# Acid activation of groundnut husk for copper adsorption: kinetics and equilibrium studies

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## ABSTRACT

In this study, the use of cheap unmodified and acid-modified agricultural waste primed from groundnut husk as adsorbents for the removal of Cu(II) ions from aqueous solution were examined in a batch process under different experimental conditions. Fourier transform infrared characterization of the adsorbent before and after the adsorption process revealed the likely involvement of various functional groups such as –COOH, –C=O, –NH$_2$ and –OH$^-$ groups. Structural and morphological changes of the biomass were equally observed by X-ray diffraction and scanning electron microscopy analysis before and after adsorption of copper ions. Optimum experimental conditions were obtained to be the initial metal concentration of 50 mg L$^{-1}$, contact time of 70 min, biomass dosage of 0.03 g and hydrogen ion concentration of 5.0. The kinetic studies showed that the sorption pattern of both biomasses followed pseudo-second-order model, while the isotherms studies revealed that the adsorption data were well governed by Freundlich adsorption isotherm. The monolayer adsorption capacity for unmodified groundnut husk was found to be 14.525 and 20.146 mg g$^{-1}$ for acid-modified groundnut husk as computed from the Langmuir model equation. It can thus be concluded that waste groundnut husk can be used as a low cost and environmentally friendly adsorbent for Cu(II) ions removal from aqueous solution.

*Keywords:* Adsorption; Copper; Equilibrium; Groundnut husk; Kinetics

## 1. Introduction

The non-biodegradable nature and long-term toxic effects of heavy metals such as cadmium, nickel, copper, manganese, lead, chromium and zinc make them major pollutants of freshwater [1,2]. Rock weathering, mining, industrial, and various anthropogenic activities are among the major factors responsible for the release of these metals into the environment [3,4]. Copper occurs naturally in rocks, soil, water, sediments, and air. However, mining and metal manufacturing are the largest sources of copper in the environment. Copper is essential for good health; however, very large single or daily intakes of copper can harm human health. Copper has a widespread usage such as fungicide, a catalyst for organic reactions, pigments for ceramics, insecticides, electroplating and as an essential element in a number of enzymes for all forms of life [5,6]. Exposure to high level of copper can

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result in vomiting and diarrhea, irritation to the nasal passage; while long-term exposure can damage the liver, kidney, brain, pancreas, reproductive and nervous system [7,8].

There exist varying methods for heavy metals remediation such as chemical precipitation, oxidation/reduction, electrochemical treatment and much more; however, they are expensive or inefficient [9]. An environmentally friendly and low-cost method known as biosorption which involves the adsorption of contaminants onto the cellular structures of biomass has been proposed as an effective method for the removal of contaminants from the environment [10–12]. A wide variety of commonly discarded waste has been investigated for effective removal of copper ions from the contaminated environment. Among these adsorbents are cocoa pod [6], peats [13], banana pith [14], rice husk [15,16], sawdust, peanut [17,18], baobab fruit shells biomass [19], cassava tuber bark waste [20], wheat bran [21], loquat leave [22], orange peel [23] and cassava waste [24]. The use of these agricultural wastes in remediation of the contaminated environment has continued to gain more interest in recent years because they are readily available, simple, low cost and do not generate sludge compared with their conventional counterparts. Nigeria is one of the largest producers of groundnut in Africa, accounting for 39% of the total production and also 51% of the total production in the West Africa region [25]. While the peanut is important to both small and large commercial producers, the husk is often left unused thus constituting environmental pollution. Therefore, the use of groundnut husk as an adsorbent for the removal of copper from aqueous solutions will not only eliminate copper contamination but also add values to agricultural waste, which is cheap when compared with other adsorbents such as commercial activated carbon. The focus of this study was to evaluate the possible use of unmodified groundnut husk (UGH) and acid-modified groundnut husk (AGH) as an effective adsorbent material for the removal of Cu(II) ions from aqueous solution. The adsorption behavior was investigated on the effect of parameters such as biomass dosage, hydrogen ion concentration and contact time. Kinetic modeling and adsorption isotherms were also evaluated.

## 2. Materials and methods

### 2.1. Chemicals

All commercial chemicals used were of analytical grade and were from Merck, India. A stock, 1,000 mg L$^{-1}$, standard solution of Cu(II) ions were prepared by dissolving 3.8 g of Cu(NO$_3$)$_2$·3H$_2$O in 1 L of distilled water. A number of concentrations of Cu(II) ions ranging from 10 to 100 mg L$^{-1}$ were prepared from these stock solutions. The pH of the solutions was adjusted by the addition of 0.2 M HCl and NaOH solutions as appropriate

### 2.2. Preparation of groundnut husk

Groundnut was purchased from Kuto Market in Abeokuta, Ogun State, South West Nigeria and washed with potable water. The husk was separated from the seed, cut into pieces and then sun dried. They were then grounded into powdery form by using a mechanical grinding machine

and sieved to get required size. The acid modification was achieved by dispersing 100 g of the powdered biomass in 500 mL solution of 0.1 M HNO$_3$ for 48 h. The slurry was then filtered, rinsed thoroughly with distilled water and oven dried at 110°C for 5 h. It was then stored in an air-tight bag prior to analysis.

### 2.3. Sorption experiments

The batch adsorption experiments were performed on a rotatory shaker at a speed of 150 rpm using 250 mL conical flask. The kinetic and equilibrium procedure follows the method of Adeogun et al. [12]. The adsorbent (0.03 g) was equilibrated with 15 mL of copper(II) ions in a 250-mL conical flask that was placed on the rotatory shaker for 70 min at a temperature of 25°C. The contents of the flask were filtered and analyzed for copper(II) ions concentrations using Atomic Absorption Spectrophotometer (AAS) UNICAM 969 model.

The uptake capacity, $q_e$, was calculated from Eq. (1):

$$q_e = \frac{C_o - C_e}{W} V \tag{1}$$

$$\text{Sorption percentage} = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

where $C_o$ and $C_e$ are the initial and equilibrium concentrations, respectively, of copper(II) ions in 'mg L$^{-1}$', $q_e$ is the amount of copper(II) ions adsorbed in 'mg g$^{-1}$', $W$ is the mass of the adsorbent in 'g' and $V$ is the volume of the solution in $L$.

### 2.4. Desorption study

The reusability of the biomass was performed using HCl as desorbing agent at different concentrations, namely 0.1, 0.2, 0.3, and 0.4 M. The biomass loaded with Cu(II) ions was placed in the various desorbing concentrations in a 250 cm$^3$ beaker and placed on orbital shaker at a speed of 150 rpm for 60 min at a temperature of 25°C. After desorption, the biomass was filtered and the supernatant was analyzed for Cu(II) ions using AAS UNICAM 969 model.

### 2.5. Characterization

The vibrational frequencies of both UGH and AGH were obtained from Fourier transform infrared (FTIR) transmission spectra by KBr method using FTIR model 8400S (Shimadzu, Japan). The ground KBr powder was pressed with Shimadzu MHP-1 mini hand press to form homogenized pellet for background measurement. A 5% dilution of either UGH or AGH with KBr was ground with agate mortar to have a homogenized mixture. Suitable pellets were used for the scan in the percent transmittance mode in the mid-IR region of 400–4,000 cm$^{-1}$. X-ray diffraction (XRD) was recorded using PANalytical (X'Pert Pro, Netherland). The diffraction patterns were collected over a range of 2θ = 10°–60° with an incremental step size of 0.02 using Cu Kα (γ = 1.54178 Å) radiation. Scanning electron microscopy (SEM) analysis was carried out to evaluate the morphology using a Hitachi

(Japan) S-3000H electron microscope with an accelerating voltage of 15 kV. The particle size distribution present was measured by using a Nanotrac equipped with Microtrac FLEX 10.5.2 software for data processing. About 0.1 g of the sample was dispersed in 50 mL of Millipore water in 100 mL beaker and sonicated for 10 min prior to analysis to minimize the degree of agglomeration of the particle. The zeta potential of the biomass sample was investigated by using 0.1 g of adsorbent in 20 mL of copper solution. The pH of the solution was adjusted using 0.1 M HCl or NaOH and analyzed using a Zetasizer Nano ZS instrument (Malvern, UK).

## 3. Results and discussions

### 3.1. Characterization of adsorbent

The functional groups of the groundnut husk were analyzed using FTIR as shown in Fig. 1. The result of the FTIR analysis of the groundnut husk showed different functional groups present on the surface; the UGH demonstrated broad peaks between 2,500 and 3,700 $cm^{-1}$, which are identified as those of O–H vibrations and/or N–H stretching associated with N-substituted amide [26], the 2,928 $cm^{-1}$ peak is –CH stretching of the alkanes group, 2,350 $cm^{-1}$ peak is that of $CO_2$ from air, the distinct peak at 1,608 $cm^{-1}$ is probably the C=O stretching of carbonyl groups, and the one at 1,417 $cm^{-1}$ is that of –$CH_3$. The peak value at 1,067 $cm^{-1}$ is attributed to the C–O stretching of the carboxylic acids and esters groups [27]. Upon activation, the peak at 2,854 $cm^{-1}$ reduced, while peaks at 2,350 and 1,716 $cm^{-1}$ were introduced. The peak at 2,854 $cm^{-1}$ corresponds to the C–H stretching of aldehyde, while the peak at 1,716 $cm^{-1}$ is assigned to C=O of the carbonyl stretching in ketone, esters, lactones, quinines, and/or carboxylic acids [28]. Furthermore, all the peaks within the range 1,003–1,516 $cm^{-1}$ were more distinct and pronounced in the activated husk (AGH). This suggested that the activation removed molecules that are bound to functional groups prior to activation, thus making them available for efficient adsorption. Fig. 2 depicts the XRD patterns of groundnut husk before and after the adsorption of copper(II) ions; the
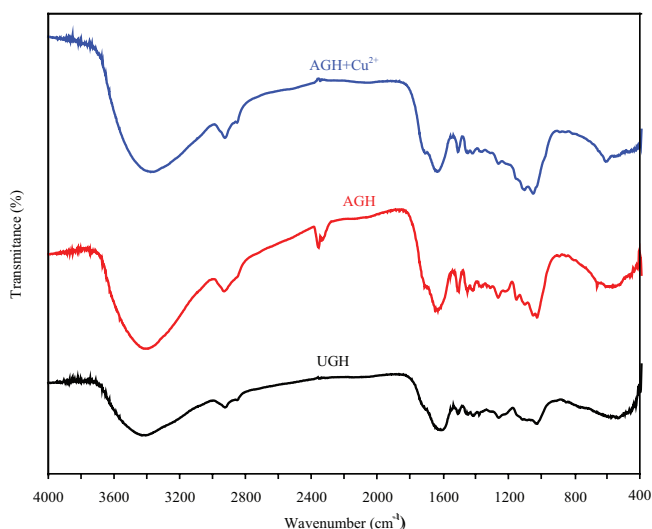
pattern observed was that of amorphous cellulose type I with main peaks at about 2θ = 16.3° and 22.4°. The diffraction peaks at 2θ = 16.3° and 22.4° correspond to the (101) and (200) planes for cellulose [29]. The decrease in peak intensities was observed after copper(II) ions uptake by the biomass. Fig. 3 shows the particle size distribution of AGH with the majority of the particle in the range of 0.6–0.8 μm. The microstructure of UGH, AGH, and AGH+$Cu^{2+}$ load is as shown in Fig. 4. Changes in the morphology after acid activation and copper(II) ions adsorption were observed on the surface of the biomass. The presence of pores was noticed after the acid treatment of the adsorbent thus providing more adsorption sites on the surface of the biomass.

### 3.2. Effect of initial metal concentrations

The experimental results for the sorption of Cu(II) ions onto the cell walls of UGH and AGH at various concentrations are shown in Fig. 5. The results showed that the amount of Cu(II) ions adsorbed increased with an increase in the initial concentration of copper. The sorption capacity ($q_e$) of UGH increased from 5.5 to 14.5 mg $g^{-1}$ on increasing the copper concentration from 10 to 50 mg $L^{-1}$. Upon treatment with acid, the biomass sorption capacity ($q_e$) showed

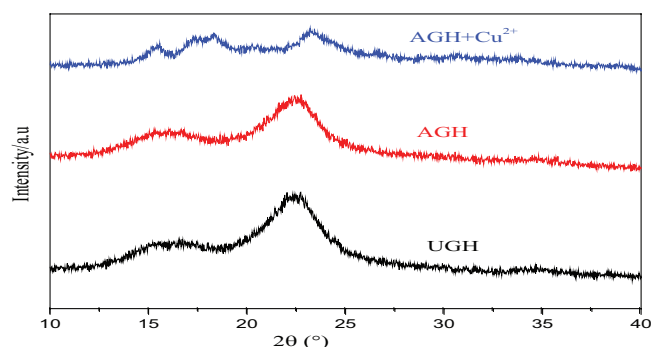Fig. 2. XRD patterns of UGH, AGH, and AGH+$Cu^{2+}$.

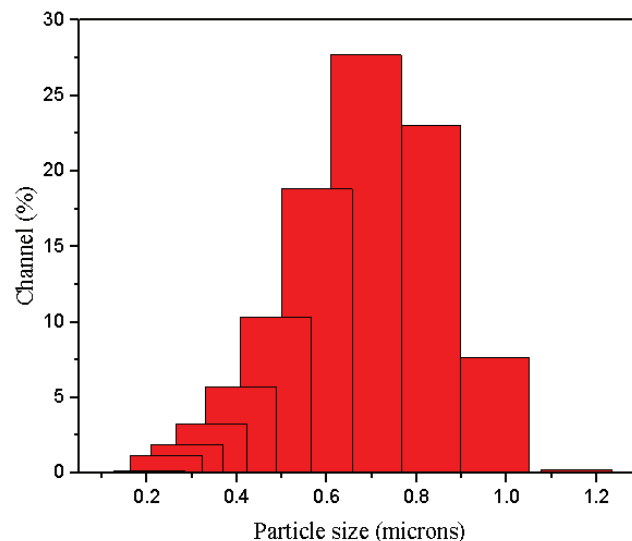Fig. 1. The FTIR spectra of UGH, AGH, and AGH+$Cu^{2+}$.

Fig. 3. Particle size of AGH.
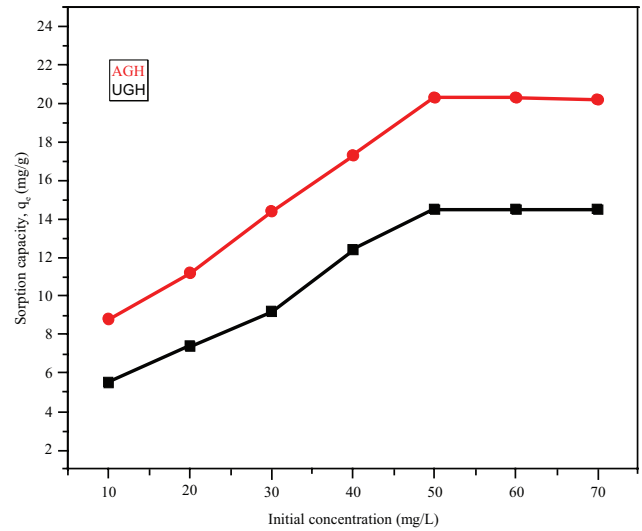
Fig. 5. Sorption capacity of Cu(II) ions against initial metal concentration by UGH and AGH at a pH of 5.0, contact time of 70 min and biomass dosage of 0.03 g.

an enormous increase from 8.8 to 20.3 mg g$^{-1}$ when the initial metal concentration was increased from 10 to 50 mg L$^{-1}$. Ho and Mckay [13] and Li et al. [30] had previously reported similar findings that a higher initial concentration provided an important driving force to overcome all mass transfer resistances of the adsorbate between the aqueous and solid phases and thus increased the uptake of the adsorbate by the adsorbent [31].

### 3.3. Effect of contact time

The effect of contact time on the sorption of Cu(II) ions is shown in Fig. 6. It is apparent from the plot that the sorption capacity of both biomasses increased with an increase in contact time. The results revealed that the maximum sorption capacities of both the unmodified and the modified adsorbents for Cu(II) ions adsorption were 14.5 and 20.3 mg g$^{-1}$, respectively, at a contact time of 70 min. It was observed that the rate of adsorption increased with the contact time and then slows down as the process attained equilibrium due to the saturation of the surface of the sorbent by copper ions. At the initial stage, there are vacant sites on the surface of the sorbent that enhances its sorption capacity. However, as the reaction progressed, these vacant sites were being crammed by the sorbate and this reduced the sorption capacity of the sorbent [27,28].

### 3.4. Effect of different masses of groundnut husk

The effect of varying the groundnut husk masses, using an initial copper(II) ions concentration of 50 mg L$^{-1}$ at a contact time of 70 min and pH of 5.0 is shown in Fig. 7. The results reveal that the sorption percentage of the adsorbate increases with an increase in the adsorbent dosage and almost constant at a dosage higher than 0.03 g. Thus, an adsorbent dosage of 0.03 g was selected for subsequent studies. As demonstrated in the plot, maximum sorption percentage by UGH and modified groundnut husk for the sorption
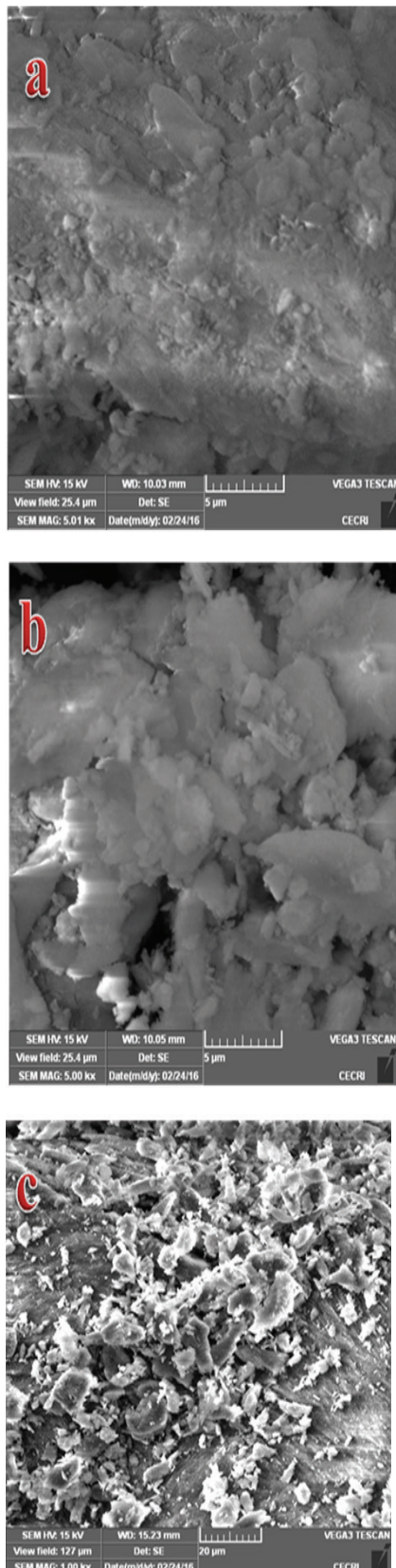


Fig. 4. SEM images of (a) unmodified groundnut husk, UGH, (b) acid-modified groundnut AGH, and (c) acid-modified groundnut +Cu$^{2+}$.

of Cu(II) ions increased from 43.5% to 77.3% for UGH and from 55.5% to 97.4% for AGH when the biomass dosage was increased from 0.01 to 0.03 g. This was attributed to the fact that higher dosage of sorbent led to an increase in the surface area thus providing more adsorption sites available for adsorbate adsorption, which gave rise to a higher removal of Cu$^{2+}$. The decrease in the sorption percentage observed at a higher adsorbent dosage above 0.03 g could be as a result of the formation of the partial aggregate of adsorbent at higher biomass values owing to the deposit of the sorbate on the pore of the sorbent there by decreasing the sorption capacities of the biomass.
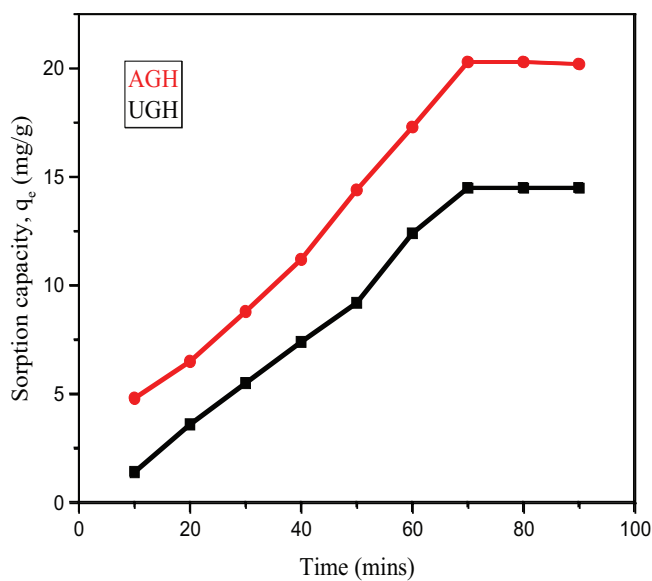
### 3.5. Effect of hydrogen ion concentration

Fig. 8 shows the results of the experimental studies of the zeta potential and effect of hydrogen ion concentration on the sorption capacities of both UGH and AGH for the removal of



Fig. 6. Sorption capacity of Cu(II) ions against contact time by UGH and AGH at a pH of 5.0, the initial metal concentration of 50 mg L$^{-1}$ and biomass dosage of 0.03 g.
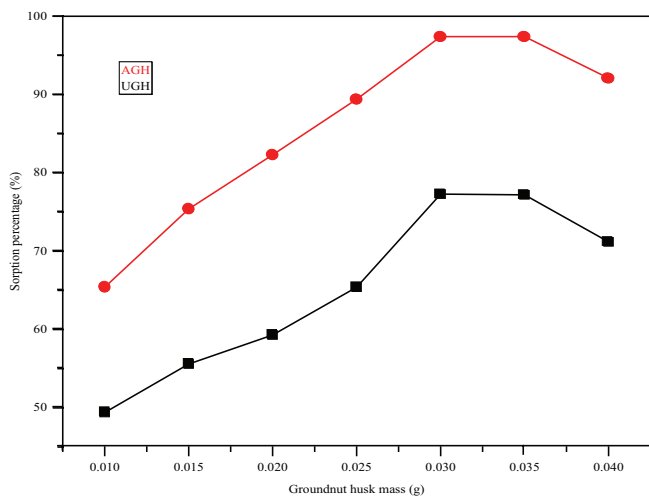


Fig. 7. Sorption capacity of Cu(II) ions against different masses of UGH and AGH at a pH of 5.0, an initial metal concentration of 50 mg L$^{-1}$ and contact time of 70 min.
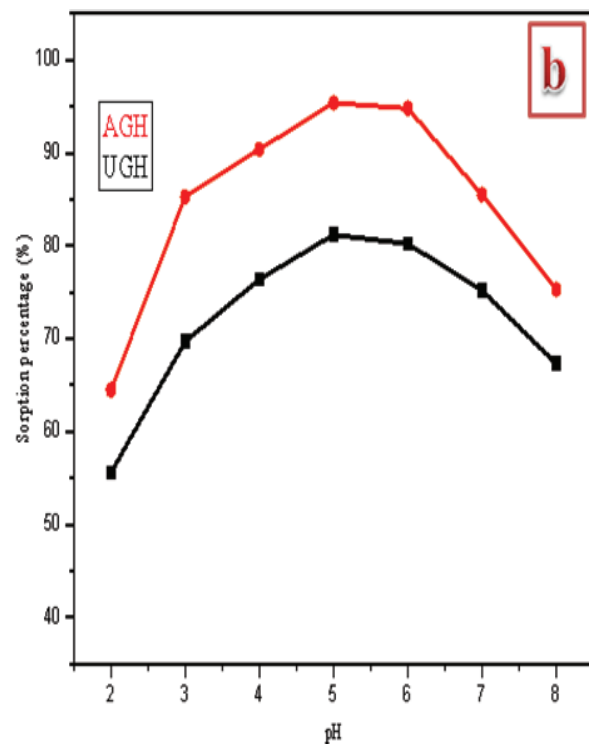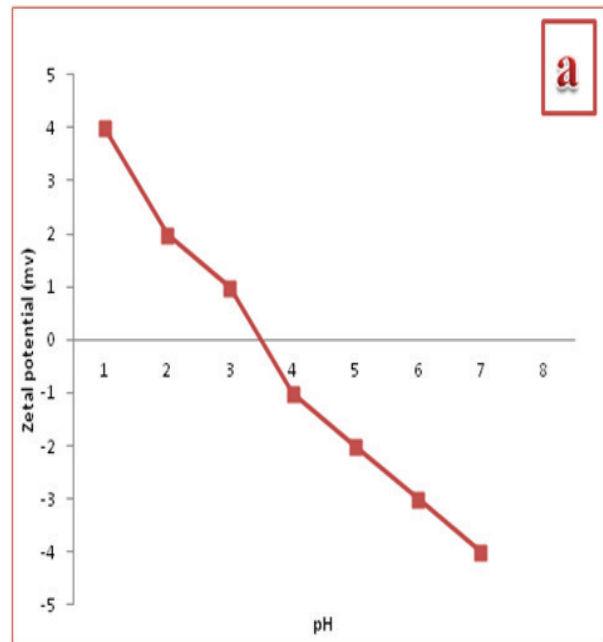


Fig. 8. Plots of (a) zeta potential and (b) sorption capacity of Cu(II) ions against pH by UGH and AGH at the initial metal concentration of 50 mg L$^{-1}$, a dosage of 0.03 g and contact time of 70 min.

Cu(II) ions from aqueous solution. The zero point charge of the biomass was obtained as 3.5 and below this value, the biomass surface is positively charged. The surface of the biomass becomes negatively charged at a pH above 3.5 that enhances the sorption of $Cu^{2+}$ onto the surface of the adsorbent. The results revealed that higher sorption capacities were achieved at a pH of 5.0 which could be due to the net negative charge on the biomass surface as revealed by the zeta potential experiment. The sorption percentage of unmodified adsorbent increases linearly from 56.3% to 81.2% when the pH was raised from 2.0 to 5.0 before showing a decrease to 67.3% at a pH of 8.0. On the other hand, when acid-treated biomass was used, the sorption percentage increased from 63.9% to 95.4% when the pH was raised from 2.0 to 5.0 and later decreased to 75.3% at a higher pH of 8.0. Thus, pH is an important parameter on the sorption of metal ions from aqueous solutions since it is responsible for the protonation of metal-binding sites, calcium carbonates solubility and metal specification in the solution as reported by Vijaya et al. [32]. It is often believed that cell walls of most adsorbents contain a wide variety of functional groups such as $-NH_2$, $-COOH$, $-C=O$, and $-OH$, which are positively charged at lower pH and negatively charged at higher pH. Thus, the adsorption of Cu(II) ions onto the cell walls of groundnut husk was impeded at low pH. However, as the pH increases, the surface becomes more negatively charged and the surface tends to absorb more Cu(II) ions. The precipitations of copper as oxide and hydroxide at higher pH of 7 and above may be responsible for the low binding of copper onto the surface of groundnut husk. Similar findings were reported by Qaiser et al. [33] and Bouhamed et al. [34].

## 3.6. Kinetics studies

In order to examine the mechanism of adsorption process of copper(II) ions by UGH and AGH, pseudo-first-order, pseudo-second-order, Elovich model and intra-particle diffusion models were employed for the evaluation of the adsorption data.

### 3.6.1. Pseudo-first-order model

The pseudo-first-order equation is generally expressed as follows [35]:

$$\frac{dQ}{dt} = k_1(Q_e - Q_t) \tag{3}$$

where $Q_e$ and $Q_t$ are the sorption capacity at equilibrium and at time $t$, respectively, in mg g$^{-1}$, and $k_1$ is the pseudo-first-order rate constant in min$^{-1}$. On integrating Eq. 3 between the limits $t = 0$, $Q_t = 0$, and $t = t$, $Q_t = Q_t$, the following equation is obtained:

$$\text{In}(Q_e - Q_t) = \text{In}Q_e - k_1 t \tag{4}$$

This can be rearranged into a nonlinear form as follows:

$$Q_t = Q_e(1 - e^{-k_1 t}) \tag{5}$$

The plots of $Q_t$ against $t$ from the least square fit method were used to estimate the values of $Q_e$ and $k_1$ as presented in Fig. 9.

### 3.6.2. Pseudo-second-order model

The rate expression for the pseudo-second-order equation is given as [13,35]:

$$\frac{t}{Q_t} = \frac{1}{k_2}Q_e^2 + \left(\frac{1}{Q_t}\right)t \tag{6}$$

This can be rearranged into a nonlinear form as:

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \tag{7}$$

where $k_2$ the equilibrium rate constant of the pseudo-second-order model in g mg$^{-1}$ min$^{-1}$, $Q_e$ is the amount of copper(II) ions adsorbed at equilibrium in mg g$^{-1}$, $Q_t$ is the amount of copper(II) ions adsorbed at time $t$ in mg g$^{-1}$. The corresponding values of $Q_e$ and $k_2$ were evaluated from the plots of $Q_t$ against $t$ of the least square fit method as shown in Fig. 9, while the physical parameters are presented in Table 1.

### 3.6.3. Elovich kinetic model

The Elovich equation has been used for describing reactions involving chemisorption of gases on a solid surface and for simulating sorption kinetics in a liquid phase. The non-linear form of the Elovich model is given as [13]:

$$Q_t = \frac{1}{\beta} In(\alpha\beta \times t) \tag{8}$$

The simplified form of the Elovich equation is given as [13]:

$$q_t = \frac{1}{\beta}(In\alpha\beta) + \left(\frac{1}{\beta}\right)Int \tag{9}$$

where $\alpha$ is the initial adsorption rate in mg g$^{-1}$ min$^{-1}$, $\beta$ is the desorption constant in g mg$^{-1}$. The corresponding constants values were evaluated from the plots of $Q_t$ against $t$ of the least square fit method as shown in Fig. 9 and their physical parameters are presented in Table 1.

### 3.6.4. Intra-particle diffusion model

The non-linear form of the intra-particle diffusion equation can be expressed as follows [36]:

$$Q_t = K_{id}t^{0.5} + C_i \tag{10}$$

where $K_{id}$ is the intra-particle diffusion rate constant (mg$^{-1}$min$^{-0.5}$) and $C_i$ is the intercept and a measure of surface thickness.
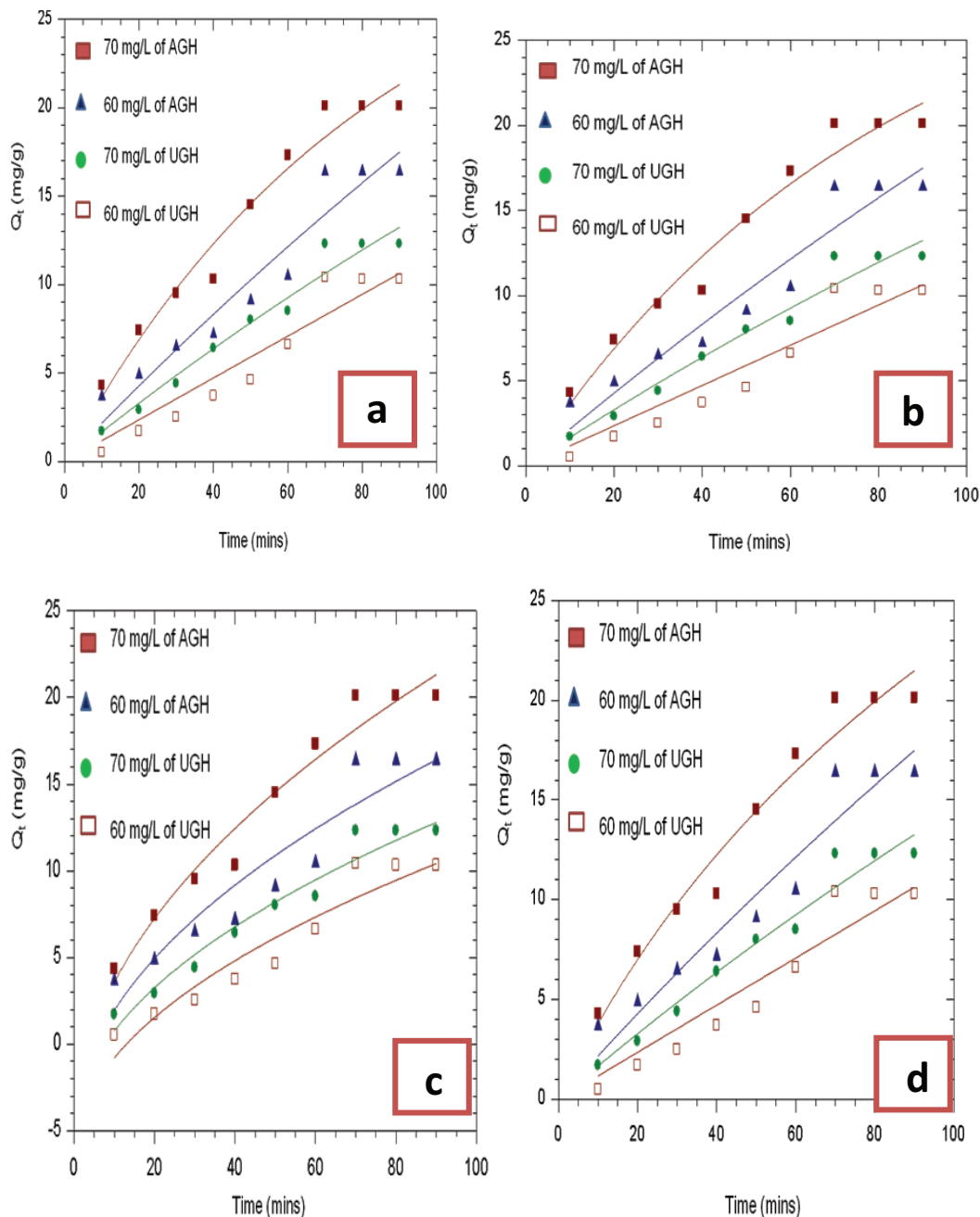
Fig. 9. Plots of (a) pseudo-first-order, (b) pseudo-second-order, (c) Elovich kinetic (d) intra-particle diffusion kinetic equations for the sorption Cu(II) ions by groundnut husk.

### 3.6.5. Fitness of kinetics models

The best fit between the kinetics models was evaluated by the sum of squared errors (SSE, %) given as follows:

$$\% \ \mathrm{SSE} = \sqrt{\frac{\left((Q_{(\exp)} - Q_{(\mathrm{Cal})}) / Q_{\exp}\right)^2}{N - 1}} \times 100 \qquad (11)$$

where $N$ is the number of data points. The smaller the %SSE values and the higher the values of $R^2$, the better the curve fitting.

The plots of $Q_t$ vs. $t$ depict (a) pseudo-first-order, (b) pseudo-second-order, (c) Elovich kinetic, and (d) intra-particle diffusion kinetic equations for the sorption Cu(II) ions by groundnut husk. A comparison of the results with the correlation coefficients showed good fits by all models but the calculated values of equilibrium adsorption capacities ($q_{e(\mathrm{cal})}$) were well agreed with the experimental values ($q_{(e.\exp)}$) for the pseudo-second-order kinetic model. In addition, the values SSE for second order were smaller than for pseudo-first-order kinetic model. Thus, the pseudo-second-order kinetic model obtained for Cu²⁺ sorption showed better correlation of results than the

Table 1
Kinetic parameters for the sorption of Cu(II) ions by UGH and AGH

|  | $C_o$ (mg L$^{-1}$) | 40 mg L$^{-1}$ UGH | 50 mg L$^{-1}$ UGH | 40 mg L$^{-1}$ AGH | 50 mg L$^{-1}$ AGH |
|---|---|---|---|---|---|
| Pseudo-first-order | $Q_{e(exp)}$ (mg g$^{-1}$) | 10.300 | 12.200 | 16.500 | 20.100 |
|  | $Q_{e(cal)}$ (mg g$^{-1}$) | 23.120 | 28.610 | 28.720 | 33.210 |
|  | $k_1$ (min$^{-1}$) | 0.041 | 0.024 | 0.044 | 0.034 |
|  | $R^2$ | 0.927 | 0.992 | 0.986 | 0.995 |
|  | %SSE | 0.719 | 0.777 | 0.428 | 0.377 |
| Pseudo-second-order | $Q_{e(cal)}$ (mg g$^{-1}$) | 9.340 | 11.250 | 15.720 | 19.250 |
|  | $k_2$ (g mg$^{-1}$ min$^{-1}$) | 0.003 | 0.003 | 0.012 | 0.653 |
|  | $R^2$ | 0.974 | 0.990 | 0.982 | 0.994 |
|  | %SSE | 0.054 | 0.045 | 0.027 | 0.024 |
| Elovich | $\alpha$ (mg g$^{-1}$ min$^{-1}$) | 0.116 | 0.172 | 0.200 | 0.418 |
|  | $\beta$ (g mg$^{-1}$) | 0.008 | 0.022 | 0.021 | 0.048 |
|  | $R^2$ | 0.974 | 0.993 | 0.986 | 0.995 |
| Intraparticle diffusion | $K_p$ (mg g$^{-1}$ min$^{-1/2}$) | 1.772 | 1.903 | 2.285 | 2.805 |
|  | $C$ (mg g$^{-1}$) | 6.395 | 5.263 | 5.276 | 5.295 |
|  | $R^2$ | 0.972 | 0.991 | 0.980 | 0.994 |

pseudo-first-order equation model. The values of $k_1$ and $k_2$ obtained varied from 0.024 to 0.044 min$^{-1}$ and from 0.003 to 0.653 (g mg$^{-1}$ min$^{-1}$), respectively. It was observed that equilibrium adsorption capacity ($Q_e$) increased with an increase in initial copper ion concentration. The two parameters ($\alpha$ and $\beta$) of the Elovich model were used to explain the copper adsorption mechanism onto groundnut husk which were estimated from the least square fit of the linear plot of $Q_t$ against $t$ (Fig. 9). A good range of $R^2$ values (0.974–0.995) were obtained suggesting the applicability of this model for Cu(II) ions adsorption as well. The obtained values of $\alpha$ and $\beta$ (Table 1) showed a general trend of changes with an increase in the initial copper concentration. It was observed that the values of $\alpha$ increased with increased initial copper concentration, suggesting that the process was chemisorptions corresponding to the heterogeneity in nature of active sites, while the values of $\beta$ showed a decreasing trend [37,38]. The intra-particle diffusion plots gives multi-linearity which inferred that adsorption process may occur in three main steps. The initial portion which is known as film diffusion involves the boundary layer diffusion of the adsorbate from the bulk solution to the adsorbent surface. The intermediate part is called pore or intra-particle diffusion and it is due to the adsorbate diffusion from the adsorbent surface into its pores, while the third stage involves the adsorption of the adsorbate onto the active sites of the pores on the adsorbent surface. According to Duran et al. [39], the last stage occurs rapidly which implies that the overall adsorption process is controlled either by film or pore diffusion, or a combination of both. The experimental data for Cu(II) ions by UGH and AGH fitted well with intra-particle model as predicted by the values of $R^2$ ranging from 0.972 to 0.994 (see Table 1). The rate constant ($K_p$) showed an increase with increase in initial copper concentration for both adsorbents.

## 3.7. Adsorption studies

Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich adsorption isotherms have been utilized to describe the sorption patterns of various metal ions on the different adsorbent.

### 3.7.1. Langmuir adsorption isotherm

The Langmuir isotherm proposed a homogeneous monolayer sorption surface in which there are no interactions between adsorbed molecules. The non-linear form of the Langmuir isotherm is given as follows [40]:

$$Q_e = \frac{Q_o b C_e}{1 + b C_e} \tag{12}$$

where $Q_0$ is the saturated monolayer sorption capacity, $b$ is the sorption equilibrium constant, $Q_e$ is the weight adsorbed per unit weight of adsorbent at equilibrium and $C_e$ is the metal concentration at equilibrium. The plots of $Q_e$ against $C_e$ which is shown in Fig. 10 was used to evaluate the values of the Langmuir parameters. The adsorption intensity ($R_L$) from the Langmuir isotherm is given as follows [40]:

$$R_L = \frac{1}{\left(1 + b C_o\right)} \tag{13}$$

where $C_o$ is the initial concentration expressed in mg L$^{-1}$. The variation of the values of $R_L$ between 0 and 1 at different initial metal concentrations suggests a favorable adsorption process.
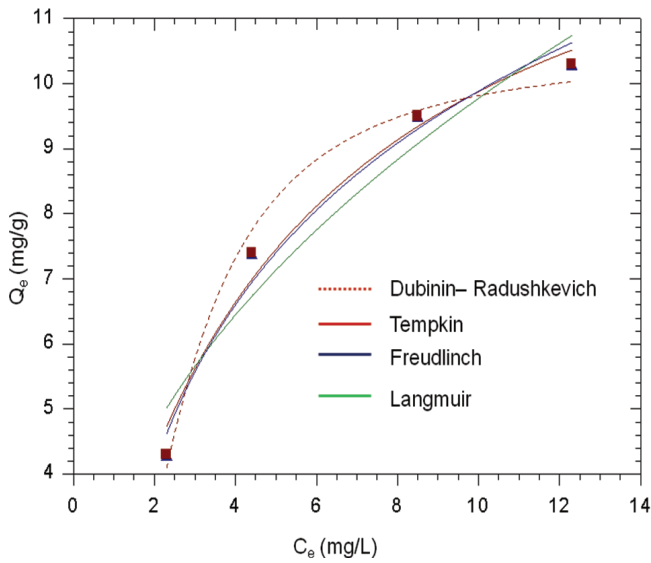
Fig. 10. Plots of Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich adsorption isotherms for the sorption of Cu(II) ions at pH of 5.0 by UGH.

### 3.7.2. Freundlich's adsorption isotherm

The Freundlich isotherm assumes a heterogeneous energetic distribution of active site in a monolayer sorption process. There are, however, interactions between adsorbed molecules. The non-linear form of Freundlich equation is given as follows [41]:

$$Q_{eq} = K_F C_e^{1/n} \tag{14}$$

where $K_F$ (mg g$^{-1}$) and $n$ are Freundlich constants representing the relative adsorption capacity and the strength of sorption process, respectively. The plots of $Q_e$ against $C_e$ shown in Fig. 10 were used to evaluate the values of the Freundlich's parameters. The Freundlich isotherm constant, $n$, gives information about the favorability of the adsorption process. The value of $n$ between unity and 10 implies favorable adsorption condition [41].

### 3.7.3. Temkin adsorption isotherm

The Tempkin adsorption isotherm assumes that the heat of adsorption decreases linearly with the sorption coverage due to adsorbent–adsorbate interactions. The non-linear form of Tempin isotherm equation is given as follows [42]:

$$Q_e = \frac{RT}{b_T} \ln a_T C_e \tag{15}$$

While the linear form of the Temkin isotherm is given as follows:

$$q_e = \frac{RT}{bT} \ln \alpha_T + \frac{RT}{bT} \ln C_e \tag{16}$$

where $\alpha_T$ (L g$^{-1}$) is the Temkin isotherm constant relating to binding energy, $b_T$ (J mol$^{-1}$) is a constant related to heat of sorption, $R$ is the ideal gas constant (8.3145 J mol$^{-1}$ K$^{-1}$) and $T$ is the absolute temperature in Kelvin.

### 3.7.4. Dubinin–Radushkevich adsorption isotherm

The Dubinin–Radushkevich (DR) equation has been used to describe the sorption of metal ions on groundnut husk [43]. The non-linear form of DR equation is given as:

$$Q_e = Q_m e^{-\beta \varepsilon^2} \tag{17}$$

where $Q_e$ is the number of metal ions adsorbed per unit weight of adsorbent (mg g$^{-1}$), $Q_m$ (mg g$^{-1}$) is the maximum sorption capacity, $\beta$ (mol$^2$ J$^{-2}$) is the activity coefficient relating to mean sorption energy and $\varepsilon$ is the Polanyi potential, which is expressed as follows:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e}\right) \tag{18}$$

where $R$ is the molar gas constant in J mol$^{-1}$ K$^{-1}$, $T$ is the absolute temperature in Kelvin and $C_e$ is the concentration of the adsorbate in mol L$^{-1}$ at equilibrium [44]. The sorption energy can also be worked out using the following relationship:

$$E = \frac{1}{\sqrt{2\beta}} \tag{19}$$

If the value of $E$ is less than 8 kJ mol$^{-1}$, the adsorption process is physical in nature, if it is between 8 and 16 kJ mol$^{-1}$, it follows ion-exchange and higher values of 24.7 ± 3.2 kJ mol$^{-1}$ indicate strong chemisorptions formation between the adsorbent and the adsorbate [43,44]. Figs. 10 and 11 show the plots Langmuir, Freundlich, Tempkin, and Dubinin–Radushkevich adsorption isotherms for the sorption of Cu(II) ions by UGH and AGH, respectively, at pH 5.0. The physical parameters for the isotherms are shown in Table 2. The correlation coefficient $R^2$ (0.913, 0.998, 0.943, and 0.959) of UGH and $R^2$ (0.925, 0.999, 0.934, and 0.980) of AGH for Langmuir, Freundlich, Tempkin, and Dubinin–Radushkavish adsorption isotherms confirm good agreement between both theoretical models and our experimental results (Table 2). It is clear that the Freundlich isotherm is best fitted for the sorption of Cu(II) on UGH and AGH, respectively. The maximum sorption capacity, $Q_e$ calculated from Langmuir equation is 14.625 and 26.467 mg g$^{-1}$ for UGH and AGH, respectively. The values of the absorption intensity ($R_L$) from the Langmuir isotherms was found to be in the range of 0 to 1; which indicate that the sorption process is favorable for both sorbents; 0 < $R_L$ < 1; adsorption is favorable. The values obtained for Cu(II) from the Freundlich isotherm showed a maximum adsorption capacity ($K_F$) of 3.435 and 6.897 mg g$^{-1}$ with an affinity value ($n$) equal to 2.202 and 2.395 for UGH and AGH, respectively. Since the value of $n$ is greater than unity, it further affirms the favorable nature of the adsorption process. The values of sorption constants, derived from UGH and AGH for

Dubinin–Radushkevich model are 10.478 and 18.453 mg g$^{-1}$ for $Q$, 9.530 and 14.256 (kJ mol$^{-1}$) for $E$. Since the values of $E$ lies within 8 to 16 kJ mol$^{-1}$, the adsorption process is of the orders of an ion-exchange mechanism [45,46].

Table 3 shows the comparison of the sorption capacity $Q_e$ in mg g$^{-1}$ of Cu(II) ions by different adsorbents in literature with those obtained from this study. It is obvious from the table that the use of UGH and AGH for the sorption of Cu(II) ions from the aqueous solution which was investigated in this work agrees with the majority of reports on various adsorbents.
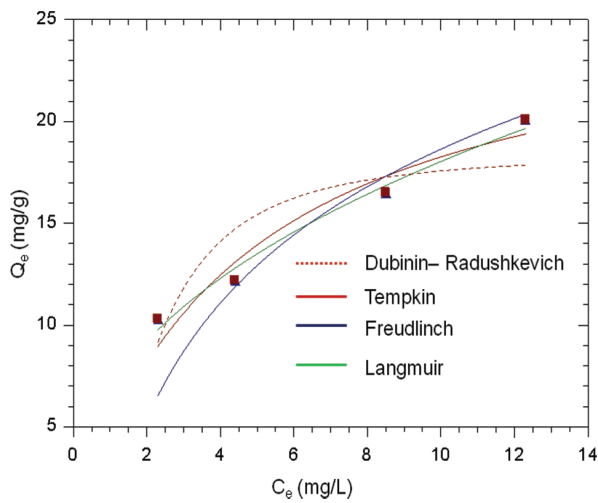


Fig. 11. Plots of Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich adsorption isotherms for the sorption of Cu(II) ions at pH of 5.0 by AGH.

Table 2
Isotherm model parameters for the sorption of Cu(II) ion by UGH and AGH

|  |  | $C_o$ (mg L$^{-1}$) | UGH | AGH |
|---|---|---|---|---|
| Langmuir | $Q_{max}$ (mg g$^{-1}$) |  | 14.625 | 26.467 |
|  | $R_L$ |  | 0.208 | 0.222 |
|  | $b$ (L mg$^{-1}$) |  | 0.362 | 0.753 |
|  | $R^2$ |  | 0.913 | 0.925 |
| Freundlich | $K_F$ (mg g$^{-1}$) (mg L$^{-1}$)$^{-1/2}$ |  | 3.435 | 6.897 |
|  | $n$ |  | 2.202 | 2.395 |
|  | $R^2$ |  | 0.998 | 0.999 |
| Temkin | $\alpha_T$ (L g$^{-1}$) |  | 0.970 | 0.960 |
|  | $b_T$ (J mol$^{-1}$) |  | 556.162 | 300.677 |
|  | $R^2$ |  | 0.943 | 0.934 |
| Dubinin–Radushkevich | $Q$ (mg g$^{-1}$) |  | 10.478 | 18.453 |
|  | $\varepsilon$ (mol J$^{-1}$)$^2$ |  | 0.357 | 0.628 |
|  | $E$ (kJ mol$^{-1}$) |  | 9.530 | 14.256 |
|  | $R^2$ |  | 0.959 | 0.980 |

## 3.8. Desorption study

In order to evaluate the reusability of the biomass, different concentrations of the desorbing agent (HCl) were used for this purpose. When untreated groundnut husk was subjected to this treatment, the percentage recovery increased from 40.7% to 68.3% with increasing concentration of HCl from 0.1 to 0.3 M before showing a decrease to 55.8% at a higher concentration of 0.4 M HCl (Fig. 12) [39]. On the other hand, the percentage recovery of the treated biomass increased from 53.8% to 81.5% when the concentration of the desorbing agent was raised from 0.1 to 0.3 M and later showed a decrease to 70.3% at a higher concentration of 0.4 M HCl. The results indicated that the reusability of groundnut husk is a function of the concentration of the desorbing agent and for this study; maximum percentage recovery was attained at a concentration of

Table 3
Comparison of sorption capacity, $Q_e$, (mg g$^{-1}$) of Cu(II) ions by different adsorbents

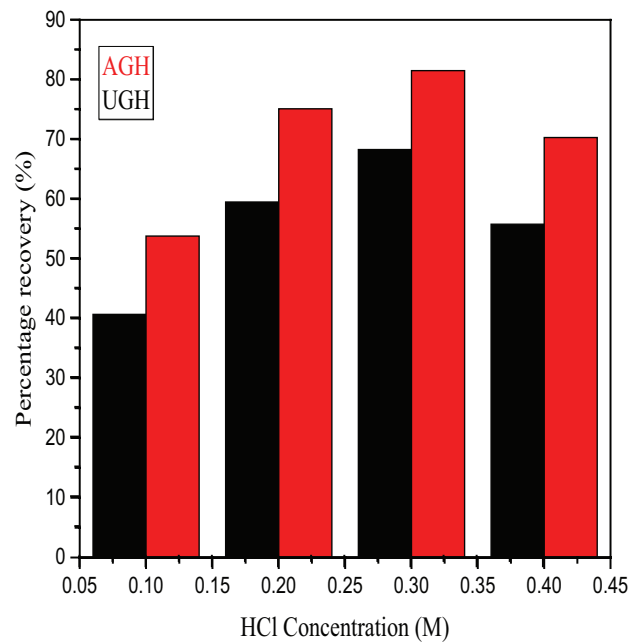| Adsorbents | $Q_e$ (mg g$^{-1}$) | References |
|---|---|---|
| Peat | 12.6 | [13] |
| Rice husk | 29 | [15] |
| Rice husk | 10.9 | [16] |
| Cassava tuber bark waste | 90.5 | [47] |
| Oak sawdust | 3.6 | [19] |
| Baobab shells | 10.56 | [20] |
| Loquat leave | 33.3 | [23] |
| Orange peel | 72.73 | [24] |
| Unmodified groundnut husk | 14.625 | Present work |
| Modified groundnut husk | 26.467 | Present work |



Fig. 12. Percentage recovery against different concentrations of a desorbing agent.

0.3 M HCl. Furthermore, the treated biomass showed better and greater reusability than the untreated biomass.

## 4. Conclusion

This study established the application of unmodified and acid modified agricultural waste which was primed from groundnut husk as adsorbents for the removal of Cu(II) ions from aqueous solution in a batch adsorption process. The binding capacities of UGH and AGH were found to be dependent on pH, contact time, contaminant concentration and adsorbent dosage. The acid modification of the adsorbent greatly enhanced the sorption capacity of the biomass. Kinetic findings revealed that copper adsorption onto groundnut husk follows the pseudo-second-order, Elovich, and intra-particle diffusion mechanisms. Thus, the present study shows that unmodified and chemically modified groundnut husk are effective adsorbents for the sorption of Cu(II) ions from aqueous solutions.

## Acknowledgment

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