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Adsorption of Cu (II) Ions from Aqueous Solution onto Chemically Prepared Activated Carbon from *Theobroma cacao*

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Authors' contributions

This work was carried out in collaboration with all authors. Authors JNG and JMK designed the study. Author DLA carried out the experiments after writing out the protocol that was validated by author JNN. Author JNG wrote the first draft of the manuscript. Authors DLA and TDN managed literature searches. Authors DLA and JNG managed the analyses of the study. All authors read and approved the final manuscript.

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ABSTRACT

This present research was aimed at studying the adsorption characteristics of Cu(II) ions from aqueous solutions onto two samples of low-cost, cocoa shell-based activated

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carbons (CSBAC) using the batch adsorption mode. Activated carbon samples were obtained by chemical treatment via pyrolysis using phosphoric acid (PAA) and potassium hydroxide (PHA) as activation agent. Findings from the studies unveiled a pH at zero-point charge (pHzpc) of 7.0 and 5.9 for PAA and PHA samples respectively. Contact time of 35 minutes for PAA and 15 minutes for PHA at $\text{pH}_{\text{max}} = 4$ by 0.1 g were observed. Optimum adsorption quantities were 62.2 mg/g for PAA and 42.2 mg/g for PHA for an initial metal ion concentration of 2400 ppm. The Langmuir model for PHA and Freundlich model for PAA best described the adsorption of Cu (II) ions from aqueous solution. The two CSBAC samples both obeyed pseudo-second order kinetics. Generally, these results indicate that CSBAC can be used as an effective and low-cost adsorbent for the removal of Cu (II) ions from aqueous solutions.

Keywords: Cocoa shell; chemical activation; activated carbon; Copper(II) ions; adsorption; kinetic model; isotherm model.

ABBREVIATIONS

PAA: Phosphoric acid activated carbon, PHA: Potassium hydroxide activated carbon, CSBAC: Cocoa shell-based activated carbons, In: Iodine number, ASTM: American Society for Testing and Materials, pHzpc: pH at zero-point charge.

1. INTRODUCTION

Voluntary or accidental water, air and soil pollution by some chemical substances of industrial (heavy metals, colorants, microorganics, toxic gases, etc.) or agricultural origin (pesticides, fungicides, fertilizers, etc) constitute a major source of environmental degradation. These problems have been receiving worldwide attention from researchers to savage the health of mankind [1]. Heavy metals on their part are well known for their non-biodegradation properties that render them very toxic even at very low concentrations to all organisms of the plant and animal kingdoms. They accumulate in living organisms even during mass transfer in trophic chain [2]. It is therefore imperative to partially or totally eliminate heavy metal ions from industrial effluents to acceptable levels.

Copper is used in cloth making, marine painting, electrical equipments, boilers, pipes, etc. International norms according to WHO prescribe limiting concentrations of Copper in drinking water to 1 mg/L of copper [3]. Although Copper constitutes one of the micronutrients in the human body, its accumulation have been reported in the liver, brain, pancreas and myocardium of humans that often leads to Wilson Disease [4,5]. Continual inhalation of Copper vapor may lead to lung cancer [6]. The development of several techniques and methods such as chemical precipitation, adsorption on mineral or organic materials, complexation, biosorption, cementation, solvent extraction, distillation, emulsified liquid membranes and membrane processes (microfiltration, ultrafiltration, nanofiltration, reverse osmosis, ion-exchange resins etc), are geared towards greater amelioration of the quality of the environment/water quality [7]. Amongst these methods, adsorption which is reported in this work has shown high potentials and simplicity in management in the depollution of industrial waste water, especially in the elimination of some heavy metals [8]. Nevertheless, its efficacy depends largely on the adsorbent (cost, availability, and its regeneration) put in place.

In this regard, much work has been carried out on diverse materials, be it of natural or biological origin in the elimination of heavy metals from aqueous solutions. Low cost and high adsorption capacity agricultural by-products such as saw-dust, coco fibers, coconut palm fibers, banana peelings, sugar cane bagasse, orange peelings and nut shells etc [9], cola nut shells in the adsorption of colorants [10] have been used as adsorbents for the removal of heavy metals from aqueous solutions. The adsorption of cadmium on bacterium cells and algae has been studied [11-13] for the adsorption of some heavy metals on cucumber pulps. Adsorption studies of crystal violet [14]; reactive yellow 2 dyes on activated carbons based on cocoa shells showed that they can serve as low-cost adsorbent material for colorants in aqueous solutions [15]. In 2011, in particular, the fixation of methylene blue in aqueous solutions by activated carbon produced from cocoa shells was reported in the literature according to which maximum monolayer adsorption capacity of 37.03 mg/g was obtained [16]. Also, 7.56 mg/g of Pb(II) ions was adsorbed maximally from aqueous solutions onto activated cocoa shells [17]. In another study, 111.1 mg/g of Cu (II) ions was found as maximum adsorption capacity in investigations carried-out on monolayer adsorption of Cu(II) ions on activated water-melon shells [18]. In yet another study, maximum adsorption capacities of Cu(II) ions from aqueous solution by activated sugar cane bagasse, orange peelings, mango saw-dust studied in 2007 stood at 3.19, 3.12, 2.89 mg/g, respectively [19]. Recently, the investigation of the adsorption of Cu (II) ions on synthetic goethite and natural red soils resulted in the following values respectively 78.2 mg/g, 41.2 mg/g, and 32.2 mg/g [20]. All these results show that the adsorbents act as substitutes or compliments to commercial activated carbon in waste-water treatment.

In the same vein, investigation of palm oil empty fruit bunch in the adsorption of Hg (II), Pb (II) and Cu (II) ions showed that the least adsorption capacity of 0.84 mg/g with respect to the others was by Cu(II) ions [21]. Maximum adsorption capacity of Cu (II) in aqueous solutions onto different initial masses of lignite (30, 45 and 60 g) gave the following values respectively: 4.045, 3.908 and 2.625 mg/g [22]. In Cameroon, the fifth largest cocoa producer in the world [23], agriculture represents an important part of total Gross National Products (GNP) and enormous quantities of agricultural waste products are generated on daily basis near agro-industrial zones/installations. Annual production of cocoa is estimated at 320,000 tons in 2015 according to reports [24]. Cocoa shells present post harvest environmental problems as large quantities are left behind as agric waste. The main purpose of this work was to valorize some of these local precursors (cocoa shells, *Theobroma cacao*) for the production of activated carbon. In this study, activated carbon was obtained by chemically treating grounded raw samples by phosphoric acid (PAA) and potassium hydroxide (PHA), followed by simple pyrolysis procedure.

2. MATERIALS AND METHODS

2.1 Collection and Pre-treatment of Raw Materials

In order to valorize low-cost local materials as activated carbons, the *forasteros* variety of cocoa shells (*Theobroma cocoa*) was used as precursors. The choice of this biomass was attributed to its availability in the sub-region in particular and in the world in general. Samples of raw-materials were collected basically one hour after the splitting of the cocoa pods after harvesting from cocoa plantations of the Santchou locality, a village situated in the West Region of Cameroon. These samples after collection were abundantly washed with distilled water to eliminate dusty and hydrosoluble substances and were sun-dried for 14

days, after which were grounded using RETCH SM 2000/1430 UPM grinder, which were further sieved to obtain fractions of diameter between 0.50 and 1.25 mm.

2.2 Chemical Activation and Pyrolysis

In this study, chemical activation was carried out with the help of phosphoric acid (H_3PO_4) and potassium hydroxide (KOH), as activation agents. The precursor materials obtained were of diameters ranging between (0.50-1.25 mm). They were chemically pre-treated before pyrolysis step, although the order could be reversed as prescribed by [25]. The method involved mixing the chosen precursor fraction of cocoa shells with either 10% wt/wt H_3PO_4 (for PAA samples) and 50% wt/wt of KOH (for PHA samples) in a 1:2 weight ratio before carbonization. The impregnated samples were placed in an oven at 110°C for 24 hours. Pyrolysis of the impregnated samples was carried-out for one hour duration in a carbolite furnace in the absence of air (oxygen) which was preheated to 400°C at a 10°C min^{-1} heating rate, which was then allowed to cool down to ambient temperature, after which a dry residue was obtained. Total elimination of phosphate ions from the acid samples of activated carbon obtained (PAA) were eliminated by abundantly washing with distilled water until a neutral pH was obtained [26]. On their part, the PHA samples were initially washed abundantly with a 10% solution of hydrochloric acid followed by abundant washing with distilled water until the pH of the resulting samples ranged from 6-7 in order to eliminate all chloride ions [27]. The resultant activated carbon samples (PAA and PHA) were then dried in an oven at 110°C for a period of 24 hours. The final material samples were grounded and then sieved to obtain particles with diameters less than 71 microns and later on conserved in desiccators for further use.

2.3 Characterization of Adsorbent

2.3.1 Iodine number (In)

The iodine number was measured according to the procedure established by the American Society for Testing and Materials (ASTM D2866-94) [28]. The iodine number is defined as the milligrams of iodine adsorbed by 1.0 g of carbon when the iodine concentration of the filtrate is 0.02 N. The iodine number is accepted as the most fundamental parameter used to characterize activated carbon performance.

Iodine number was employed in this study as a test for micro porosity via volumetric analysis. This fundamental test for the potentials of the prepared activated carbon determines its microporosity up to values as small as 2 nm. Iodine number is often correlated with sample specific surface area from BET studies, and is obtained from the following expression:

$$\text{Iodine number} = \frac{25.4 \times (20 - V_n)}{m_{AC}} \quad (1)$$

Where, m_{AC} (g) is the mass of the activated carbon and V_n (mL) the volume of the sodium thiosulphate solution at the equivalence point.

2.3.2 Standardization of iodine solution

10 mL of 0.02 N iodine solutions were pipetted into a conical flask. 2-3 drops of starch solution were added. The pale yellow color of iodine solution turned blue and was titrated with 0.005 N sodium thiosulphate till it became colorless.

2.3.3 Surface fonction determination by the boehm method

Titration of total surface acidity and basicity of the activated carbons was carried out via the Boehm method [29,30]. In the determination of acidic surface functions (carboxylic, lactonic, phenolic), 40 mL each of decimolar solutions of NaHCO_3 , Na_2CO_3 , NaOH and HCl , were introduced into different reactors and each put in contact with 0.10 g of activated carbon sample. Titration of excess base was done by HCl solution. In the determination of the basic functions, 0.1 g of activated carbon was put in contact with 40 mL of a decimolar solution of HCl and the excess acid titrated with NaOH . Stirring was maintained during 48 hours with the aid of a magnetic agitator.

2.3.4 Determination of pH at zero-point charge (pHzpc)

pH of zero charge, pHzpc, corresponds to a pH at which the surface charge is nul. pHzpc of the activated carbon was estimated according to standard procedure [31]. 50 mL of a decimolar solution of NaCl was introduced each into a reactor each containing 0.1 g of activated carbon to be analyzed. The pH of each solution was adjusted by addition of decimolar solutions of NaOH or HCl (by varying values of pH between 3 and 11). pHzpc was determined by the intersection point of the representative curves $\text{pH}(\text{final}) = f[\text{pH}(\text{initial})]$ and the first bisector curve. Stirring was maintained at 27°C for 48 hours with the aid of a multi-agitator system. The contents of the reactors were then filtered with Whatman N°4 filter paper after which the pH of the final solutions was measured.

2.3.5 Analysis by fourier-transform-IR spectrophotometer (FTIR)

In order to determine the surface functional groups existing on the carbon samples, FTIR were carried out on samples using infrared spectrophotometer (trade-mark bruker alpha-p spectrometer) with ethanol as solvent with a resolution of 4cm^{-1} within the interval $400\text{-}4000\text{ cm}^{-1}$.

2.4 Batch Adsorption Experiments (Equilibrium Studies)

2.4.1 Preparation of Cu(II) Ion solution

The UV-Visible absorption spectrum of Cu(II) ions was obtained by spectral scanning of a 3 g/L mother solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ between 770 and 870 nm. Results show a wavelength of maximum absorption of Cu(II) at 830 nm. The mother solution was prepared by dissolving 8.04834 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ($M = 170$, 48 g/mol at 99% purity by mass) in a liter of freshly prepared distilled water contained inside a volumetric flask, and homogenized (agitation for 1 hour). Successive dilution of mother solution gave rise to the working solutions.

2.4.2 Batch adsorption experiments

Kinetic and equilibrium studies of Cu(II) ions adsorption were carried out in a batch reactor maintained at 27°C . In each trial (in a total of ten), 0.1 g of carbon sample preserved as described above was weighed and introduced into 20 mL of a Cu(II) ions solution in a volumetric flask. The pH of the mixture was then adjusted by 0.1 N solution of HCl or NaOH to a pre-determined value to permit maximum adsorption. The different mixtures obtained were agitated within a time interval of 5-60 minutes in order to determine the time required for equilibrium to be attained. The residual Cu(II) ions concentration in each sample, after filtration of the residual solutions with Whatman filter paper N°4 was determined by UV-

visible spectrophotometer (CORNING 259) at 830 nm wavelength. The sorption capacity of samples at equilibrium (Q_e) and the percentage removal (% R) are given by the relations (2) and (3) below:

$$Q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

$$R = \frac{C_0 - C_t}{C_0} \times 100 \quad (3)$$

Where C_0 is the initial concentration of Cu (II) ions, C_e is the equilibrium concentration, while V is the volume of the Cu (II) ions solution.

2.5 Kinetic Models

Several kinetic models are often used in modeling the adsorption mechanism of dissolved solutes on adsorbents. In this study, four kinetic models have been studied in describing the adsorption phenomenon of Cu (II) ions onto the two activated carbon samples studied herein: Pseudo-first order, pseudo-second order, Elovich's model and intra-particle diffusion model.

2.5.1 Pseudo first-order

Pseudo-first order or Lagergren [32] model was established for liquid phase adsorption and is applicable only in the first few minutes of adsorption. It requires pre-knowledge of the adsorbed quantity at equilibrium. This model takes the form of the following differential equation [33].

$$\frac{dQ_t}{dt} = K_1(Q_e - Q_t) \quad (4)$$

where, k_1 is the pseudo-first-order rate constant (min^{-1}); Q_e and Q_t are the adsorption capacities at equilibrium and at a given time t expressed in (mg/g).

By integration of equation (4) within the time interval $t = 0$, and $t = t$ corresponding to $Q_t = 0$ and $Q_t = Q_t$, the following relation is obtained :

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad \text{with} \quad \ln C_t = -k_1 t + \ln C_0 \quad \text{after reduction} \quad (5)$$

Linear plot of $\ln(Q_e - Q_t)$ versus $f(t)$ should provide values for k_1 and Q_e from the gradient and y-intercept respectively.

2.5.2 Pseudo second-order model

Represented by equation (6) below, the pseudo-second order model [34,35] has been frequently used in diverse experiments involving the adsorption of organics and heavy metals on activated carbon. The pseudo-second order chemisorption kinetic rate equation is expressed as [36]

$$\frac{dQ_t}{dt} = K_2(Q_e - Q_t)^2 \quad (6)$$

Where, k_2 is the pseudo-second-order rate constant ($\text{mg.g}^{-1}.\text{min}^{-1}$).

By integration between $t = 0$ and $t = t$ corresponding to $Q_t = 0$ and $Q_t = Q_t$, we obtain the following relation:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e e^2} + \frac{t}{Q_e} \quad (7)$$

The parameters k_2 and Q_e are obtainable from the intercepts and the slope of the graph of t/Q_t versus t .

2.5.3 Elovich model

This model (equation 9), which is often used in modeling chemisorptions of gases on solids can also satisfactorily be applied to solid-liquid adsorption systems especially those with heterogeneous adsorption surfaces [37].

$$\alpha \cdot dQ/dt \cdot \exp(-\beta qt) \quad (8)$$

where, α is the initial adsorption rate (mg/g.min) and β , the desorption rate constant (g/mg) during any one experiment. The integrated and simplified equation is:

$$Q = \frac{1}{\beta} \ln(\alpha \beta t) + \frac{1}{\beta} \ln(t) \quad (9)$$

The value of the constants can be obtained from the slope and intercepts of a plot of $Q_t = f(\ln\{t\})$.

2.5.4 Intra-particle diffusion model

The intra-particle diffusion model or the Weber and Morris equation [38] models the type of diffusion mechanism involved in adsorption processes. It is given here by equation (10):

$$Q_t = k_{id} t^{1/2} + C \quad (10)$$

Where k_{id} is the intra-particle diffusion constant (mg.g⁻¹.min^{-1/2}). The linear form of this equation takes the following form [39].

$$\ln R = \ln K_{id} + a \ln t \quad (11)$$

Where; R is the percentage of Cu(II) ions removed at instant t and a is a constant that depends on the adsorption mechanism. When intra-particle diffusion plays a significant role in controlling the kinetics of the sorption process, the plots of $\ln R$ versus $\ln t$ yield straight lines passing through the origin and the slope gives the rate constant, k_{id} . However, when the transport of the solute molecules from the liquid phase up to the solid phase boundary plays the most significant role in adsorption, the liquid film diffusion model may be applied.

2.6 Isotherm Models

Maximum sorption capacities at a given temperature are obtainable from adsorption isotherm models. In this study, three adsorption models of Cu (II) ions on two activated carbons derived from cocoa shells have been investigated: Langmuir, Freundlich and Dubinin-Radushkevich-Kaganer (D-R-K) models.

2.6.1 Langmuir adsorption isotherm

In this model valid for monolayer adsorption (equation 14), the quantity adsorbed Q_e (mg/g) is related to the maximum adsorption capacity of the adsorbent Q_m (mg/g), equilibrium adsorbate concentration C_e (mg/L) at a given temperature. The general form of the Langmuir equation is [33].

$$\frac{Q_e}{Q_m} = \frac{K_L C_e}{1 + K_L C_e} \quad (12)$$

Where, K_L is the Langmuir adsorption constant (L/mg). The linear transformation of this model takes the following expression:

$$\frac{1}{Q_e} = \frac{1}{Q_m K_L C_e} + \frac{1}{Q_m} \quad (13)$$

A graph of $1/Q_e$ versus $1/C_e$ provides values for the constants $1/KQ_m$ (gradient) and $1/Q_m$ (y-intercept) respectively.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L , which is defined as:

$$R_L = \frac{1}{1 + K C_0} \quad (14)$$

The R_L value indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) as shown in Table 3 in this work.

2.6.2 Freundlich adsorption Isotherm

Adsorption of micro pollutants is best modeled by Freundlich isotherm which takes the following mathematical expression [36]:

$$Q_e = K_f C_e^{1/n_f} \quad (15)$$

where, Q_e is the quantity of Cu^{2+} ions adsorbed per gram of adsorbent material (mg/g); and C_e is the concentration of Cu^{2+} ions at equilibrium (mg/L).

K_f and $1/n_f$ are Freundlich constants that characterize adsorbent efficiency with respect to a given adsorbate. Equation (14) is the linear form of the Freundlich isotherm.

$$\ln Q_e = \ln K_f + \frac{1}{n_f} \ln C_e \quad (16)$$

A linear graph of $\ln Q_e$ versus $\ln C_e$ gives the values of $1/n_f$ (gradient) and $\ln K_f$ (y-intercept). The $1/n$ values indicate the type of isotherm to be irreversible $1/n = 0$, favorable $0 < 1/n < 1$, unfavorable $1/n > 1$.

2.6.3 Dubinin – Radushkevich - Kaganer adsorption model

Langmuir and Freundlich isotherms are insufficient to explain the physical and chemical characteristics of adsorption. D-K-R isotherm is commonly used to describe the sorption isotherms of single solute systems. The D-K-R isotherm, apart from being an analogue of

Langmuir isotherm, is more general than Langmuir isotherm as it rejects the homogeneous surface or constant adsorption potential. The D-K-R isotherm is expressed as [33].

$$Q_e = Q_{\max} \exp \left[\frac{\left(RT \ln \left(1 + \frac{1}{C_e} \right) \right)^2}{-2Ea^2} \right] \quad (17)$$

where, Ea is the main energy of adsorption and gives information about the physical and chemical features of adsorption. The linear form of the D-K-R isotherm equation is:

$$\ln Q_e = \ln Q_{\max} - \beta \epsilon^2 \quad (18)$$

Where, $\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right)$ is called the Polanyi Potential.

3. RESULTS AND DISCUSSION

3.1 Characterization of Adsorbents

3.1.1 Chemical composition of raw cocoa shells

The chemical composition of raw cocoa shells was determined by X-ray fluorescence using Bruker-S4 Pioneer Wavelength Dispersive Fluorescence Spectrometer (WDFS) analyzer. In this study, X-ray fluorescence showed the following percentage compositions for the raw materials (cocoa shells): K_2O (83.28%); CaO (4.905%); MgO (1.04%); SiO_2 (0.671%); SO_3 (0.652%); P_2O_5 (0.52 7%); Fe_2O_3 (0.467%); Al_2O_3 (0.329%); MnO (0.224%); TiO_2 (0.112%); Rb_2O (0.0867%); ZnO (0.0793%); CuO (0.0468%); Na_2O (0.041%); SrO (0.0259%); LOI (7.21%); Sum (99.6967%).

3.1.2 Iodine number test (In)

Iodine number (In) is a fundamental parameter used to characterize activated carbon performance. It is a measure of the micropore content of the activated carbon and is obtained by adsorption of iodine from solution by the activated carbon sample. The micropores are responsible for the large surface area of activated carbon particles and are created during the activation process [28]. Tests were carried out according to the ASTM D2866-94 procedures, and the results obtained for activated carbons prepared by chemical activation (Fig. 1) suggest that the values of (In) obtained for PHA based-carbon is greater than the value obtained for PAA based-carbons with values 538 mg/g and 500 mg/g respectively. This implies that there are more micropores in PHA than PAA.

3.2 Determination of pH at Zero-point Charge (pH_{zpc})

Basic or acidic character of the activated carbon samples are often indicated by values of pH_{zpc} obtained and consequently, knowledge of net surface charge (according to the pH of the solution). Thus, for manipulations for which pH_{zpc}>pH activated carbon samples studied have positively charged surfaces while negatively charged ones are obtained for pH_{zpc}<pH [40]. In the liquid phase, knowledge of pH_{zpc} is of great importance in interpreting the electrostatic interactions between molecules and adsorbent material. pH at zero-point charge (pH_{zpc}) was obtainable from the graph of pH_{final} versus pH_{initial} (Fig. 2)

from which we infer neutral character for PAA ($pH_{zpc} = 7.0$) and acidic character for PHA ($pH_{zpc} = 5.9$).

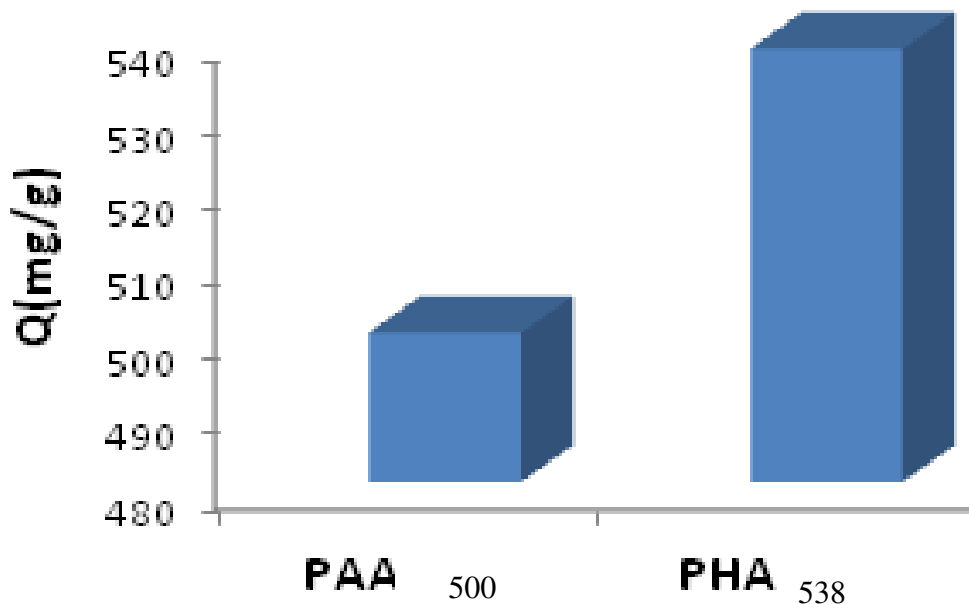


Fig. 1. Iodine number test for PAA and PHA

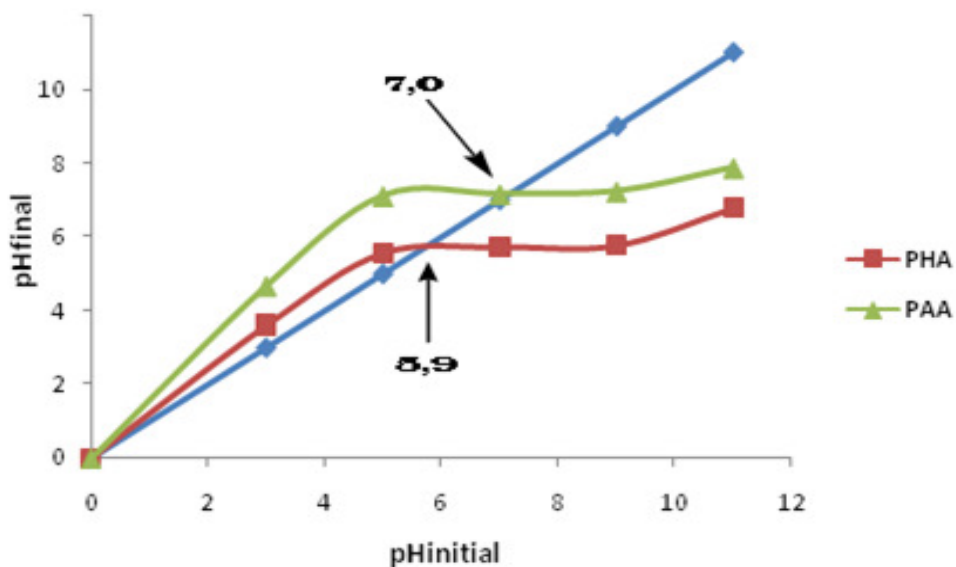


Fig. 2. Graph for the determination of pH_{zpc} for PAA and PHA

3.3 Determination of Oxygen Containing Functional Groups

Nature and quantity of functional groups on the activated carbons were obtained from the titration of surface functional groups [29,30]. The quantification of the surface functions

(basic or acidic) of the two activated carbon samples have been presented on (Table 1). The validation of our results was through Boehm titration which was carried out in triplicate measurements. Results in (Table 1) show that the two activated carbon samples PAA and PHA have different chemical properties. PAA-based CSBAC present an equivalent quantity of oxygen-based surface groups (acid and basic) therefore confirming its neutral character while PHA-based CSBAC show more acidic than basic groups, confirming its acidic character. We can therefore conclude that the quantification of the surface functional groups by the Boehm method is coherent with pH_{zpc} values obtained for each carbon sample (Fig. 2) [41]. The two carbon samples PAA and PHA contains carboxylic groups and very small quantities of lactonic groups, on the other hand, PAA-based carbon contains more phenolic groups than PHA based carbons (Table 1).

Table 1. Quantification of surface oxygen-containing groups by the Boehm method

Activated carbon	Carboxylic (meq g ⁻¹)	Lactonic (meq g ⁻¹)	Phenolic (meq g ⁻¹)	Total acid (meq g ⁻¹)	Total basic (meq g ⁻¹)	Total (meq.g ¹)	Character
PAA	0.271	0.008	0.058	0.337	0.293	0.620	Neutral
PHA	0.222	0.005	0.015	0.242	0.131	0.373	Acid

3.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis have been used in confronting obtained results to those from Boehm test and from pH_{zpc} measurements. IR spectra of PAA and PHA activated carbons are represented in (Figs. 3 and 4) below.

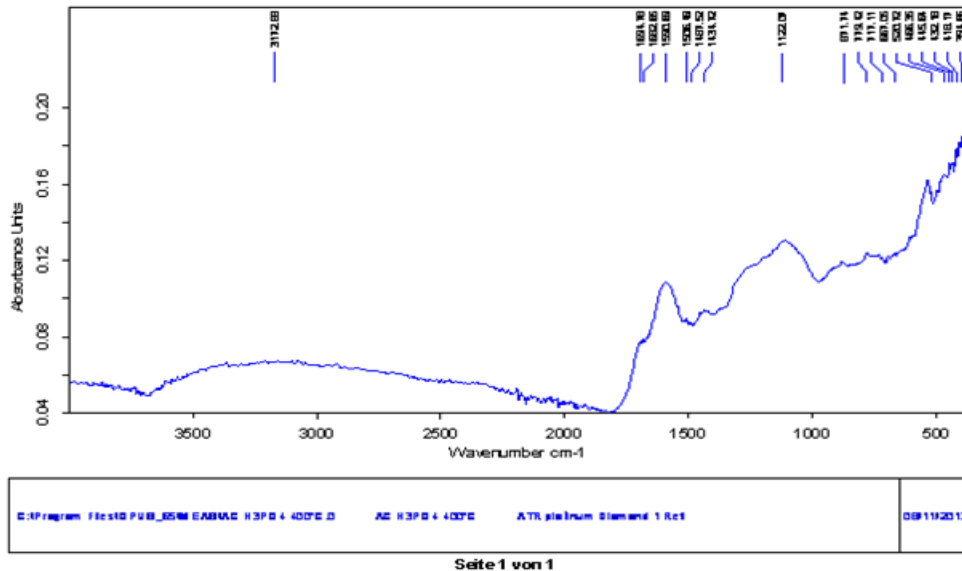


Fig. 3. FTIR spectrum for PAA

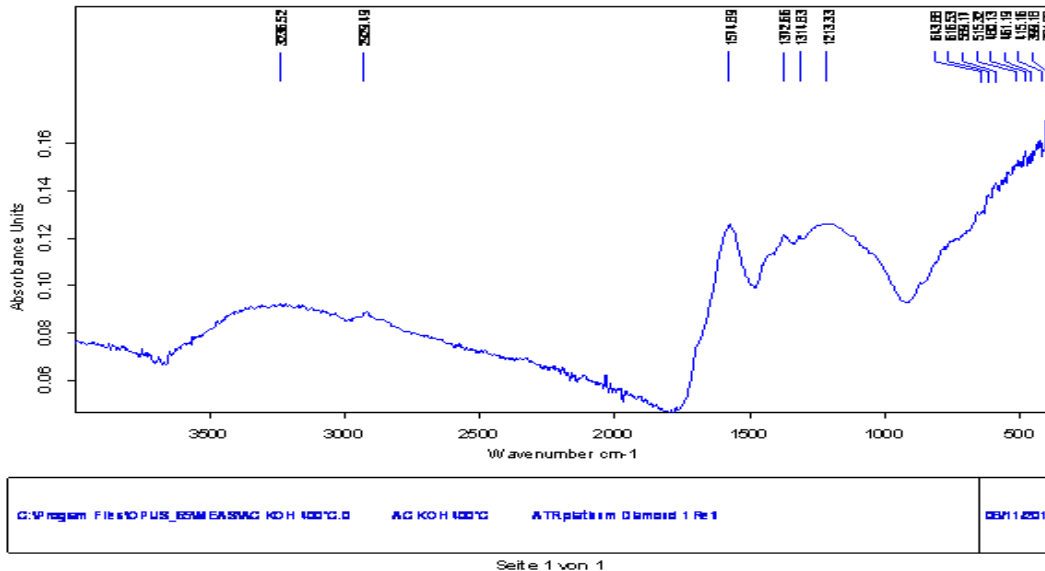


Fig. 4. FTIR spectrum for PHA

The most intense bands in the IR spectrum of phosphoric acid-based activated carbon (PHA) were: 418, 520, 667, 871, 1122, 1487, 1434, 1487, 1506, 1590, 1682, 1694, 3172 cm^{-1} . The large absorption band observed at 3172 cm^{-1} is attributed to hydrogen bond-stretching and may be the characteristic peak of the carboxylic, phenolic or alcohol hydroxyl groups or water adsorbed activated carbon. Absorption bands between 1700–1650 cm^{-1} with maximum at 1694 cm^{-1} and 1682 cm^{-1} is attributed to C=O bond stretching of the carboxylic anhydride groups. The pic observed at 1590 cm^{-1} is attributed to the carbonyl functional group. The region towards 1506, 1487, 1434 cm^{-1} provide some clues to the relative abundance of bending of CH_2 and CH_3 or of the O-H bending supported by the existence of phenols or carboxylic groups. The pick observed at 1122 cm^{-1} is attributed to the ionized chemical bond, P^+-O^- , found in the esters of phosphate acids [42] and to symmetric vibrations of the P-O-P chains (polyphosphate) [43]. The absorption band from 900–600 cm^{-1} can be attributed to C – O – C groups of esters or ethers.

On the IR spectrum of PHA-based CSBAC (Fig. 4), we observe a large absorption band from 3600-2000 cm^{-1} and presents a maximum at 3236 cm^{-1} and 2929 cm^{-1} . The pick corresponding to 3236 cm^{-1} is assigned to O–H stretching vibrations of hydrogen bonded hydroxyl, or carboxylic groups, and the pick situated at 2929 cm^{-1} is attributed to C=O bond stretching of ketones. The spectra of PHA based CSBAC equally show a pick situated at 1574 cm^{-1} due to C=C bond vibrations of aromatic rings. The shoulder at 1371.53 cm^{-1} can be ascribed to N-O stretching of aliphatic nitro compounds of the activated carbon derived from sodium hydroxide activation [40]. The band between 600–400 cm^{-1} corresponds to C-H bond vibrations in the aromatic ring. From the foregoing, the functional groups present on PAA-based CSBAC are phenols, carboxylic, esters or ethers while those present on PHA-based CSBAC are carboxylic, ketones, aliphatics, which are all in line with other results from the Boehm method.

3.5 Influence of Contact Time

During adsorption processes, the rate of mass transfer from the liquid to the solid phase is influenced by contact time between the two phases. In order to determine the effect of the contact time on the extent of adsorption, 0.1 g of the adsorbent was stirred with a 20 mL solution of Cu(II) ions of initial concentration 2400 mg/L for a time interval of 5 - 60 minutes for PAA and PHA at pH = 4.0. The experimental results obtained for the adsorption of Cu(II) ions during various contact times are illustrated in (Fig. 5). It can be observed that the quantity adsorbed increases with time, then attains a constant value beyond which no further adsorption took place. It can be inferred from these results that adsorption takes place in two stages: an initial rapid phase which attains saturation point within 15 and 35 minutes for PHA and PAA, attributed to the presence of free adsorption sites at the surface of the adsorbents [44]. Once the Cu(II) ions are adsorbed from solution onto these sites, they block the adsorption pores (which are of smaller sizes) from subsequent adsorption. As a consequence, adsorption speed decreases and that marks the onset of the slow second phase (step) from 35 to 60 and 15 to 16 minutes corresponding to PAA and PHA respectively. Therefore, surface adsorption sites are exhausted with time. The remaining vacant sites are difficult to be occupied by the cation due to repulsive forces between adsorbate present in solid and bulk phases [45]. We also observed from (Fig. 5) that adsorption reach equilibrium within 35 and 15min for PAA and PHA, respectively.

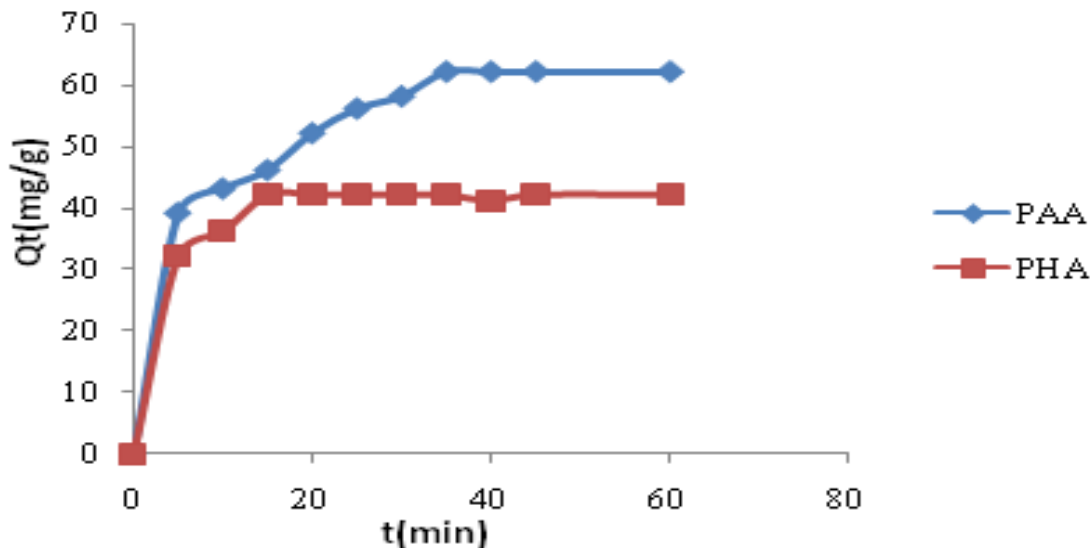


Fig. 5. Effect of contact time on the adsorption of Cu(II) ions on PAA and PHA

3.6 Influence of pH

Sorption of metallic ions from aqueous solutions depends very much on pH as it influences surface charge, degree of ionization and the nature of the adsorbent ionic species in solution [46]. (Fig. 6) represents the effect of initial pH of the solution on the sorption of Cu (II) ions onto PAA and PHA using 2400 mg/L initial Cu (II) concentration and 0.1 g of adsorbent. pH was varied between 2 and 4 in the present study. Sorption potentials of PAA and PHA for

Cu(II) ions were seen to increase with solution pH appreciably up to pH 4.0 as shown in (Fig. 6). The optimum pH for Cu (II) ions adsorption by PAA and PHA was found to be 4.0.

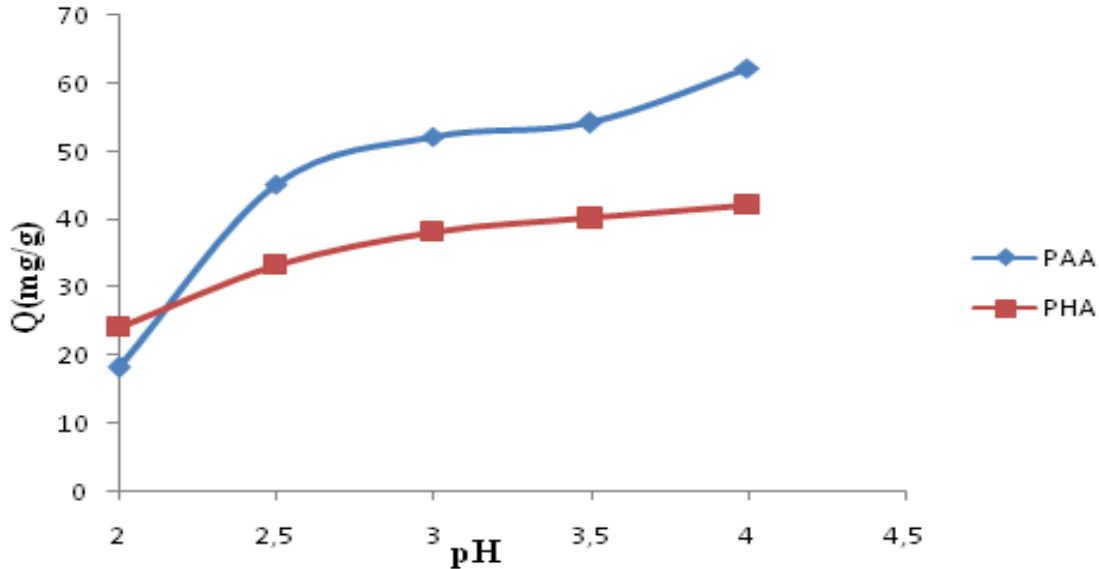


Fig. 6. Influence of pH on copper (II) ion adsorption on PAA and PHA

At strong pH range ($\text{pH} < 3$) we observed low values of adsorbed quantities. This is attributed to the fact that H^+ ion concentration is high in solution which induces competition (in favor of H^+) for free adsorption sites between Cu (II) and H^+ ions [47]. Adsorbed quantities have been found to decrease as surface becomes negatively charged (excess OH^- ions) at $\text{pH} > 4$ and this too is attributed to the precipitation of $\text{Cu}(\text{OH})_2$ and adsorption becomes impossible [48]. From these results we can conclude that maximum adsorption/retention capacity of adsorbents for Cu (II) ions is at $\text{pH} = 4.0$.

3.7 Influence of Adsorbent Dose

The influence of the adsorbent concentration on the removal of Cu (II) ions from aqueous solution was studied by varying their concentration from 0.1 to 0.6 g. (Fig. 7) represents the influence of adsorbent dose on the adsorption of Cu (II) ions onto PAA and PHA using 2400 mg/L initial Cu (II) ions concentration at $\text{pH} = 4.0$. Adsorbed quantity decreased with increasing adsorbent dose. This is explained by the fact that an increase in adsorbent dose leads to an agglomeration of unit cells and consequently a decrease in intercellular distances which in turn produces a screening effect leading to the protection of the adsorption sites of the adsorbent [49]. Furthermore, maximum quantity adsorbed, $Q_e = 62.2$ and 42.2 mg/g for PAA and PHA respectively, was reached for 0.1 g of each of the adsorbents as presented on (Fig. 7).

3.8 Influence of Initial Concentration

On the basis of the results of the preceding paragraph, the analysis of the effect of the initial concentration of Cu (II) ions were hence carried out at $\text{pH} 4.0$ on 0.1 g of each adsorbent samples (both PAA and PHA), mixed with 20 mL of the aqueous solution at $(27 \pm 1)^\circ\text{C}$ for a

duration of 35 and 15 minutes respectively for PAA and PHA. (Fig. 8) shows the variation of amount adsorbed versus concentration of Cu (II) ions for each adsorbent. The results obtained show that an increase in the initial concentration between 900 and 2400 ppm leads to a change in the quantity adsorbed from 32.2 mg/g to 62.2 mg/g for PAA and from 29.2 mg/g to 42.2 mg/g for PHA. This increase in adsorbed quantity with initial concentration of metal ion is due to the fact that an increase in the concentration of metal ion increases the collisions between the molecules of the metal and the adsorption sites. Also, with increasing metal concentrations the binding sites become more quickly saturated as the amount of adsorbent concentration remained constant [50]. This result also show that maximum adsorption capacity for both adsorbents PAA and PHA is reached at initial adsorbate concentrations of 2400 ppm.

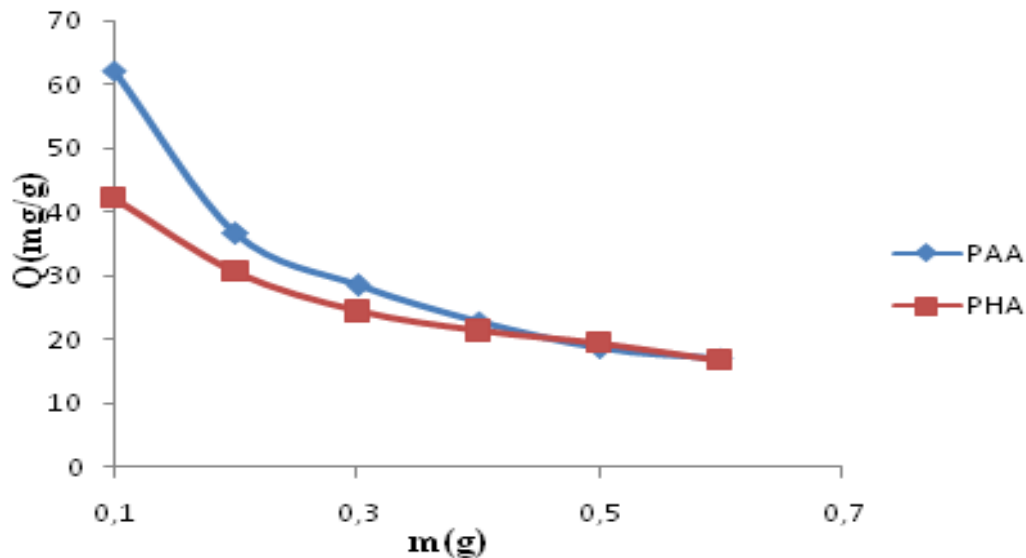


Fig. 7. Influence of adsorbent dose for the uptake of copper (II) ions on PAA and PHA

From these results we observe that, of the two activated carbon samples studied, PAA (62.2 mg/g) adsorbs better than PHA (42.2 mg/g). This is in contradiction with the awaited results [28], because iodine number of PHA (538 mg/g) is greater than that of PAA (500 mg/g). This can then be directed toward the size of the Cu (II) ions and the micro pores.

3.9 Kinetic Model

Sorption performances of the CSBAC samples (PAA and PHA) were estimated through kinetic and equilibrium studies. Four Kinetic models that were applied in this study provided pieces of information on the sorption mechanisms of Cu (II) ions onto the two samples. The straight-line plots have been represented on (Figs. 9, 10, 11, 12 and Table 2) gives all the kinetic parameters deduce from the plot. Correlation coefficients, R^2 obtained (0.995 for PAA and 0.998 for PHA respectively) show that the pseudo second-order model best describes the adsorption of Cu (II) ions from aqueous solutions. This implies that adsorption of Cu (II) ions onto both adsorbents may occur through a chemical process involving the valence forces of the shared or exchanged electrons [34,35]. This means that chemisorption reaction or an activated process becomes more predominant in the rate-controlling step for the

system. A comparison of the R^2 values for intraparticle diffusion (Fig. 12) for both samples show that the rate limiting step governing the adsorption of Cu (II) onto CSBAC is by pore diffusion for PAA but not PHA.

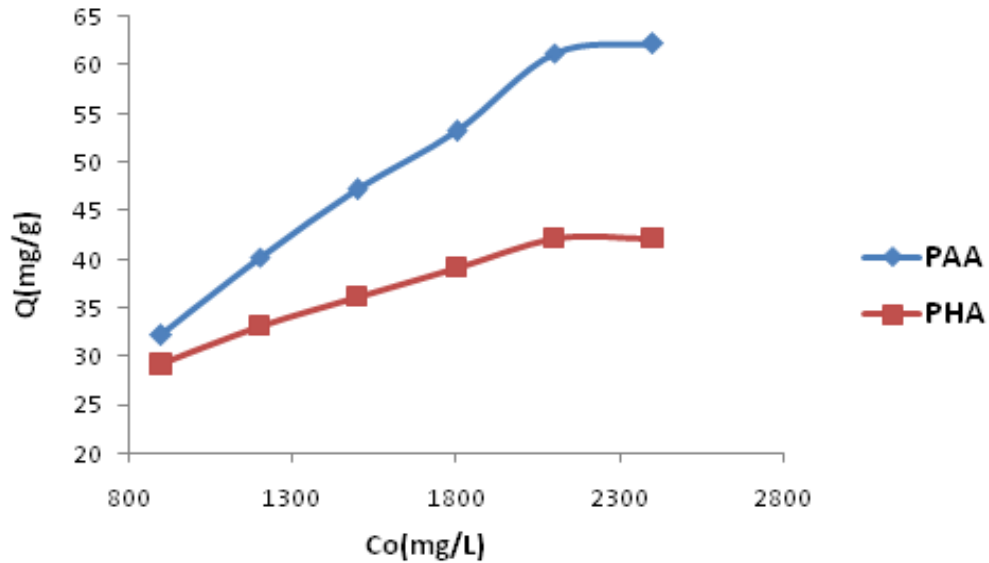


Fig. 8. Effect of initial concentration on copper (II) ion adsorption on PAA and PHA

3.9.1 Pseudo first-order model

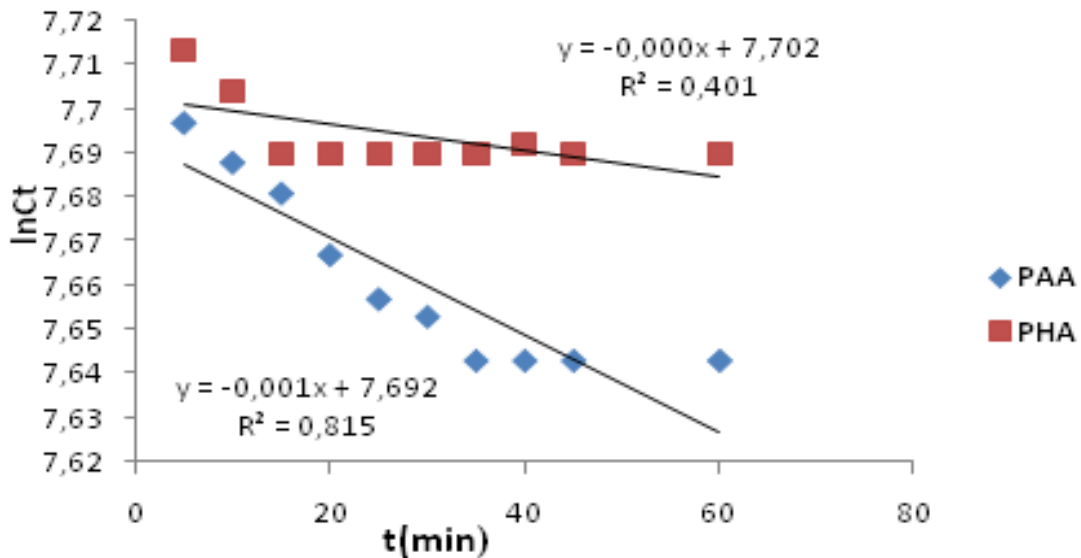


Fig. 9. Linearized pseudo-first order plots for $C_0=2400\text{mg/L}$, $V=20\text{mL}$, $\text{pH}=4$, $m=0.1\text{g}$ adsorbent

3.9.2 Pseudo second-order model

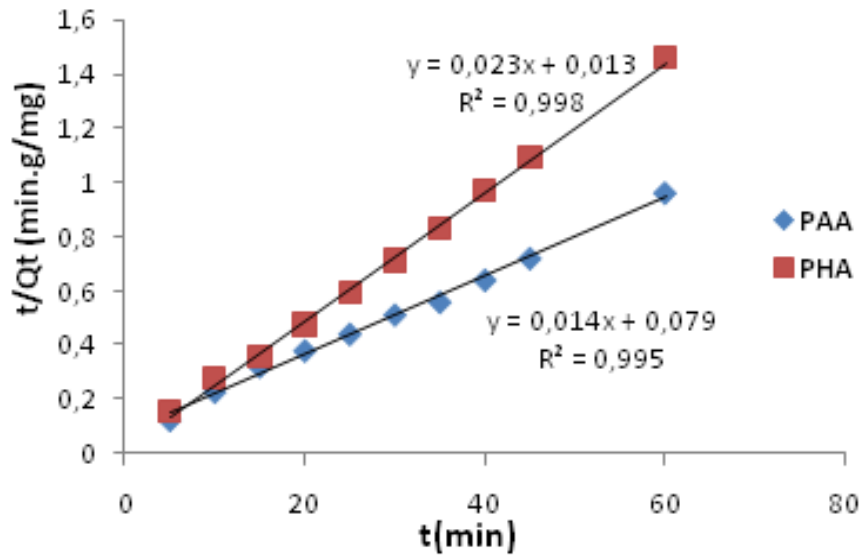


Fig. 10. Linearized pseudo-second order plots for $C_0=2400\text{mg/L}$, $V = 20 \text{ mL}$, $\text{pH} = 4.0$, $m = 0.1 \text{ g adsorbent}$

3.9.3 Elovich model

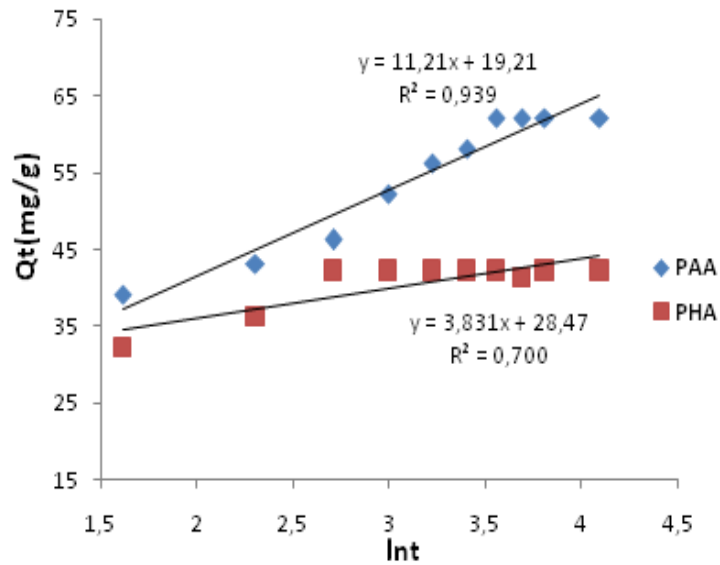


Fig. 11. Linearized elovich plots for $C_0 = 2400 \text{ mg/L}$, $V=20 \text{ mL}$, $\text{pH} = 4.0$, $m = 0.1 \text{ g adsorbent}$

3.9.4 Intra-particulaire diffusion model

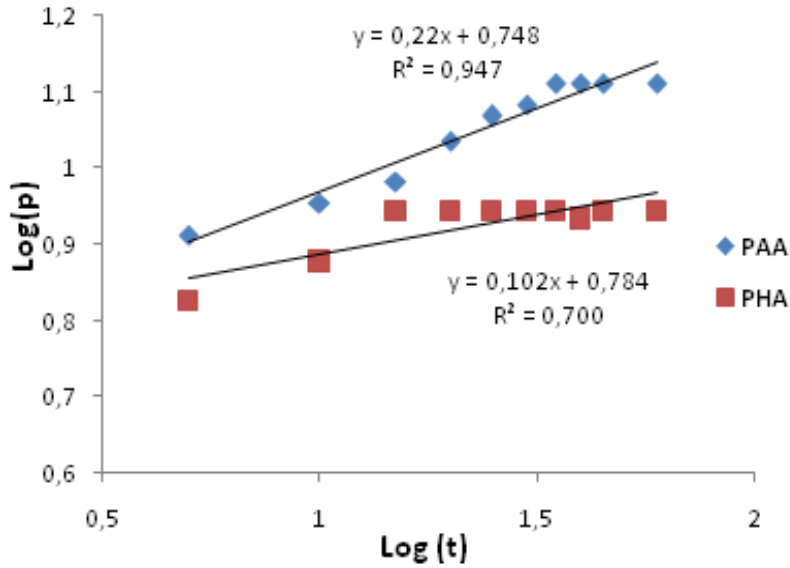


Fig. 12. Linearized intraparticle diffusion plots for $C_0 = 2400 \text{ mg/L}$, $V = 20 \text{ mL}$, $\text{pH} = 4.0$, $m = 0.1 \text{ g adsorbent}$

3.10 Adsorption Isotherms

Equilibrium adsorption isotherm is one of the most important data used in understanding the mechanism of adsorption systems. The equilibrium adsorption data were analyzed by the Langmuir, Freundlich, and Dubinin-Kaganer-Radushkevich (D-K-R) adsorption isotherm models. These isotherm models are characterized by certain constants whose values represent surface properties as well as sorbent affinities of the adsorbed species. These parameters for the two carbon samples (PAA and PHA) have been assembled in (Table 3) and the modeling of the adsorption isotherm presented on (Figs. 13, 14 and 15).

Table 2. Adsorption parameters for the different models

Models	Parameters	Adsorbents	
		PAA	PHA
Pseudo-first order	R^2	0.815	0.401
	$K_1 (\text{min}^{-1})$	0.001	0.000
Pseudo-second order	R^2	0.995	0.998
	$K^2 (x10^{-3} \text{g/mg. min})$	2.481	40.70
	$Q_e (\text{mg/g})$	71.42	43.47
Elovich	R^2	0.939	0.700
	$\beta (\text{g/mg})$	0.090	0.261
	$\alpha (\text{mg/g min}) x10^{-9}$	62.60	4.701
Intra-particle diffusion	R^2	0.947	0.700
	$K_{id} (\text{min}^{-1})$	2.112	2.190
	$a (\text{mg/g})$	0.220	0.102

Linear curves, obtained by plotting C_e/Q_e versus C_e , indicate the validity of Langmuir isotherm and $\ln Q_e$ versus $\ln C_e$, indicate the validity of Freundlich isotherm and $\ln Q_e$ versus

ϵ^2 , indicate the validity of Dubinin-Radushkevich-Kaganer isotherm. The values of the correlation coefficients from (Table 3) show that all three isotherm models describe the sorption process fairly well (for both samples) but the very best correlation for PHA samples is from Langmuir with $R^2=0.994$. Maximum adsorption capacity according to Langmuir (monolayer adsorption) is equal to 58.82 mg/g. From the different values of R_L (Table 4 and for $R_L < 1$), we can conclude that Cu (II) ions adsorption onto PHA carbon sample is favorable within the concentration range studied [51]. (Table 3) shows that the best correlation of the experimental results is obtained with the Freundlich isotherm model with PAA ($R^2=0.995$). This result suggest that Cu (II) ions are adsorbed onto the adsorbent surface of the PAA carbon in different ways. Also from the values of the parameter $1/n$, it comes out that adsorption is favorable for $1/n < 1$ for the two adsorbents, which implies an increase in the adsorption capacity and the appearance of new adsorption sites, and as such, a homogenous adsorption at the surface of PAA and PHA. The positive values of sorption energy ($E_a = 2.411$ and 3.194 kJ/mol) indicate that the adsorption of Cu (II) ions by PAA and PHA respectively is endothermic and the value is less than 8 kJ/mol. This also is indicative of weak interactions between the adsorbent (PAA and PHA) and the Cu (II) ions [52]. The Q_m values obtained for the present system in comparison with those reported in the literature for sorption of Cu (II) ions onto various adsorbents (Table 5) revealed that PAA and PHA are effective adsorbents in removing copper from aqueous solutions.

Table 3. Isotherm models parameters of adsorption

Models	Parameters	Adsorbents	
		PAA	PHA
Langmuir isotherm	R^2	0.969	0.994
	Q_{max} (mg/g)	166.66	58.82
	K_L ($\times 10^{-4}$ L/mg)	2.877	11.83
Freundlich isotherm	R^2	0.995	0.980
	$1/n$	0.722	0.375
	K_F (L/g)	0.252	2.363
D-K-R isotherm	R^2	0.950	0.954
	K_D	0.086	0.049
	Q_{max} (mg/g)	66.75	43.81
	E_a (kJ/mol)	2.411	3.194

Table 4. Langmuir isotherm with separation factor (R_L)

Concentration (ppm)	900	1200	1500	1800	2100	2400
Adsorbents	R_L					
PAA	0.794	0.743	0.698	0.658	0.623	0.591
PHA	0.484	0.413	0.360	0.319	0.287	0.260

Table 5. Comparison of adsorption capacity of copper (II) with other adsorbents

Adsorbents	Q_m (mg/g)	References
Watermelon shell	111.1	[18]
Orange peel, sawdust bagasse	3.19; 3.12; 2.89	[19]
Palm oil empty fruit bunch	0.84	[21]
Kolubara lignite	4.045 ; 3.908 ; 2.625	[22]
PAA	62.2	Present Study
PHA	42.2	Present Study

3.10.1 Langmuir isotherm

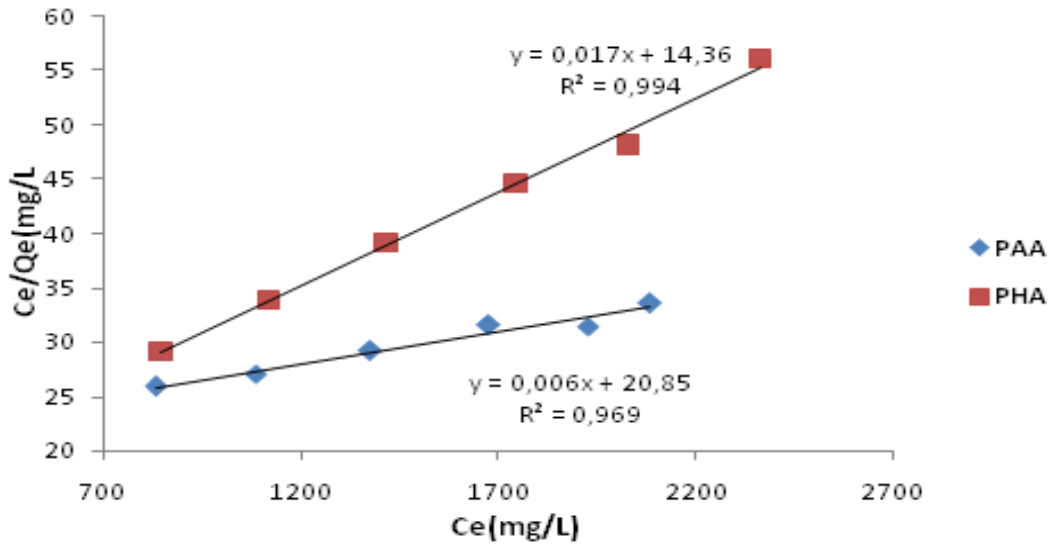


Fig. 13. Linear plot of langmuir model, for $C_o = 2400$ mg/L, $V = 20$ mL, $pH = 4.0$, $m = 0.1$ g adsorbent

3.10.2 Freundlich adsorption isotherm

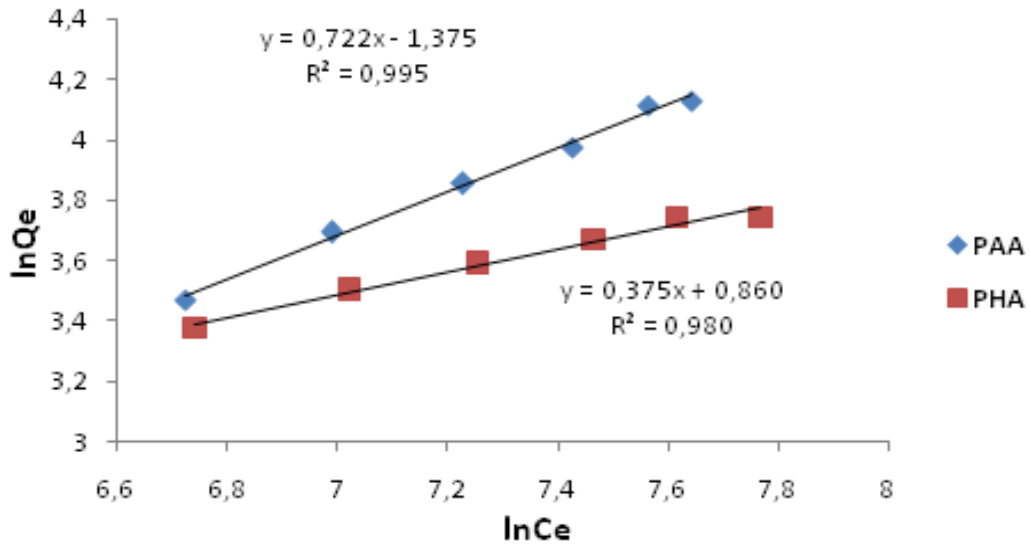


Fig. 14. Linear Plot of the model of freundlich for $C_o = 50$ mg/L, $V = 20$ mL, $pH = 4.0$, $m = 0.1$ g adsorbent

3.10.3 Dubinin et radushkevich kaganer (DRK) isotherm model

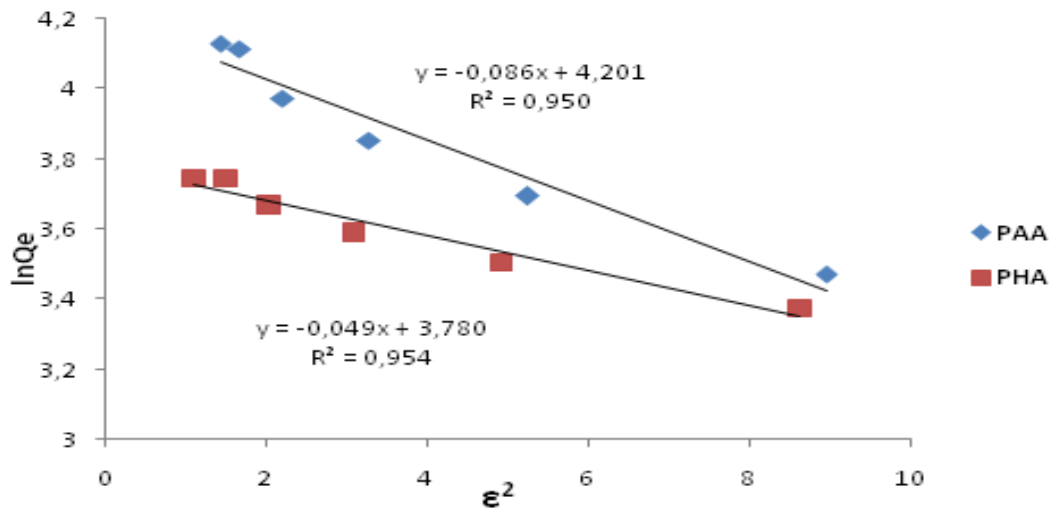


Fig. 15. Linear transform of the model of D-K-R for $C_0 = 2400$ mg/L, $V = 20$ mL, pH = 4.0, $m = 0.1$ g Adsorbent

4. CONCLUSION

A basic investigation on the adsorption of Cu (II) ions from aqueous solution by cocoa shell-based activated carbon (CSBAC) was carried out under batch mode. Sorption of Cu (II) ions were influenced by various parameters such as contact time, adsorbent dosage, initial pH and initial Cu (II) ions concentration within the range 900-2400 mg/L. The maximum removal of Cu (II) ions observed at pH 4.0 and sorbent dose of 0.1 g were 62.2 mg/g for PAA and 42.2 mg/g for PHA for an initial metal ion concentration of 2400 ppm. Iodine number for both PAA and PHA samples were obtained as 500 mg/g and 538 mg/g respectively. Results revealed by titration via Boehm method showed predominance of acidic functional groups on the surface of PAA (0.337 meq/g) and basic groups on PHA (0.103 meq/g). FTIR analysis for both the raw cocoa shells and activated carbon showed that hydroxyl, carbonyl, aliphatic, ethers, alcohol, phenol and carboxylic groups were present on their surfaces. A pH at zero-point charge (pHzpc) of 7.0 and 5.9 were obtained for PAA and PHA samples respectively. Sorption equilibrium time was observed in 35 minutes for PAA and 15 minutes for PHA. X-ray fluorescence showed that the chemical composition of the oxide level in raw material (cocoa shell) is composed mainly of potassium oxide (K_2O) of 83.28% followed by calcium oxide (CaO) 4.905%. The Langmuir model for PHA and Freundlich model for PAA best described the sorption of Cu (II) ions from aqueous solution by the two adsorbents. The two activated carbon samples both obeyed pseudo-second order kinetics. The results indicated that CSBAC can be used as an effective and low-cost adsorbent to remove Cu (II) ions from aqueous solutions.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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