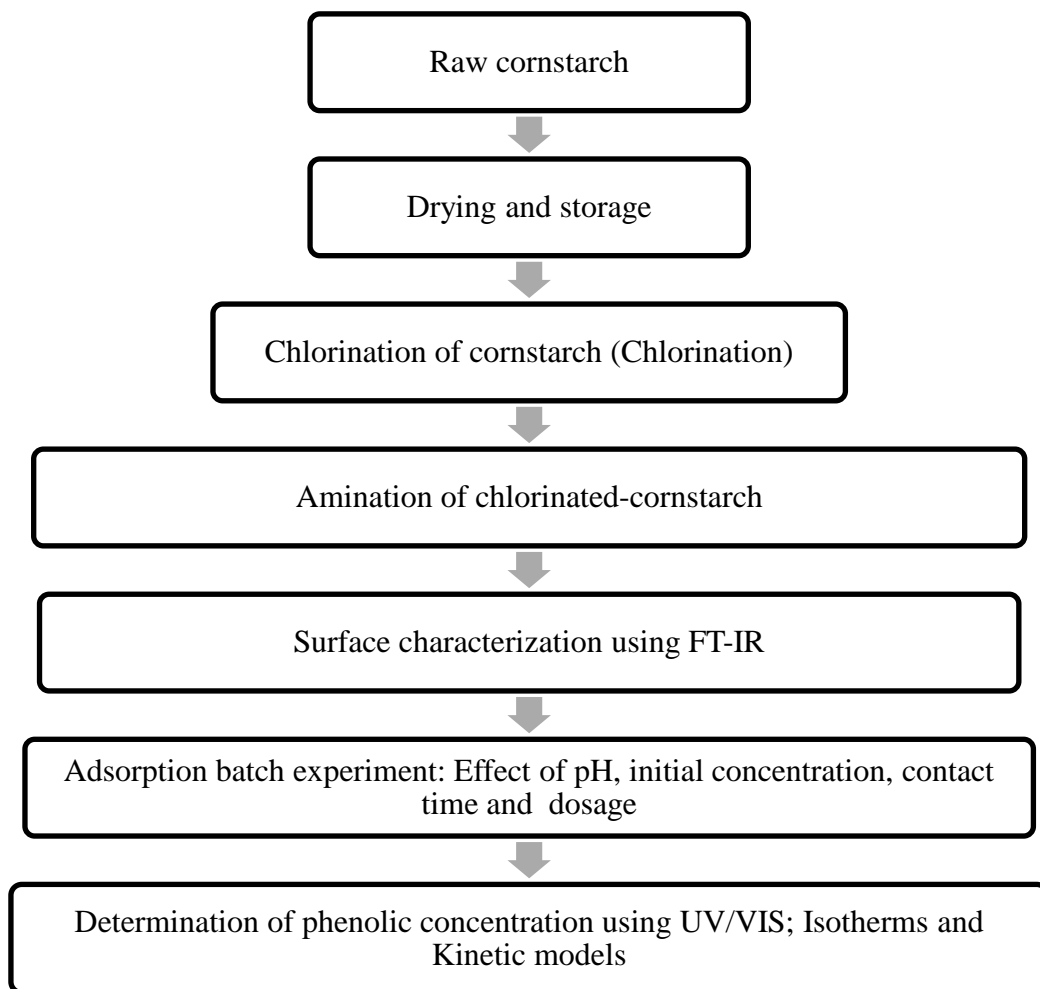
### **MATERIALS AND METHODS**

#### **3.1 Introduction**

This chapter involves sample collection, preparation and modulation of collected cornstarch. Discussion of methods and instruments for characterization of bioadsorbent. Batch experiments, adsorption models and uptake of PCs from aqueous media are discussed in this chapter

#### **3.2 Research Design**

Modulation of dried cornstarch (maize flour) was achieved by first chlorinating it with acetyl chloride under reflux in aniline solvent and then amination using tertiary amine (triethanolamine). Characterization of the modified biopolymer and then subsequently the biomaterial was applied in removal of phenolics from spiked/model solutions. The optimization of sorption variables was carried out and finally application of adsorbent in determination of adsorption capacities as well as reaction mechanism as shown in Figure 3.1.



**Figure 3.1. The Research Designs.**

### **3.3 Apparatus Cleaning**

All glassware used during laboratory work and collection of samples were first immersed in warm water with a caustic soda and detergent for 3 hours and scrubbed with brushes. They were soaked in aqua regia (royal water: the mixture of nitric(v) acid and hydrochloric in the ratio 1:1) overnight and then scrubbed with brush to remove all the ionic contaminants. Followed by rinsing severally with double deionized water, and then immersed in chromic acid for four (4) hours to oxidize any organic contaminants. Finally, glassware was cleansed with double deionized water and placed in a modern double oven at 50 °C overnight (12 hours) to dry.

Nickel/ steel apparatus were washed in hydrochloric acids followed by detergent. They were then rinsed with double-deionized water. Plastic apparatus was washed with detergent and caustic soda and then soaked in nitric (V) acids for 3 hours. They were subsequently cleansed with double de-ionized water and then dried.

### **3.4 Reagents, Chemicals and Solvents**

Starch used in this study was obtained from maize (corn) enriched flour purchased from a local market, Maragua and Mukuyu in Murang'a County, Kenya. All solutions were prepared using double deionized water obtained from Kenyatta University Chemistry Laboratory. Chemicals and reagents used were of analytical grade (AR). Tertiary amine (triethanolamine), hydroquinone and 2-naphthol were supplied by RFCL, Rankem, India. Phenol ( $C_6H_5OH$ ), 2, 4-dichlorophenol (2, 4-DCP), acetyl chloride and thionylchloride were sourced from BDH Chemical Ltd. Poole, England. Ammonium hydroxide ( $NH_4OH$ ), aniline solvent, sodium hydroxide ( $NaOH$ ), sodium acetate (buffer), potassium bromide ( $KBr$ ), hydrochloric acid ( $HCl$ ) of 37% purity, sulphuric acid (98% purity) and nitric acid ( $HNO_3$ ) were supplied by Sigma Aldrich (Kobian, Nairobi Kenya). Acetyl chloride (98% purity) was sourced from Fluka, Sigma Aldrich, Buchs Switzerland.

### **3.5 Instrumentation**

The characterization of unmodulated and modified cornstarch was done using FT-IR spectroscopy (FT-IR-8400 model, Shimadzu Tokyo, Japan) to identify the functional groups present. The phenolics concentration in aqueous media was determined using UV/Vis spectroscopy (Analytik Jena Specord 200 Plus model, Germany). A digitally calibrated pH meter (Hanna, model pH 210, Italy) was used in determination of all the pH. The solutions were shaken at 120 rpm speed for a given duration (30 minutes) using DKZ series digital reciprocating shaker (model SHR-2D, Korea). The mass

measured using BPS-4500-C1, (d=10 mg) electronic balance supplied by MRC Ltd, London UK. The oven used in this study was 78532 Tullingen /Germany oven model.

### **3.6 Stock Solution Preparation**

The stock solutions of selected soluble phenolic compounds: phenol and hydroquinone were prepared by dissolving 1.0 g/L (1000 ppm) in distilled water and 1.0 g of sodium acetate buffer was added. For 1000ppm 2-naphthol stock solution of pH 7 was prepared by first dissolving 1.0 g of 2-naphthol in 100 mL of 2-Propanol. Solution obtained was placed in a 1000 mL volumetric flask and then was filled up to the mark with distilled water (Barrera, 2020). Dilution of stock solutions were done to obtain standard working solutions used. The pH of working solution was measured and adjusted to have pH values of 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0 and 10.0 using 0.1 M hydrochloric acid and 0.1 M sodium hydroxide and dropwise (Mwangi *et al.*, 2014; Mwangi *et al.*, 2016).

### **3.7 Preparation of Adsorbent Biopolymer**

Bioadsorbent was prepared in two steps; Initial method was chlorination of cornstarch using suitable chlorinating agent, acetyl chloride refluxed in aniline. The final step was amination of intermediate product using tertiary amine and then characterization of the bioadsorbent.

#### **3.7.1 Chlorination of Cornstarch**

Cornstarch was dried at 60 °C for twelve (12) hours, cooled in a desiccator and later kept in an oven at 30 °C in a screwed clean plastic container. Glass apparatus used were dried in an oven at 100 °C for one hour before set up. A sample of 15.0 g dried cornstarch was mixed with 200 mL aniline solvent in a 500 mL three-neck flask. A 80 mL acetyl chloride, the chlorinating agent, was added dropwise from a separatory

funnel under mechanical rabbling at a temperature of 70 °C for 5 hours. The solid chlorinated cornstarch was recovered from the three-neck flask and unreacted chlorine was removed by washing with double de-ionized water and thus, adjusting its pH to neutrality, which was checked by universal indicator paper. It was then dried for 48 hours at room temperature (Mwangi *et al.*, 2014; Muhammad *et al.*, 2016).

### **3.7.2 Amination of the Chlorinated Cornstarch**

A mass of 15.00 g chlorinated cornstarch was mixed with 100 mL tertiary amine (triethanolamine) and refluxed under a mechanical mixer for 3.5 hours at 40 °C. The solid aminated cornstarch obtained was recovered from the mixture by vacuum filtration (with suction bump) using sintered glass crucible no.3 and Whatmann filter paper no.1. The residue was cleansed with double de-ionized water until its pH was neutral and dried at room temperature for one day. The synthesized solid derivative biomaterial was then packed in screwed clean plastic container and used for batch adsorption experiments (Muhammad *et al.*, 2016; Mwangi *et al.*, 2016).

### **3.7.3 Characterization of Starch Biopolymer**

The characterization of dried raw cornstarch (untreated) (RCS), chlorinated cornstarch (CCS), aminated cornstarch (ACS) and the aminated cornstarch after removal of phenolics (ACS) was done using FT-IR. The purpose of this stage was to find the functional/active groups present at each step and transformation of cornstarch after modulation. A 1.0 mg of dried sample of each of RCS, CCS, ACS and ACS were mixed thoroughly with 50.0 mg of potassium bromide (KBr). The mixture was pulverized and then pressed in a vacuum into pellets. The pellets were then put into Fourier Transform Infrared spectrophotometer machine (FT-IR-8400 model, Shimadzu Tokyo, Japan) for analysis. The adsorbents spectra were measured in the wavelength range 4500 cm<sup>-1</sup>–250 cm<sup>-1</sup>.

### **3.8 Adsorption Experiments**

The adsorption experiments were done in mechanical shaker set at 120 revolution per minute at controlled temperature, adjusted pH, contact time of the samples, biomaterial resin dosage used and initial concentration of phenolic using 0.1 g of the modulated cornstarch. The regeneration of the biomaterial resin was done using dilute hydrochloric acid (3.0 mol/L) and the eluent solution was analyzed using UV/Vis to determine the phenolic compounds present. The calibration of UV/Vis was done by first running blank sample at the set maximum wavelength for each PCs used. The standard solutions were then run in UV/Vis at their respective wavelength: phenol ( $\lambda_{\text{max}}=270$  nm), hydroquinone ( $\lambda_{\text{max}}=290$  nm) and 2-naphthol ( $\lambda_{\text{max}}=295$  nm). The concentration of the standards solution that were used were 5, 10, 15, 20, 25, 30, 35 and 40 ppm for each PCs. The calibrations graphs obtained were used for standardization, as in appendix VII.

#### **3.8.1 Effects of pH on Adsorption of PCs**

The optimum pH values were investigated by batch adsorption experiment on removal of phenolic from model solutions using 0.1 g of modulated cornstarch at different pH levels. The pH levels of the model solutions were adjusted from pH 3.0 to pH 10.0 using 0.1 M HNO<sub>3</sub> acid and 0.1 M NaOH solutions (Nayak *et al.*, 2020). The pH levels were measured using digital pH meter. A 20 mL of 25 mg/L phenol, 30 mL of 30 mg/L hydroquinone and 20 mL of 25 ppm 2-naphthol solutions were separately mixed with 0.1 g of the modulated cornstarch biopolymer and added to model solutions at varying pH levels (3, 4, 5, 6, 7, 8 and 9) in 25 mL screwed plastic bottles (Girish and Murty, 2014; Nayak *et al.*, 2020). The mixtures were equilibrated for predetermined time of 1 hour on a shaker machine at 120 rpm (Nayak *et al.*, 2020). The mixtures were then filtered at the end of one hour and the concentration of phenolics in the filtrate were

investigated using UV/Vis (Biglari *et al.*, 2016). All experiments were done at room temperature ( $25 \pm 1$  °C) and the entire procedure was repeated twice to ascertain the reproducibility, reliability, accuracy and precision of the data that were collected (Saha *et al.*, 2013).

### **3.8.2 Optimization of Initial Concentration on PCs Adsorption**

The optimization of initial concentration of phenolics was done according to Mwangi *et al.* (2014). The optimum initial concentration on uptake of phenolics were determined using 25 mL model phenolic solutions (phenol, hydroquinone and 2-naphthol) of 5, 10, 15, 20, 25, 30, 35 and 40 mg/L (ppm) in plastic bottles with 0.1 g each of the modulated cornstarch biopolymer on shaker kept at  $25 \pm 1$  °C. The solution pH level was fixed at a pH of 5.0. The mixtures were agitated at a speed of 120 rpm for one hour at a constant temperature. After the agitation time, the mixtures were then filtered and concentration of phenolics in the filtrate were analyzed using UV/Vis. The entire procedure was repeated twice to ascertain accuracy and precision.

### **3.8.3 Optimization of Adsorbent Dosage on Adsorption of PCs**

The optimization was done as described by Girish and Murty, (2014) and Nayak, *et al.*, (2020). The effect of the modulated biopolymer dose on the removal of phenolics was determined by mixing 40 mL phenol, hydroquinone and 2-naphthol of concentration 30 mg/L (ppm) with different amount of bioadsorbent 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 g in 25 mL screwed plastic bottles. The pH of the model solutions was adjusted to pH 5.0 using 0.1 M NaOH and 0.1 M HCl solutions. The mixtures were stirred at 120 rpm for 1hr at  $25 \pm 1$  °C. The mixtures were then filtered at the end of the contact time and the concentration of phenolic compounds in the filtrate were assessed using UV/Vis. The entire procedure was repeated twice.

### 3.8.4 Optimization of Contact Time on Adsorption of Phenolics

The optimization of agitation duration on phenolics uptake was performed according to Biglari *et al.*, (2016). The optimum contact time on phenolics removal were studied at different contact time of 5, 10, 20, 40, 60, 80, 100 and 120 minutes using 20 mL of phenol, hydroquinone and 2-naphthol 30 mg/L (ppm) of model solutions in the screwed plastic bottles. A mass of 0.1 g of the modulated biopolymer were put in each model solution. The pH of the model solutions was fixed at pH 5.0. The mixtures were shaken at 120 rpm and at the constant temperature ( $25 \pm 1$  °C). The mixtures were then filtered after each contact time. Thereafter, the concentration of phenolic in the filtrate was determined using UV/Vis. The entire procedure was repeated twice.

### 3.8.5 Determination of Adsorption Capacities of Raw and Modulated Cornstarch

The adsorption capacities were investigated by adding 0.1g of dried raw and modulated cornstarch separately to 25 mL of changing initial concentration of the model solution. The solutions were buffered at optimum pH (5-6) of each PCs. The mixture was agitated at 120 rpm for contact time 0.5 hr at constant temperature of  $25 \pm 1$  °C. After the time of contact, the mixtures were filtered and the amount of phenolics in the filtrate were analyzed using UV/Vis. The entire procedure was done in three replicates. The capacities of adsorption were determined by Langmuir and Freundlich isotherms.

## 3.9 Data Analysis

The quantity of phenolic compounds adsorbed by modulated cornstarch during the batch experiment was calculated as expressed in Equation 3.1.

$$q_e = \frac{(C_i - C_e)}{M} V \text{ ----- Equation 3.1}$$

where,  $q_e$  is the quantity of PCs uptake per unit of modulated biopolymer at



equilibrium,  $C_i$  is the initial concentration of PCs in ppm ( $\text{mgL}^{-1}$ ),  $C_e$  is the equilibrium concentration of PCs in  $\text{mgL}^{-1}$ ,  $M$  is the mass of the modulated cornstarch in grams and  $V$  is the volume of adsorbate in L (Barrera, 2020; Mbugua, 2020). The removed percentage of PCs in solution was calculated using Equation 3.2 shown below,

$$R\% = \left( \frac{C_i - C_e}{C_i} \right) \times 100 \text{ ----- Equation 3.2}$$

where,  $R\%$  is the percentage of removed PCs in solution,  $C_e$  and  $C_i$  are the equilibrium and the initial concentration of PCs respectively (Barrera, 2020).

The data obtained were analyzed using sorption models/ isotherms to determine the quantity of PCs removed. Langmuir and Freundlich equation, Equation 2.2 and 2.3 respectively were used in determination of absorption capacities of the adsorbent. (APHA *et al.*, 2017).

### 3.10 Kinetic Studies

The experimental data were applied to the Lagergren's pseudo – first order ( $K_1$ ) and the Ho's pseudo – second order ( $K_2$ ) rate kinetics in order to determine the rate controlling mechanism of phenol, hydroquinone and 2-naphthol uptake by the aminated cornstarch (ACS) biomaterial. The kinetics were studied by using 0.1 g of ACS and 30 mg/L (ppm) of 20 mL each model solution in a 50 mL screwed plastic bottles (Barrera, 2020). The pH of the model solutions was fixed at pH 5.0. The mixture was shaken for 5, 10, 20, 40, 60, 80, 100 and 120 minutes at the speed of 120 rpm and at the constant temperature ( $25 \pm 1$  °C). The mixtures were then filtered after each contact time. Thereafter, the concentration of phenolics in the filtrate were determined. The experimental data obtained were fitted in the pseudo – first order ( $K_1$ ) and the pseudo – second order ( $K_2$ ) kinetic models and analyzed by using linearized equations 2.5, 2.6 and the graphical analysis are as shown in Appendices I-III.

### **3.11 Chapter Summary**

This chapter comprehensively discussed collection and cleaning of apparatus, materials used and the methods to be followed in all procedures in order to achieve the specific objectives of the study. It includes the research design, instrumentation, modulation of cornstarch, characterization of cornstarch, adsorption batch experiments, data analysis methods and adsorption capacity determination using isotherm and kinetic models.

## CHAPTER FOUR

### RESULTS AND DISCUSSION

#### 4.1 Introduction

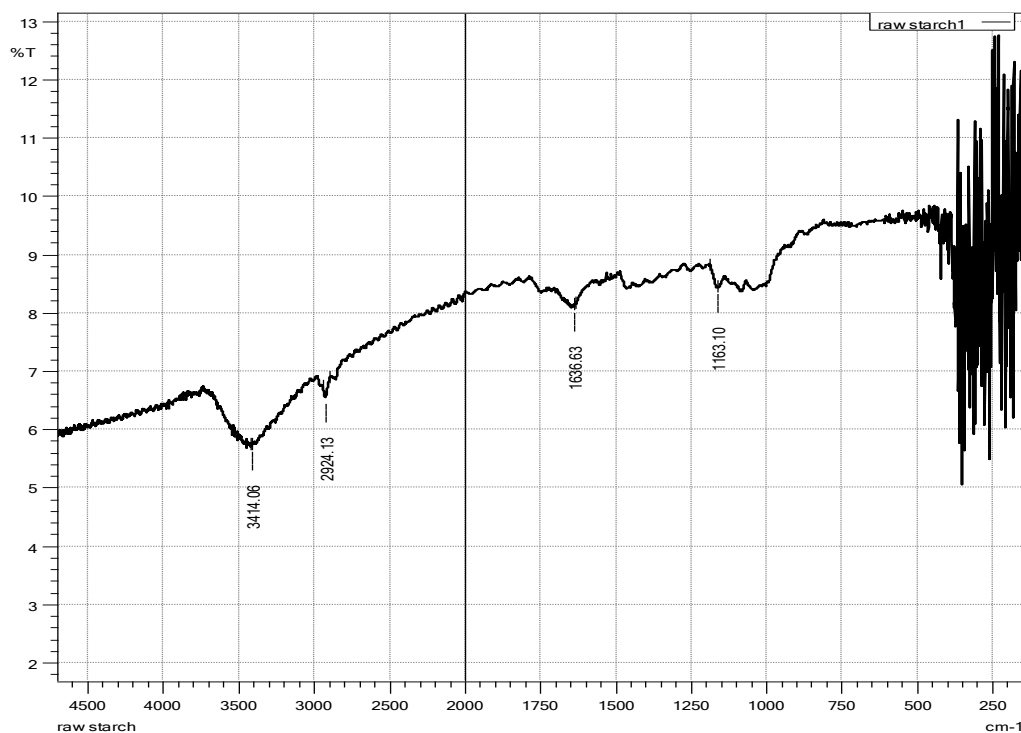
The chapter reports on the findings derived from this research which involved the modulation of cornstarch using triethanolamine which is tertiary amine. The resultant was characterized using FT-IR spectrophotometer and the biomaterial applied for the phenolics adsorption from water. The removal parameters of phenolic compounds were optimized using model solutions and the optimal values used for the adsorption of PCs in aqueous solution. The regeneration (reusability) of the phenolated bioadsorbent was investigated and it was observed that the adsorbed phenolic material could be easily removed by treating the phenolated material with a mineral acid. The following subsections give the discussions of the results obtained.

#### 4.2 FT-IR Characterization of the Biopolymer

The Fourier transform infra-red is an important tool in identification of functional groups in the biomaterials (Skoog *et al.*, 2007; Nthiga, 2016; Mbugua, 2020). The characterization of biomaterial was done using 8400 FT-IR spectroscopy Shimadzu model in the region of 4500 and 250  $\text{cm}^{-1}$ . The results obtained are as shown in the following sub-units.

#### 4.2.1 Characterization of the Raw Cornstarch

The FT-IR spectrum of raw cornstarch (RCS) result is shown in the Figure 4.1.



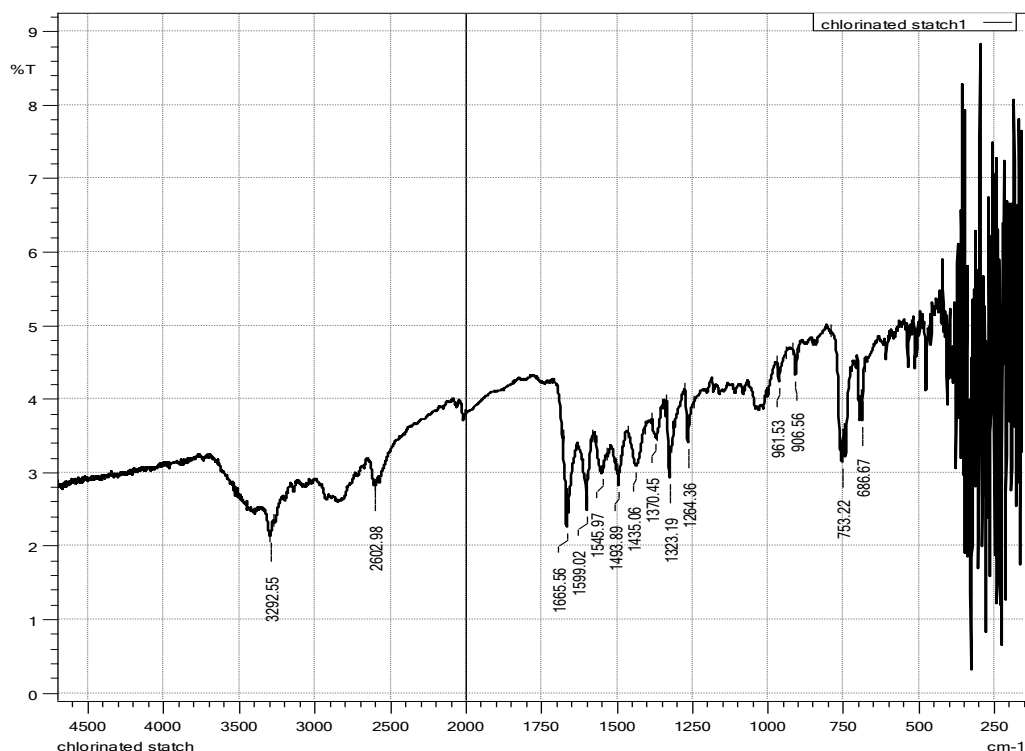
**Figure 4.1: FT-IR Spectrum of the Raw Cornstarch (RCS).**

The FT-IR spectrum (Figure 4.1) showed an intense broad band at 3414.06 cm<sup>-1</sup> assigned to O-H stretching in alcohols intermolecular bonded (Girish and Murty, 2014). For -NH group in amine absorbs in the region 3400-3300 cm<sup>-1</sup> (John, 2000; Mbugua, 2020). The intense peak at 2924.13 cm<sup>-1</sup> indicates O-H stretching in carboxylic group or in alcohols intramolecular bonded. The peak at 2924.13 cm<sup>-1</sup> also attributed to C-H bonds stretching vibration while at 1636.63cm<sup>-1</sup> to carbonyl functional group of esters and lactones (Liouna *et al.*, 2022). The bands observed at 1163.10 cm<sup>-1</sup> is due to C-OH stretching in tertiary alcohols (or anhydroglucose unit) and ethers which absorbs from the range 1250-1000 cm<sup>-1</sup>. A wide band at 1500-1250 cm<sup>-1</sup> attributed to C-C bending (John, 2000; Liouna *et al.*, 2022). The compounds

present in cornstarch based on the functional groups identified are alcohols, carboxylic acid in starch, aldehydes, amides, ether, esters and amines (Figure 4.1).

#### 4.2.2 Characterization of the Chlorinated Cornstarch

The spectrum of chlorinated cornstarch (CCS) is represented in the Figure 4.2.



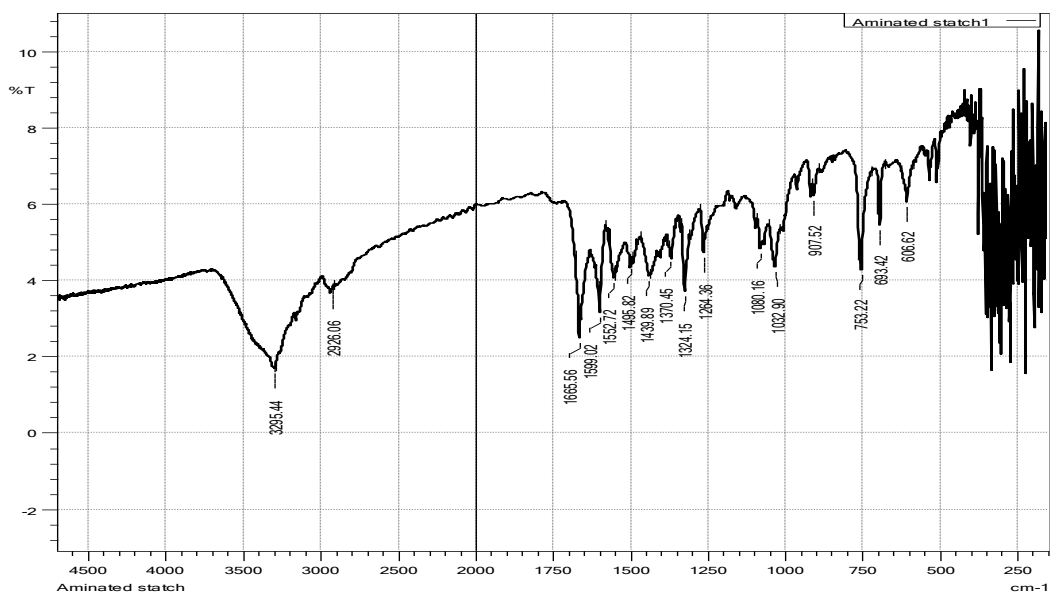
**Figure 4.2:** FT-IR Spectrum of the Chlorinated Cornstarch (CCS)

FT-IR spectrum of CCS (Figure 4.2) revealed the shifting of existing bands, disappearance of bands (Figure 4.1) and appearance of new bands of some absorption bands frequencies due to hydroxyl, carboxylic and halogen group (Nayak *et al.*, 2020). Significant shifting of absorption peak frequencies, examples of the bands at 3414.06 cm<sup>-1</sup> (Figure 4.1) to 3292.55 cm<sup>-1</sup> due to one of -OH group being displaced by chlorine, 2924.13 cm<sup>-1</sup> to 2602.98 cm<sup>-1</sup> and 1636.13 cm<sup>-1</sup> to 1599.02cm<sup>-1</sup> respectively was observed upon chlorination. Appearance of the new absorption peak frequencies at 753.22 and 686.67cm<sup>-1</sup>was observed which was assigned to C-Cl bond stretching

vibration which ranges from 850-500  $\text{cm}^{-1}$  (John, 2000; Nayak *et al.*, 2020). The frequency band at 1163.10  $\text{cm}^{-1}$  which was characteristics of C-OH group stretching vibration in alcohols in the raw cornstarch (RCS) disappeared upon the replacement of -OH group with the halide (Mwangi, *et al.*, 2016). The absorption peaks at various wavelengths (Figure 4.2) were due to different functional groups identified, such as at 2602.98 (C-H stretch), 1665.56 (carboxylate, C=O stretching), 1493.89 (C-H bending), 1435.06 (O-H stretch), 1370.45 (O-H bending) and 1323.19-1264.36 (C-O stretch from carboxylic acids, alcohols, ethers, esters and lactones) (John, 2000; Nayak, *et al.*, 2020).

#### 4.2.3 Characterization of the Aminated Cornstarch

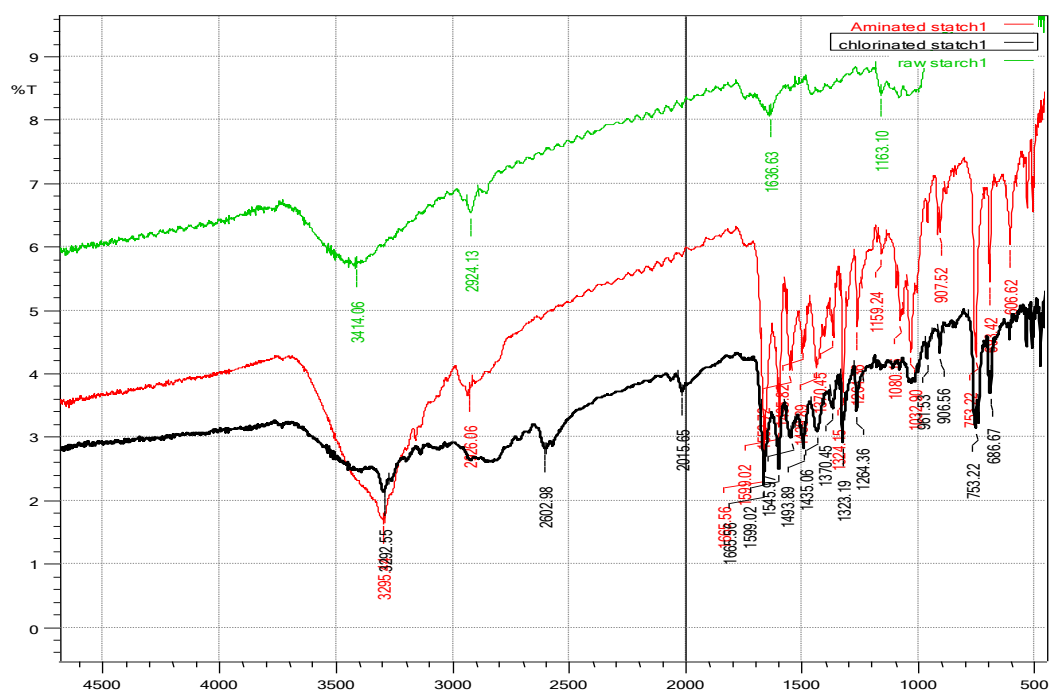
Figure 4.3 shows results of FT-IR spectrum of aminated cornstarch (ACS).



**Figure 4.3:** FT-IR Spectrum of the Aminated Cornstarch (ACS) with Triethanolamine.

The new peak absorption frequencies at 1080.16 and 1032.90  $\text{cm}^{-1}$  corresponded to C-N bond stretching vibration of amine group (John, 2000). This confirmed the formation of the C-N bond of amine group. Significant shifting of some bands from

3292.55, 1493.89, 1435.06, 1323.19  $\text{cm}^{-1}$  in chlorinated cornstarch (Figure 4.2) to 3295.44, 1495.82, 1439.89, 1324.15  $\text{cm}^{-1}$  in aminated cornstarch (Figure 4.3) were observed after modulation with triethanolamine (amination). The band at 2602.98 and 2015.65  $\text{cm}^{-1}$  in chlorinated cornstarch (Figure 4.2) disappeared in aminated cornstarch (Figure 4.3) upon amination which showed the substitution of chlorine with triethanolamine (Mwangi *et al.*, 2016). Strong broad band with increased intensity at 3295.44  $\text{cm}^{-1}$  in aminated cornstarch (Figure 4.3 and 4.4) confirmed C-N stretch of amine functional group and N-H stretch of amine salt which ranges from 3300-2800  $\text{cm}^{-1}$  (John, 2000). The peak at 1552.72  $\text{cm}^{-1}$  is due to  $-\text{CH}_3$  groups of the compounds containing nitrogen (Nayak *et al.*, 2020).



**Figure 4.4: FT-IR Spectra of RCS, CCS and ACS Overlaid**

Figure 4.4, illustrated distinct FT-IR spectra differences of the RCS, CCS and ACS. It shows functional groups in RCS, CCS and ACS. The overlaid spectra of RCS, CCS and ACS (Figure 4.4) gives a clear difference between them with aminated chlorinated-cornstarch having peaks with high intensity. This confirmed that

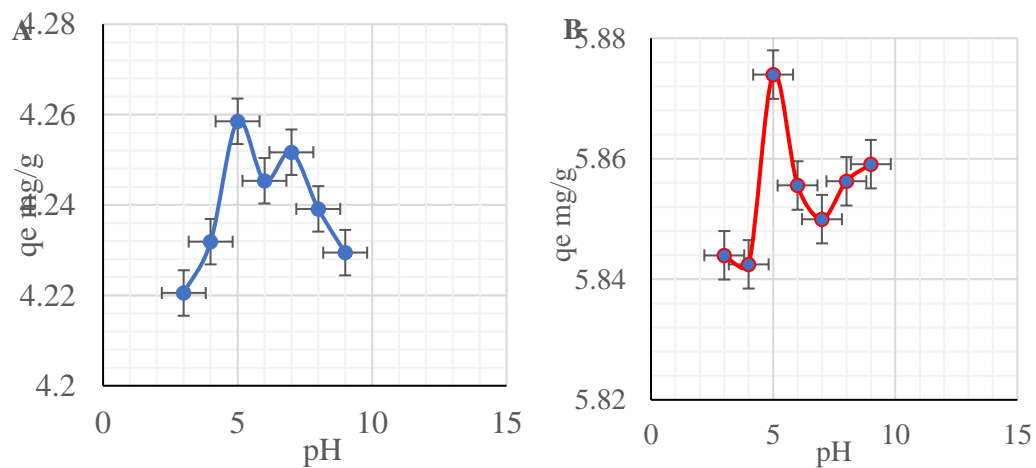
triethanolamine (tertiary amine) was successfully anchored on the cornstarch biomaterial. Results reported in this study were similar with those reported on sawdust (Nayak *et al.*, 2020), quaternized maize tassels (Mwangi *et al.*, 2014) and on shea residue- *Vitellaria paradoxa* (Liouna *et al.*, 2022).

### 4.3 Adsorption Experiments Results

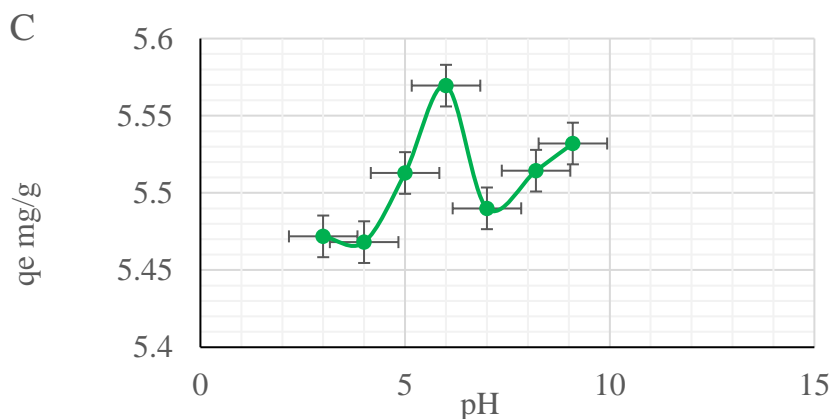
The results of optimization of adsorption parameters are discussed in the following subsections. All the batch adsorption experiments were done at a fixed temperature using horizontal mechanical shaker at the constant 120 rpm speed.

#### 4.3.1 Effect of pH on Adsorption of PCs

The uptake of PCs in aqueous media relies on the pH of solution. The effect of pH on the uptake of PCs was carried out in section 3.8. The results of the effect obtained are presented in tabular form in appendix X and graphical representation as shown in Figure 4.5.







**Figure 4.5. Effect of pH on the adsorption of Phenol (A), Hydroquinone (B) and 2-Naphthol (C) onto ACS adsorbent. (Initial concentration: 25 ppm phenol & 2-naphthol and 30 ppm hydroquinone; agitation time: 60 mins; ACS dosage: 0.1 g; temperature:  $25 \pm 1$  °C; shaking speed: 120 rpm).**

The results (in Figure 4.5) and in appendix VIII show that pH has significant effect on sorption of phenolics in aqueous media. It was noted that adsorption was low at pH values below 4.0 and above 7.5. The maximum sorption capacities were found to be between pH 5.0 and 6.0. This was attributed to high concentration of hydrogen ions/hydroxonium ions resulting to increase of the positive surface charge density of the adsorbent, resulting to greater removal of PCs (Mukherjee, *et al.* 2007). In figure 4.5 and appendix VIII show that maximum uptake of phenol was at pH of 5.0 with capacity  $q_e$  of 4.257 mg/g (85.17%) as observed in Figure 4.5 (A) and in appendix VIII and hydroquinone was at pH 5.0 with  $q_e$  of 5.874 mg/g (97.90%) as observed in Figure 4.5 (B) and appendix VIII. For 2-naphthol, the optimum pH was 6.0 with  $q_e$  of 5.570 mg/g (92.83%) as indicated in Figure 4.5 (C) and appendix VIII. The adsorbent and the adsorbate/ analyte have deprotonation and protonation relying on pH environments.

The trend of the adsorption of PCs increases from pH 3 to pH 6 due to high density of positively charge ions. From the pH of 7 to pH of 9, the percentage removal decreases

due to the increase in negatively charge ions, resulting to increase in repulsive effect between adsorbate and adsorbent. Therefore, low pH environment neutralizes starch surface negative particles, lowers the hinderance to diffusion of phenolic compounds ions, increases electrostatic attraction due to  $\pi$ - $\pi$  interactions between ions and consequently increases the probability of their adsorption (Kaman *et al.*, 2016; Nayak *et al.*, 2020). This attributes to a chemisorption adsorption mechanism.

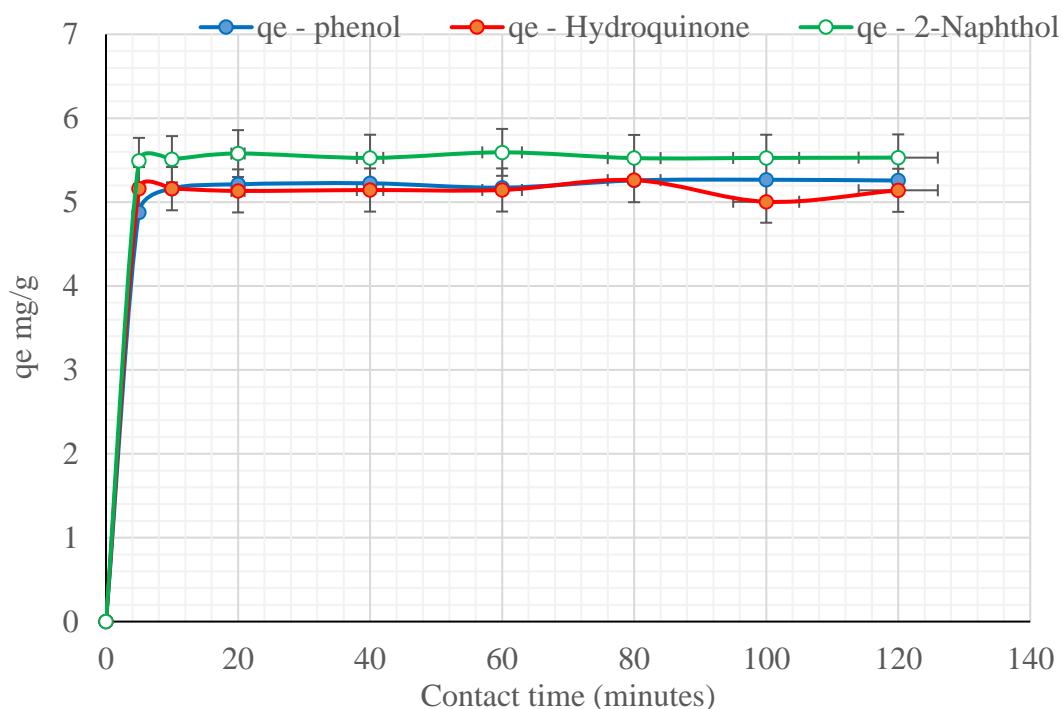
At high pH values  $>7$ , there was high concentration of  $\text{-OH}^-$  ions (negatively charge ions) which increases the development of the repulsive forces between ions of PCs and hydroxide ions. Consequently, increases the hindrance to diffusion of PCs ions resulting in low uptake of PCs, thus reduces their adsorption of PCs at high pH values (Nayak *et al.*, 2020). At that pH environment, the phenolate ions forms strong salts with alkali metal of the base (Barrera, 2020).

At optimal pH environment, the percentage removal was 85.17% for phenol, for 2-naphthol has optimum pH of 6.0 and 92.83% and for hydroquinone (hydroxyl benzene) was 97% as indicated in appendix VIII. Size of the phenolate ion and the number of hydroxyl groups also affected the percentage removal. The observation could be due to electron density resonating in their benzene ring structure (Barrera, 2020). The order of uptake efficiencies was ascribed to the acidity strength of the PCs which depends on the kinds, positions and nature of the substituent groups attached to aromatic ring (Bożena and Sylwia, 2003). Similar findings have been reported in studies on the PCs removal using adsorption process by quaternized maize tassels, (Mwangi *et al.*, 2014), tamarind seed powder (Abu *et al.*, 2018) and the  $\text{Fe}_2\text{O}_3$  impregnated sawdust (Nayak *et al.*, 2020) as adsorbents.

The maximum removal of model PCs in solution were realized at the pH 5 for phenol, pH 5 for hydroquinone and pH 6 for 2-naphthol in this study. Therefore, it was established that maximum removal of PCs in aqueous solutions can be successfully achieved in the pH 5.0-6.0 range and was used in subsequent batch experiment.

#### 4.3.2 Effect of Contact time on Adsorption of PCs

Contact time is very significant factor affecting the efficiency and establishing the kinetic process (Biglari *et al.*, 2016). The data obtained when contact time was varied as in the section 3.8.4. The results obtained in this study were as presented in Figure 4.6, in appendix IV as well as in tabular form as shown in appendix X.



**Figure 4.6: Effect of Contact time on the Removal of PCs from Aqueous Solutions.**

(Initial concentration: 30 ppm; agitation speed: 120 rpm; ACS dosage: 0.1 g; temperature:  $25 \pm 1$  °C; pH: 5.0).

From the findings in Figure 4.6, it was clearly seen that the uptake of PCs increases rapidly with time for the first 5 minutes contact time, which then slowed down and flattened for longer contact time. At the 10 minutes, the removal efficiencies of phenol, hydroquinone and 2-naphthol were 5.160 mg/g ,5.161 mg/g and 5.511 mg/g respectively. Beyond the contact time of 10 minutes, also as in Appendix IV, there was no significant changes on adsorption of PCs ascribed to state of equilibrium condition was reached for maximum uptake. This trend can be attributed to the presence of a high number of available active binding sites on the adsorbent surface resulting to relatively high rate of adsorption initially, which then remains without any remarkable changes (Nayak *et al.*, 2020). The results estimate the rate at which the phenolic ions were removed from solution and provide details of the adsorption mechanism (Mwangi, *et al.*, 2014; Nayak, *et al.*, 2020). The results also indicate that for maximum removal of phenolic ions, ACS would need low residence time of adsorbate at solid – solution equilibrium interface which controls the rate of uptake (Kaman, *et al.*, 2016).

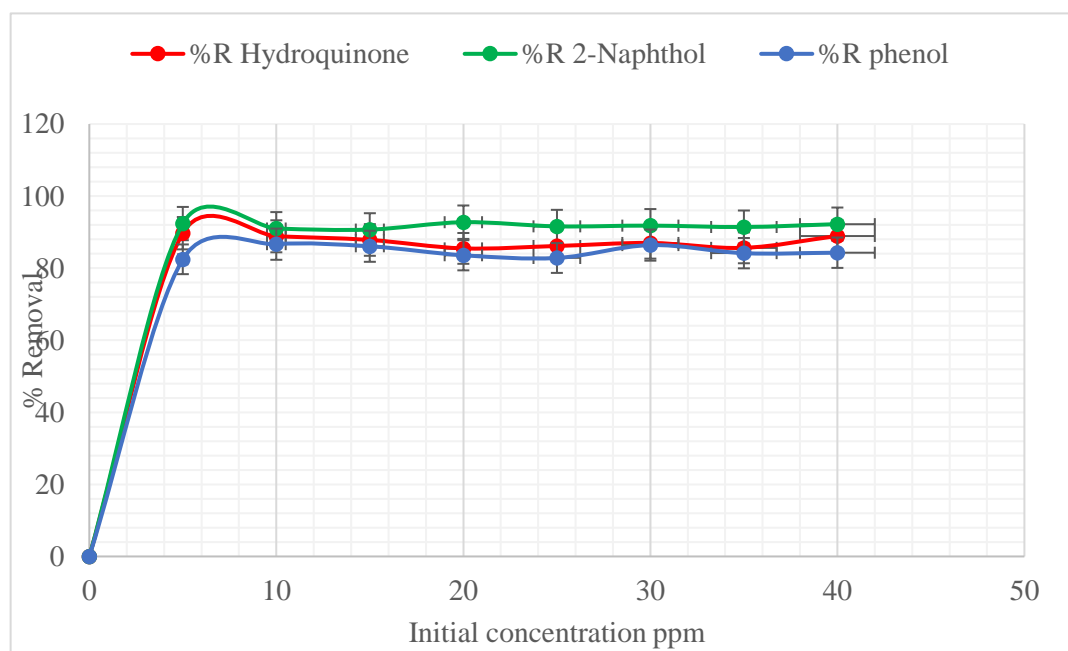
Consequently, the slowed down in rate of adsorption in longer agitated time, after optimum time may be due to a possible adsorbate molecules aggregation and thus leading to resistance to further ions diffusion. As the time progressed the active binding sites for ion exchange reaction becomes exhausted decreasing the sites to adsorb phenolic compounds. Thereby, increasing repulsive forces between solid-solution ions interface lowering the uptakes/ adsorption rate (Abu *et al.*, 2018).

The maximum uptake occurred within 10 minutes of the adsorption process. An equilibrium was established after the binding sites have been saturated with ionic PCs and there was minimal adsorption taking place. Results found agreed with what was

reported on quarternized maize tassels and sawdust (Mwangi, *et al.*, 2014; Nayak, *et al.*, 2020). Therefore, for the maximum PCs removal from aqueous media, the optimum period for equilibration was kept at 30 minutes and is utilized in the subsequent experiments.

#### 4.3.3 Effect of Adsorbate Initial Concentration on Adsorption of PCs

The initial concentrations of PCs were varied when investigating its effect on the removal of phenolic compounds from aqueous solution. The other physicochemical parameters were kept constant, refer to the section 3.8.2. The findings obtained were as shown in Figure 4.7 and in appendix IX as well as in the table shown in appendix X.



**Figure 4.7: Effect of Initial Concentration on the Removal of PCs from Aqueous Solutions.**

(Contact time: 60 min; shaking speed: 120 rpm; ACS dosage: 0.1 g; temperature: 25  $\pm$  1  $^{\circ}$ C; pH: 5.0).

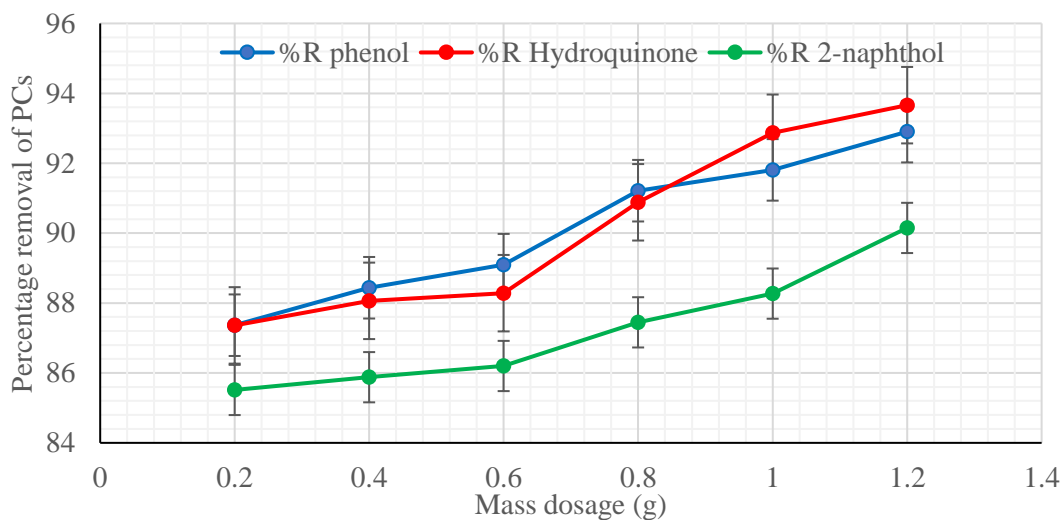
The general observations in Figure 4.7 and appendix IX for all the PCs were that the uptake (percentage removal) increases with increase in initial concentration up to an initial concentration of 5.0 ppm the sorption attains a plateau profile.,  $q_e$  mg/g, approached steady state. Beyond 10 ppm, the ACS adsorbent is said to be saturated and attained its operational optimum adsorption capacities (Mwangi *et al.*, 2014; Barrera, 2020). This is because increase of mass transfer driving force between adsorbate and adsorbent, and thus the fruitful diffusion of phenolic ions / binding to the surface of adsorbent from solutions (Nayak *et al.*, 2020).

The fixed active binding sites on ACS surface are successfully occupied by the phenolate ions as initial concentration of phenolics increases. This accounts for the observed increase in the percentage removal of PCs (Figure 4.7), since more of active sites are fully occupied resulting in saturation of binding sites and slowed down the adsorption efficiencies.

In this study, the maximum of 86.65% of phenol at 10 ppm, 89.70% of hydroquinone and 92.37% of 2-naphthol at 5 ppm were removed. The results also show that 2-naphthol has the highest binding affinity power towards ACS compared to other PCs. The difference in the binding power of PCs towards ACS could be ascribed to traits like solubility, kind of functional group(s) and position on the aromatic ring, as have been reported by Bożena and Sylwia (2003), Mwangi *et al.*, (2014) and Barrera, (2020).

#### 4.3.4 Effect of Dosage of Modulated Adsorbent on Adsorption of PCs

The effect of ACS adsorbent dosage on uptake of PCs was examined by varying mass, refer to the section 3.8.3. The results obtained on adsorption of PCs by various masses of ACS adsorbent in the equilibration were presented in Figure 4.8 and in appendix X.



**Figure4.8: Effect of Dosage of ACS Adsorbent on Removal of PCs from Aqueous Solution.**

(Initial concentration :30 ppm; Contact time: 30 min; shaking speed: 120 rpm; temperature:  $25 \pm 1$  °C; pH: 5.0 for phenol and hydroquinone, pH 6 for 2-naphthol).

From the Figure 4.8, the findings show that the percentage removal of PCs increases gradually with the increase in the mass of the ACS adsorbent. The observed phenomenon in figure 4.8 can be explained by the fact that the volume of binding active sites or pores for interaction increases with increase in mass of ACS which leads to increase the amount of PCs removed from aqueous phase. This observation was assigned to increased adsorptive surface area and availability of more effective active adsorption sites resulting from the stoichiometrically increased dose of ACS. This showed that the number of active binding adsorptive sites increases with the increase

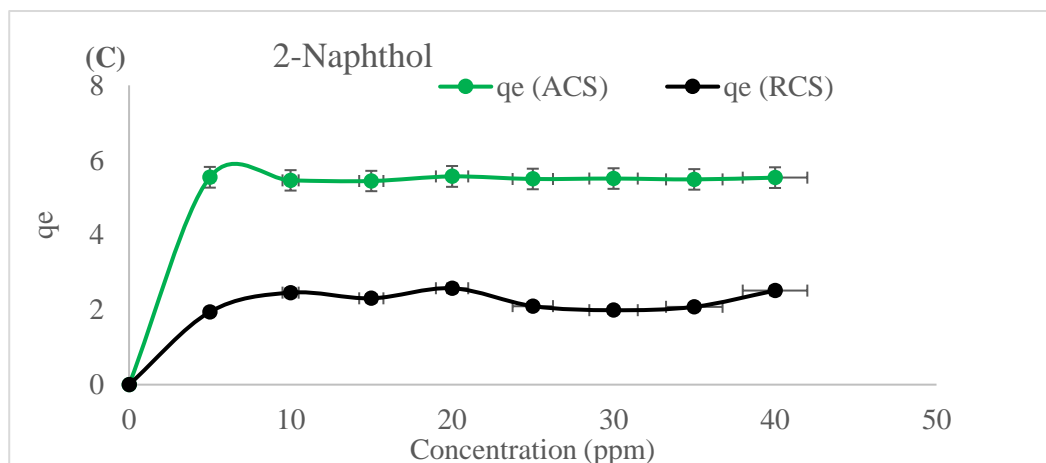
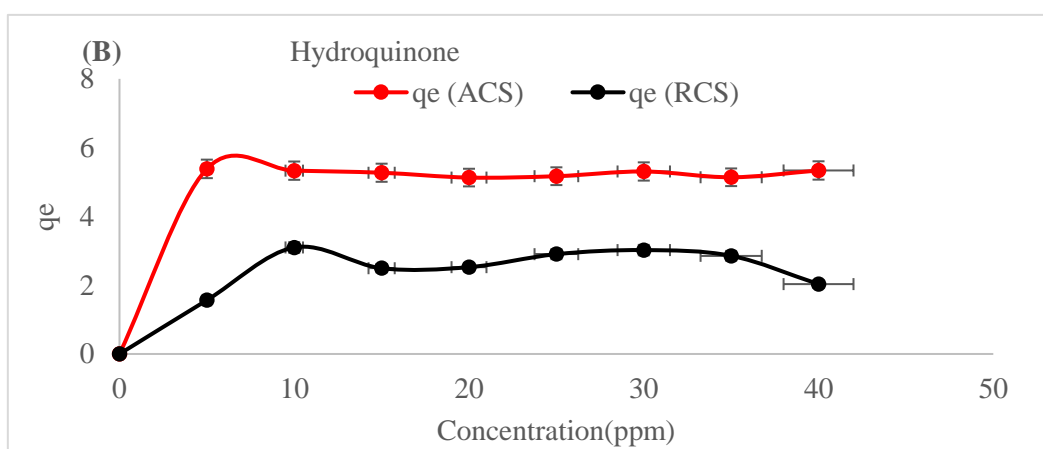
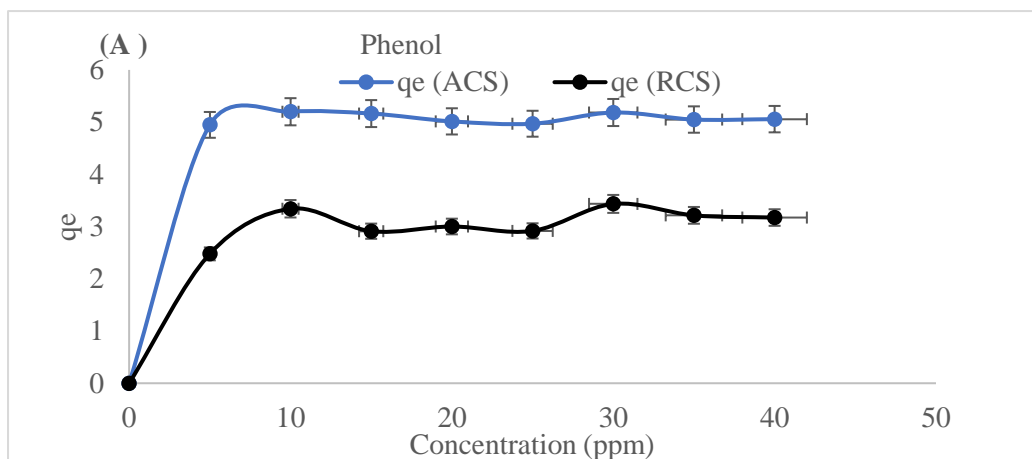
in ACS biomaterial dose and inadequate of active sites at less doses which retards the removal onto the surface of adsorbent.

The increase of uptake of PCs show that there are still active sites on the surface of ACS adsorbent that are not saturated. Thus, adsorbent is said to be saturated when all active sites are fully occupied, this is where the adsorption process profile is plateaued. These findings are in congruent to those reported in the literature (Saha *et al.*, 2013; Mwangi *et al.*, 2014; Sarker & Fakhruddin, 2017; Abu *et al.*, 2018). The optimum dosage in process unit depends on the chemistry of the solution: concentration of adsorbates, the volume of adsorbates and the ion size (Saha *et al.*, 2013). In all the subsequent equilibration studies, therefore, the mass dosage was 0.1grams.

#### **4.4 Comparison of Efficacy of Modified and Raw Cornstarch as Adsorbent**

The comparison of the efficacy of adsorbents were done by adding 0.1 g of dried modulated (ACS) and raw (RCS) cornstarch separately to 25 mL of the initial concentration ranging from 5 ppm to 40 ppm of phenol, hydroquinone and 2-naphthol at their optimum pH. For phenol and hydroquinone optimum pH was 5 and 2-naphthol was pH 6. The mixtures were agitated using reciprocating mechanical shaker at the speed of 120 rpm for 30 minutes. The batch experiments were performed at Lab. temperature. Results were as presented in Figure 4.9.





**Figure 4.9:** Effect of Initial Concentration on Uptake of PCs with both ACS and RCS Adsorbents. (Contact time: 30 min; shaking speed: 120 rpm; temperature:  $25 \pm 1$  °C; pH: 5.0 for phenol and hydroquinone, pH 6 for 2-naphthol, 0.1 g dose).

The general observations in Figure 4.9 for both ACS and RCS adsorbents were that the maximum uptake occurred rapidly and then slowed down after 10 ppm for phenol, hydroquinone and 2-naphthol. It seems that the adsorption did not vary significantly with change in initial concentration of the PCs. This accounts to the fully occupied of the fixed available active binding sites on adsorbents at the first stage as initial concentration increase. At equilibrium the adsorption efficacies lowered as a consequence of saturation of binding sites. The profile of modulated cornstarch recorded higher maximum uptake of PCs than raw cornstarch for all model solutions. Modulation enhances the adsorptive properties of biopolymer by insertion of functional group responsible for adsorption of PCs. This is in parallel with the literature reported, (Abu *et al.*, 2018; Barrera, 2020; Nayak *et al.* 2020).

#### **4.5 Adsorption Isotherms/ Adsorption Capacities for PCs**

In the determination of adsorption capacities and chemisorption mechanism of the PCs using ACS as adsorbent, the experimental results obtained was integrated into Freundlich and Langmuir isotherms denoted by equation 2.2, 2.3 and equation 2.4. The initial concentration of PCs was varied as in section 3.8.6 and refer figure 4.7 (a) and (b). The corresponding isotherms parameters and the linear regression coefficients from each isotherm were evaluated for all PCs used and the results presented in Table 4.1.

**Table 4.1: Results for the Freundlich and Langmuir Isotherms for PCs Adsorption Capacities**

Phenolic Compounds (pcs)	Langmuir Model			Freundlich Model			Best Model Fitted
	Parameters	$q_{\max}$ (mg/g)	$b / K_L$ (dm <sup>3</sup> /g)	$R^2$	1/n	$K_f$ (mg/g)	
Phenol	4.298	1.428	0.9998	0.1725	3.897	0.9172	Langmuir
Hydroquinone	4.585	2.142	0.9999	- 0.1379	6.290	0.9928	Langmuir
2-Naphthol	5.048	4.895	1.000	- 0.0899	5.970	0.9984	Langmuir

From the results in the Table 4.1 and appendices V and VI, the maximum adsorption capacities ( $q_{\max}$ ) for phenol, hydroquinone and 2-naphthol were 4.298, 4.585 and 5.048 mg/g respectively by the aminated cornstarch adsorbent this shows that the nature and position of substituent group influence the adsorption capacities. For 2-Naphthol, had a higher b value of 4.895 dm<sup>3</sup>/g while phenol and hydroquinone had 1.428 and 2.142 dm<sup>3</sup>/g respectively. Thereby, 2-naphthol has higher affinity power and energy to ACS adsorbent than phenol and hydroquinone, this could be due to strong Van der Waal attractions. The Langmuir constant (b) shows the magnitude of affinity of binding sites and a measure of absorption energy (Nthiga, 2016). The 1/n values are less than one as observed in the Table 4.1, indicates that the adsorbent binding sites is homogeneous and favourable normal adsorption process. The negative 1/n values are relatively uncommon but are often observed at low concentration ranges for compounds containing a polar functional group. They are in competition with water for adsorption sites. Freundlich linear equation is purely empirical and is valid only up to a particular concentration, above which it tends to non-linear (Laura *et, al.*,

2021). Thus, negative values show that adsorption data does not fit Freundlich isotherm model.

Therefore, Langmuir linear equation gave higher values of regression coefficients ( $R^2 > 0.9998$ ) as compared to Freundlich linear equation ( $R^2 > 0.9172$ ). This shows that the experimental data perfectly suited or conformed to the Langmuir isotherm (Laura *et al.*, 2021). A similar observation was made by Saha *et al.*, (2013), Mwangi *et al.*, (2014) and Nayak *et al.*, (2020) in their adsorption studies. The Langmuir isotherm explains the fact that the adsorption equilibrium of PCs occurred at a specific homogeneous surface of bioadsorbent and that no more uptake could occur at saturated sites, thus suggesting a chemisorption and a monolayer coverage adsorption (Kaman *et al.*, 2016; Barrera, 2020). The adsorption capacity values reported in this study were relatively higher than for many other reported processes in literature. This indicates that removal of PCs from aqueous media using ACS was effective.

#### **4.6 Adsorption Kinetics**

The Lagergren's pseudo – first order ( $K_1$ ) and Ho's pseudo – second order ( $K_2$ ) kinetic rate models, as in Equation 2.5 and 2.6, were integrated to the experimental data obtained (Lagergren, 1898; Ho and McKay, 1999). They were used to investigate the molecularity of the adsorption and the rate-limiting step mechanism. The results obtained of the kinetics parameters for the three PCs are shown in Table 4.2.

**Table 4.2: Results for Kinetic Parameters for Adsorption of PCs onto ACS**

Phenolic Compounds (PCs)	Pseudo – first order ( $K_1$ )			Pseudo – second order ( $K_2$ )			Best Model Fitted
	Parameters	$q_e$ (mg/g)	$K_1$ (mg/ g min <sup>-1</sup> )	$R^2$	$q_e$ (mg/g)	$K_2$ (mg/ g min <sup>-1</sup> )	
Phenol	0.9410	0.0021	0.6356	3.6738	0.1648	0.9978	Pseudo-second order
Hydroquinone	1.1182	-0.0049	0.1694	4.3783	0.2393	0.9767	Pseudo-second order
2-Naphthol	2.3453	0.0017	0.1813	2.3458	0.4507	0.9946	Pseudo-second order

From the results in the Table 4.2 and Appendices I-III show that  $q_e$  mg/g (capacities) of phenol, hydroquinone and 2-naphthol were higher in pseudo-second order than in the first order. The adsorption rate was higher in 2-naphthol (0.4507 mg/g.min) followed by hydroquinone 0.2393 mg/g/min and then phenol with least 0.1648 mg/g/min. The rate of reaction was generally higher in pseudo-second order as compared to the first order kinetic model but hydroquinone has negative  $K_1$  the explanation of negative gradient of hydroquinone adsorption is due to its dihydroxy factor and low concentration. That phenomenon enables chemisorption process due to its high polarizing charge favouring a chemisorption process and not physisorption (Laura *et al.*, 2021). The linear coefficient of correlation,  $R^2$ , values recorded by  $K_1$  were lower than values recorded by  $K_2$ , which will be denoted as  $K_1 < K_2$ . The experimental results showed that optimum changes were realized with  $K_2$  since it gives the best  $R^2$  values. Therefore, pseudo-second order kinetic model ( $K_2$ ) fitted best to the experimental data than pseudo-first order ( $K_1$ ). From the data the rate-determining mechanism of the adsorption process is chemisorption, which agreed with previous reports by Kaman *et al.* (2016), Barrera, (2020) and Nayak, *et al.* (2020).

## 4.7 Chapter Summary

The conclusion of this chapter is as highlighted below:

The cornstarch was successfully modified using acetyl chloride as a chlorinating agent in aniline by shaking at a temperature of 70 °C for 5 hours followed by amination of the chlorinated cornstarch using triethanolamine by refluxing for 3.5 hours at 40°C and this was confirmed by the FT-IR analysis obtained. The analysis revealed the functional groups and kinds of chemical bonds responsible for adsorption of PCs.

The adsorption process was influenced by the dosage of adsorbent, contact time, solution pH and initial concentration of phenol, hydroquinone and 2-naphthol. Batch mode studies showed that high removal of PCs was noted at a contact time of 10 mins, pH of 5.0-6.0 and constant temperature of  $25 \pm 1$  °C and agitation speed of 120 rpm for the three compounds selected. The dose of aminated cornstarch and initial concentration increases with the increase in removal of phenolic compounds.

The modified cornstarch has higher adsorption capacity than the raw cornstarch. The data obtained fitted well into the Langmuir isotherm compared with the Freundlich isotherm, with linear regression coefficient,  $R^2=0.9998$ , 1.000, 0.9999 and monolayer adsorption capacities of 4.298, 4.584 and 5.048 mg/g for phenol, hydroquinone and 2-naphthol respectively. The adsorption process was best described by the linear regression coefficient of pseudo-second order was fairly higher than that of pseudo-first order kinetic model.

## CHAPTER FIVE

### CONCLUSION AND RECOMMENDATIONS

#### 5.1 Conclusion

The cornstarch was successfully modified using acetyl chloride as a chlorinating agent in aniline by rabbling at a temperature of 70 °C for 5 hours followed by amination of the chlorinated cornstarch using triethanolamine by refluxing for 3.5 hours at 40°C and this was confirmed by the FT-IR analysis. The spectra showed strong broad band with increased intensity at 3295.44cm<sup>-1</sup> which confirmed C-N stretch of amine group and N-H stretch of amine salt were anchored. The analysis revealed the functional groups and kinds of chemical bonds responsible for adsorption of PCs.

The quantity of PCs adsorbed by the modulated bioadsorbent were influenced by the following adsorption parameters viz dosage of adsorbent, contact time, solution pH and initial concentration of adsorbate. Batch mode studies showed that high removal of PCs was noted at a contact time of 10 mins, pH of 5.0-6.0 and constant temperature of 25 ± 1 °C and agitation speed of 120 rpm for the three compounds selected. The dose of aminated cornstarch and initial concentration increases with the increase in removal of phenolic compounds. The maximum adsorption of PCs happened at initial concentration of 10ppm and then flatten.

The modified cornstarch has higher adsorption capacity than the raw cornstarch. The data obtained fitted well into the Langmuir isotherm with regression coefficient, R<sup>2</sup>=0.9998, 1.000, 0.9999 and monolayer adsorption capacities of 4.298, 4.584 and 5.048 mg/g for phenol, hydroquinone and 2-naphthol respectively. These adsorption

capacities were relatively higher than some reported processes, thus making the aminated cornstarch (ACS) an alternative adsorbent for removal of phenolic compounds from aqueous media. The adsorption process was best described by the pseudo-second order kinetic model. The rate controlling mechanism of this adsorption was chemisorption.

## **5.2 Recommendations**

### **5.2.1 Recommendations from this Study**

- i. The method is recommended for modification of other biopolymers to be used for water purification.
- ii. The optimized adsorption parameters are recommended for use in water purification.
- iii. The adsorption capacity of aminated cornstarch was higher than the raw biopolymer. The aminated cornstarch is recommended for removal of phenolic compounds from wastewater.

### **5.2.2 Recommendations for Further Research**

- i. Further research to be done on multi-component or combined adsorption of phenolics with metal (Cu, Pb, Zn, Cd etc.) pollutants and other contaminants (fluorides ions) available in domestic water, to provide solution to wastewater treatment.
- ii. Further studies to use aminated cornstarch in adsorption using column operations apart from batch operations. Since most studies are conducted using batch operations and less recorded adsorption studies using column experiments.
- iii. Surface morphology of aminated cornstarch should be carried out.



## REFERENCES

- Abu Auwal, Md., Jewel Hossen and Md. Rakib-uz-Zaman, (2018). Removal of Phenol from Aqueous Solution Using Tamarind Seed Powder as Adsorbent, *IOSR Journal of Environmental Science, Toxicology and Food Technology*, Vol. 12, (3) Ver.I. Pp 41-48. ISSN: 2319-2399. <https://www.iosrjournals.org>.
- Azizi, A.; Abouseoud, M. and Amrane A. (2017). Phenol removal by a sequential combined fenton-enzymatic process, *Nature Environment and Pollution Technology Journal*, 16(1), 321–330
- Antonio, T. and Cosimino, M. (2020). Removal of Phenolic Compounds from Olive Mill Wastewater by a Polydimethylsiloxane/oxMWCNTs Porous Nanocomposite, *Water* 2020, 12, 3471; doi:10.3390/w12123471: <http://www.mdpi.com/journal/water>
- APHA., Eaton, A.D.; Mary, A. and Franson, H. (2017). Standard Methods for the Examination of Water and Wastewater, 23<sup>rd</sup> Edition, American Public Health Association, American Water Works Association, Water Environment Federation. Washington DC 20001-3710. ISSN 55-1979.
- Bailey, S.E.; Olin, T.J.; Bricka, R.M. and Adrian, D.D. (1999). A review of potentially low-cost sorbents for heavy metals, *Water Resources Journal*, 33:2469–2479.
- Barrera, A. (2020). Synthesis of Nanotemplated, Glucose-derived Adsorbents for the Removal of Organic and Inorganic Pollutants from Water. Open Access Theses & Dissertations. 3082. University of Texas at El Paso. [https://scholarworks.utep.edu/open\\_etd/3082](https://scholarworks.utep.edu/open_etd/3082).
- Bentaleb, K.; Bouberka, Z.; Chinoune, K.; Nadim, A. and Maschke, U. (2017) Enhanced adsorption of 2,4-dichlorophenol from aqueous solution using modified low-cost Algerian geomat. *J. Taiwan Inst. Chem. Eng.*, 80, 578–588.
- Bhatnagar, A.; Sillanpää, M. and Witek-Krowiak, A. (2015). Agricultural waste peels as versatile biomass for water purification – A review. *Chemical Engineering Journal*, 270: Pp 244-271.
- Biglari, H.; Afsharnia, M.; Javan, N. and Sajadi, SA. (2016). Phenol Removal from Aqueous Solutions by Adsorption on Activated Carbon of Miswak's Root Treated with KMnO<sub>4</sub>. *Iranian Journal of Health Sciences*; 4(1):20-30. <http://jhs.mazums.ac.ir>.
- Bożena Bukowska and Sylwia Kowalska (2003). The Presence and Toxicity of Phenol derivatives-their effect on human erythrocytes, *Current Topics in Biophysics* 2003, 27(1-2), 43-51
- Chiong, T.; Lau, SY.; Khor, EH. and Danquah MK., (2014). Enzymatic approach to phenol removal from wastewater using peroxidases, *Critical review. OA Biotechnology*, 10; 3(1):9.
- Diana Soto, José U.; Kelly P.; Orietta L.; Alexandra M. and Marta F. (2014). Heavy metals (Cd<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup> and Ni<sup>2+</sup>) adsorption in aqueous solutions by oxidized starches. *Polymers for Advanced Technologies*, Vol. 26 (2)
- Droste, R. L. (1997). Theory and practice of water and wastewater treatment. New York: Wiley & Sons. (Book).
- Edet, U. A. and Ifelebuegu, A. O. (2020). Kinetics, Isotherms and Thermodynamic Modeling of the Adsorption of Phosphates from Model Wastewater Using Recycled Brick Waste. *Processes*, 8, 665; doi:10.3390/pr8060665.
- El-Ashtoukhy, E-S.Z.; El-Taweel Y.A.; Abdelwahab, O. and Nassef, E.M. (2013). Treatment of Petrochemical Wastewater Containing Phenolic Compounds by Electrocoagulation

- Using a Fixed Bed Electrochemical Reactor, *International Journal of Electrochemical Science*, 8, 1534 – 1550.
- Haq F.; H. Yu.; L. Wang.; L. Teng.; M. Haroon.; R.U. Khan.; S. Mehmood.; Bilal-Ul-Amin.; R.S. Ullah.; A. Khan and A. Nazir. (2019). Advances in chemical modifications of starches and their applications, *Carbohydrate Research*, doi: <https://doi.org/10.1016/j.carres.2019.02.007>.
- Ho, Y. S. and McKay G. (1999). Pseudo-second order model for sorption processes. *Process Biochem.* 34, 451–465; doi:10.1016/S0043-1354(99) 00232-8
- Feng, N. and Guo, X. (2012). Characteristics of adsorptive capacity and mechanisms on adsorption of copper, lead and zinc by treated orange peels. *Transactions of Nonferrous Metals Society of China*, 22: 1224-1231.
- Ferreira, R; Sousa, F. W. De, Oliveira, V; Neto, S; Basilio, P; and Fachine, A. (2012). Biomass adsorbent for Removal of Toxic Metal Ions from Electroplating Industry Wastewater. Posted in <http://www.interchopen.com>, Pp. 678-689
- Franck, D.; Grégorio, C.; Joël, V.; Michael, K.; Gilles, S. and Emmanuel, C. (2003). Starch-modified Filters used for the Removal of Dyes from Waste Water, *Macromol. Symp.* 203,165-171. DOI: [10.1002/masy.200351315](https://doi.org/10.1002/masy.200351315).
- Fuller, R.; Rahona, E.; Fisher, S.; Caravanos, J.; Webb, D.; Kass, D. and Matte, T. (2018). Pollution and non – communicable diseases: time to end the neglect. United Nations Development Programme, Pure Earth, New York, USA. Vol.2.
- Girish C. R. and Murty V. R. (2014). Adsorption of Phenol from Aqueous Solution Using *Lantana camara*, Forest Waste: Kinetics, Isotherm, and Thermodynamic Studies, *International Scholarly Research Notices*, Volume, Article ID 201626. <http://dx.doi.org/10.1155/2014/201626>.
- Grangier, C; Qadir, M. and Singh, M., (2012). Health Implications for Children in Wastewater-Irrigated Peri-urban Aleppo, Syria. *Water Quality, Exposure and Health* 4(4):187-195. Springer. <http://link.springer.com/article/10.1007/s12403-012-0078-7>
- Griffiths, P. and Hasseth, J. A. (2007). *Fourier Transform Infrared Spectrometry*, 2nd Ed. Wiley-Blackwell. ISBN 0-471-19404-2
- Gude, V. (2017). Desalination and water reuse to address global water scarcity. *Reviews in Environmental Science and Biotechnology*, 16: 591-609.
- Guppy, L. and Anderson, K. (2017). *Water Crisis Report*. United Nations University Institute for water, Environment and Health, Hamilton, Canada. <http://inweh.unu.edu>. ISBN:978-92-808-6083-2
- Haskem, A.; Abdel-Halim, E.S.; El-Tahlawy, K.F.; Hebeish, A. (2005). Enhancement of the adsorption of Co (II) and Ni (II) ions onto peanut hulls through esterification using citric acid, *Adsorption Science Technology*, 23: 367-380.
- Hossain, M. A; Ngo, H. H; Guo, W. S. and Nguyen, T. V. (2012). Biosorption of Cu (II) from water by banana peels based biosorbent experiments and models of adsorption and desorption. *Journal of Water Sustainability*, 2(1): 87-104.
- Hossain, M.A; Hao N; Guo, H. W.S. and Nguyen, T.V. (2012). Removal of Copper from water by Adsorption onto Banana Peels as Bioadsorbent, *International Journal of Geomaterial*, 2: 227-234.
- Ibrahim, R.K.; Fiyadh, S.S.; Al Saadi, M.A.; Al Omar, M.K.; Hin, L.S.; Mohd, N.S.; Ibrahim, S.; Afan, H.A; Fai, C.M.; Ahmed, A.N. and Elshafie, A. (2020). Feedforward Artificial Neural Network-Based Model for Predicting the Removal of Phenolic Compounds from Water by Using Deep Eutectic Solvent-Functionalized CNTs. *Molecules*, 25, 1511; doi:10.3390/molecules25071511.
- ICA. (2012). *Global water security*. IC-coordinated paper. Intelligence Community Assessment, Washington, DC, Pp. 1125

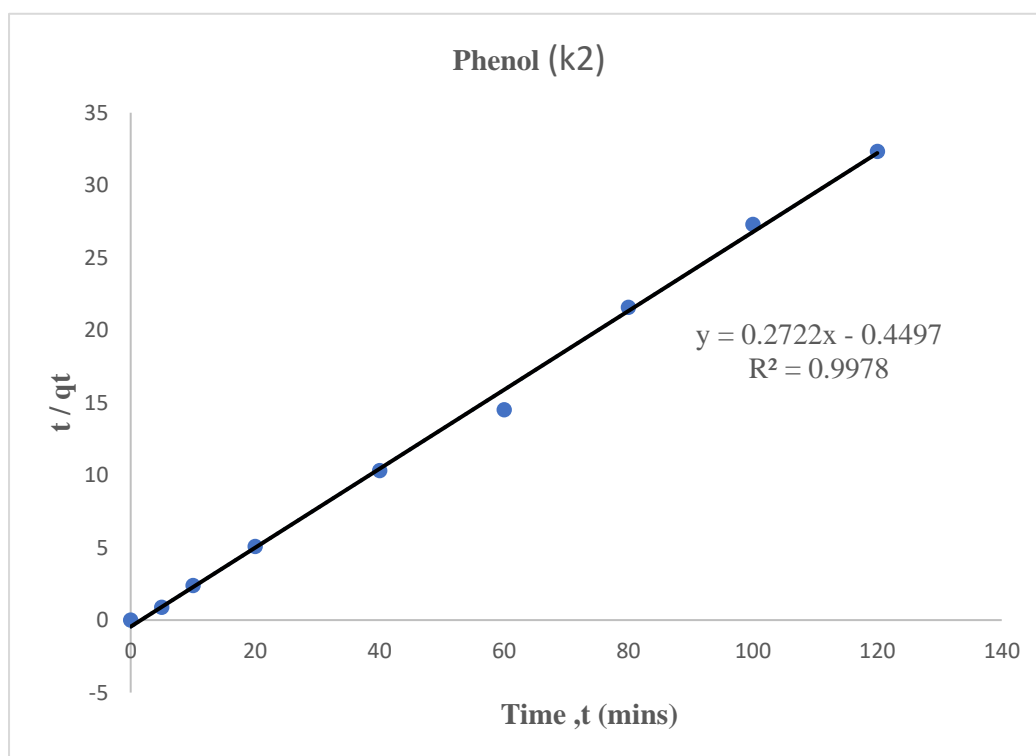
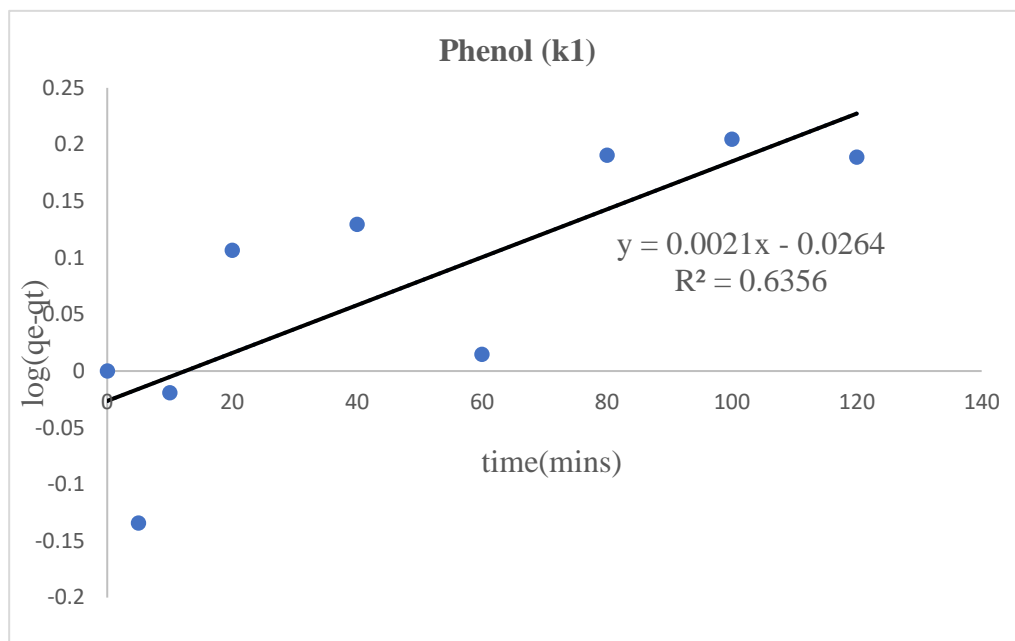
- Jabeen, A.; Huang, X.S. and Aamir, M. (2015). The Challenges of Water Pollution, Threat to Public Health, Flaws of Water Laws and Policies in Pakistan, *Journal of Water Resource and Protection*, 7, 1516-1526.  
<http://dx.doi.org/10.4236/jwarp.2015.717125>
- John, C. (2000). Interpretation of infrared spectra, a practical approach. Encyclopaedia of analytical chemistry. Chichester, John Wiley and Sons Ltd. pp 10815–10837.
- Joshua, N. H. and M, Nazrul I. (2015). Water Pollution and its Impact on the Human Health, *Journal of Environment and Human*, Vol. 2, ISSN: 2373-8332
- Kaur, B.; Ariffin, F.; Bhat, R. and Karim, A. A. (2012). Food Hydrocolloids, *Elsevier*, 26(2), 398–404. ISSN: 0268-005X.
- Kaman Singh, B. Chandra and M. Gautam (2016). Development of Inexpensive Adsorbent from Agro-Waste for Phenol Adsorption. *Journal of Scientific & Industrial Research, ResearchGate*, 75; 444-451.
- Kelland, Kate (2017). "Study links pollution to millions of deaths worldwide". Reuters.
- Kjällstrand J. and Petersson G. (2001). Phenolic antioxidants in alder smoke during industrial meat curing. *Food Chemistry Journal*, 74, 85-89.
- Köhler, S. J.; P. Cubillas, J. D.; Rodriguez-Blanco.; C. Bauer, and M. Prieto (2007) "Removal of cadmium from wastewaters by aragonite shells and the influence of other divalent cations," *Environmental Science & Technology*, vol. 41, no. 1, pp. 112–118.
- Kulkarni S. J.; R. W. Tapre; S. V Patil and M. B. Sawarkar, (2013). Adsorption of Phenol from Wastewater in Fluidized Bed Using Coconut Shell Activated Carbon, *Procedia Engineering*, 51, Pp 300–307
- Kumar, R; Mudhoo, A; Lofrano, G. and Chandra, M. (2014). Adsorbent modification and activation methods and adsorbent regeneration: Biomass-derived biosorbents for metal ions sequestration, *Journal of Environmental Chemical Engineering*, 2:239-259.
- Landrigan, P. J.; Fuller, R.; Acosta, N. J. R.; Adeyi, O.; Arnold, R.; Basu, N. N.; Baldé, A. B.; Bertollini, R.; Bose-O'Reilly, S.; Boufford, J. I.; Breysse, P. N.; Chiles, T.; Mahidol, C.; Coll-Seck, A. M.; Cropper, M. L.; Fobil, J.; Fuster, V.; Greenstone, M.; Haines, A. and Zhong, M. (2018). The Lancet Commission on pollution and health. *The Lancet*, 391(10119),462-512.Elsevier Science. ISSN 0140-6736.  
[https://doi.org/10.1016/S0140-6736\(17\)32345-512](https://doi.org/10.1016/S0140-6736(17)32345-512).
- Laura Senft; Jamonica L. Moore; Alicja Franke; Katherine R. Fisher; Andreas Scheitler; Achim Zahl; Ralph Puchta; Dominik Fehn; Sidney Ison; Safaa Sader; Ivana Ivanović-Burmazović and Christian R. Goldsmith. (2021). Quinol-containing ligands enable high superoxide dismutase activity by modulating coordination number, charge, oxidation states and stability of manganese complexes throughout redox cycling. *Chemical Science*, -. doi:10.1039/d1sc02465e
- Lagergreg, S. (1898). The theory of so-called adsorption of soluble substances. *Handlingar* 24 (4): 1-39.
- Liouna A. A.; Theophile K.; Rufis F. T. T.; Cyrille D. A.; Idris-Hermann T. K. and Solomon Gabche A. (2022). Optimized Removal of Hydroquinone and Resorcinol by Activated Carbon Based on Shea Residue (*Vitellaria paradoxa*): Thermodynamics, Adsorption Mechanism, Nonlinear Kinetics, and Isotherms, *Hindawi Journal of Chemistry*, Volume, Research Article ID 1125877,  
<https://doi.org/10.1155/2022/1125877>.
- Marrot, B.; Barrios-Martinez, A.; Moulin, P. and Roche, N. (2006). Biodegradation of high phenol concentration by activated sludge in an immersed membrane bioreactor, *Biochemical Engineering Journal*, 30(2): Pp. 174-183.

- Mbugua W. G. (2020). Facile remediation of fluoride in aquatic media using modified polyethylene container, (Doctoral dissertation, Kenyatta University, Kenya).
- Miretzky, P; Saralegui, A. and Cirelli, A. F. (2006). Simultaneous heavy metal removal mechanism by dead macrophytes. *Journal of Chemosphere*, 62: 247-254
- Muhammad Haroon; Li Wang; Haojie Yu; Nasir M. Abbasi; Zain-ul-Abdin; Muhammad Saleem; Rizwan Ullah Khan; Raja Summe Ullah; Qing Chen and Jialiang Wu (2016). Chemical modification of starch and its application as an adsorbent material, *RSC Adv.*, 2016, 6, 78264, DOI: 10.1039/c6ra16795k.
- Mulei, S. K. (2012). Water Quality Degradation Trends in Kenya over the Last Decade, *Water Quality Monitoring and Assessment*, Dr. Voudouris (Ed.), ISBN: 978-953-51-0486-5
- Mwangi, C.K.; Mwangi, I.W.; Wanjau, R.N.; Swaleh, S.; Ram, M. and Ngila, J.C. (2016). Remediation of Fluoride Laden water by Complexation with trimethylamine modified Maize Tassels, *Environment and Natural Resources Research*, 6(1): 44. ISSN 1927-0488.
- Mwangi, I.W.; Ngila, J.C.; Ndungu, P. and Msagati, T.A. (2014). Removal of phenolics from aqueous media using quaternized maize tassels. *Journal of Environmental Management*, 134, Pp. 70-79. <http://dx.doi.org/10.1016/j.jenvman.2013.12.031>
- Nawal N.; Ebrahim M. and Sami E., (2013). Removal of Heavy Metals Fe<sup>3+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> from Wastewater by Using Rice Straw as Low-Cost Adsorbent. *Academic Journal of Interdisciplinary Studies*, 6: Pp 85.
- Nayak, A.; Bhushan, B. and Gupta, V., (2020). Removal of Phenolics from Wastewater by Fe<sub>2</sub>O<sub>3</sub> Impregnated Sawdust as Adsorbent: Adsorption Isotherm and Kinetic Studies. *Journal of Graphic Era University*, Vol. 8, Issue 1, Pp 1-15.
- Nuhu, D. M.; Nabeel, J.; Mukarram, Z. and Omar, A., (2017). Removal of Phenolic Compounds from Water Using Sewage Sludge-Based Activated Carbon Adsorption: A Review. *International Journal of Environmental Research and Public Health* 2017, 14, 1094; doi:10.3390/ijerph14101094. [www.mdpi.com/journal/ijerph](http://www.mdpi.com/journal/ijerph).
- Nthiga, E. W. (2016). *Efficacy and kinetics of adsorption of single and multiple heavy metal cations from aqueous solutions by fruit waste products* (Doctoral dissertation, Kenyatta University)
- Oki, T. and Kanae, S. (2006). Global hydrological cycles and world water resources, *Science*, 313(5790): 1068-1072.
- Roostaei, N. and F.H., Tezel. (2004). Removal of phenol from aqueous solutions by adsorption, *Journal of Environmental Management*, 70(2): 157-164
- Róžański L. (1998). Przemiany pestycydów w organizmach żywych i środowisku. *Agra-Enviro. Lab.*, Poznań.
- Saha Das P.; Jaya Srivastava and Shamik, Chowdhury. (2013). Removal of phenol from aqueous solution by adsorption onto seashells: equilibrium, kinetic and thermodynamic studies, *Journal of Water Reuse and Desalination*, National Institute of Technology-Durgapur, India (WB) 713209.
- Samantha, M. (2011). Water crisis in Kenya: causes, effects and solutions. *Journal of Global Majority*, 2(1): 31-45.
- Sarker, Nandita and Fakhruddin, A. N. M. (2017). Removal of phenol from aqueous solution using rice straw as adsorbent, *Appl. Water Sci.* 7:1459–1465. DOI 10.1007/s13201-015-0324-9.
- Skoog, D.; Holler, F. and Crouch, S. (2007). *Fundamental analytical chemistry: Principles of instrumental analysis*, 6<sup>th</sup> edition. United States, Thomson, Brooks/Cole. Pp 169–173, 454-455, 672-673. ISBN 9780495012016.

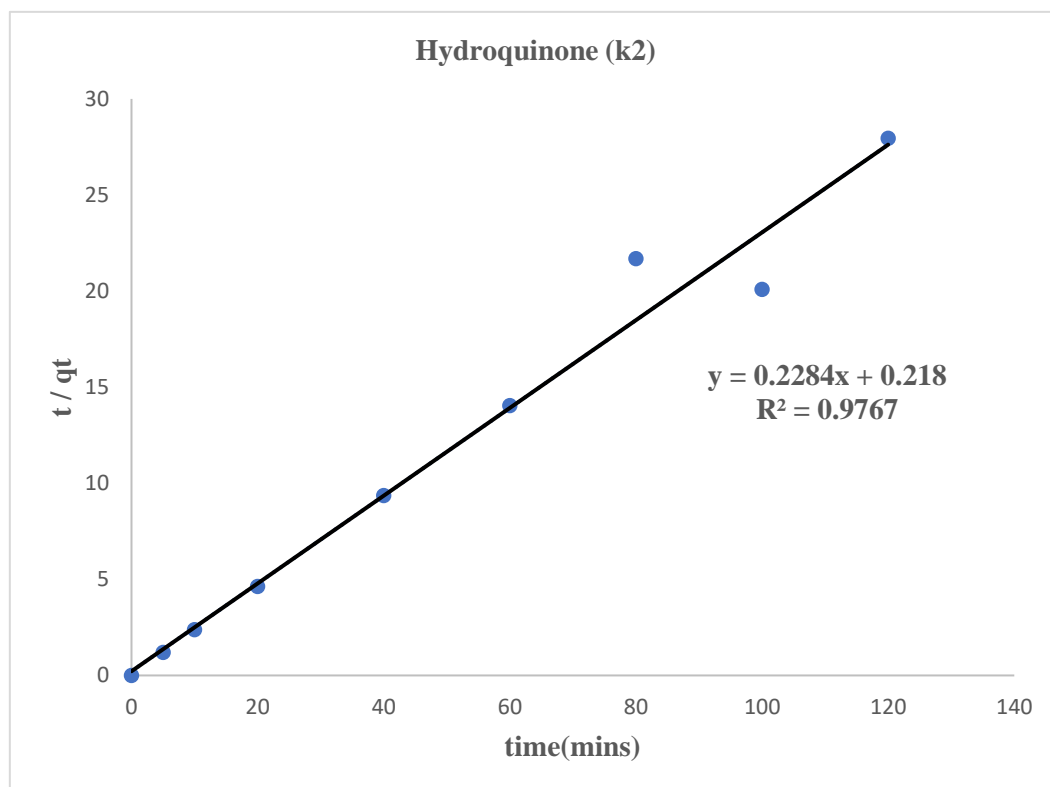
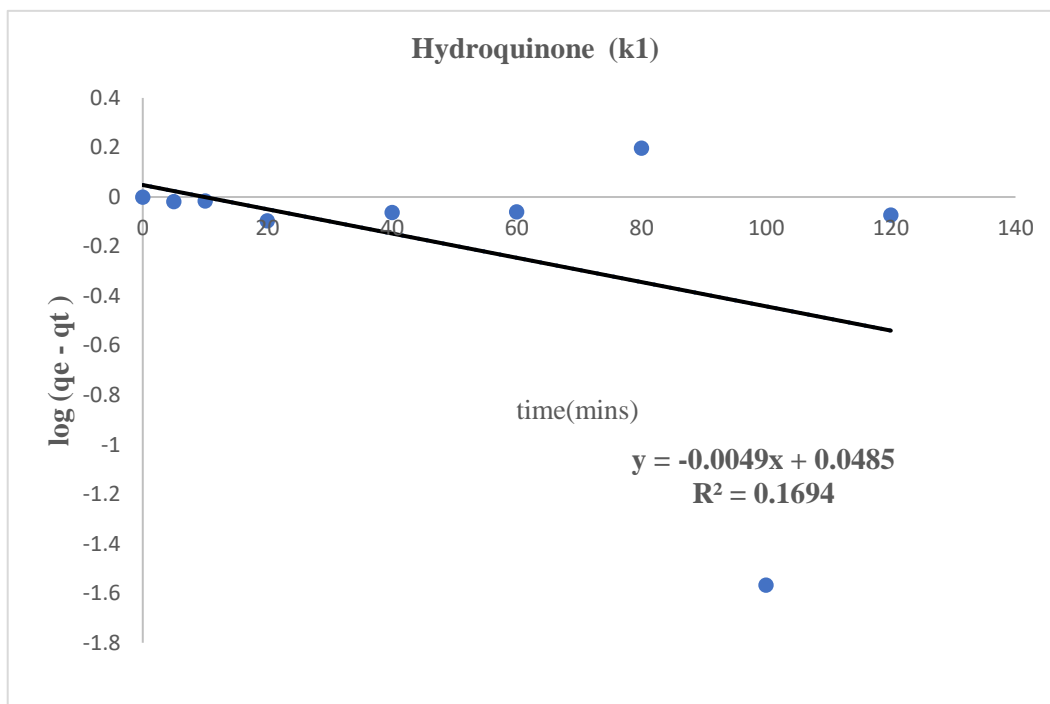
- Suresh, S.; Srivastava, V. C. and Mishra, I. M. (2012). Adsorption of catechol, resorcinol, hydroquinone, and their derivatives: a review. *International Journal of Energy and Environmental Engineering* 2012 3:32; doi:10.1186/2251-6832-3-32
- Mukherjee, S.; S., Kumar; A.K. Misra and Maohong F. (2007). Removal of phenols from water environment by activated carbon, bagasse ash and wood charcoal. *Chemical Engineering Journal* 129, Pp133–142.
- Sud Dhiraj.; Mahajan, G. and Kaur, M.P. (2008). Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions-a review, *Journal of Bioresource Technology*, 99:6017....6027
- Swarts, M.; Verhagen, F. J.; Field, J. A. and Wijnberg, J. B. (1998). Trichlorinated phenols from *Hypholoma elongatum*. *Phytochem.* 49, 203-206.
- Tan, I.A.W.; A.L. Ahmad, and B.H. Hameed, (2009). Fixed-bed adsorption performance of oil palm shell-based activated carbon for removal of 2,4,6-trichlorophenol. *Bioresource Technology*, 100(3): 1494-1496.
- Tsutsui T.; Mayashi N.; Maizumi H.; Huff J. and Barrett J.C. (1997). Benzene-, catechol-, hydroquinone- and phenol- induced cell transformation, gene mutation, chromosome aberrations, aneuploidy, sister chromatid exchanges and unscheduled DNA synthesis in *Syrian hamster embryo cells*. *Mut. Res.* 373, 113-123.
- UNICEF/WHO (2012). Joint monitoring programme for water supply and sanitation United States Environmental Protection Agency. [cited 2019 July 15]; <http://water.epa.gov/scitech/methods/cwa/pollutants.cfm>.
- US Environmental Protection Agency (UEPA) (2008). Supplement to 5<sup>th</sup> Edition of manual for Certification of Laboratories Analyzing Drinking water: EPA 815-F-08-006.Off. Water. Off. Ground water and Drinking water. Technical Support Center, Cincinnati, Ohio.
- US Environmental Protection Agency (UEPA) (1999). Alternative disinfectants and oxidants guidance manual, EPA Office of Water Report 815-R-99- 014
- Verhagen, F. J.; Swarts M.; Field, J. A. & Wijnberg J. B. (1998). Biotransformation of the major fungal metabolite 3,5-dichloro-p-anisyl alcohol under anaerobic conditions and its role in information of bis (3,5-dichloro-4-hydroxyphenyl) methane, *Appl. Environmental. Microbiol.*, 64, 3225-3231.
- West, Larry (March 26, 2006). "World Water Day: A Billion People Worldwide Lack Safe Drinking Water", *About.com*.
- William W. Anku; Messai A. Mamo and Penny P. Govender, (2017). Phenolic Compounds in Water: Sources, Reactivity, Toxicity and Treatment Methods. <http://dx.doi.org/10.5772/66927>
- (WHO) World Health Organization (1993). Guidelines for drinking water quality, World Health Organization [http://www.who.int/water\\_sanitation\\_health/dwq/gdwq2v1/en/](http://www.who.int/water_sanitation_health/dwq/gdwq2v1/en/).
- (WHO) World Health Organization (1996). Guidelines for drinking water quality, World Health Organization. Geneva. [http://www.who.int/water\\_sanitation.../](http://www.who.int/water_sanitation.../).
- (WHO) World Health Organization (2019). WHO, African. Water management.
- (WWAP) World Water Assessment Programme, (2017). The United Nations World Water Development Report 2017: Wastewater the Untapped Resource. United Nations Educational, Scientific and Cultural Organization (UNESCO), Paris. <http://unesdoc.unesco.org/images/0024/002471/247153e.pdf>
- Zhang, D.; Yan, D.; Lu, F.; Wang, Y. and Feng, J., (2015). Copula-based risk assessment of drought in Yunnan province, *China Natural Hazards*, 75:2199–2220. <http://link.springer.com/article/10.1007/s11069-014-1419-6>.

## APPENDICES

**Appendix I: Phenol Pseudo - First order (k1) and Pseudo – Second order (k2)  
for ACS**

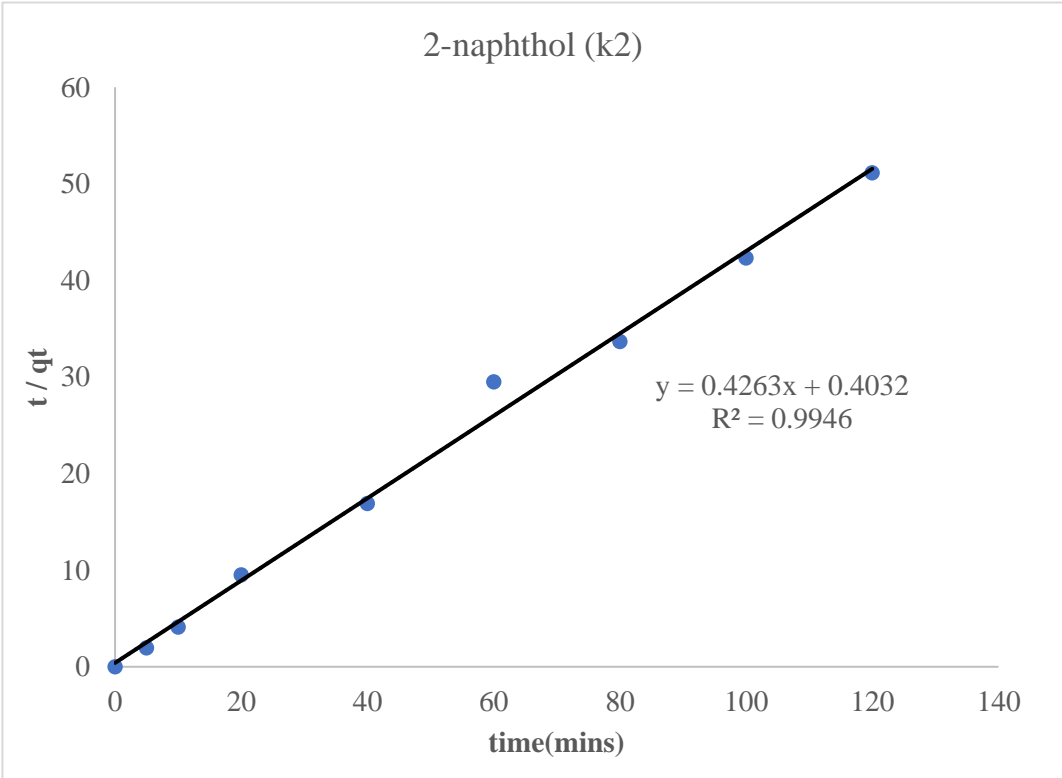
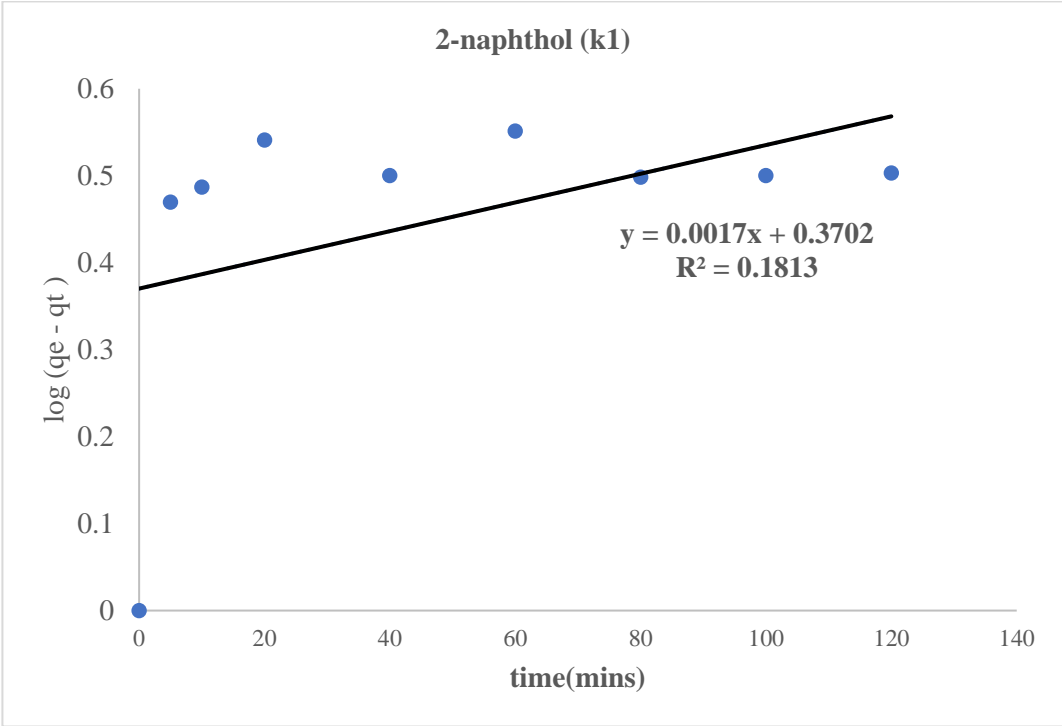


**Appendix II: Hydroquinone Pseudo - First order (k1) and Pseudo – Second order (k2) for ACS**

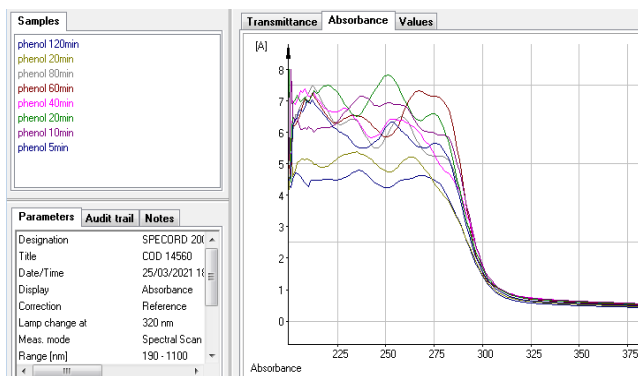
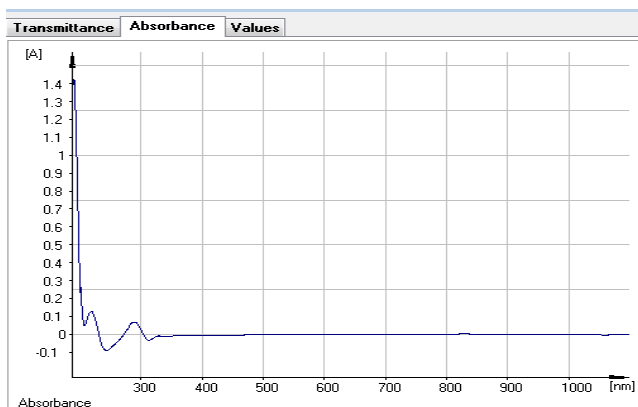
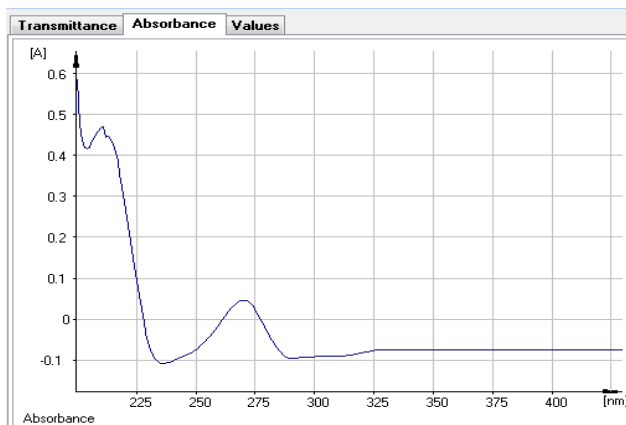
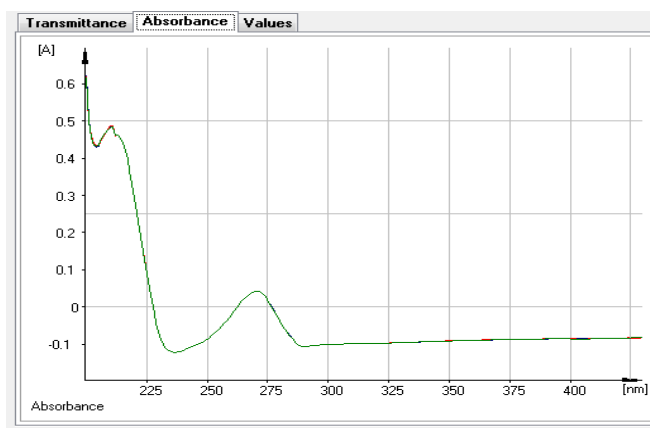




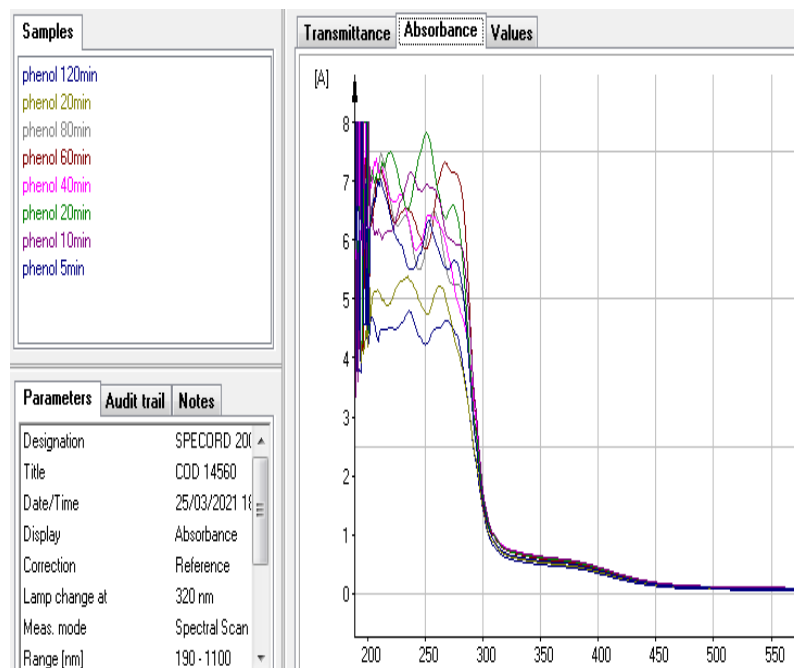
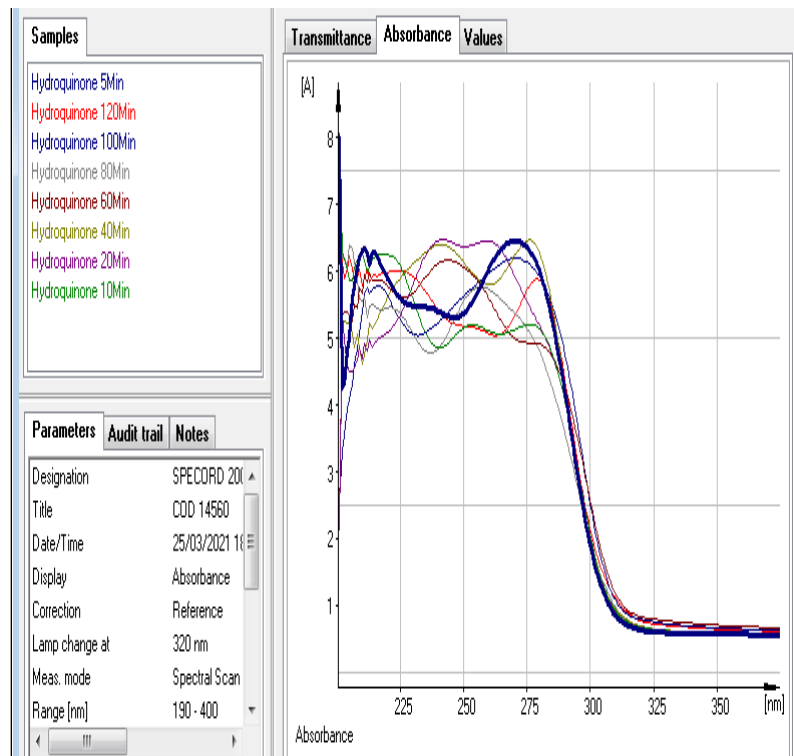
**Appendix III: 2-Naphthol Pseudo - First order (k1) and Pseudo – Second order (k2) for ACS**



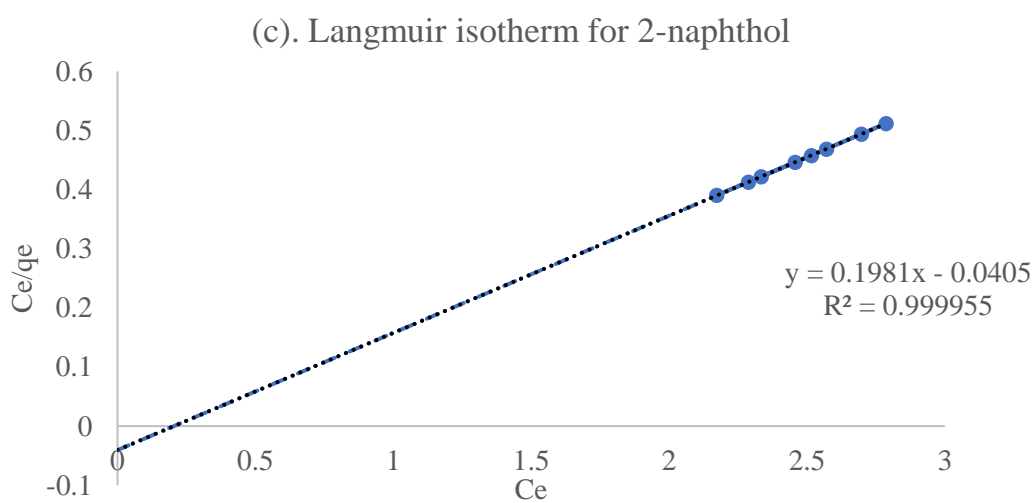
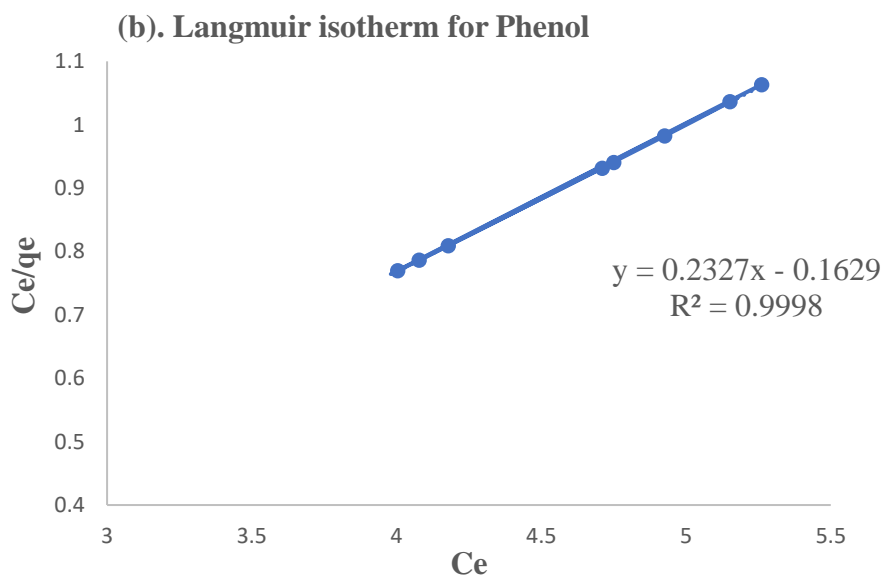
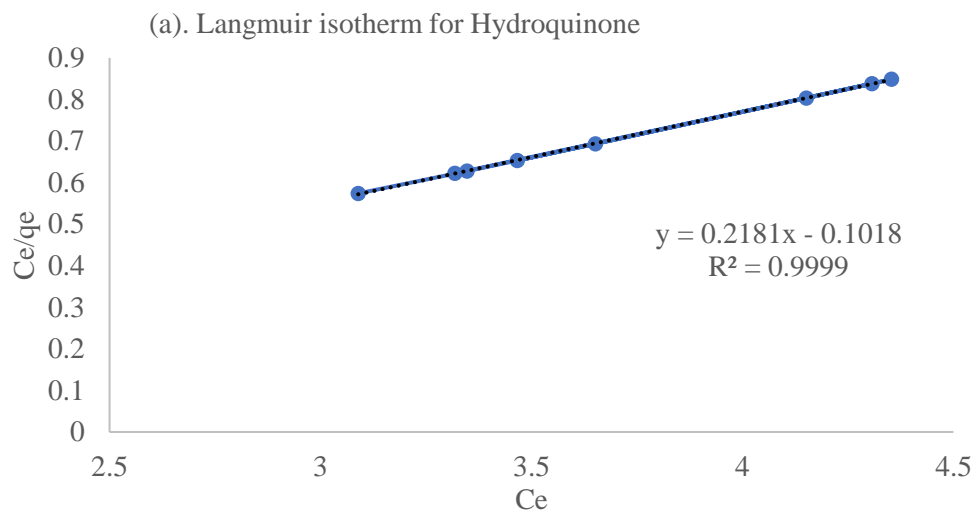
## Appendix IV: UV-Vis Spectra for PCs



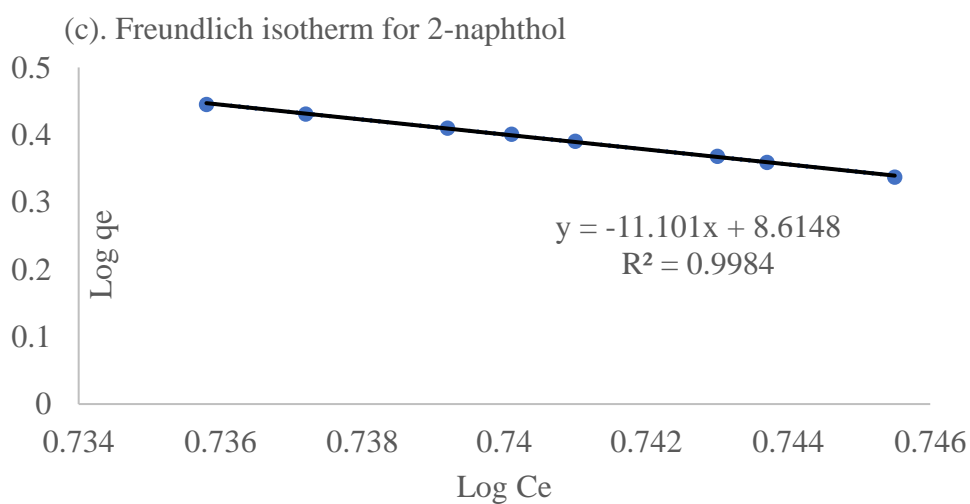
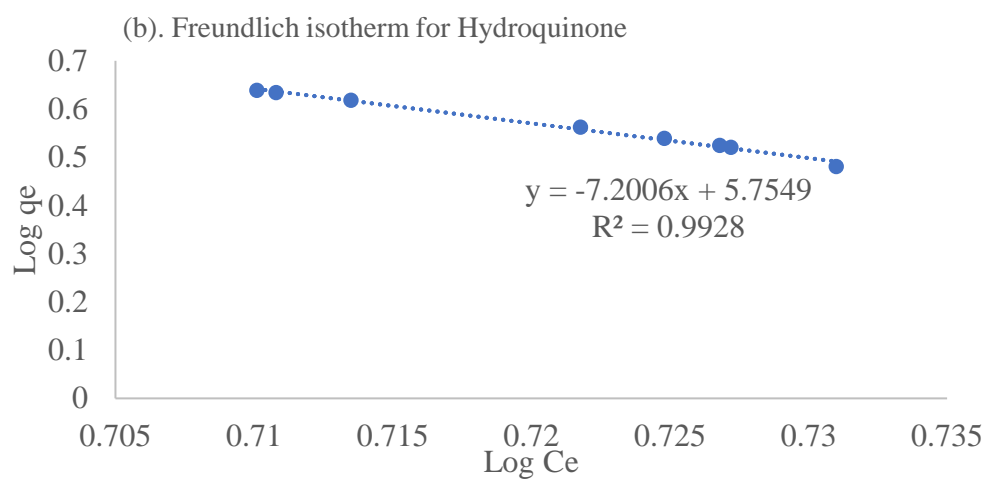
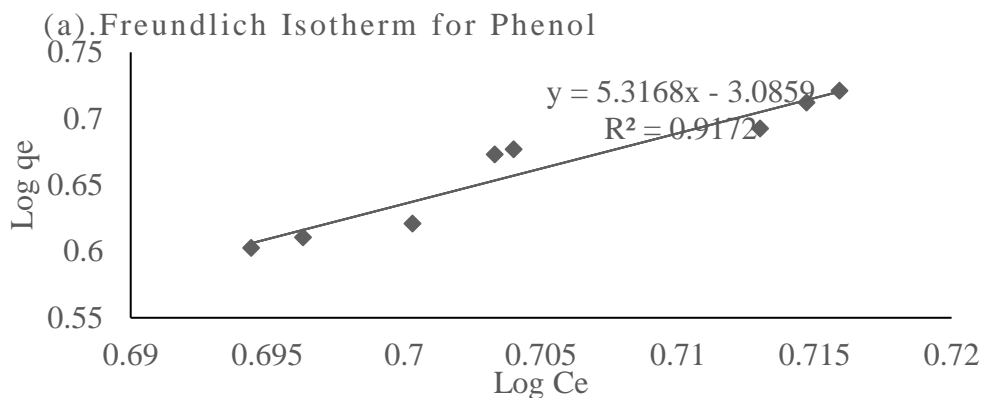
## Overlaid of contact time of phenol



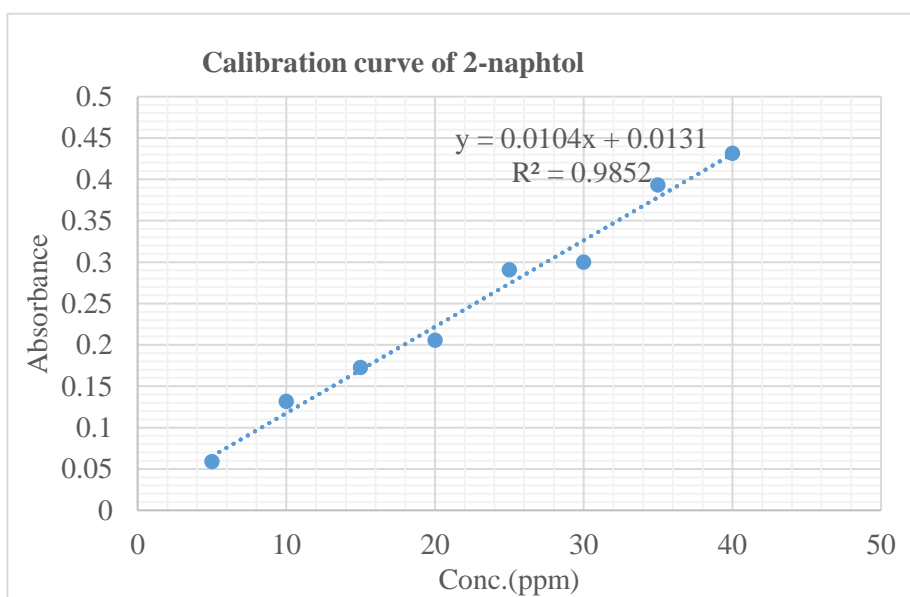
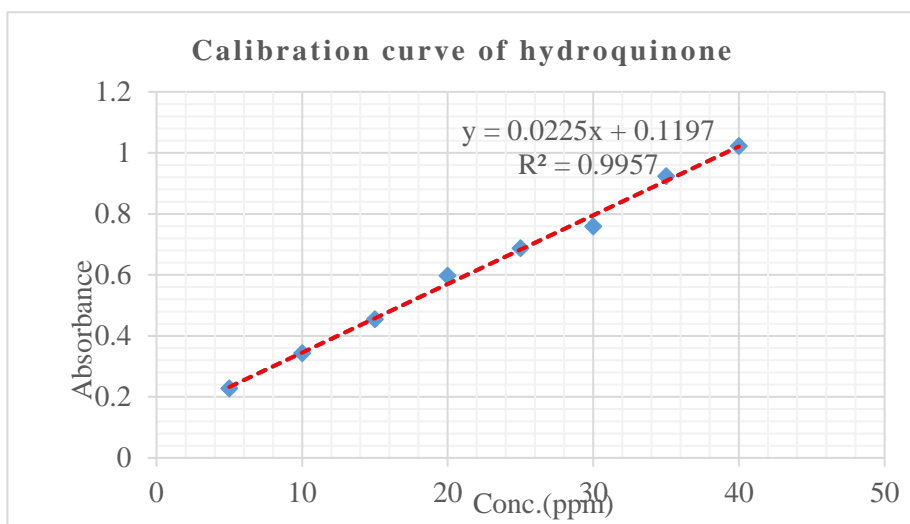
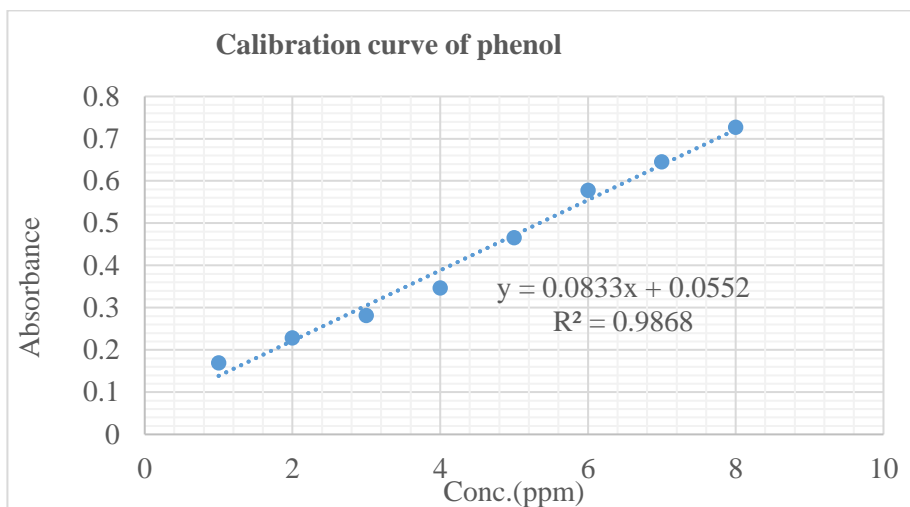
**Appendix V: Langmuir isotherm for hydroquinone (a), phenol (b) and 2-Naphthol (c)**



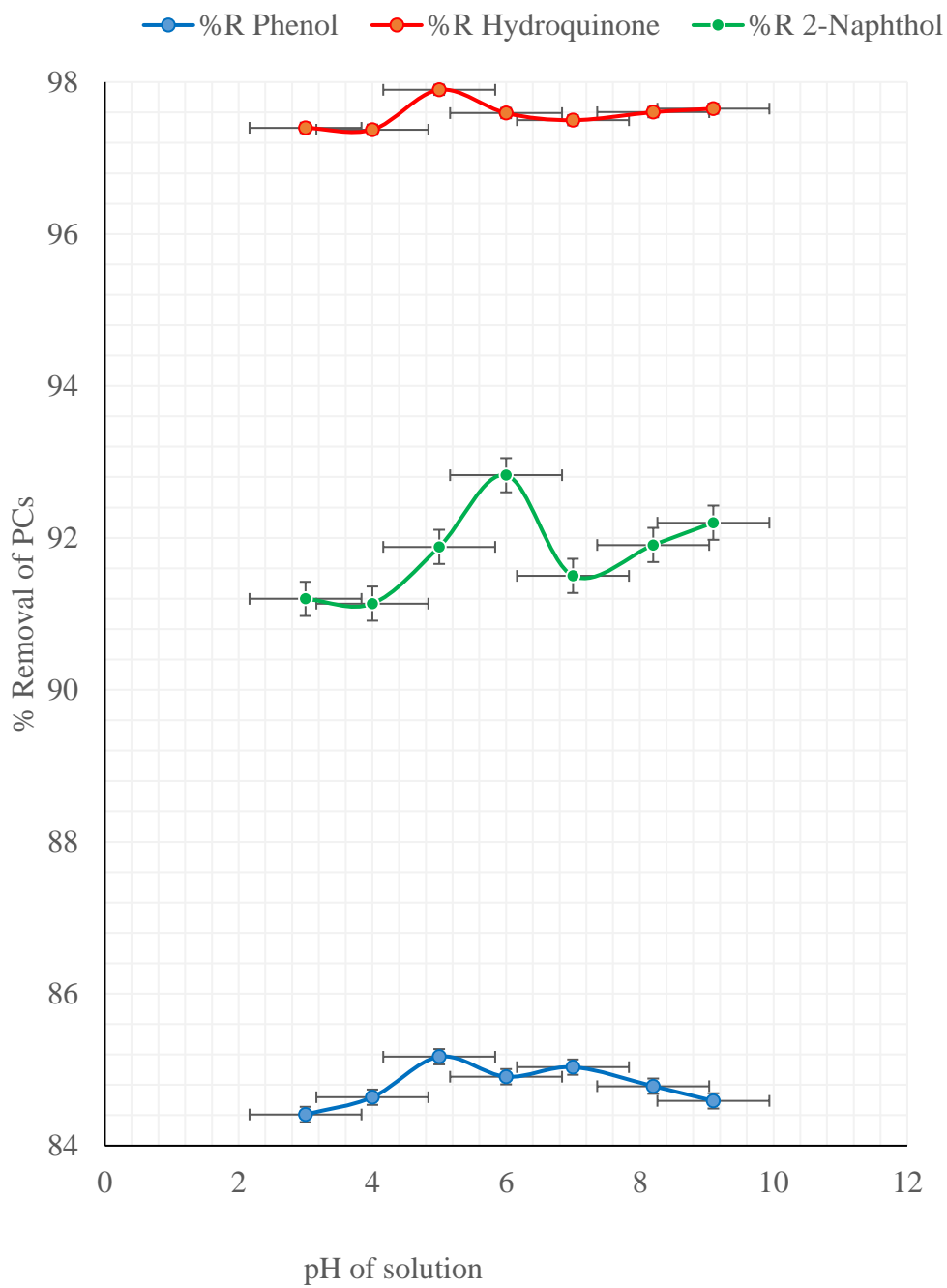
**Appendix VI: The Freundlich isotherms for phenol (a), hydroquinone(b) and 2-Naphthol (c)**



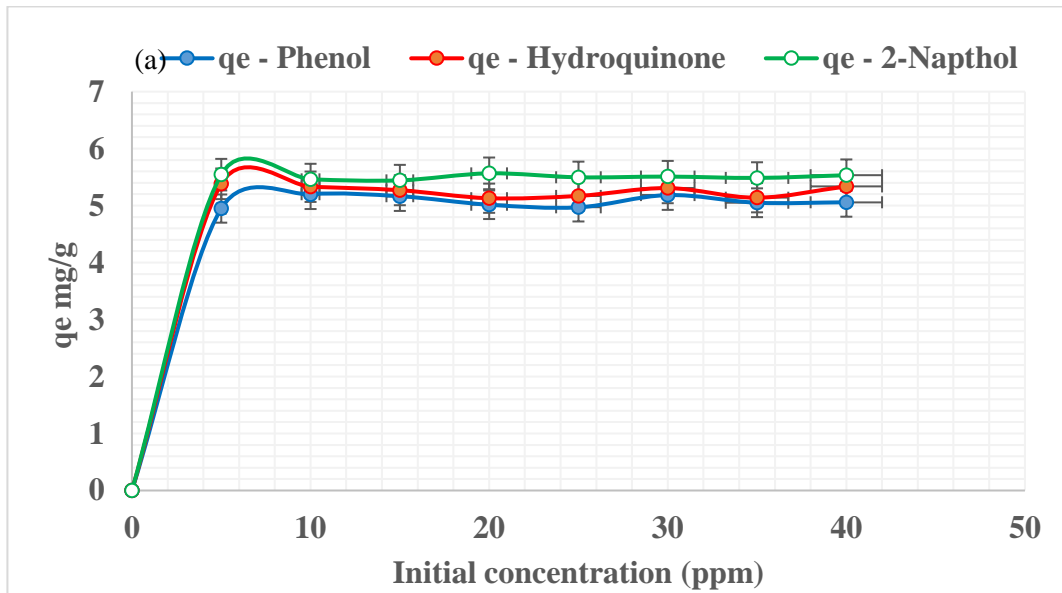
**Appendix VII: Calibration curve of phenol ( $\lambda_{\text{max}}=270 \text{ nm}$ ), hydroquinone ( $\lambda_{\text{max}}=290 \text{ nm}$ ) and 2-naphthol ( $\lambda_{\text{max}}=295 \text{ nm}$ )**



### Appendix VIII: Effect of pH on the adsorption of Phenol, Hydroquinone and 2-Naphthol.



**Appendix IX: Effect of initial Concentration on the removal of PCs from aqueous solutions.**





**Appendix X: Effect of adsorption parameters on removal of PCs from aqueous solutions**

<b>Effect of pH on adsorption of PCs</b>									
<b>pH values</b>	3	4	5	6	7	8	9		
<b>qe(Phenol)</b>	4.221±0.002	4.232	4.259	4.245	4.252	4.239	4.229		
<b>qe(Hydroquinone)</b>	5.844	5.842	5.874	5.856	5.850	5.856	5.859		
<b>qe(2-naphthol)</b>	5.472	5.468	5.513	5.570	5.490	5.514	5.532		
<b>Effect of contact time on adsorption of PCs</b>									
<b>Time (min)</b>	0	5	10	20	40	60	80	100	120
<b>qe(Phenol)</b>	0.000	4.878	5.160	5.213	5.225	5.172	5.259	5.267	5.258
<b>qe(Hydroquinone)</b>	0.000	5.160	5.161	5.134	5.144	5.145	5.262	5.005	5.141
<b>qe(2-naphthol)</b>	0.000	5.491	5.511	5.579	5.527	5.593	5.525	5.527	5.531
<b>Effect of initial concentration on adsorption of PCs</b>									
<b>Conc.(ppm)</b>	0	5	10	15	20	25	30	35	40
<b>qe - Phenol</b>	0.000	4.948	5.199	5.164	5.015	4.970	5.184	5.050	5.058
<b>qe - Hydroquinone</b>	0.000	5.382	5.331	5.270	5.129	5.170	5.307	5.139	5.336
<b>qe - 2-Naphthol</b>	0.000	5.542	5.460	5.443	5.565	5.497	5.509	5.486	5.533
<b>Effect of dosage of ACS on adsorption of PCs</b>									
<b>Mass(g)</b>	0.2	0.4	0.6	0.8	1	1.2			
<b>%R phenol</b>	87.37	88.44	89.10	91.21	91.81	92.90			
<b>%R Hydroquinone</b>	87.36	88.06	88.28	90.88	92.87	93.66			
<b>%R 2-naphthol</b>	85.51	85.88	86.20	87.45	88.27	90.15			

## Appendix XI: Research authorization (MUT)



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DIRECTORATE OF POSTGRADUATE STUDIES

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Ref: MUT/BPS/M/04

Date: 16<sup>th</sup> September 2020

Dear Mr. Bosuben K. Haron [SC401/5067/2017]

**RE: APPROVAL OF RESEARCH PROPOSAL AND SUPERVISORS**

I am pleased to inform you that the directorate of Postgraduate Studies on the 15<sup>th</sup> September 2020 considered and approved your MSc proposal entitled "**Removal of Phenolic compounds from aqueous solutions using tertiary amine modulated corn starch**" and appointed the following as supervisors:

1. Dr. Peter W. Njoroge [School of Pure Applied and Health Sciences]
2. Prof. Sylvia A. Opiyo [School of Pure Applied and Health Sciences]
3. Dr. Mwangi W. Isaac [Kenya University]

You may now proceed with your data collection subject to obtaining research permit from NACOSTI, if required. You should also begin consulting your supervisors and submit through them quarterly progress reports to the Director Postgraduate Studies through your COD and School Dean. Progress Reports can be accessed in the University Website.

It is the policy and regulations of the University that you observe deadlines. The Guidelines on Postgraduate supervision can be accessed in the post graduate Handbook.

Your responsibilities as a student will include, among others;

- I. Maintain regular consultation with your supervisor(s), at least once a month
- II. Submit quarterly reports on time, through your supervisors, COD, Dean and to the Director of Postgraduate studies;
- III. Ensure quality work all through;
- IV. Present your research findings at 2- 3 seminars/conferences prior to thesis examination.
- V. Publish one article from your research findings in a refereed journal prior to thesis examination

For any further clarification, please contact the undersigned.

Yours Sincerely,

**Dr. Andrew Makori**

**Ag Director, Directorate of Postgraduate Studies**

CC : Registrar- ASA

## **Appendix XII: Publication**

The following paper has been published from this thesis results:

Bosuben, H.; Njoroge, P W.; Opiyo, S A. and Mwangi, I W. (2022). Facile removal of phenol from aqueous solution using modulated cornstarch impregnated with triethanolamine as adsorbent: Sorption isotherms and Kinetics, *IOSR Journal of Applied Chemistry (IOSR-JAC)*, Volume 15, Issue 8 Ser. II, PP 34-45.