



# ELEMENTARY REMOVAL OF HYDROQUINONE AND 2-NAPHTHOL FROM AQUEOUS SOLUTIONS BY AMINATED CORNSTARCH WITH TRIETHANOL AMINE AS BIOADSORBENT: Isotherms and Kinetics studies

Haron Bosuben<sup>1</sup>, Peter W. Njoroge<sup>1</sup>, Sylvia A. Opiyo<sup>1</sup>

<sup>1</sup>(Department of Physical and Biological Sciences, Murang'a University of Technology, Nairobi, Kenya)

## ABSTRACT

**Background:** The sources of phenolics pollutants in water are mainly chemical industries and pharmaceutical. They are harmful and toxic even at modest concentrations. Despite substantial achievements for water treatment using adsorption, there is need to search for bio-adsorbent which is user-friendly, ecofriendly and efficient. **Materials and Methods:** Characterization of raw and modified cornstarch, was done using Fourier Transform Infrared (FT-IR) spectrophotometer. The modulated cornstarch was used in the removal batch experiment on model solutions. The efficiency of modified cornstarch in hydroquinone and 2-naphthol removal at different batch adsorption parameters at room temperature were investigated. 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 aminated corn-starch (ACS). **Results:** 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. Batch studies revealed that maximum removal of phenolic compounds (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 hydroquinone and 2-naphthol. 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 ( $k_2$ ). The maximum uptake of PCs occurred at initial concentration of 10 ppm and then plateaued. The batch experimental data obtained best fitted into the Langmuir isotherm, and monolayer adsorption capacities of 4.585 and 5.048 mg/g for hydroquinone and 2-naphthol respectively. **Conclusion:** According to this study, 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 hydroquinone and 2-naphthol from aqueous solutions.

**Index Terms:** Adsorption; Amination; Bioadsorbent; Modulation; Cornstarch; Hydroquinone; 2-naphthol.

## I. INTRODUCTION

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 [31]. Untreated and poorly treated wastewater or grey water is put in use for agricultural activities in a number of developing countries [15]. 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 [15]. 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 [27, 31]. Pollution of water is a serious worldwide challenge and is one of the leading global geneses of diseases and death [17]. 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 [13]. Water pollution caused the deaths of 1.8 million people in 2015 about 3.7 percent of disability-adjusted life years (DALYS) worldwide [21, 25]. Modern society is perplexed with water pollution and contamination in rural and urban areas.

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 [10, 34]. 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 [34].

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 [35]. 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 [47]. 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 [44].

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, sulphydryl groups, starch and lipids having a variety of functional groups [4,18, 44]. These constituents have high attraction for both organic and inorganic compounds in aqueous media to yield complexes and other organic moieties [44]. 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 [6, 26].

Starch is a polymeric biomolecule derived from plants which is affordable, available in large quantities and has numerous applications in various industries [32]. Bio adsorbents obtained from readily available starch are effective, efficient and have high sorption capacity for uptake of phenolic compounds from aqueous solution [12]. 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 [23, 32]. Therefore, this study focused on chemical modulation of starch using tertiary amine (triethanolamine) for adsorptive removal of phenolics from aqueous solution.

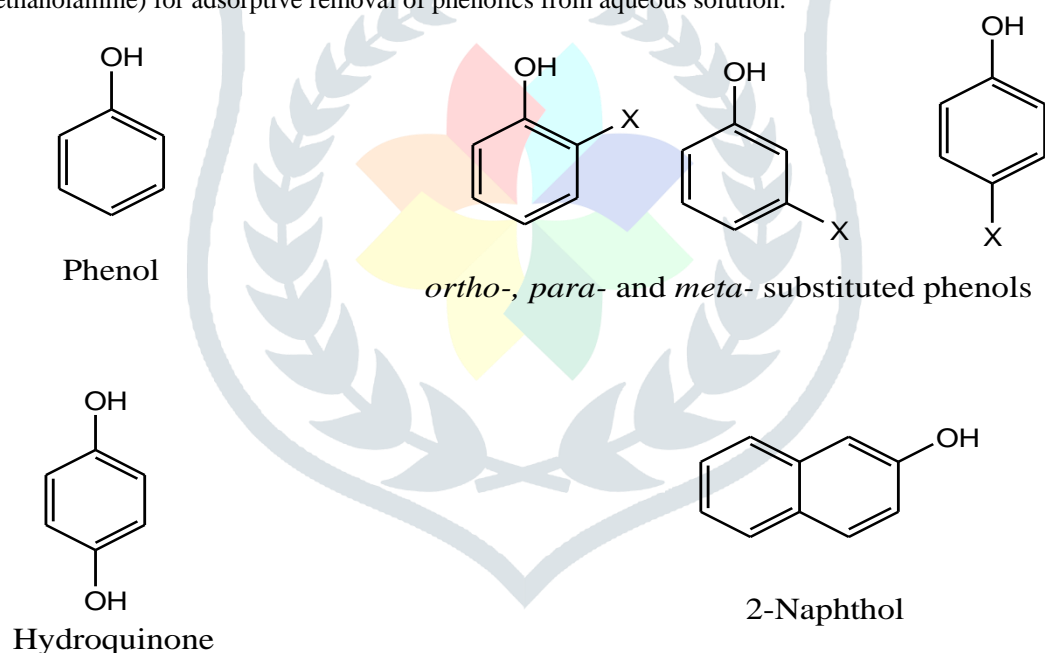
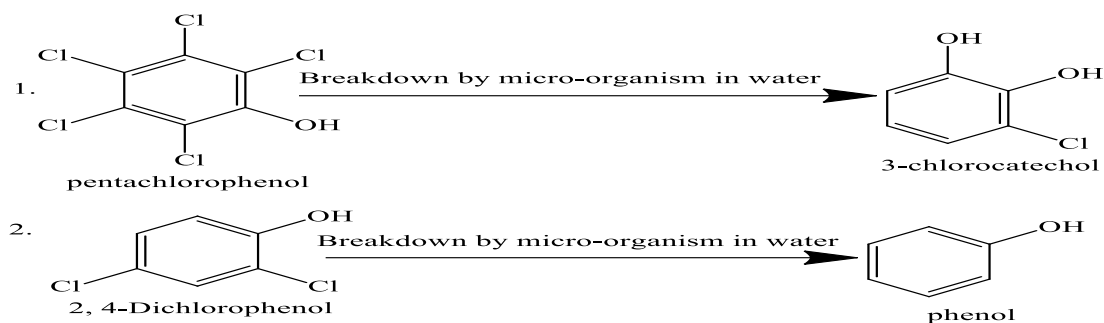
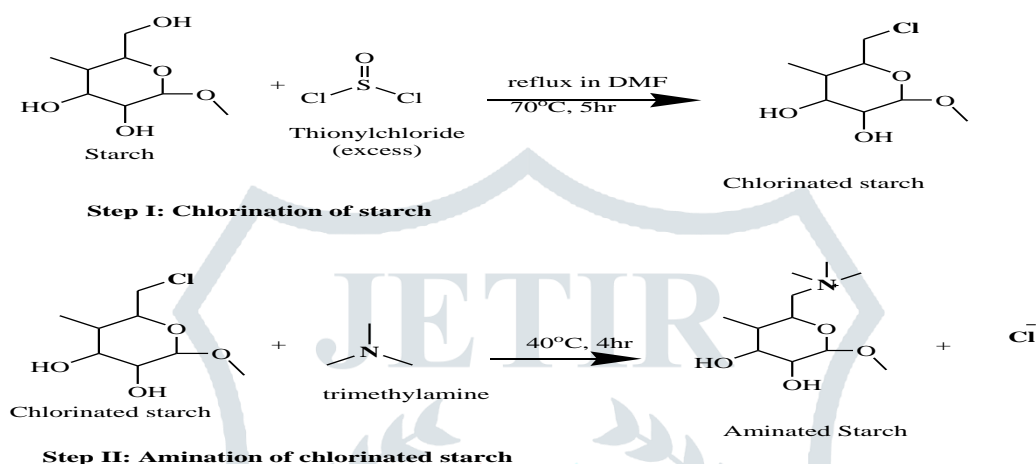


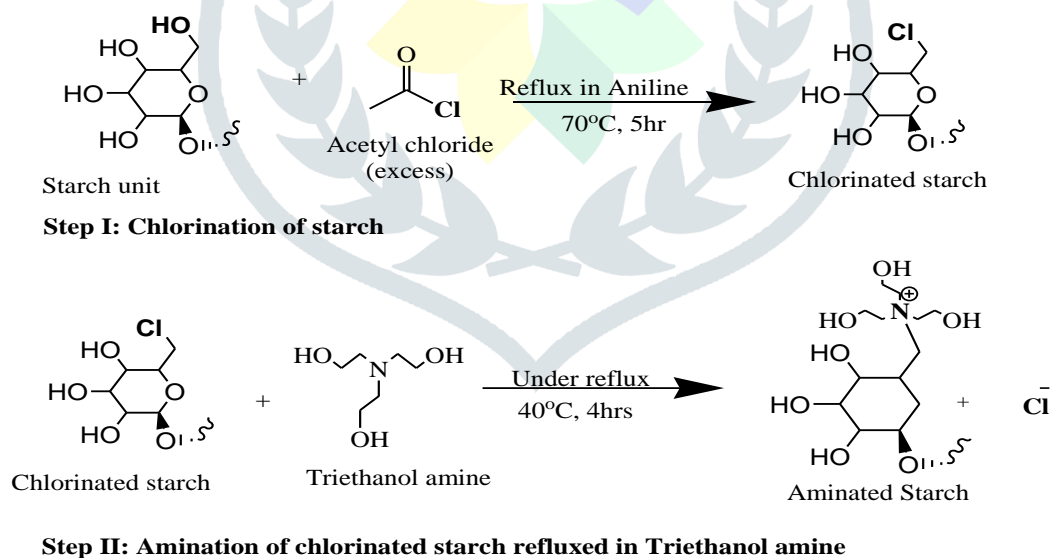
Figure 1: Structures of Simple Phenolics



Scheme 1. Breakdown of some phenolics by micro-organism in water [38], [45]; [32].



Scheme 2. The Chemical Modulation of Starch [33]



Scheme 3: The steps involved in Amination of dried cornstarch using triethanolamine [34].

## 1.1 Analytical Techniques

### 1.1.1 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 [41]. 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 [16].

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 [41]. 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 [16]. 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 cm<sup>-1</sup> to about 1250 cm<sup>-1</sup> is used in determination of functional groups [41]. 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 [31, 37].

### 1.1.2 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 [16].

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 and undergo electronic transitions [41]. 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 [41]. 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 [41]. 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. 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 [34], rice straws [40], tamarind seeds [1], sawdust [35].

## 1.2 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 [31]. 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 [31]. The two isotherms are discussed in the following sub-units.

### 1.2.1 Langmuir Model

The Langmuir model deals with adsorption at monolayer homogeneous on the adsorbent surface [19, 20, 36]. 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 [46]. As for solid–liquid interactions results, the Langmuir model is expressed in the linear equation as shown in **Equation 2.2**;

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

where, C<sub>e</sub> is the phenolics concentration remaining in the solution at equilibrium in mg/L, K<sub>L</sub> is the equilibrium constant (Langmuir constant), apparent energy of sorption, q<sub>e</sub> is the amount of phenolic adsorbed at equilibrium (mg/g) and q<sub>max</sub> is the complexation capacity. q<sub>max</sub> and K parameters are determined by plotting a graph of C<sub>e</sub>/q<sub>e</sub> against C<sub>e</sub>, and give a straight line of intercept 1/K<sub>L</sub>·q<sub>max</sub> and slope 1/q<sub>max</sub>. Langmuir model accounts for the adsorbent's surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium) [5].

### 1.2.2 Freundlich Model

The Freundlich model describes a multilayer nature of complexation which takes place on a heterogeneous system [19, 20, 36]. 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 [2, 36]. 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.

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

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

Where, q<sub>e</sub> is the maximum uptake amount of adsorption (mg/g), K<sub>f</sub> 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 [2]. If 1/n is tending to zero it shows that the system is homogeneous. n and K<sub>f</sub> are determined by plotting a graph of log q<sub>e</sub> versus log C<sub>e</sub>, where the slope is 1/n and the intercept is K<sub>f</sub> [19, 20, 36].

### 1.3 Kinetic Studies

Adsorption chemical kinetics explains how fast the reaction rate occurs, and are vital in understanding reactions and their application [9]. 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 [42]. 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 [9].

The pseudo-first-order kinetic model was first proposed by Lagergren (Lagergren, 1898; [42]. 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 [42]. 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 [11]. 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 [9, 42]. The linearized form of Ho's equation is expressed as in **Equation 2.6**.

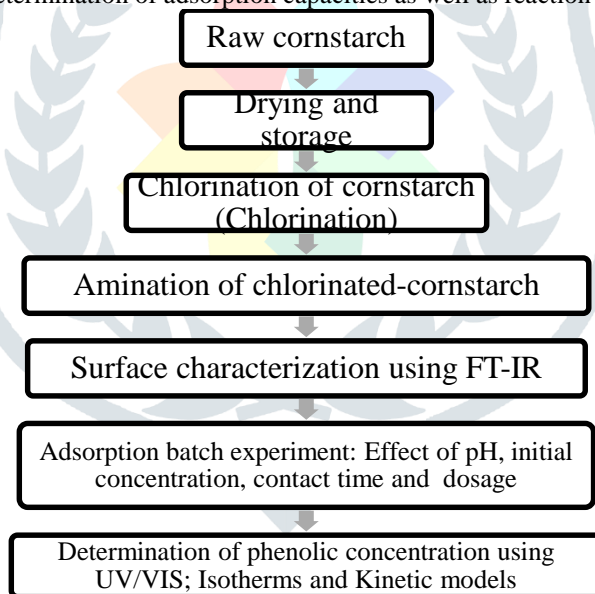
$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \dots \dots \dots \text{Equation 2.6.}$$

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 [5].

## II. MATERIALS AND METHODS

### 2.1 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 2**.



**Figure 2.** The Research Designs.

### 2.2 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.

### 2.3 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., 2,4-dichlorophenol (2, 4-DCP), acetyl chloride and thionylchloride were sourced from BDH Chemical Ltd. Poole, England. Ammonium hydroxide (NH<sub>4</sub>OH), 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<sub>3</sub>) were supplied by Sigma Aldrich (Kobian, Nairobi Kenya). Acetyl chloride (98% purity) was sourced from Fluka, Sigma Aldrich, Buchs Switzerland.

#### 2.4 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.

#### 2.5 Stock Solution Preparation

The stock solutions of selected soluble phenolic compounds: hydroquinone was 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 [5]. 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 [33, 34].

#### 2.6 Preparation of Adsorbent Biopolymer

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

##### 2.6.1 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 [32, 34].

##### 2.6.2 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 sunction 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 neural 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 [32, 33].

##### 2.6.3 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>.

#### 2.7 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: hydroquinone (λ<sub>max</sub>=290 nm) and 2-naphthol (λ<sub>max</sub>=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.

##### 2.7.1 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 [35]. 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 [14, 35]. The mixtures were equilibrated for predetermined time of 1 hour on a shaker machine at 120 rpm [35]. The mixtures were then filtered at the end of one hour and the concentration of phenolics in the filtrate were investigated using UV/Vis [7]. All experiments were done at room temperature (25 ± 1 °C) and the entire procedure was repeated twice to ascertain the reproducibility, reliability, accuracy and precision of the data that were collected [39].

### 2.7.2 Optimization of Initial Concentration on PCs Adsorption

The optimization of initial concentration of phenolics was done according to [34]. The optimum initial concentration on uptake of phenolics were determined using 25 mL model phenolic solutions (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.

### 2.7.3 Optimization of Adsorbent Dosage on Adsorption of PCs

The optimization was done as described by [14] and [35]. The effect of the modulated biopolymer dose on the removal of phenolics was determined by mixing 40 mL 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.

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

The optimization of agitation duration on phenolics uptake was performed according to [7]. 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 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.

### 2.7.5 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.

### 2.8 Data Analysis

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

$q_e = \frac{(C_i - C_e)}{M} V$  ----- 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 [5, 31]. The removed percentage of PCs in solution was calculated using Equation 3.2 shown below,

$R\% = \left( \frac{C_i - C_e}{C_i} \right) \times 100$  ----- 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 [5].

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 [3].

### 2.9 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 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 [5]. 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 and 2.6.

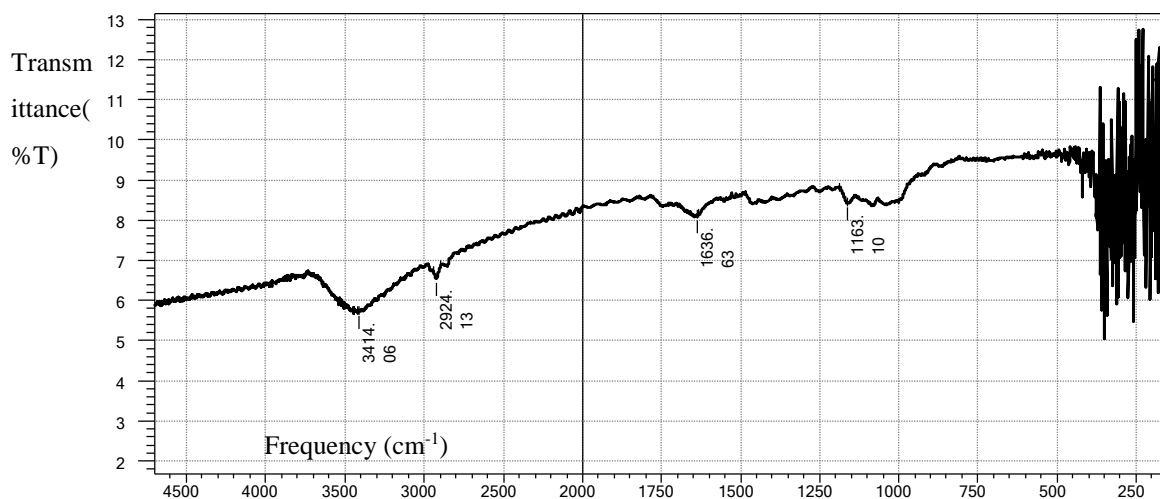
## III. RESULTS AND DISCUSSION

### 3.1 FT-IR Characterization of the Biopolymer

The Fourier transform infra-red is an important tool in identification of functional groups in the biomaterials [31, 37, 41]. 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.

### 3.1.1 Characterization of the Raw Cornstarch

The FT-IR spectrum of raw cornstarch (RCS) result is shown in the **Figure 3**.

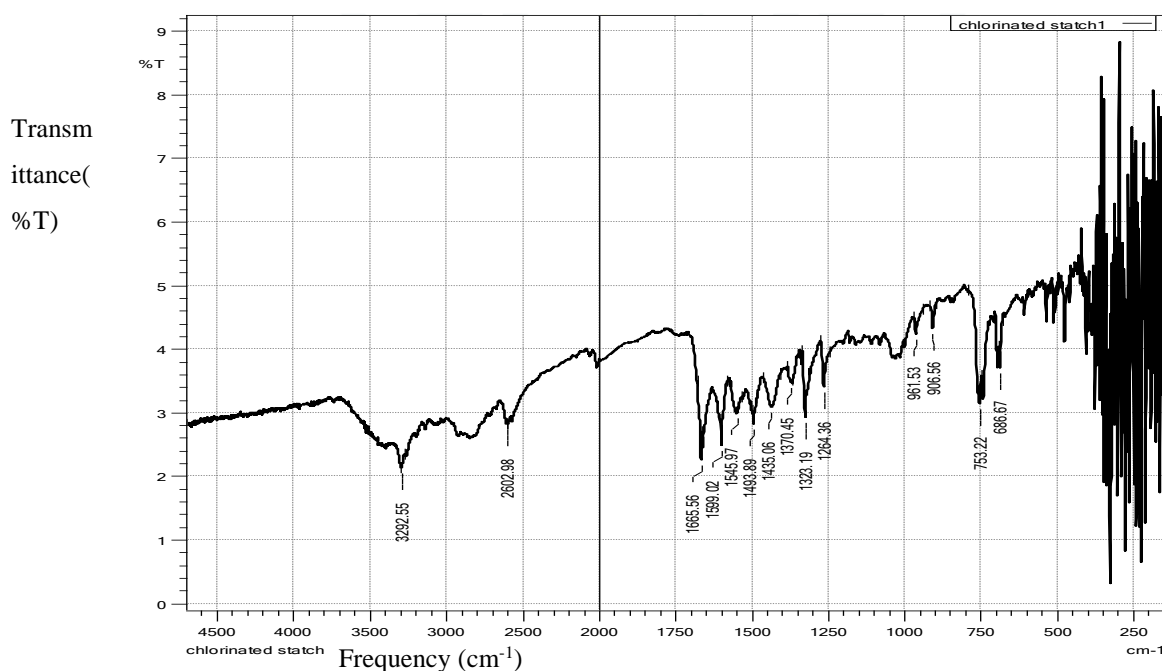


**Figure 3:** FT-IR Spectrum of the Raw Cornstarch (RCS).

The FT-IR spectrum (**Figure 3**) showed an intense broad band at  $3414.06\text{ cm}^{-1}$  assigned to O-H stretching in alcohols intermolecular bonded [14]. For -NH group in amine absorbs in the region  $3400\text{--}3300\text{ cm}^{-1}$  [22, 31]. The intense peak at  $2924.13\text{ cm}^{-1}$  indicates O-H stretching in carboxylic group or in alcohols intramolecular bonded. The peak at  $2924.13\text{ cm}^{-1}$  also attributed to C-H bonds stretching vibration while at  $1636.63\text{ cm}^{-1}$  to carbonyl functional group of esters and lactones [30]. The bands observed at  $1163.10\text{ cm}^{-1}$  is due to C-OH stretching in tertiary alcohols (or anhydroglucose unit) and ethers which absorbs from the range  $1250\text{--}1000\text{ cm}^{-1}$ . A wide band at  $1500\text{--}1250\text{ cm}^{-1}$  attributed to C-C bending [22, 30]. The compounds present in cornstarch based on the functional groups identified are alcohols, carboxylic acid in starch, aldehydes, amides, ether, esters and amines (**Figure 3**).

### 3.1.2 Characterization of the Chlorinated Cornstarch

The spectrum of chlorinated cornstarch (CCS) is represented in the **Figure 4**.



**Figure 4:** FT-IR Spectrum of the Chlorinated Cornstarch (CCS)

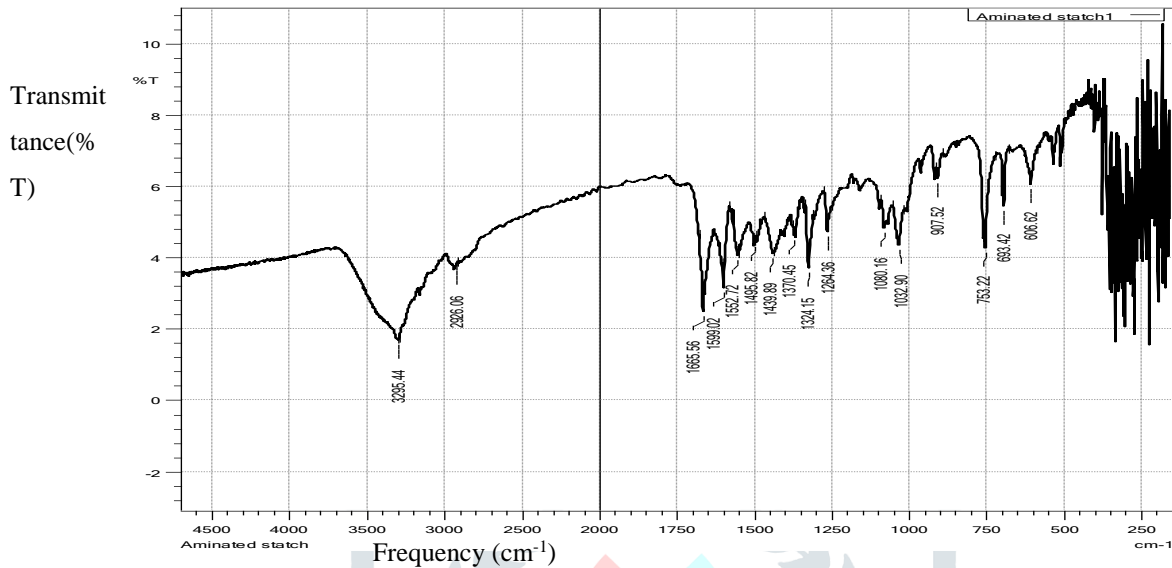
FT-IR spectrum of CCS (**Figure 4**) revealed the shifting of existing bands, disappearance of bands (**Figure 3**) and appearance of new bands of some absorption bands frequencies due to hydroxyl, carboxylic and halogen group [35]. Significant shifting of absorption peak frequencies, examples of the bands at  $3414.06\text{ cm}^{-1}$  (**Figure 3**) to  $3292.55\text{ cm}^{-1}$  due to one of -OH group being displaced by



chlorine, 2924.13  $\text{cm}^{-1}$  to 2602.98  $\text{cm}^{-1}$  and 1636.13  $\text{cm}^{-1}$  to 1599.02  $\text{cm}^{-1}$  respectively was observed upon chlorination. Appearance of the new absorption peak frequencies at 753.22 and 686.67  $\text{cm}^{-1}$  was observed which was assigned to C-Cl bond stretching vibration which ranges from 850-500  $\text{cm}^{-1}$  [22, 35]. 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 [34]. The absorption peaks at various wavelengths (**Figure 4**) 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) [22, 35].

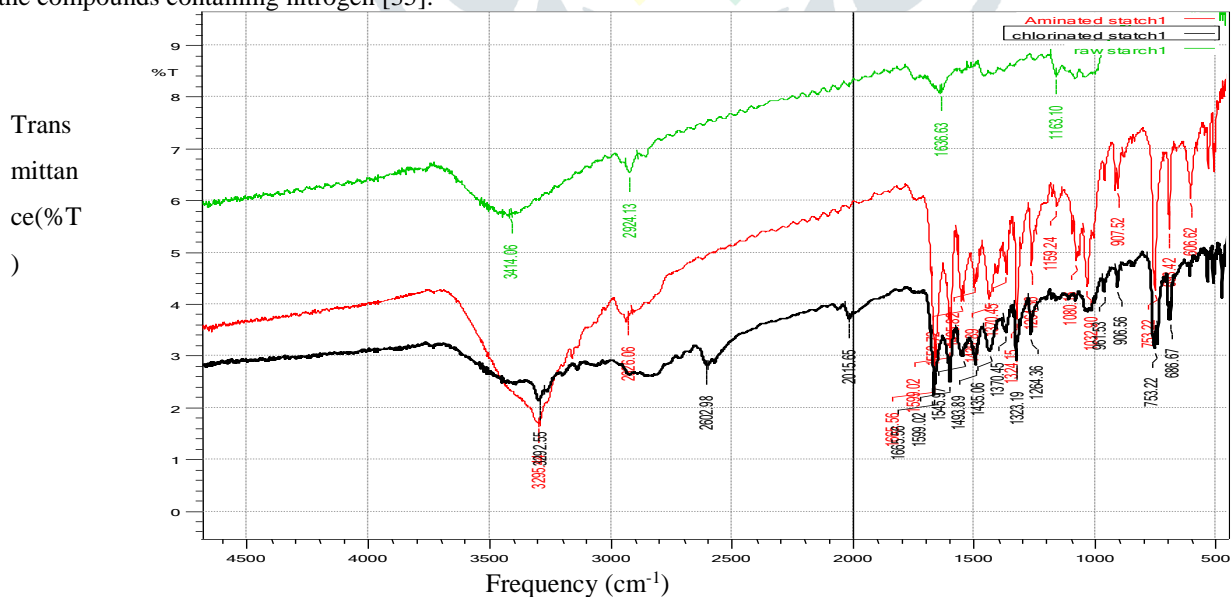
### 3.1.3 Characterization of the Aminated Cornstarch

**Figure 5** shows results of FT-IR spectrum of aminated cornstarch (ACS).



**Figure 5:** 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 [22]. 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**) to 3295.44, 1495.82, 1439.89, 1324.15  $\text{cm}^{-1}$  in aminated cornstarch (**Figure 5**) were observed after modulation with triethanolamine (amination). The band at 2602.98 and 2015.65  $\text{cm}^{-1}$  in chlorinated cornstarch (**Figure 4**) disappeared in aminated cornstarch (**Figure 5**) upon amination which showed the substitution of chlorine with triethanolamine [33]. Strong broad band with increased intensity at 3295.44  $\text{cm}^{-1}$  in aminated cornstarch (**Figure 4 and 5**) confirmed C-N stretch of amine functional group and N-H stretch of amine salt which ranges from 3300-2800  $\text{cm}^{-1}$  [22]. The peak at 1552.72  $\text{cm}^{-1}$  is due to -CH<sub>3</sub> groups of the compounds containing nitrogen [35].



**Figure 6:** FT-IR Spectra of RCS, CCS and ACS Overlaid

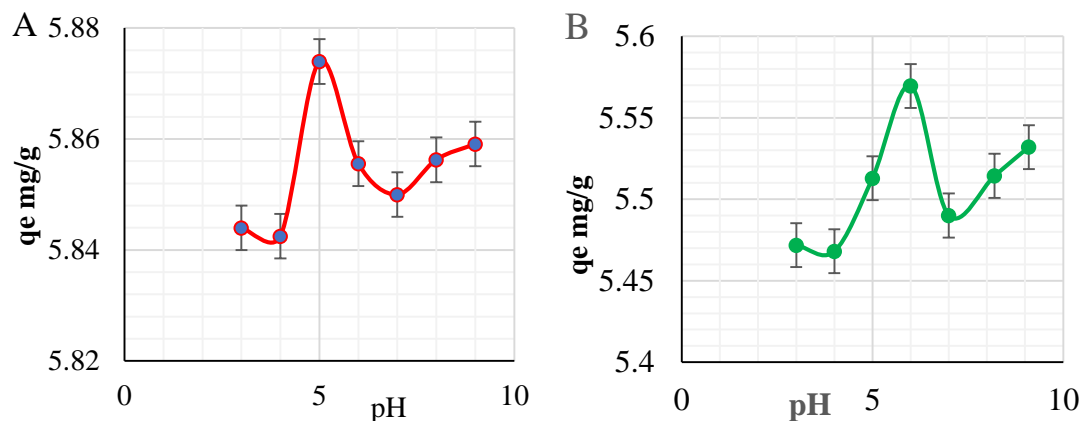
**Figure 6**, illustrated distinct FT-IR spectra differences of the RCS, CCS and ACS. It shows functional groups in RCS, CCS and ACS. The overlaid spectra of RCS, CCS and ACS (**Figure 6**) gives a clear difference between them with aminated chlorinated-cornstarch having peaks with high intensity. This confirmed that triethanolamine (tertiary amine) was successfully anchored on the cornstarch biomaterial. Results reported in this study were similar with those reported on sawdust [35], quaternized maize tassels [34] and on shea residue- *Vitellaria paradoxa* [30].

### 3.2 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.

#### 3.2.1 Effect of pH on Adsorption of PCs

The uptake of PCs in aqueous media relies on the pH of solution. The results of the effect obtained are presented in tabular form in graphical representation as shown in **Figure 7**.



**Figure 7.** Effect of pH on the adsorption of Hydroquinone (A) and 2-Naphthol (B) onto ACS adsorbent. (Initial concentration: 25 ppm 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 7**) 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 [43]. In **Figure 7** hydroquinone was at pH 5.0 with q<sub>e</sub> of 5.874 mg/g (97.90%) as observed in **Figure 7** (A). For 2-naphthol, the optimum pH was 6.0 with q<sub>e</sub> of 5.570 mg/g (92.83%) as indicated in **Figure 7** (B). 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 [24, 35]. This attributes to a chemisorption adsorption mechanism.

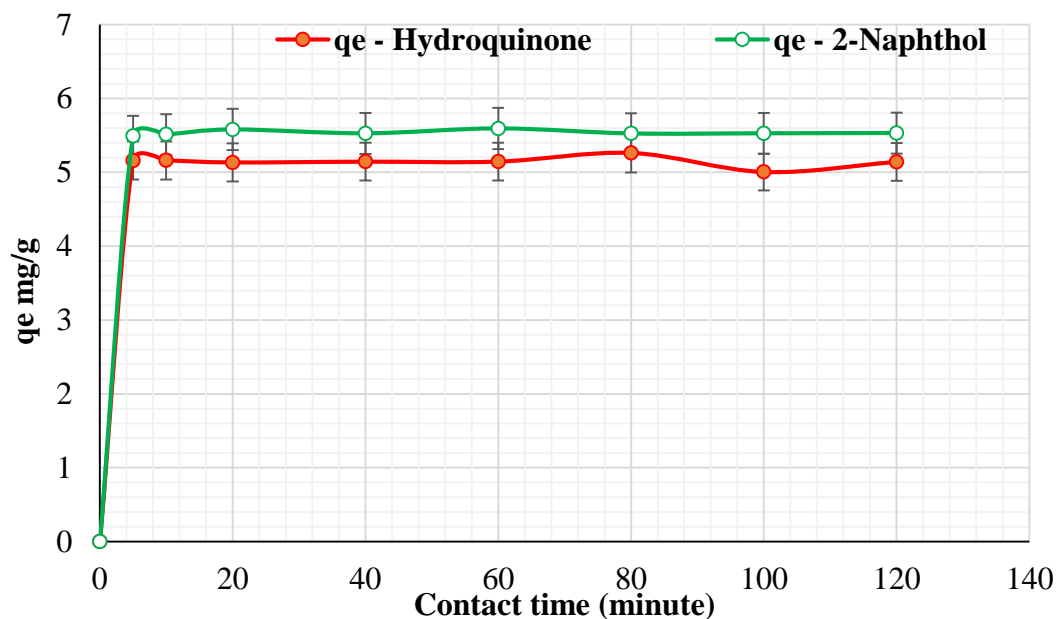
At high pH values >7, there was high concentration of  $\text{-OH}^-$  ions (negatively charge ions) which increases the development of the repulsive forces between ions of PCs and hydroxide ions. Consequently, increases the hindrance to diffusion of PCs ions resulting in low uptake of PCs, thus reduces their adsorption of PCs at high pH values [35]. At that pH environment, the phenolate ions forms strong salts with alkali metal of the base [5].

At optimal pH environment, the percentage removal was 92.83% for 2-naphthol at optimum pH of 6.0 and for hydroquinone (hydroxyl benzene) was 97%. 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 [5]. 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 [8]. Similar findings have been reported in studies on the PCs removal using adsorption process by quaternized maize tassels, [34], tamarind seed powder [1] and the  $\text{Fe}_2\text{O}_3$  impregnated sawdust [35] as adsorbents.

The maximum removal of model PCs in solution were realized at the 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.

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

Contact time is very significant factor affecting the efficiency and establishing the kinetic process [7]. 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 8**.



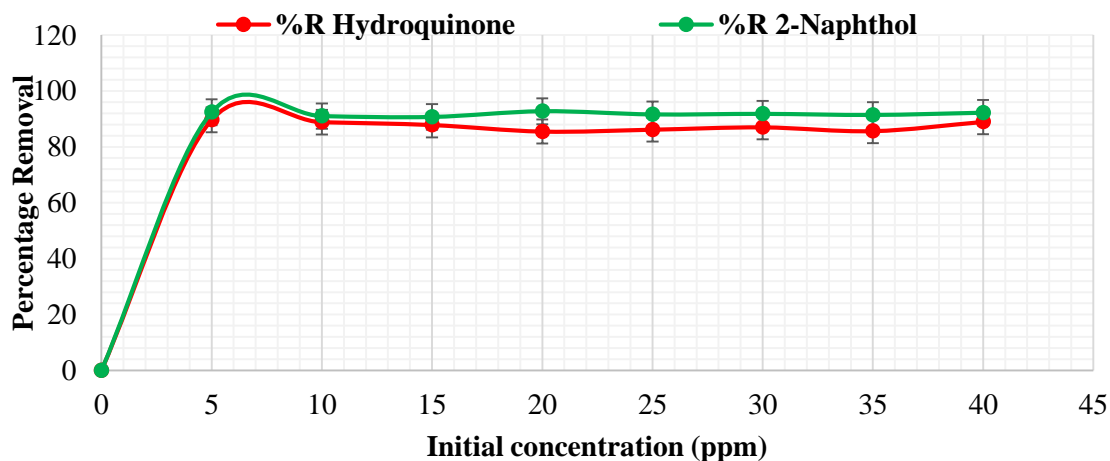
**Figure 8:** Effect of Contact time on the Removal of PCs from Aqueous Solutions. (Initial concentration: 30 ppm; agitation speed: 120 rpm; ACS dosage: 0.1 g; temperature:  $25 \pm 1$  °C; pH: 5.0).

From the findings in **Figure 8**, 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 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 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 [35]. The results estimate the rate at which the phenolic ions were removed from solution and provide details of the adsorption mechanism [34, 35]. 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 [24]. 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 [1].

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 were in agreement with what was reported on quarternized maize tassels and sawdust [34, 35]. 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.

### 3.2.3 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 9**.



**Figure 9:** 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:  $25 \pm 1$  °C; pH: 5.0).

The general observations in **Figure 9** 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 [5, 34]. This is because

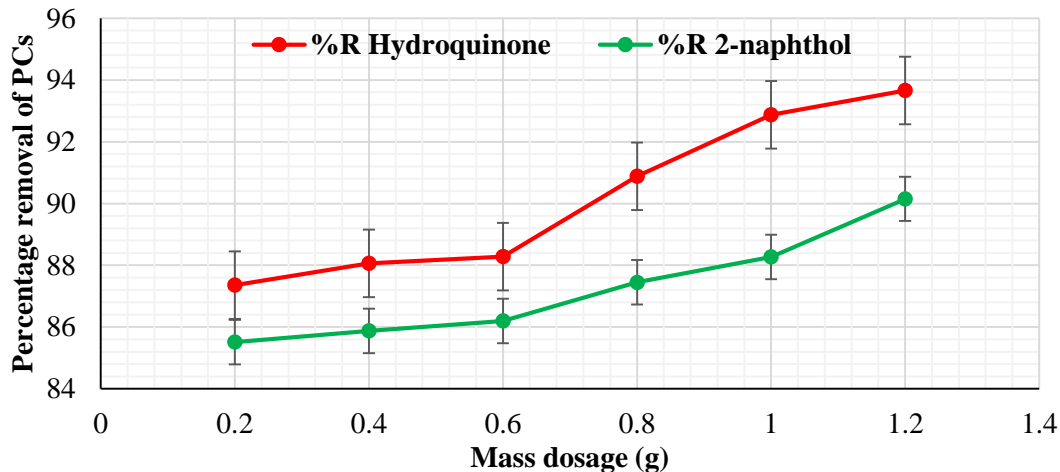
increase of mass transfer driving force between adsorbate and adsorbent, and thus the fruitful diffusion of phenolic ions / binding to the surface of adsorbent from solutions [35].

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 9**), 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 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 [5, 8] and [34].

### 3.2.4 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. The results obtained on adsorption of PCs by various masses of ACS adsorbent in the equilibration were presented in **Figure 10**.



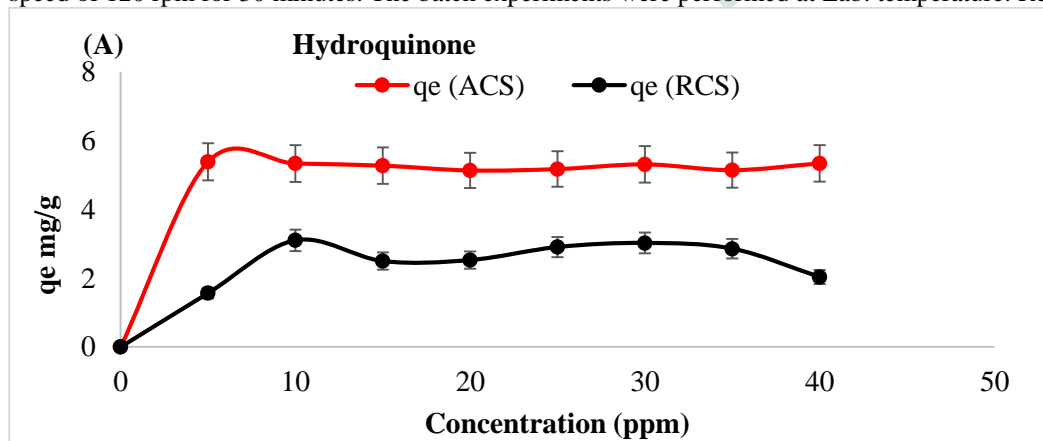
**Figure 10:** Effect of Dosage of ACS Adsorbent on Removal of PCs from Aqueous Solution. (Initial concentration :30 ppm; Contact time :30 min; shaking speed: 120 rpm; temperature:  $25 \pm 1$  °C; pH 5.0 for hydroquinone and pH 6 for 2-naphthol).

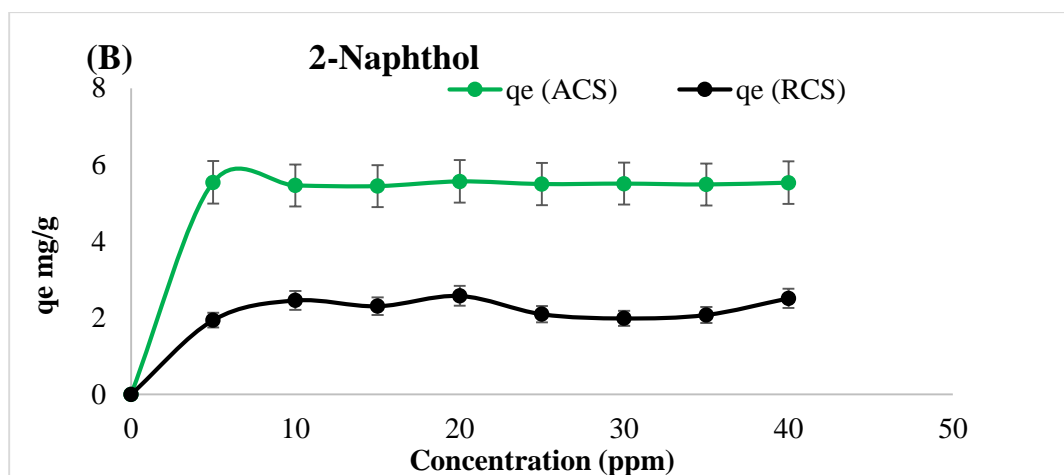
From the **Figure 10**, the findings show that the percentage removal of PCs increases gradually with the increase in the mass of the ACS adsorbent. The observed phenomenon in **Figure 10** can be explained by the fact that the volume of binding active sites or pores for interaction increases with increase 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 shows 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 [1, 34, 39, 40]. The optimum dosage in process unit depends on the chemistry of the solution: concentration of adsorbates, the volume of adsorbates and the ion size [39]. In all the subsequent equilibration studies, therefore, the mass dosage was 0.1grams.

### 3.2.5 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 hydroquinone and 2-naphthol at their optimum pH. For 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 11**.





**Figure 11:** 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 hydroquinone and pH 6.0 for 2-naphthol, 0.1 g dose).

The general observations in **Figure 11** for both ACS and RCS adsorbents were that the maximum uptake occurred rapidly and then slowed down after 10 ppm for 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, [1, 5, 35].

### 3.3 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 shown in **Figure 11** (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 1**.

**Table 1:** Results for the Freundlich and Langmuir Isotherms for PCs Adsorption Capacities

Phenolic Compounds (pcs)	Langmuir Model			Freundlich Model			Best Model Fitted
	$q_{\max}$ (mg/g)	$b / K_L$ ( $\text{dm}^3/\text{g}$ )	$R^2$	$1/n$	$K_f$ (mg/g)	$R^2$	
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 1, the maximum adsorption capacities ( $q_{\max}$ ) for hydroquinone and 2-naphthol were 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  $4.895 \text{ dm}^3/\text{g}$  while hydroquinone had  $2.142 \text{ dm}^3/\text{g}$ . Thereby, 2-naphthol has higher affinity power and energy to ACS adsorbent than 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 [37]. The  $1/n$  values are less than one as observed in the Table1, 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 [29]. 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 [29]. A similar observation was made by [39], [34] and [35] 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 [24]; [5]. 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.

### 3.4 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 [11]). 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 2.

**Table 2:** Results for Kinetic Parameters for Adsorption of PCs onto ACS

Phenolic Compounds (PCs)	Pseudo – first order ( $K_1$ )			Pseudo – second order ( $K_2$ )			BestModel Fitted
	Parameters	qe (mg/g)	$K_1$ (mg/ g min <sup>-1</sup> )	$R^2$	qe (mg/g)	$K_2$ (mg/ g min <sup>-1</sup> )	
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 show that qe 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) than hydroquinone 0.2393 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 favoring a chemisorption process and not physisorption [29]. 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 [5, 24] and [35].

## IV. CONCLUSION

The spectra 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 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  $25 \pm 1^\circ\text{C}$  and agitation speed of 120 rpm. The dose of aminated cornstarch and initial concentration increases with the increase in removal of PCs. 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,  $R^2=1.000$  and  $0.9999$  and monolayer adsorption capacities of  $4.584$  and  $5.048$  mg/g for 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.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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**Ethnic statement:** The study fulfills ethical requirements of the research/study.

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