

Facile Removal of Phenol from Aqueous Solution Using Modulated Cornstarch Impregnated With Triethanolamine as Adsorbent: Sorption Isotherms and Kinetics

Haron Bosuben¹, Peter W. Njoroge¹, Sylvia A. Opiyo¹, Isaac W. Mwangi²

¹(Department of Physical and Biological Sciences, Murang'a University of Technology, Kenya)

²(Department of Chemistry, Kenyatta University, Kenya)

Abstract

Background: The sources of phenolics pollutants in water are mainly pharmaceutical and chemical industries. The compounds are carcinogenic, cytotoxic, mutagenic and teratogenic even at modest concentrations. These health effects are unrectifiable and it is prudent to remove phenols from water to overcome them. Despite substantial achievements on modern methods for removal of phenol from aqueous media, there is need to search for bio-adsorbent which is non-toxic, ecofriendly, cost-effective and efficient. This study reports on the modulation of cornstarch by chlorination followed by amination using triethanolamine, to be used as adsorbent.

Materials and Methods: Starch was derived from corn (maize) enriched flour purchased from Mukuyu and Maragua in Murang'a County, Kenya. All solutions were prepared using double deionized water obtained from Kenyatta University (K.U) Chemistry Laboratory. Reagents and chemicals used were of analytical grade (AR). Characterization of raw and modulated cornstarch, was done using Fourier Transform Infrared (FTIR) spectrophotometer. The modulated cornstarch was used in the removal batch experiments (optimization of adsorption parameters) on model solutions. The efficiency of modified cornstarch in phenol removal at different pH levels (pH3.0-10), contact time (5-120 minutes), initial phenolics concentration (5-40ppm) and bioadsorbent dosage (0.1-1.2g) of aminated cornstarch (ACS) in aqueous media at laboratory temperature ($25 \pm 1^\circ\text{C}$) were investigated.

Results: The results showed that the maximum uptake of phenol was realized at equilibrium contact time of 10 mins, pH of 5.0. The uptake of phenol increased with increase in dosage of ACS and initial concentration of phenol. The maximum uptake of phenol occurred at initial concentration of 10ppm and then plateaued. In kinetic models, the adsorption mechanism of phenol was best described by the pseudo – second order (K_2) kinetic model with $R^2=0.9978$. The batch experimental data obtained best fitted into the Langmuir isotherm with regression coefficient $R^2=0.999839$ and monolayer adsorption capacities of 4.2977mg/g for phenol.

Conclusion: These adsorption capacities were relatively higher than reported processes, indicating that aminated cornstarch (ACS) is an effective adsorbent for removal of phenol from aqueous media. The findings from this study will provide remedy to water treatment using effective ecofriendly adsorbent and recycling of wastewater for reuse.

Key Word: Adsorption; Amination; Bioadsorbent; Modulation; Phenol; Cornstarch.

Date of Submission: 20-08-2022

Date of Acceptance: 04-09-2022

I. Introduction

Water is extremely salient for human being, animals and growth of plants. Natural processes and increasing human 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 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).

Phenolic compounds (PCs) 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 end up in wastewater (El-Ashtoukhy *et al.*, 2013). Some of phenolics are used in chemical synthesis and as solvent, like phenol, in large quantities. Pollutions caused by phenols have been associated with a lot of health risks and poor organoleptic properties of water and fish. Therefore, it is very prudent to remove phenols from wastewater before being used

or released into the ecosystem as the compound and its derivatives have carcinogenic, mutagenic, teratogenic, malformation and cytotoxic properties. In addition, phenol and its derivatives change activity of enzymes and the metabolism of cell upon entry into the living organism (Bożena and Sylwia, 2003; Haq *et al.*, 2019).

According to the US Environmental Protection Agency (EPA) phenol has 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. EPA has set allowable limit of 0.1mg/L of a phenolic compound in wastewater whereas WHO sets a 0.001mg/L as the limit of phenols concentration in portable water (Nayak *et al.*, 2020). The permissible concentration limit of phenol in water should be at most 1-2 µg/L. The world health organization (WHO) set a maximum permissible concentration of 1g/L of overall phenolic compounds in drinking water (Bentaleb *et al.*, 2017; Ibrahim *et al.*, 2020).

Methods that have been utilized for removal of phenol from wastewater are adsorption, polymerization, ozonation, photocatalytic degradation, electrocoagulation, electroFenton, electrolysis, extraction, biological methods, ion exchange and membrane - based separation (William *et al.*, 2017; Nayak *et al.*, 2020). Some methods are linked with high capital, poor efficiency, maintenance and operational costs which includes; ultra-filtration, nano-filtration and reverse osmosis. This has led to a wide range of intervention and methods for removal of phenols contaminant in water and wastewater using natural or synthetic materials such as clay, membranes, activated carbon, nanomaterials, zeolites and carbon nanotubes. (Haq *et al.*, 2019, Antonio and Cosimino, 2020). Adsorption method is the most famous and preferred because of its additional benefits of level of effectiveness, eco-friendly, user-friendly, low-cost and availability of various bioadsorbents (Barrera, 2020; Mbugua, 2020).

Agricultural product has cellulose/ biopolymers that show potentials application for adsorption of hazardous/ toxic organic and inorganic contaminants in aqueous media. The pre-eminent constituents 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).

Cornstarch is a polymeric biomolecule derived from plants which is cheap, available in large quantities at low cost and has numerous applications in various industries (Muhammad *et al.*, 2016). Bio adsorbents obtained from cheap readily available starch are effective, efficient and have high sorption capacity for uptake of phenols from contaminated water (Franck *et al.*, 2003). Cornstarch can be modified by numerous methods such as physical, genetic and chemical modifications. 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 cornstarch using tertiary amine (triethanolamine) for adsorptive removal of phenol from contaminated water/ wastewater.

II. Material And Methods

Chemicals and reagents

The starch material used in this study was derived from corn (maize) starch enriched flour purchased from Mukuyu and Maragua in Murang'a County, Kenya. All solutions were prepared using double deionized water obtained from Kenyatta University Chemistry Laboratory. Reagents and chemicals used were of analytical grade (AR) and supplied by RFCL, Rankem, India and Sigma Aldrich (Kobian, Nairobi Kenya).

Modulation of cornstarch

Cornstarch was dried at 60⁰C for twelve (12) hours, cooled in a desiccator and later kept in an oven at 30⁰C in a screwed clean plastic container. A sample of 15.0 g dried cornstarch was mixed with 200 ml aniline solvent in a 500ml three-neck flask. Eighty (80) ml acetyl chloride, was added dropwise from a separatory funnel under mechanical stirring at a temperature of 70 ⁰C for 5 hours. The solid chlorinated cornstarch was recovered from the three-neck flask and washed with double de-ionized water to remove unreacted chlorine and thus, adjusting its pH to neutrality. It was then dried for two days at laboratory temperature (Mwangi *et al.*, 2014; Muhammad *et al.*, 2016).

A mass of 15.0 g chlorinated cornstarch was mixed with 100 ml tertiary amine (triethanolamine) and refluxed under a mechanical mixer for 3.5 hours at 40⁰C, as represented in **scheme1**. The solid aminated cornstarch obtained was recovered from the mixture by vacuum filtration 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).

Scheme1: The steps involved in Amination of dried cornstarch using triethanolamine.

Characterization of the adsorbents

Characterization of dried raw cornstarch (untreated) (RCS), chlorinated cornstarch (CCS) and aminated cornstarch (ACS) was done using Fourier Transform Infrared spectrophotometer machine (FTIR-8400 model, Shimadzu Tokyo, Japan). The purpose of this stage was to determine the functional groups present at each step and transformation of cornstarch after modulation. One (1.0) mg of dried sample of each of RCS, CCS and ACS were mixed thoroughly with 50.0 mg of potassium bromide (KBr). The mixture was grinded into a fine powder and then pressed in a vacuum into pellets. The pellets were then put into FTIR for analysis. The adsorbents spectra were measured in the wavelength range 4500 cm^{-1} – 250 cm^{-1} .

Adsorption Experiments

The adsorption experiments were done in DKZ series digital reciprocating shaker (model SHR-2D, Korea) 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 0.1g of the modulated cornstarch. The phenol concentration in filtrate / aqueous media was determined using UV/VIS spectroscopy (Analytik Jena Specord 200 Plus model, Germany).

The pH levels of the model solutions were adjusted from pH 3.0 to pH 10.0 using 0.1M HNO₃ acid and 0.1M NaOH solutions. They were measured using digital pH meter. Twenty (20) mL of 25 mg/L phenol 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, 9 and 10) in 25ml screwed plastic bottles. Mixture filtered at the end of contact time.

The optimum initial concentration on uptake of phenol were determined using 25 mL model phenol 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 $25 \pm 1^{\circ}\text{C}$ and a fixed pH of 5.0.

The effect of the dose of adsorbent on the removal of phenol was determined by mixing 40 ml phenol 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 25ml screwed plastic bottles. The pH was fixed at pH 5.0 using 0.1M NaOH and 0.1M HCl solutions.

The optimum contact time on phenol removal was studied at different contact time of 5, 10, 20, 40, 60, 80, 100 and 120 minutes using 20 ml of 30mg/L phenol solutions in the screwed plastic bottles. Mixture filtered at the end of contact time and filtrate analyzed

The quantity of phenol adsorbed by modulated cornstarch during the batch experiment was calculated as expressed in Equation 2.

$$q_e = \frac{(C_i - C_e)}{M} V$$
 ----- Equation 2 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 (mgL^{-1}), C_e is the equilibrium concentration of PCs in 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** shown below,

$$R\% = \left(\frac{C_i - C_e}{C_i} \right) \times 100$$
 -----Equation 3

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).

Adsorption isotherms

Freundlich and Langmuir models were used to determine the effectiveness of biomaterial based on data obtained and the maximum sorption capacity of modulated cornstarch on removal of phenolics (Mwangi *et al.*, 2016; Nthiga, 2016). The Langmuir model is expressed in the linear equation as shown in Equation 2.1:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}} C_e \text{-----Equation 4}$$

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 adsorbed 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 $1/K_L \cdot q_{max}$ 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).

The Freundlich model is 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 a linear form as shown in the Equation 2.2

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \text{..... Equation 5}$$

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).

Kinetic studies

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 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 2.3.

$$\log (q_e - qt) = \log q_e - K_1 t \text{.....Equation 6}$$

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

The pseudo-second order kinetic (K_2) model 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 2.4.

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \text{..... Equation 7}$$

where qt and q_e 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) ($g/mg \cdot \text{min}^{-1}$). The graph of the $\frac{t}{qt}$ against time, t (min) gives a straight line which is used to calculate K_2 and q_e from the intercept and the slope respectively (Barrera, 2020).

III. Results

Characterization studies of adsorbents

The FTIR 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 FTIR spectroscopy Shimadzu model in the region of 4500 and 250 cm^{-1} . Figure 1 shows results of FTIR spectra of raw cornstarch (RCS), chlorinated- cornstarch (CCS) and aminated chlorinated cornstarch (ACS).

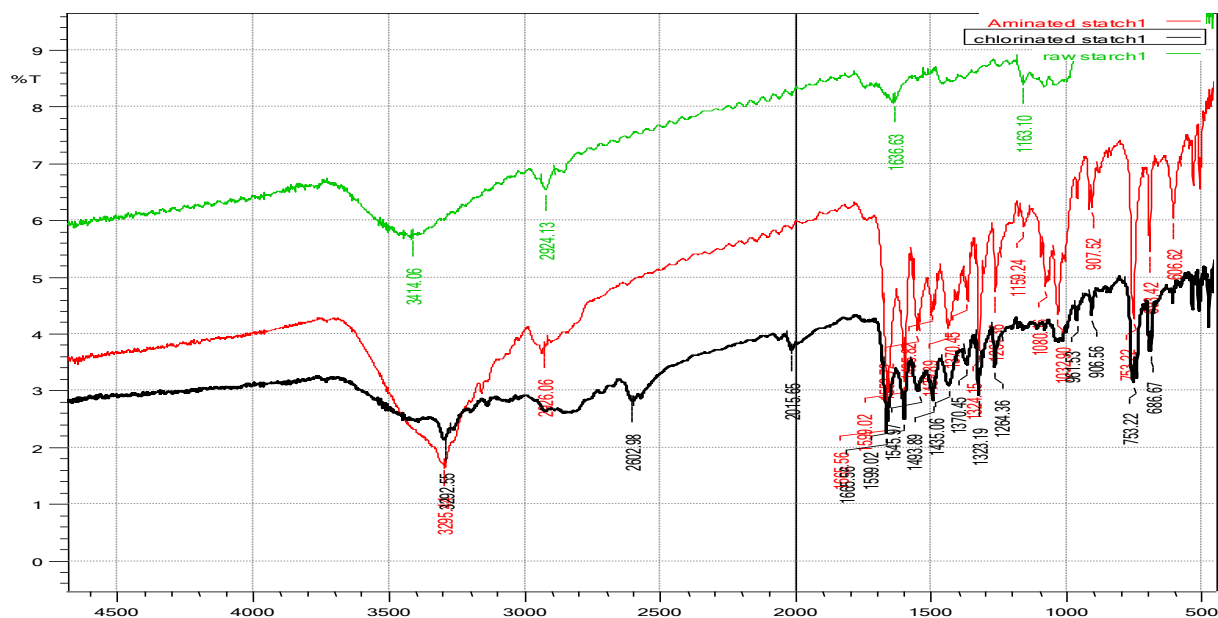


Figure 1: FTIR Spectra of RCS, CCS and ACS overlaid

The overlaid spectra of RCS, CCS and ACS (Figure 3.1) gives a clear difference between them with aminated chlorinated-cornstarch having peaks with high intensity. This confirmed that triethanolamine (tertiary amine) was successfully anchored/ impregnated on the cornstarch biomaterial.

Batch experiments studies

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 120rpm speed.

Effect of pH on adsorption of phenol

The uptake of PCs in aqueous media depends on the pH of solution. The effect of pH on the uptake of PCs was carried out over the range from 3 to 9. The results of the effect obtained are presented in graphical representation as shown in Figure 2.

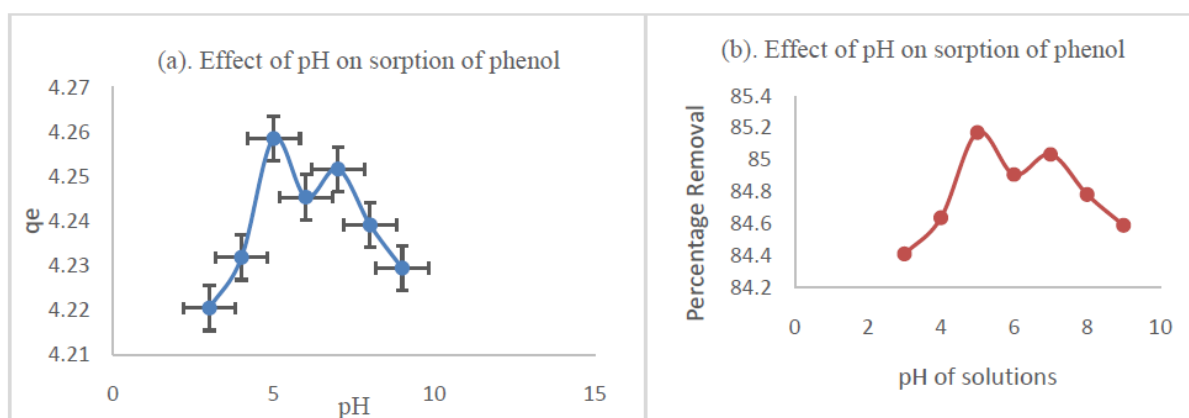


Figure 2 (a & b): Effect of pH on the adsorption of Phenol (Initial concentration: 25ppm phenol agitation time: 60mins; ACS dosage: 0.1g; temperature: 25 ± 1⁰C; shaking speed: 120rpm).

Effect of contact time on adsorption of phenol

Contact time is very significant factor affecting the efficiency and establishing the kinetic process (Biglari, *et al.*, 2016). In this experiment contact time was varied (5, 10, 20, 40, 60, 80, 100 and 120 minutes) using 20 ml of 30mg/L(ppm) phenol while the pH was maintained at optimal value pH 5.0 when mass of the adsorbent was 0.1 g, (physicochemical parameters were fixed). The temperature was fixed at 25 ± 1⁰C and the mechanical shaker was set at a shaking speed of 120rpm. The results obtained in this study were as presented in Figure 4

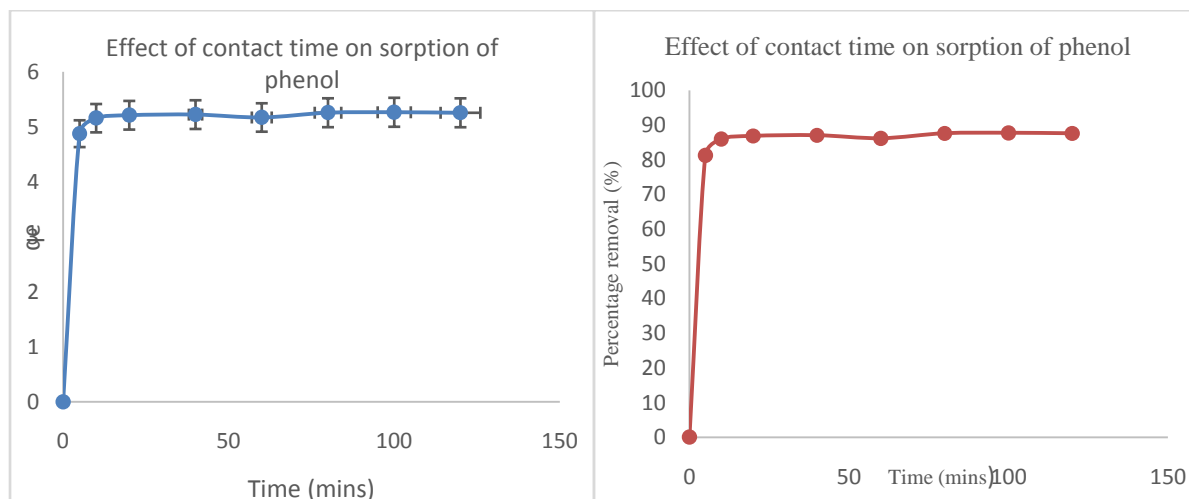


Figure 3: Effect of contact time on the removal of phenol from aqueous solutions. (Initial concentration: 30ppm; agitation speed: 120rpm; ACS dosage: 0.1g; temperature: $25 \pm 1^{\circ}\text{C}$; pH: 5.0).

Effect of adsorbate initial concentration on adsorption of phenol

The initial concentrations of phenol were 5, 10, 15, 20, 25, 30, 35 and 40ppm while investigating the effect of the initial concentration on the removal of phenol. The other physicochemical parameters were kept constant. The findings obtained were as shown in Figure 5 (a) and (b).

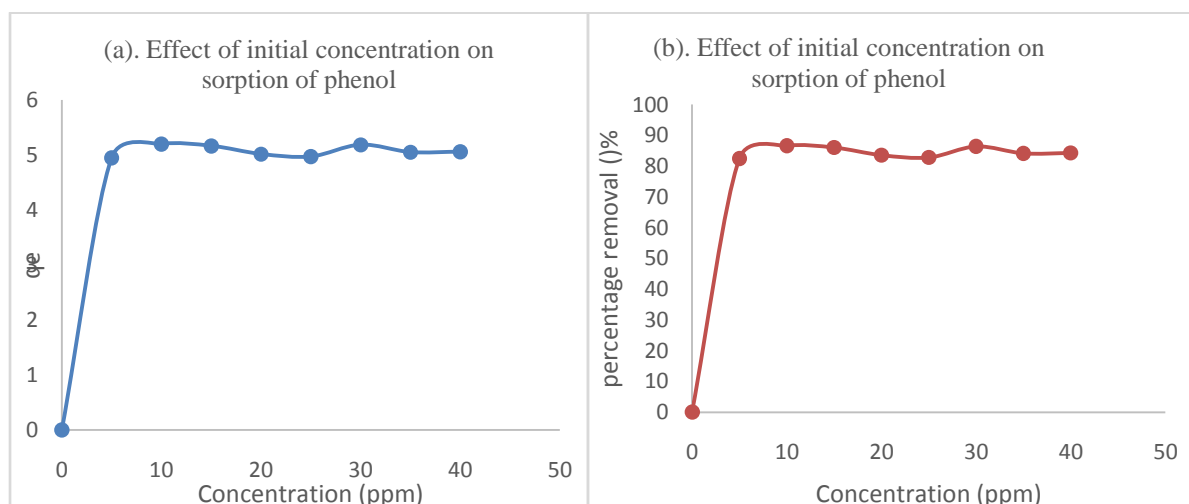


Figure 4(a) and (b): Effect of initial Concentration on the removal of phenol from aqueous solutions. (Contact time: 60min; shaking speed: 120rpm; ACS dosage: 0.1g; temperature: $25 \pm 1^{\circ}\text{C}$; pH: 5.0).

Effect of dosage of modulated adsorbent on adsorption of phenol

The effect of ACS adsorbent dosage on uptake of phenol was examined by varying mass doses (0.2, 0.4, 0.6, 0.8, 1.0 and 1.2g) of ACS biomaterial resin at a fixed initial concentration (30ppm of phenol), pH=5.0 and 60 minutes agitation time. The batch experiments reported were all performed at lab temperature of $25 \pm 1^{\circ}\text{C}$. The results obtained on adsorption of phenol by various masses of ACS adsorbent in the equilibration were presented in Figure 6.

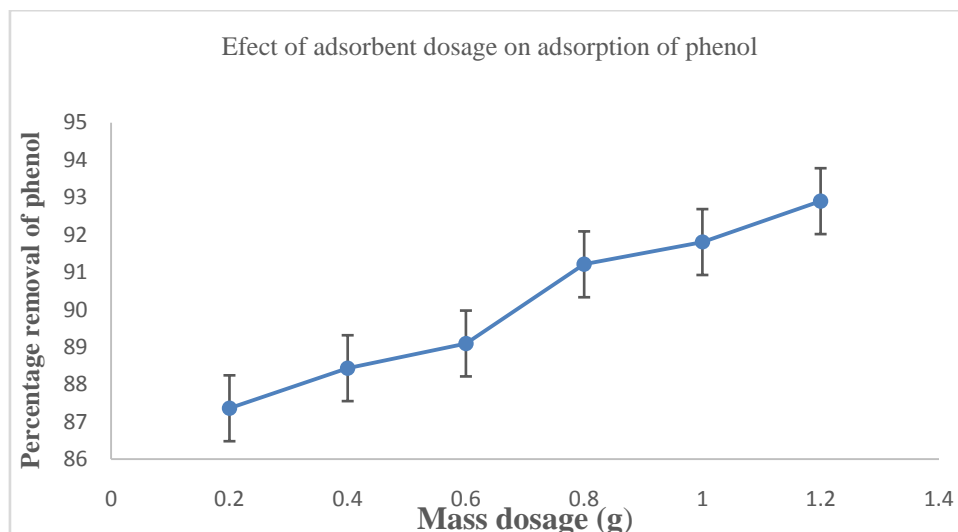


Figure 5: Effect of dosage of ACS adsorbent on removal of phenol from aqueous solution. (Initial concentration :30ppm; Contact time: 30min; shaking speed: 120rpm; temperature: $25 \pm 1^{\circ}\text{C}$; pH: 5.0).

Adsorption isotherms/ adsorption capacities for phenol

In the determination of adsorption capacities and chemisorption mechanism of the phenol using ACS as adsorbent, the experimental results obtained was fitted into Langmuir and Freundlich isotherms represented by equation 4 and 5. The initial concentration of phenol was varied from 0 to 40 ppm at a fixed pH of 5.0 and 0.1g of ACS adsorbent dose biomaterial, as presented in Figure 4(a) and (b). Then, the content was agitated for 30 minutes at 120rpm and constant temperature of $25 \pm 1^{\circ}\text{C}$. The results were presented in the graphs of the isotherms for the adsorption of phenol shown in Figure 6(a) and(b).

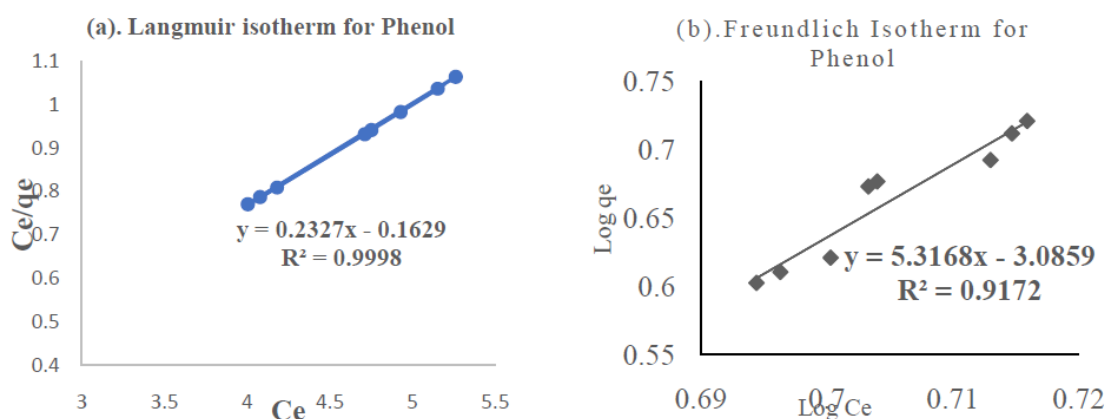


Figure 6: Results for the Freundlich and Langmuir isotherms for phenol adsorption capacities

Adsorption kinetics

The Lagergren's pseudo – first order (K_1) and Ho's pseudo – second order (K_2) kinetic rate models, as in Equation 6 and 7, were fitted 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 phenol are shown in Figure 7.

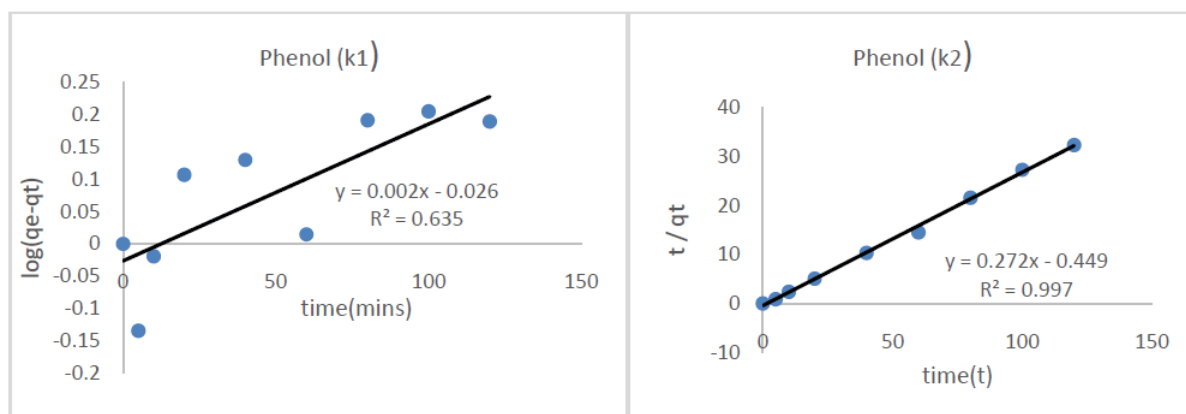


Figure 7: Results for kinetic parameters for adsorption of phenol onto ACS

IV. Discussion

Characterization studies of adsorbents

The FTIR spectrum of raw cornstarch (RCS) showed a strong broad band at 3414.06 cm^{-1} assigned to O-H stretching in alcohols intermolecular bonded (Girish and Murty, 2014). For -NH group in amine absorbs in the region $3400\text{-}3300\text{ cm}^{-1}$ (John, 2000; Mbugua, 2020). The strong peak at 2924.13 cm^{-1} indicates O-H stretching in carboxylic group or in alcohols intramolecular bonded. The peak at 2924.13 cm^{-1} also attributed to C-H bonds stretching vibration while at 1636.63 cm^{-1} to carbonyl functional group of esters and lactones (Liouna, *et al.*, 2022). The compounds present in raw cornstarch based on the functional groups identified are alcohols, carboxylic acid in starch, aldehydes, amides, ether, esters and amines (**Figure 1**).

FTIR spectrum of chlorinated cornstarch (CCS) (**Figure 1**) revealed the shifting of existing peaks, disappearance of peaks (RCS) and appearance of new peaks of some absorption bands frequencies due to hydroxyl, carboxylic and halogen group (Nayak, *et al.*, 2020). Significant shifting of a number of absorption peak frequencies from 3414.06 cm^{-1} (RCS) to 3292.55 cm^{-1} , 2924.13 cm^{-1} to 2602.98 cm^{-1} and 1636.13 cm^{-1} to 1599.02 cm^{-1} was observed upon chlorination. Appearance of the new absorption peak frequencies at 753.22 and 686.67 cm^{-1} was observed which was assigned to C-Cl bond stretching vibration which ranges from $850\text{-}500\text{ cm}^{-1}$ (John, 2000; Nayak, *et al.*, 2020). The absorption peaks at various wavelengths (CCS) were due to different functional groups identified, such as at 2602.98 (C-H stretch), 1599.02 (carboxylate, C=O stretching), 1493.89 (C-H bending), 1435.06 (O-H stretch), 1370.45 (O-H bending) and $1323.19\text{-}1264.36$ (C-O stretch from carboxylic acids, alcohols, ethers, esters and lactones) (John, 2000; Nayak, *et al.*, 2020).

The new peak, absorption frequencies at 1080.16 and 1032.90 cm^{-1} in aminated cornstarch (ACS) spectra 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 , and 1323.19 cm^{-1} in chlorinated cornstarch to 3295.44 , 1495.82 , 1439.89 , and 1324.15 cm^{-1} in aminated chlorinated-cornstarch were observed after modulation with triethanolamine (amination). The bands at 2602.98 and 2015.65 cm^{-1} in chlorinated cornstarch disappeared in aminated chlorinated-cornstarch upon amination which showed the substitution of chlorine with triethanolamine (Mwangi, *et al.*, 2016). Strong broad band with increased intensity at 3295.44 cm^{-1} in aminated chlorinated-cornstarch confirmed C-N stretch of amine functional group and N-H stretch of amine salt which ranges from $3300\text{-}2800\text{ cm}^{-1}$ (John, 2000). The peak at 1552.72 cm^{-1} is due to $-\text{CH}_3$ groups of the compounds containing nitrogen (Nayak, *et al.*, 2020). The overlaid spectra of RCS, CCS and ACS (**Figure 1**) gives a clear difference between them with aminated chlorinated-cornstarch having peaks with high intensity. This confirmed that triethanolamine (tertiary amine) was successfully anchored/ impregnated on the cornstarch biomaterial.

Effect of pH on adsorption of phenol

The results in **Figure 2** show that pH has significant effect on sorption of phenol in aqua media. It was observed that adsorption was low at pH values below 4.0 and above 7.5. The best sorption was found to be between 5.0 and 7.0. 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 phenol (Mukherjee, *et al.* 2007). From the results, maximum uptake of phenol was at pH of 5.0 with percentage removal efficiencies of 85.17% as observed in **Figure 2**. The adsorbent and the adsorbate/ analyte have deprotonation and protonation relying on pH environments. Therefore, low pH environment neutralizes cornstarch surface negative particles, lowers the hinderance to diffusion of phenolic compounds ions, increases electrostatic attraction due to $\pi\text{-}\pi$ 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.

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 phenols 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 phenolic compounds removal using adsorption process by quaternized maize tassels, (Mwangi, *et al.*, 2014), tamarind seed powder (Abu, *et al.*, 2018) and the Fe₂O₃ impregnated sawdust (Nayak, *et al.*, 2020) as adsorbents. The maximum uptakes of model phenol in solution were realized at the pH values of 5 in this study. Therefore, it was established that maximum removal of phenol in aqueous solutions can be successfully achieved in the pH 5 and was used in subsequent batch experiment.

Effect of contact time on adsorption of phenol

In the **Figure 3**, it was observed that the uptake of phenol increased rapidly with time for the first 5 minutes contact time, which then slowed down and flattened for longer contact time. Beyond the 10 minutes, there was no significant changes on adsorption of phenol ascribed to state of equilibrium condition was reached for maximum uptake. The results also indicate that for maximum removal of phenolate ions, ACS would need low residence time of adsorbate at solid – solution equilibrium interface which controls the rate of uptake (Kaman, *et al.*, 2016). At the 10 minutes, the removal efficiencies of phenol was 5.1595mg/g (85.99%) as shown in **Figure 3**.

This 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). 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 ability of the sites to adsorb phenol- thereby, increasing repulsive forces between solid- solution ions interface lowering the uptakes/ adsorption rate (Abu, *et al.*, 2018)

An equilibrium was established after the binding sites had been saturated with phenolate ions and there was minimal adsorption taking place. Therefore, for the maximum phenol removal from aqueous media, the optimum period for equilibration was at 10 minutes. In the subsequent experiments for maximum uptake agitation time was kept at 30 minutes.

Effect of adsorbate initial concentration on adsorption of phenol

The general observations in **Figure 4** for phenol were that the uptake (percentage removal) increases with increase in initial concentration up to concentration of 5.0 ppm, the sorption attains a plateau profile., q_e mg/g, approached steady state. Beyond 10ppm, the ACS adsorbent is said to be saturated and attained its operational optimum adsorption capacities (Mwangi, *et al.*, 2014). This is due to increase of mass transfer driving force between adsorbate and adsorbent, and thus the fruitful diffusion of phenolate ions / binding to the surface of adsorbent from solutions (Nayak, *et al.*, 2020). A similar profile was observed in the removal profile as shown in **Figure 4** due to the same reasons. In this study, the maximum percentage removal of 86.65% of phenol at 10ppm was reported as shown in **Figure 4**. This is in agreement with findings that have been reported by Bożena and Sylwia (2003), Mwangi *et al.* (2014) and Barrera (2020).

Effect of dosage of modulated adsorbent on adsorption of phenol

The findings show that the percentage removal of phenol increases gradually with the increase in the dose of adsorbent (Figure 5). This observation was attributed to increased adsorptive surface area and availability of more effective active adsorption sites resulting from the stoichiometrically increased dose of ACS. This implied that the number of active binding adsorptive sites increases with the increase in ACS biomaterial dose. These findings are in agreement to those reported in the literature (Saha, *et al.*, 2013; Mwangi, *et al.*, 2014; Sarker & Fakhruddin, 2017; Abu, *et al.*, 2018). In all the subsequent equilibration studies, therefore, the mass dosage was 0.1 grams.

Adsorption isotherms studies

The corresponding isotherms parameters and regression coefficients from each isotherm were evaluated for phenol and the results presented in **Table 1**

Table 1: Results for the Freundlich and Langmuir isotherms for phenol adsorption capacities

Parameters	Langmuir Model			Freundlich Model			Best Model Fitted
	Q _{max} (mg/g)	b / K _L (dm ³ /g)	R ²	1/n	K _f (mg/g)	R ²	
Phenol	4.2977	1.4284	0.999839	0.17252	3.8971	0.9172307	Langmuir

From the results in the **Table 1**, a Langmuir linear equation gave higher values of regression coefficients ($R^2 > 0.999839$) as compared to Freundlich linear equation ($R^2 > 0.9172307$). This shows that the experimental data perfectly suited or conformed to 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 phenol 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). And $1/n$ is less than one as observed in the **Table1**, indicates that the adsorbent binding sites is homogeneous and favourable normal adsorption. The maximum adsorption capacities (q_{max}) for phenol was 4.2977mg/g by the aminated cornstarch adsorbent.

Adsorption kinetics

The results obtained of the kinetics parameters for phenol are shown in **Table 2**.

Table 2: Results for kinetic parameters for adsorption of phenol onto ACS

Parameters	Pseudo – first order (K_1)			Pseudo – second order (K_2)			Best Model Fitted
	q_e (mg/g)	K_1 (mg/ g min ⁻¹)	R^2	q_e (mg/g)	K_2 (mg/ g min ⁻¹)	R^2	
Phenol	0.9410	0.0021	0.6356	3.6738	-0.1648	0.9978	Pseudo-second order

From the results in the **Table 2**, show that the 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, it was concluded that pseudo – second order kinetic model (K_2) fitted best to the experimental data than pseudo – first order (K_1). This was in agreement with studies by Kaman *et al.* (2016), Barrera, (2020) and Nayak, *et al.* (2020).

V. Conclusion

Based on the findings of the present study, it is concluded that modulated aminated cornstarch can be utilized as a novel, facile, low-cost and effective biopolymer resin for the uptake of phenol from aqueous media. The modulated cornstarch was successfully synthesized by anchoring amino functional group (triethanolamine) on it and this was confirmed by the FTIR spectra outcomes. The analysis revealed the functional groups and kinds of chemical bonds responsible for adsorption of PCs. The findings presented that the quantity of PCs adsorbed by the bioadsorbent were influenced by the following parameters viz dosage of adsorbent, solution pH, initial concentration of adsorbate and contact time. Batch mode studies showed that maximum removal of phenol was realized at a contact time of 10 mins, pH of 5.0 and constant temperature of 298 K. The dosage of ACS and initial concentration increases with the increase in uptake of phenolics. The maximum uptake of phenol occurred at initial concentration of 10ppm and then plateaued. The batch experimental data obtained best fitted into the Langmuir isotherm with regression coefficient, $R^2=0.999839$ and monolayer adsorption capacities of 4.2977mg/g for phenol. These adsorption capacities were relatively higher than reported processes, thus making the aminated cornstarch (ACS) an effectual adsorbent for removal of phenolic compounds from aqueous media. The adsorption mechanism was best described by the pseudo – second order (K_2) kinetic model.

Acknowledgement

Author is grateful to the Department of Physical and Biological Sciences, School of Pure, Applied and Health sciences, Murang'a University of Technology and the Department of Chemistry, Kenyatta University for provision of instruments/ facilities for analysis and logistics assistance accorded during the research periods of this study.

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

References

- [1]. 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. ISSN: 2319-2399. <https://www.iosrjournals.org>.
- [2]. 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>

- [3]. 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.
- [4]. 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
- [5]. 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 geomaterial. *J. Taiwan Inst. Chem. Eng.*, 80, 578–588.
- [6]. 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
- [7]. 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* 2020, 8, 665; doi:10.3390/pr8060665.
- [8]. El-Ashtouky, 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 (2013) 1534 – 1550.
- [9]. Haq F.; H. Yu.; L. Wang.; 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* (2019), doi: <https://doi.org/10.1016/j.carres.2019.02.007>.
- [10]. Ho Y. S. and McKay G. (1999). Pseudo-second order model for sorption processes. *Process Biochem.* 34, 451–465 (1999); doi:10.1016/S0043-1354(99)00232-8
- [11]. 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.
- [12]. 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 March 2018.
- [13]. 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 2014, Article ID 201626. <http://dx.doi.org/10.1155/2014/201626>.
- [14]. Griffiths, P.; Hasseth, J. A. (2007). *Fourier Transform Infrared Spectrometry*, 2nd Ed. Wiley-Blackwell. ISBN 0-471-19404-2
- [15]. 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
- [16]. 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.
- [17]. 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.
- [18]. 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.
- [19]. Ibrahim, R.K.; Fiyadh, S.S.; AlSaadi, 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.
- [20]. John, C. (2000). Interpretation of infrared spectra, a practical approach. *Encyclopaedia of analytical chemistry*. Chichester, John Wiley and Sons Ltd. pp 10815–10837.
- [21]. Kaur, B.; Ariffin, F.; Bhat, R. and Karim, A. A. (2012). *Food Hydrocolloids*, Elsevier, 26(2), 398–404. ISSN: 0268-005X.
- [22]. 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.
- [23]. 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.
- [24]. 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; 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
- [25]. Lagergren, S., (1898). The theory of so-called adsorption of soluble substances. *Handlingar* 24 (4): 1-39.
- [26]. 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 2022, Research Article ID 1125877, <https://doi.org/10.1155/2022/1125877>.
- [27]. Mbugua W. G. (2020). Facile remediation of fluoride in aquatic media using modified polyethylene container, (Doctoral dissertation, July 2020, Kenyatta University, Kenya).
- [28]. 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.
- [29]. 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, 133–142.
- [30]. 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.
- [31]. 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, 70-79. <http://dx.doi.org/10.1016/j.jenvman.2013.12.031>
- [32]. Nayak, A., Bhushan, B. and Gupta, V., (2020). Removal of Phenolics from Wastewater by Fe₂O₃ Impregnated Sawdust as Adsorbent: Adsorption Isotherm and Kinetic Studies. *Journal of Graphic Era University*, Vol. 8, Issue 1, 1-15. ISSN: 0975-1416 (Print), 2456-4281 (Online)
- [33]. 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.

- [34]. 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)
- [35]. 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.
- [36]. 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.
- [37]. Skoog, D., Holler, F. and Crouch, S. (2007). *Fundamental analytical chemistry: Principles of instrumental analysis*, 6th edition. United States, Thomson, Brooks/Cole. pp 169–173, 454-455, 672-673. ISBN 9780495012016.
- [38]. 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
- [39]. SudDhiraj. 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
- [40]. 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.
- [41]. 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>.
- [42]. US Environmental Protection Agency (2008). Supplement to 5th 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.
- [43]. US Environmental Protection Agency (1999). Alternative disinfectants and oxidants guidance manual, EPA Office of Water Report 815-R-99-014
- [44]. 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. Environ. Microbiol.* 64, 3225-3231.
- [45]. 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>
- [46]. World Health Organization (WHO) (1993). Guidelines for drinking water quality, World Health Organization. http://www.who.int/water_sanitation_health/dwq/gdwq2v1/en/.
- [47]. World Health Organization (WHO) (1996). Guidelines for drinking water quality, World Health Organization. Geneva. http://www.who.int/water_sanitation.../.
- [48]. World Health Organization (WHO) (2019). WHO, African. Water management.
- [49]. 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>

Haron Bosuben, et. al. "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)*, 15(08), (2022): pp 34-45.