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Characterization and Cu(II) adsorption properties of activated carbons prepared from cotton stalk by one-step H3PO4 activation.

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ABSTRACT

In the present study adsorption of copper (II) ions from aqueous solution by activated carbon was produced from cotton stalks husk via thermal pretreatment preceding chemical modification with phosphoric acid was investigated under batch mode. The biosorbent was characterized by thermo-gravimetric analysis, Fourier transform infrared (FT-IR) and iodine number. The influence of copper concentration, contact time, and temperature was studied. Sorption equilibrium time was observed in 30 min. The equilibrium adsorption data were correlated with Freundlich and Langmuir adsorption isotherm models. The kinetics of the adsorption process was tested by pseudo- first-order, pseudo-second order and Intra-particle diffusion. It was shown that adsorption of copper could be described by the pseudo-second order kinetic model. Thermodynamic parameters such as Gibbs free energy (ΔG0), the enthalpy (ΔH0) and the entropy change of sorption (ΔS0) have also been evaluated and it has been found that the adsorption process was spontaneous, feasible and endothermic in nature. The results indicated that Activated carbon was produced from cotton stalks husk can be used as an effective and low-cost adsorbent to remove copper (II) from aqueous solution.

Keywords: Heavy metals, adsorption, isotherms, kinetics, thermodynamics.

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1. Introduction

The increasing discharge of industrial wastewaters containing heavy metals to the environment has been on the increase as a result of rapid growth of industries. This is a serious problem because heavy metals at high concentrations are toxic to aquatic eco-systems causing harmful effects to living organisms, plants and humans [1]. Copper can cause serious health problems such as damage to heart, kidney, liver, pancreas, brain, intestinal distress and anemia [2]. The World Health Organization (WHO) recommended a maximum acceptable concentration of Cu (II) in drinking water of 1.5 mg /L [3]. Therefore, the concentrations of copper must be reduced to levels that satisfy environmental regulations for various bodies of water. Conventional treatment methods for heavy metals containing wastewater treatment include chemical precipitation, ultrafiltration, solvent extraction, ion exchange, reverse osmosis and adsorption. Among these techniques, adsorption is one of the most economically favorable and technically simple method [4,5]. The adsorption technique has been found to be one of the most effective for the removal of metal ions from solution [6,7]. As a result many researchers have reported the use of different materials for adsorption, such as biomass materials [8–19], fertilizer waste [20], tea waste [21], microorganism [22], charcoal [23], yeast [24], sludge ash [25], date pits [26], lateritic minerals [27], red mud [28] and clay [29,30]. However, owing to the high cost and difficult procurement of activated carbon, efforts are being directed towards finding efficient and low cost adsorbent materials. A number of researchers have utilised wide variety of adsorbents to remove heavy metal ions from aqueous solutions.

In this study activated carbons were obtained from cotton stalk will be investigated as a potential and low cost adsorbent for the removal of Cu(II) ions from aqueous solutions.

The main objective of this study is the use of the activated carbon as a low-cost adsorbent for Cu(II) ions from aqueous solution. This is to minimize the problem of high cost involved in the treatment of industrial wastewaters in most developing nations. The effect of initial metal ion concentration, contact time and temperature were investigated. Equilibrium, kinetic and thermodynamic parameters were also determined to help provide a better understanding of the sorption process.

2. Experimental

2.1. Reagents and reference materials

All the chemicals used were of analytical reagent grade. Deionized doubly distilled (DDD) water was used throughout the experimental studies. Cu^{2+} standard solutions (10 mg/L, Atomic Spectroscopy Standard, PerkinElmer, Inc, U.SA) were prepared by diluting 10 mg/L in a volume of 500 mL deionized water. Working standards were prepared by progressive dilution of the Cu^{2+} stock solution with DDD water. GACS reagent grade HCl, NaOH and buffer solutions (Merck, Germany) were used to adjust the solution pH to the required value.

The cotton stalks husks were obtained from a farm in Djelmé, in the north region of Cameroon. They were filtered through Whatman paper #4 (USA) to remove suspended particles and then stored in a laboratory fridge at 4 ^{0}C until analysis before one week.

2.2. Preparation of activated carbon

The preparation of activated carbon was carried out according to the procedure recommended by Martinez et al., 2006. The solid residue of cotton stalks was manually chosen, cleaned with deionized water, dried at 100 °C for 24 hours, ground and passed through a sieve to obtain samples of 1–2.5 mm particle size. This raw material was treated with phosphoric acid at different concentrations (0.5/1, 1/1, 1.5/1, 2/1, 3/1, char/H_3PO_4) and pyrolysed in a tubular oven (Nabertherm S.A.S), at 600°C. These ratios were selected from previous investigations [7] which showed that the adsorption capacity increases remarkably with increasing char/H_3PO_4. After the activation, the steam flow was stopped and the obtained ACs were cooled down to room temperature and washed with distilled water to a pH of 7.

2.3 Characterization of the precursor and prepared samples

The raw Cotton stalk, activation temperature was fixed using thermogravimetry and differential thermal analysis (TG- DTA). The prepared activated carbon, surface functional groups were analysed from FT-IR spectra obtained by the KBr pellet method using Perkin Elmer Spectrum RXI FTIR spectrometer in the range 4000–400 cm^{-1}.

2.4. Iodine number

The iodine number was determined by using the sodium thiosulfate volumetric method. Standard iodine solution was added over activated carbon (10 mg) and after an equilibration time of 4h, the residual iodine concentration was determined by titration with standard sodium thiosulfate using starch as an indicator. The iodine number was defined as the adsorbed quantities of iodine (in molg-1of carbon) obtained by subtracting the residual concentration at equilibrium Ce, from the initial concentration Co.

$$Q_0 = \frac{C_0 - C_e}{m} V$$

(1)

Where m and V are the mass of activated aarbons sample and the volume of adsorbing solution respectively.

2.5. Batch adsorption studies

2.6 Data treatment

2.6.1 Isotherm models

The sorption equilibrium data for Cu^{2+} on activated carbons was analyzed by means of the Freundlich and Langmuir isotherm models [8]. The Freundlich isotherm equation x/m = $k_f C^{1/n}$ can be written in the linear form as given in equation 1.

$$\log\left(\frac{x}{m}\right) = \log K_F + \frac{1}{n}\log C_e$$

(2)

where x/m and Ce are the equilibrium concentrations of Cu^{2+} in the adsorbed and liquid phases in mg/g, and k_F and n are the Freundlich constants that are related to the sorption capacity and intensity, respectively. The Freundlich constants K_F and n can be calculated from the slope and intercept of the linear plot of log (x/m) a logCe.

The Langmuir sorption isotherm equation $\frac{x}{m} = \frac{Q_{\max} K_L C_e}{1 + k_L C_e}$ on linearization becomes:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{\max}} + \frac{1}{Q_{\max}} C_e$$

(3)

where Qmax is the maximum adsorption capacity (mg g^{-1}) when all adsorption sites are occupied, Ce(mg) is the equilibrium concentration of copper, Qe is the equilibrium adsorption capacity and the Langmuir constant K_L (L/mg) is derived from the ratio of the adsorption rate constant to the desorption rate constant.

2.6.2 Kinetics models

Kinetics adsorption data were fitted to the pseudo-first-order kinetics model [29].

$$\frac{dq_t}{dt} = k_1(q_e - q_t)$$

(4)

Where qe and q_t refer to the amount of Cu^{2+} adsorbed (mg g^{-1}) at equilibrium and at any time, t (min), respectively, and k1 is the rate constant for pseudo-first-order sorption (min^{-1}). Integration of equation 4 for the boundary conditions t = 0 to t and q_t = 0 to qt, gives equation 5:

$$\log \frac{q_e}{(q_e - q_t)} = \log q_e - \frac{k_1 t}{2.303}$$

(5)

Equation 4 is rearranged to give equation 5:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$

(6)

The slope of a plot of $\log(q_e - q_t)$ versus t was used to determine the first-order rate constant, k1. In many cases, the first-order equation of Lagergren does not fit well for the whole range of contact times and is generally applicable over the initial stage of the adsorption processes [30]. Kinetics data were further treated with the pseudo-second-order kinetic model [30]. The pseudo-second-order equation is also based on the sorption capacity of the solid phase. Contrary to the other model, it predicts the behaviour over the whole range of adsorption and is in agreement with an adsorption mechanism involving the rate-controlling step. The differential equation is given by equation 7:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2$$

(7)

Where k_2 is the rate constant for pseudo-second-order adsorption (g mg-1 min-1). Integrating Eq.(7) for the boundary conditions t = 0 to t and q_t = 0 to qt, gives equation 8:

$$\left(\frac{t}{q_t}\right) = \left(\frac{t}{q_e}\right) + \left[\left(\frac{1}{k_2 q_e^2}\right)\right] \quad (8)$$

This is the integrated rate law for a pseudo-second-order reaction.

The slope and intercept of a plot of t/qt versus t were used to calculate the second-order rate constant, k2. This model is more likely to predict the behaviour over the whole range of adsorption and is in agreement with the chemisorption mechanism being the rate-controlling step [28].

2.6.3 Adsorption mechanism

In order to gain insight into the mechanism and rate-controlling step affecting the kinetics of adsorption, the kinetics experimental results were fitted to the Weber and Morris intra-particle diffusion model (1963), in which the rate of intra-particle diffusion is a function of t1/2 and can be defined according to equation 9:

$$q = f\left(\frac{D_t}{r_p^2}\right)^{1/2} = k_w t^{1/2} + C_i$$

(9)

Where rp is the particle radius, Dt is the effective diffusivity of solutes within the particle, and kw is the intra-particle diffusion rate. Values of k_w can be obtained by linearizing the curve q = f ($t^{1/2}$). Such types of plots may present multi-linearity, implying that the overall adsorption process may be controlled by one or more steps, such as film or external diffusion, intra-particle diffusion and a chemical reaction on the pore surface, or a combination of more than one step. Weber and Morris (1963) reported that if intra-particle diffusion was involved in the adsorption process, then a plot of the square root of time versus the adsorption amount would result in a linear relationship, and that the intra-particle diffusion would be the controlling step if this line passes through the origin.

3. Results and discussion

3.1. Characterization of raws materials

In this work, cotton stalk pod husk an industrial effluent abundantly available from the cotton processing plants, was utilized as a feedstock for preparation of activated carbon at 600 °C GAC1(0.5/1 for 3h), GAC2 (1/1 for 3h), GAC3 (1.5/1 for 3h), GAC4 (2/1 for 3h) and GAC5 (3/1 for 3h) via microwave induced (w/w) of H_3PO_4 activation

3.1.1. Thermal analysis of adsorbent

Thermal behaviour of raw cotton stalk obtained from the thermogravimetric (TG) and differential thermal analysis (DSC) is depicted in Fig.1. The decomposition of cotton stalk pod husk is found to occur in three stages. The first stage corresponds to an approximate weight loss of 6.2% at 50°C -200 °C. It is mainly attributed to release of H_2O by evaporation and dehydration reactions [31] as well as decomposition of hemicellulose. The low moisture content of the dried stalk resulted in low weight loss. The second stage has a greater weight loss of about 46.1% at 200°C–353°C. This corresponds to the primary carbonization and involves degradation of cellulose and lignin [32]. Third stage weight loss is approximately 37.7% at 353°C–900°C. In this stage, weight loss is exponential. As most of the volatile constituents have already been removed, this stage corresponds to the formation of activated carbon. Thus from TG and DSC analyses, it is observed that a temperature above 353°C can be chosen for preparation of the activated carbon from GACs.

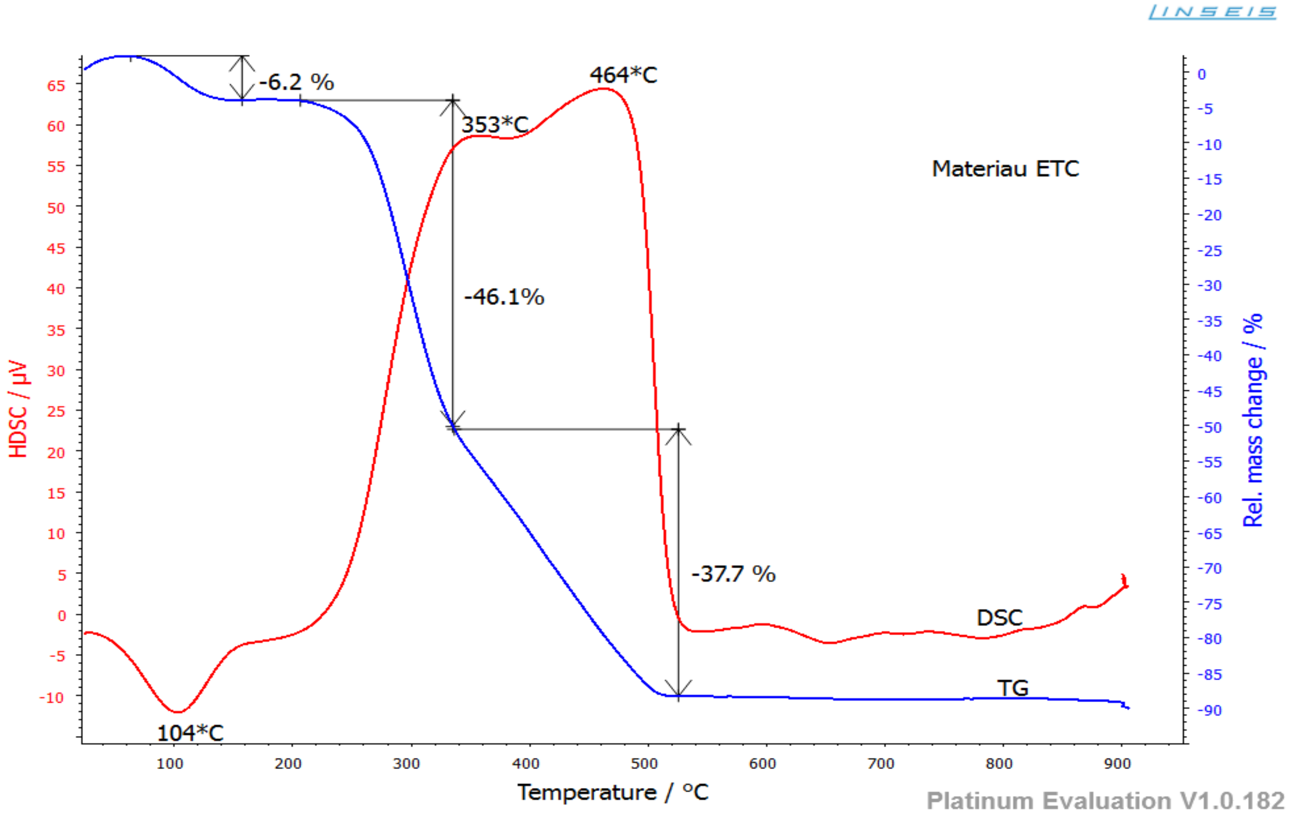


Fig 1. Curve of thermo-gravimetric analysis (TG and DSC) of cotton stalk pod husk.

3.1.2. Functionalization

The Fourier transform infrared (FTIR) spectra of the activated carbons are shown in Fig. 2.

The absorption between 2750-2560 cm^{-1} corresponds to the elongation vibrations of hydrogen of the hydroxyl groups OH of (carboxyls, phenols or alcohols) and of the absorbed water [33] it also corresponds to vibration of OH elongation of cellulose and lignin [34]. A broad band between 2260-2190 cm^{-1} which corresponds to a $C\equiv C$ elongation in disubstituted alkyne. A small band around 1710-1690 cm^{-1} attributed to the C = O elongation vibration of the carboxylic acid. A band at 1680-1630 cm^{-1} which corresponds to a C = C alkene. A band around 1565-1475 cm^{-1} corresponding to the N-H deformation in the secondary amide. At around 1120-1080 cm^{-1}, a band corresponding to a C-O elongation of the C-OH group in secondary or tertiary alcohol is observed. The intense peak observed at 960-900 cm^{-1} corresponds to a deformation vibration outside the CH_2 plane which is associated with the vinyl compounds. At about 860-760 cm^{-1} we have a deformation vibration outside the NH_2 plane of the $R-NH_2$ group of the primary amine. The band observed at 520-430 cm^{-1} corresponds to the C-O-C vibration in ether.

Table 1: Bandes infrarouges observées dans les spectres IRTF des différents matériaux.

Adsorbants	Nombres d'onde (cm^{-1})								
	O-H	C≡C	C=O	C=C	N-H	C-OH	CH=CH2	R-NH2	C-O-C
GAC1	2681.85	2234.97	1692.34	-	1541.37	1120.55	954.59	-	467.07
GAC2	2702.82	2240.27	-	1678.08	1555.93	1118.64	949.18	-	453.44
GAC3	2574.30	-	1692.53	-	1556.73	1194.70	901.12	-	-
GAC4	2675.22	2205.48	-	1678.66	1588.67	1163.05	969.64	-	439.34
GAC5	2658.02	2192.30	-	-	1557.81	1112.04	918.13	840.03	446.03

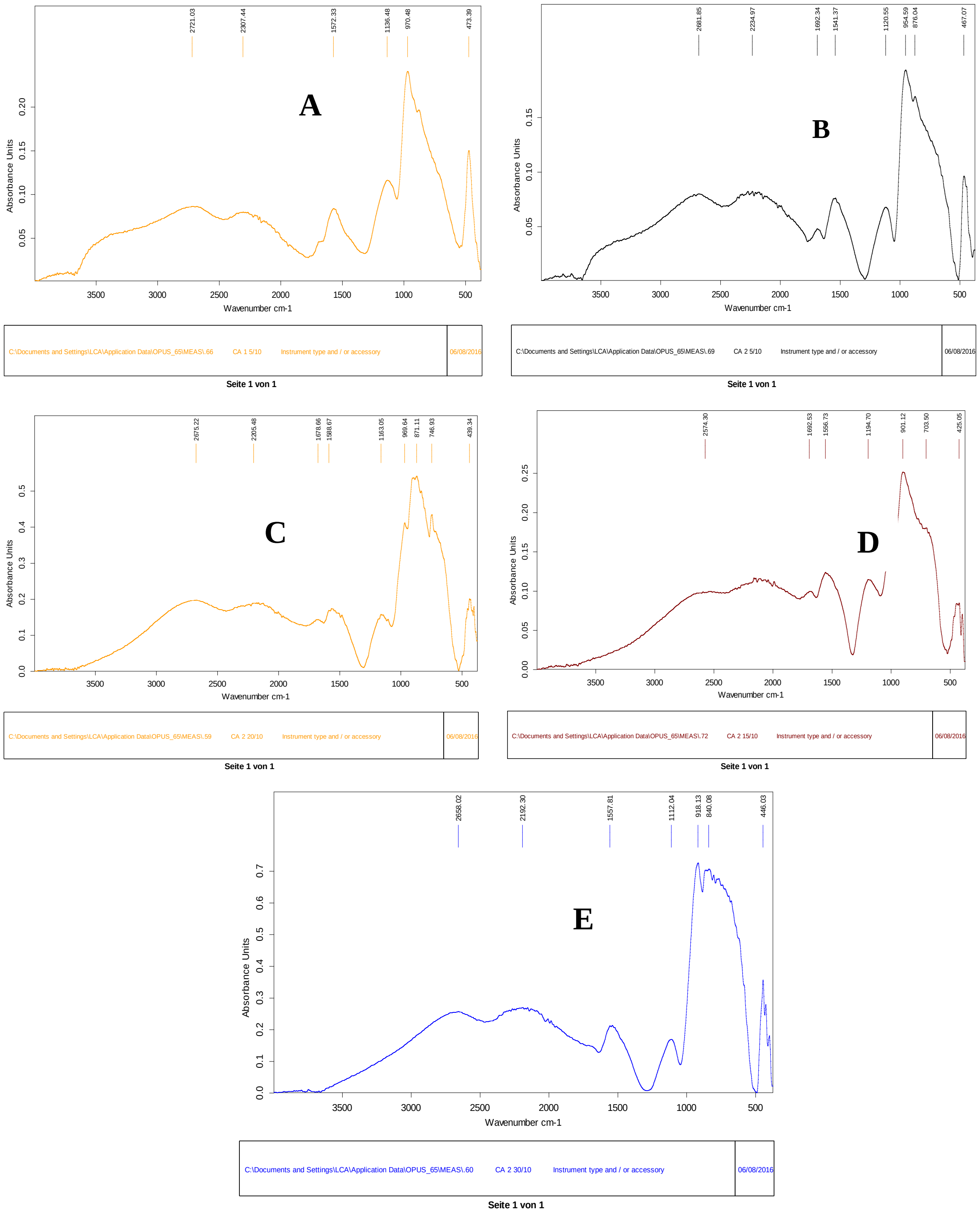


Fig.2: FTIR spectra for GAC1 (A), GAC2 (B), GAC3(C), GAC4(D) and GAC5 (E).

3.1.3 Iodine number

Determining the iodine number is one of the methods to determine the adsorption capacity of activated carbons. It is a measure of the micropore (0–20 Å) content of the activated carbon by adsorption of iodine from solution. The typical range is 500–1200 mg/g, which is equivalent to surface area of carbon between 900 and 1100 m^2/g [35].

It can be seen from Fig 3 that iodine adsorption of activated carbon prepared with activation at 600°C slightly increases with increasing impregnation ratios. It was shown that micropore content on surface of activated carbon is slightly increased with increasing impregnation ratios. This is attributed to more extensive reaction between H_3PO_4 and surface carbon [36], leading to increased release of CO_2 and CO gases and creating micropores inside of the mesopores [37].

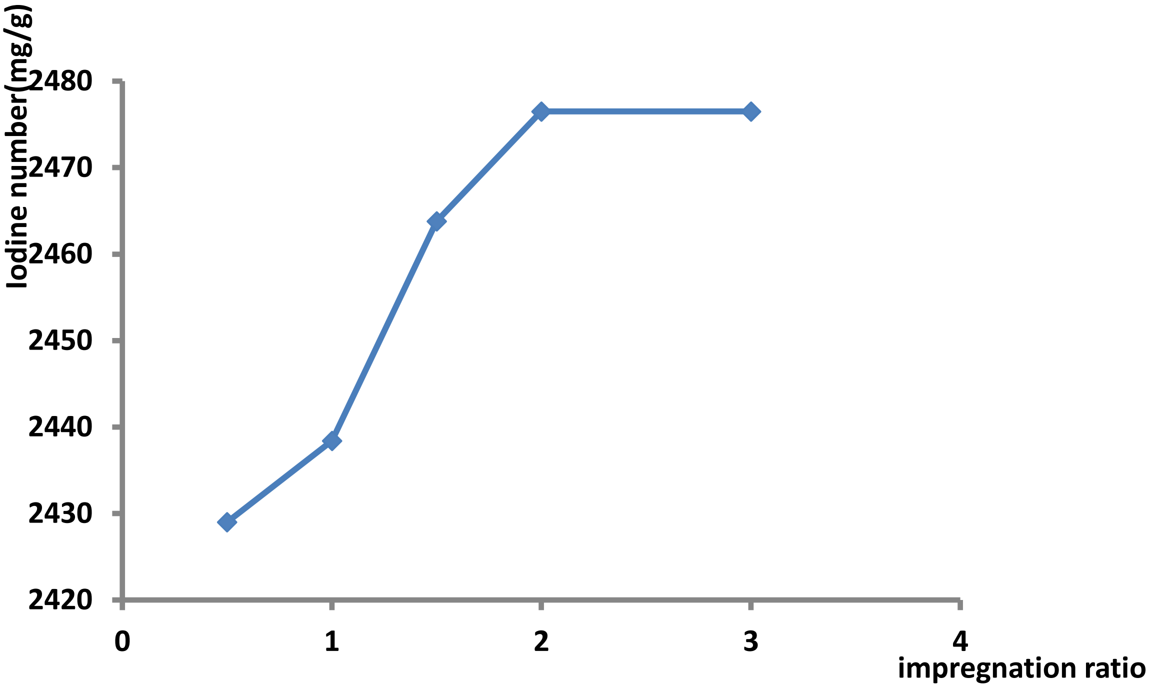


Fig.3 . Effect of impregnation ratio at the activation temperature of 600°C.

3.2 Batch adsorption studies

3.2.1. Effect of contact time

Fig. 4 shows the effect of contact time on the removal of Cu^{2+}. Experimental studies were carried out with varying adsorbents (GAC1, GAC2, GAC3, GAC4 and GAC5) with 100 mgL-1 of the initial copper ion concentration. Equilibrium adsorption was established within 60 min for the metal ion. It is very clear from the results that the agitation time required for maximum uptake of metal ions by activated carbon was dependent on the initial metal ion concentration. This data is important because equilibrium time is one of the parameters for economical wastewater treatment plant application [18]. According to these results; the agitation time was fixed at 2h for the rest of the batch experiments to make sure that equilibrium was attained.

3.2.2. Equilibrium isotherms

Adsorption isotherms provide information on the nature of the solute–surface interaction as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto the adsorbent surface at constant temperature. These equilibrium experiments were performed at room temperature with an adsorbent mass of 0.5 g and an adsorbate concentration (C_0) ranging from 25 – 125 mg/L. In order to understand the adsorption mechanism of copper onto activated carbon, two adsorption isotherm models, Langmuir and Freundlich, were used to fit the experimental data. The isotherm parameters were determined by non-linear regression with Origin version 7.0 B a Microsoft Windows-based statistical software. The adsorption isotherms obtained for the various GACs are illustrated in Fig. 5A and Fig. 5B. The values of the parameters and the correlation coefficients obtained for the different adsorbents are listed in Table 2. It is well known that the Langmuir model is usually used with an ideal assumption of a monolayer adsorption surface [27]. The value of the correlation coefficients (R^2) for the two models for different GACs shows that the best fit for both models. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L, which is defined

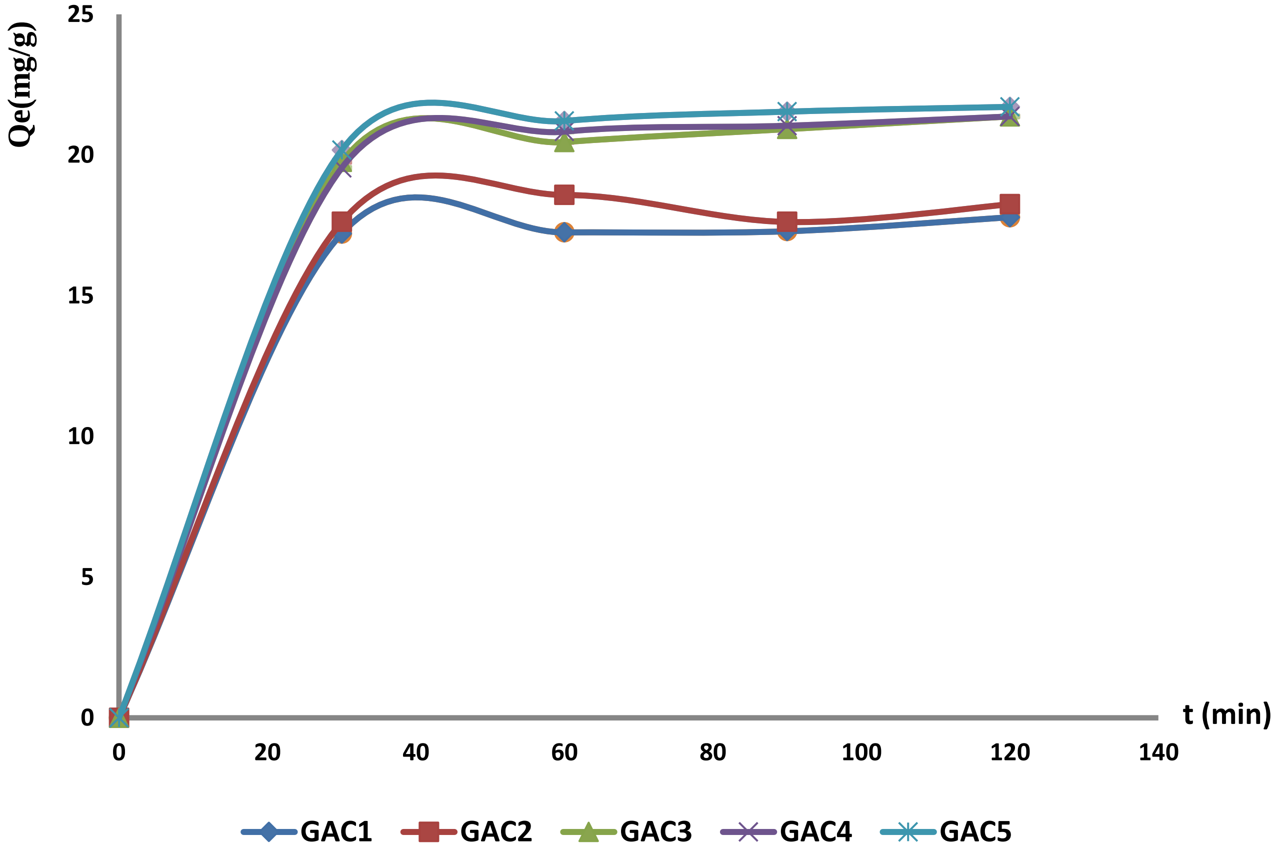


Fig.4: Effect of agitation time and initial concentration of Cu^{2+}on the adsorption of $Cu^{2+}$for GACs. Conditions: carbon concentration, 0.5 g/50 ml.

as $$R_L = \frac{1}{1 + K_L C_0}$$

where K_L is the Langmuir constant and C_0 is the initial concentration of Cu^{2+}. The R_L value indicates the shape of the is otherm as follows.

$R_L > 1$ Unfavourable

$R_L = 1$ Linear

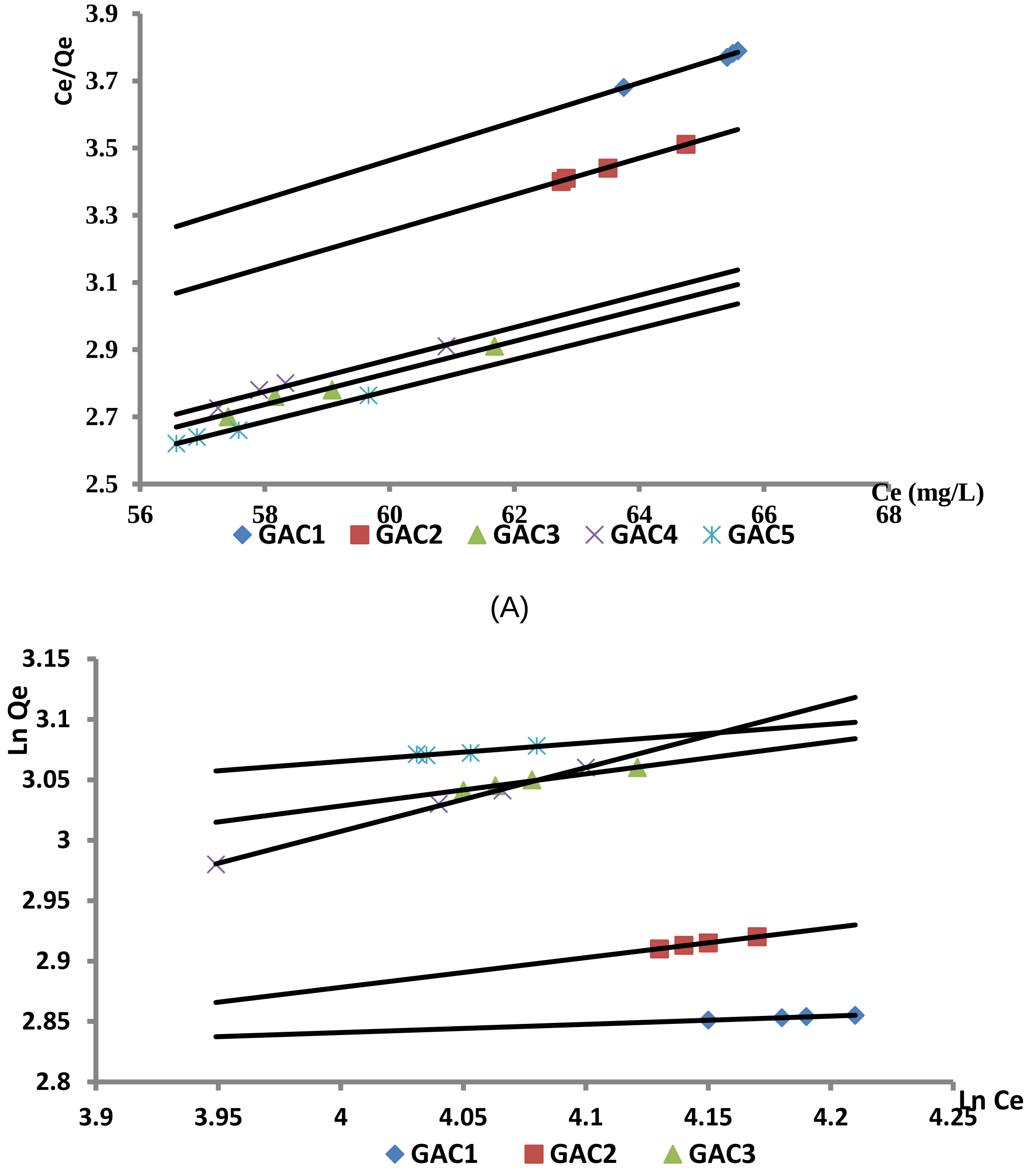
$0<R_L < 1$ Favourable

$R_L = 0$ Irreversible

According to Mckay et al., 1982. RL values between 0 and 1 indicate favourable adsorption. The RL value for copper was respectively 0.46, 0.99, 0.38, 0.59 and 0.3 for GAC1, GAC2, GAC3, GAC4 and GAC5 for 100 mgL^{-1}. Hence, the adsorption of the Cu^{2+} on GACs seems to be favourable.

Table 2: Isotherm parameters for Cu^{2+} adsorption onto GAC1, GAC2, GAC3, GAC4 and GAC5.

adsorbents	Langmuir				Freundlich		
	Qmax	K_L	R_L	R^2	K_f	n	R^2
GAC1	17.54	11.4	0.46	0.994	13.03	1.47	0.990
GAC2	18.51	9	0.99	0.996	6.65	4.08	0.996
GAC3	21.27	15.66	0.38	0.983	7.08	3.78	0.992
GAC4	21.27	6.71	0.59	0.979	2.44	1.897	0.998
GAC5	21.73	23	0.3	0.994	13.92	9.25	0.995



(A)

(B)

Fig.5: Langmuir (A) and Freundlich (B) isotherms for Cu^{2+} adsorption onto GACs at room temperature.

3.2.3 Kinetics studies

In order to investigate the kinetics of adsorption of Cu^{2+}, the Lagergren-first-order model and Ho's pseudo-second-order model were used. The values of the parameters and the correlation coefficients obtained by using non-linear regression with Origin version 7.0 at room temperatures are listed in Table 3. The fit of the experimental data to the kinetics models are illustrated in Fig.6A and Fig.6B. It was found that Ho's pseudo-second-order model gave the highest values of the correlation coefficients and predicted qe more accurately than the other model investigated. Therefore, Ho's pseudo-second-order model could be used for the prediction of the kinetics of adsorption of Cu^{2+} on the activated carbon.

Table 3: Kinetics parameters for Cu^{2+}adsorption onto cotton stalk pod husk activated carbons.

Model	Lagergren		Pseudo second order			Intra-particle Diffusion		
	K_1/min^{-1}	R^2	K_{2app}/g.mg-1.min^{-1}	R^2	h/mg.g^{-1}.min^{-1}	Kw/mg/gmin$^{0.5}$	R^2	I
CAC1	0.071	0.788	0.200	0.999	66.102	0.057	0.633	16.61
GAC2	0.025	0.907	1.450	0.996	496.799	0.091	0/079	17.53
CAC3	0.083	0.978	0.060	0.999	29.623	0.280	0.998	17.97
CAC4	0.120	0.955	0.067	0.999	33.079	0.293	0.903	18.15
GAC5	0.094	0.771	0.130	0.999	64.184	0.323	0.918	18.79

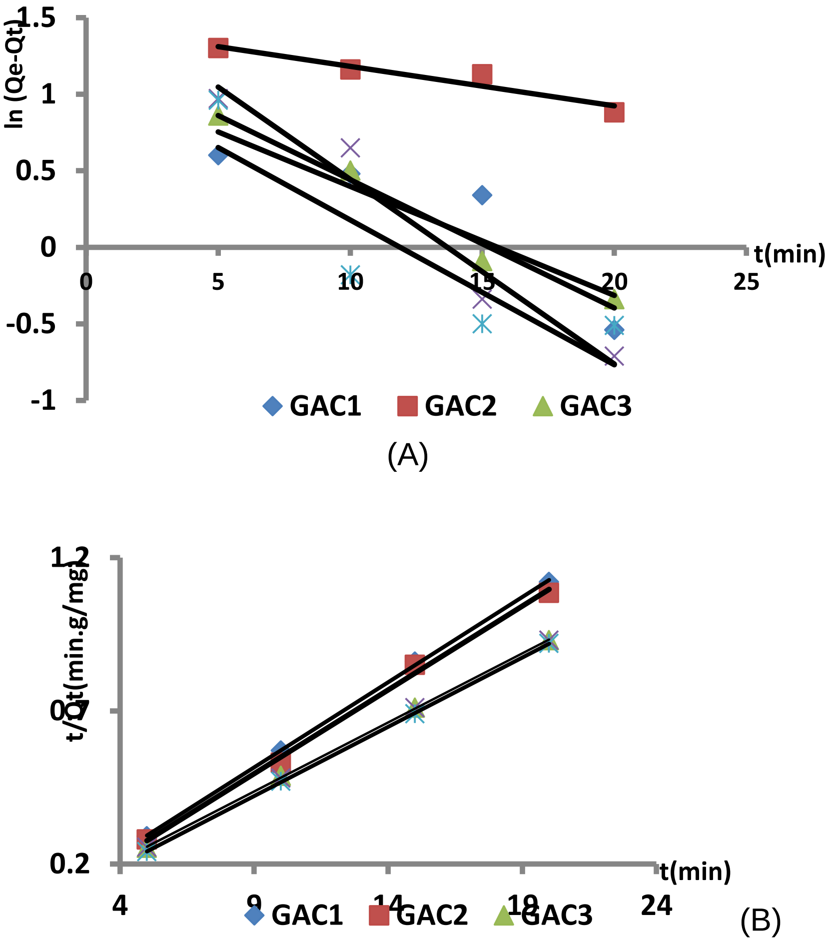


Fig.6: Fit of the pseudo-first-order (A) and pseudo-second-order (B) kinetics models for the adsorption of Cu^{2+} onto GACs for C_0 = 100 mgL^{-1}.

3.2.4. Adsorption mechanism

Fig.7. shows the intra-particle diffusion plot for the adsorption of Cu^{2+} on the five activated carbons GAC1, GAC2, GAC3, GAC4 and GAC5. From Fig. 7, it can be seen that the plots for GAC1, GAC2, GAC3, GAC4 and GAC5 show similar features; the first stage is attributed to external surface adsorption. The second stage represents intra-particle diffusion. The last stage illustrates the final equilibrium stage where maximum adsorption was presented attained.

In these observations, the adsorption of Cu^{2+} occurred in two phases, surface sorption followed by the intraparticle diffusion. This observation is also similar to the observation discussed by Ofomaja [34]. As shown in Fig. 7, the task to of distinguishing between film diffusion (first stage) and particle diffusion mechanisms (second stage) is difficult. The kw value evaluated from the first linear parts of these curves for GAC1, GAC2, GAC3, GAC4 and GAC5 were 16.61, 17.53, 17.97, 18.15 and 18.79 (mg/gmin$^{0.5}$), respectively. The kw value increased with increasing impregnation of H_3PSO_4, which showed that the adsorption rate increased with increasing impregnation of H_3PSO_4.

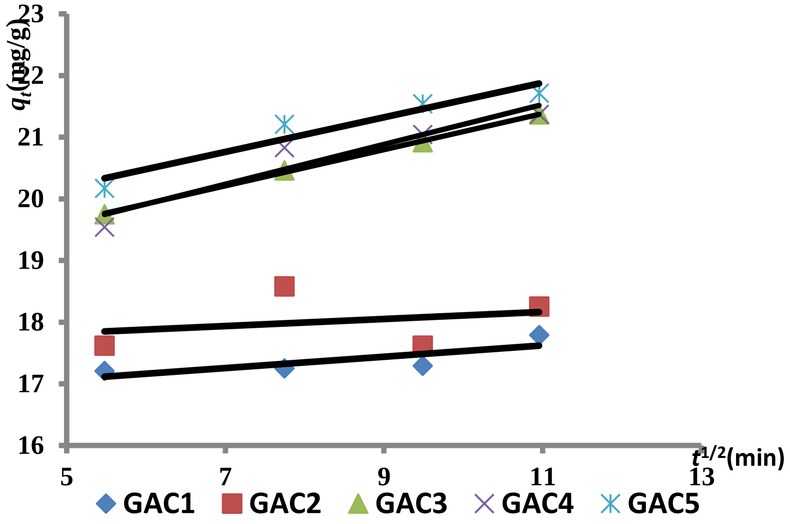


Fig.8: Plot of the intra-particle diffusion model for the adsorption of Cu^{2+} on GACs for C_0 = 100 mgL^{-1}.

3.2.5. Adsorption thermodynamics

The result on the effect of temperature on the adsorption of Cu(II) ions unto GACs is presented in Fig.8. From the graph, a slight increase in adsorption of metal ions with increase in solution temperature from 300 to 328 K was obtained. This shows that the process is endothermic in nature. The increase in percentage removal of metal ions at higher temperature may be due to a greater kinetic energy acquired by the metal ions with temperature increase resulting in an easier diffusion from the bulk solution unto the surface of GACs. The standard free energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) thermodynamic parameters were determined to evaluate the feasibility of the adsorption process [38]. The standard free energy of the adsorption is related to the thermodynamic equilibrium constant (Kc) by the following equation:

$$\Delta G^0 = -RT \ln K_c \quad (10)$$

Where T is temperature (K), R is the ideal gas constant (8.314 J/mol K) and Kc is defined by the equation:

$$K_C = \frac{C_a}{Ce} \quad (11)$$

where Ca is the metal ion concentration adsorbed from solution at equilibrium (mg/L) and Ce is the equilibrium metal ion concentration in solution (mg/L). Also, the Gibb's free energy is related to the enthalpy change (ΔH^0) and entropy change (ΔS^0) at a constant temperature by the Van't Hoff [7] equation:

$$\ln K_C = -\left(\frac{\Delta G^0}{RT}\right) = -\left(\frac{\Delta H^0}{RT}\right) + \left(\frac{\Delta S^0}{R}\right) \quad (12)$$

The values of (ΔH^0) and (ΔS^0) were calculated from the slope and intercept of the plot (lnKc versus 1/T) and the calculated thermodynamic parameter values are presented in Table 4. The values of (ΔH^0) obtained for the metal ions are positive, indicating the endothermic nature of the adsorption process, which explains the fact that adsorption efficiency increased with increase in temperature. Positive values of (ΔS^0) also indicated an increase in randomness at the solid/liquid interface. During the sorption process while low values of (ΔS^0) that no remarkable change on entropy occurred. It is clear that the reaction is spontaneous in nature as negative values of (ΔG^0) were obtained at all temperatures studied. It was also observed that the change in (ΔG^0) indicated increased with increase in temperature which indicates an increase in the spontaneity of the process with temperature. The magnitude of the enthalpy change (ΔH^0) provides information about the type of sorption. The heat evolved during physisorption generally lies in the range of 2.1 – 20.9 kJ/mol, while the heat of chemisorptions generally falls in the range of 80-200kJ/mol [38]. From table 4, the values of (ΔH^0) for Cu(II) ions are 7.356 ; 6.667 ; 13.02 ; 3.735 and 8.453 kJ/mol, respectively. This indicates that the adsorption of Cu(II) ions unto GACs may be attributed to a physical adsorption process. This may be one of the reasons why the data did not fit the pseudo second equation, since the pseudo-second order equation depicts a chemisorptions mechanism. This low energy is desirable, as physisorption processes usually require a low energy barrier to be overcome by metals ions for binding onto the surface of GACs and also enhances easy desorption of the metal ions from the surface, when regeneration of the adsorbent is required.

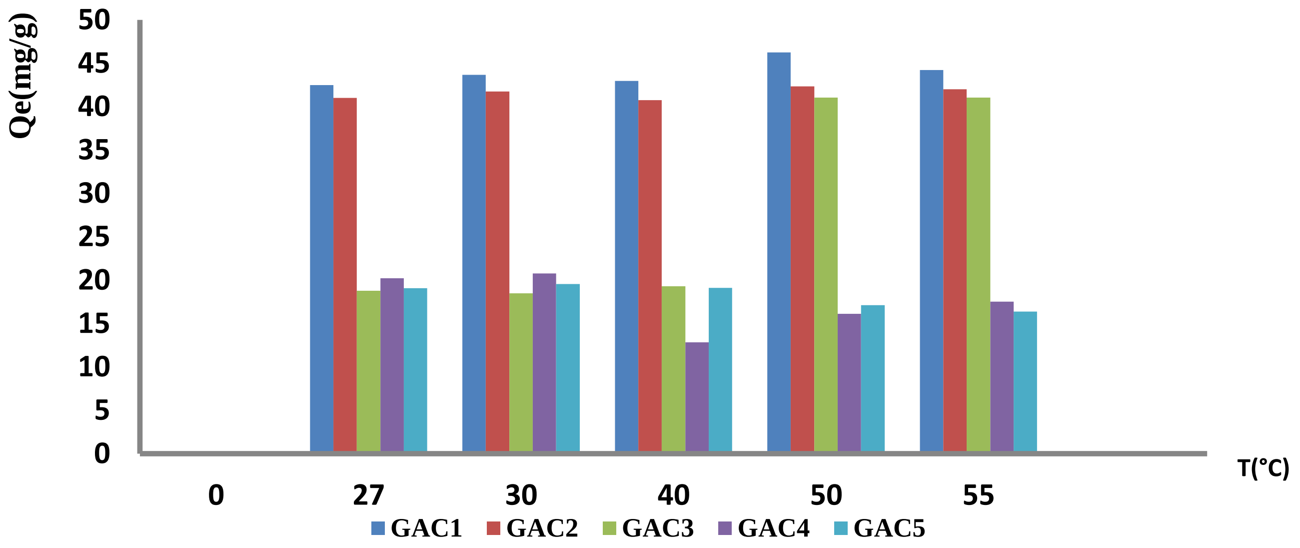


Fig 9. The effect of solution temperature on the percentage removal of Cu(II) ions from solution unto GACs. Metal concentration 100 mg/L, adsorbent dose 0.1 g, contact time 120 min.

Table 4: Thermodynamic parameters for adsorption of Cu(II) ions form solution unto GACs

Adsorbents	Température (°C)	ΔG°(KJ/mol)	ΔH° (KJ/mol)	ΔS° (J.mol-1.k-1)
GAC1	27	-2.85	7.356	34.02
	30	-2.95		
	40	-3.29		
	50	-3.632		
	55	-3.802		
GAC2	27	-1.97	6.667	28.79
	30	-2.056		
	40	-2.344		
	50	-2.535		
	55	-2.632		
GAC3	27	-2.7	13.02	52.4
	30	-2.86		
	40	-3.38		
	50	-3.9		
	55	-4.17		
GAC4	27	-2.08	3.735	19.415
	30	-2.147		
	40	-2.341		
	50	-2.535		
	55	-2.632		
GAC2	27	-2.78	8.453	35.312
	30	-2.86		
	40	-3.23		
	50	-3.8		
	55	-4.68		

4. Conclusions

Activated carbon was produced from cotton stalks husk was successfully utilized as a low-cost adsorbent for the removal of Cu(II) ions from aqueous solution by batch adsorption method. The adsorption process was found to be dependent on many factors such as the initial concentration of copper ions, contact time and also effect of impregnation ratio. The equilibrium data were tested using the Langmuir and Freundlich, isotherm model and the best fit was obtained with the Langmuir and Freundlich model. Kinetic parameters were also analyzed using the Lagergren pseudo-first order, pseudo-second order, and intraparticle diffusion rate equation. The pseudo-second order provided the best fit to the experimental data and the result also indicated the presence of intraparticle diffusion on the sorption of copper ions, although it was not the sole rate determining step. Thermodynamic analysis showed that the process was spontaneous and endothermic in nature. The value of the enthalpy change ΔH^0 indicated a physisorption mechanism for copper ions unto the adsorbent. The Langmuir and Freundlich isotherms showed a favorable adsorption process between the adsorbent and metal ions in solution. It was also found that pore diffusion played an important role in the adsorption.

Conflicts of interest

The authors declare no conflicts of interests.

References

[1] Ahluwalia SS, Goyal D. Microbial and plant derived biomass for removal of heavy metals from wastewater. Biores Technol 2007;98:2243–57.

[2] Abu Al-Rub, F.A., El-Naas, M.H., Ashour, I., Al-Marzouqi, M., Process biochem. 41 (2006) 457

[3] Ayhan, I.Ş., Özacar, M., J. Hazard. Mater. 157 (2008) 277.

[4] Karthikeyan, T.S., Rajgopal, S., Miranda, L.R., J. Hazard. Mater. 124 (2005) 192.

[5] Kanan, N., Rengasamy G., Water Air and Soil Pollut. 163 (2005) 185.

[6] Amuda, O.S., Giwa, A.A., Bello, I.A., Biochemical Eng. J. 36 (2007) 174.

[6] Kurniawan TK, Chan GYS, Lo W, Babel S. Comparison of low-cost adsorbents for treating wastewaters laden with heavy metals. Sci Total Environ 2006;366:409–26.

[7] Liang S, Guo X, Feng N, Tian Q. Isotherms, kinetics and thermodynamic studies of adsorption of Cu2+ from aqueous solution by Mg2+ /K+ orange peel adsorbents. J Hazard Mater 2010;174:756–62.

[8] Annadurai A, Juang R.S, Lee D.J. Adsorption of heavy metals from water using banana and orange peel. Water Sci Technol 2002;47:185–90.

[12] Lawal O.S, Sanni I.A, Ajayi I.A, Rabiu O.O. Equilibrium, thermodynamics and kinetic studies for the biosorption of aqueous lead(II) ions onto the seed husk of Calophyllum inophyllum. J Hazard Mater 2010;177:829–35.

[13] Vazquez G, Mosquera O, Freire M.S, Antorrena G, Alvarez J.G. Alkaline pretreatment of waste chestnut shell from a food industry to enhance cadmium, copper, lead and zinc ions removal. Chem Eng J 2012;184:147–55.

[14] Boudrhem F, Benissad F.A, Soualah A. Adsorption of lead (II) from aqueous solution by using leaves of date trees as an adsorbent. J Chem Eng Data 2011;56:1804–12.

[15] Huang K, Zhu H. Removal of Pb (II) from aqueous solution by adsorption on chemically modified muskmelon peel. Environ Sci Pollut Res 2013;20(7):4424–34.

[16] Saka C, Sahin O, Demir H, Kahyaoglu M. Removal of lead (II) from aqueous solution using pre-boiled and formaldehyde treated onions skins as a new adsorbent. Sep Sci Technol 2011;46:507–17.

[17] Meitei MD, Prasad MNV. Lead (II) and cadmium (II) biosorption on spirodela polyrhiza (L) Schleiden biomass. J Environ Chem Eng 2013;1:200–7.

[18] Legva-Ramos R, Landin-rodriguez LE, Legva-Ramos S, Medellin-Castillo NA. Modification of corncob with citric acid to enhance its capacity for adsorbing cadmium (II) from water solution. Chem Eng J 2012;180:113–20.

[19] Chen S, Yue Q, Gao B, Li Q, Xu X. Removal of Cr (VI) from aqueous solution using modified corn stalks: characterization, equilibrium, kinetic and thermodynamic study. Chem Eng J 2011;168:909–17.

[20] Gupta V.K, Rastogi A, Nayak A. Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material. J Colloid Interface Sci 2010;342:783–842.

[21] Mondal M.K. Removal of Pb (II) from aqueous solution by adsorption using activated tea waste. Korean J Chem Eng 2010; 27(11):144–51.

[22] Guler U.A, Sarioglu M. Single and binary biosorption of Cu (II) and Ni (II) and methylene blue by raw and pretreated Spirogyra sp: Equilibrium and kinetic modeling. J Environ Chem Eng 2013;1:369–77.

[23] Yadav S.K, Singh D.K, Sinha S. Chemical carbonization of papaya seed originated charcoals for sorption of Pb (II) from aqueous solution. J Environ Chem Eng 2014;2:9–19.

[24] Li T, Liu Y, Peng Q, Hua X, Liao T, Wanga H, et al. Removal of lead (II) from aqueous solution with ethylenediamine-modified yeast biomass coated with magnetic chitosan microparticles: kinetic and equilibrium modeling. Chem Eng J 2013;214:189–97.

[25] Ahmad S, Khalid N, Daud M. Adsorption studies of lead on lateritic minerals from aqueous media. Sep Sci Technol 2002;37(2):343–62.

[26] Hamidpour M, Kalbasi M, Afguni M, Shariatmadari H, Hlm PE, Hansen HCB. Sorption hysteresis of Cd (II) and Pb (II) on natural zeolite and bentonite. J Hazard Mater 2010;181:686–91.

[27] Folasegun Anthony Dawodu, Kovo Godfrey Akpomie. simultaneous adsorption of Ni(II) and Mn(II) ions from aqueous solution unto a Nigerian kaolinite clay. j mater res technol. 2014, 3(2) , 129–141.

[28] Kede C.M., Etoh M.A., Ndibewu P.P., Ngomo H.M., Ghogomu P.M. Equilibria and kinetic studies on the adsorption of cadmium onto Cameroonian wetland clays.

British J of Applied Sci and Technology, 2014, 4(7), 1070-1088.

[29] Lagergren S., about the theory of so-called adsorption of soluble substances, Kungliga Svenska Vetenskapsakademiens Handling 1898, 24, 1–39.

[30] Ho Y.S., McKay G., Pseudo-second order model for sorption processes, Process Biochem. 1999, 34, 451 – 465.

[31] Jayaramudu, J., Maity, A., Sadiku, E.R., Guduri, B.R., Varadu Rajulu, A., Ramana, CH.V.V., and LI,R. Structure and properties of new natural cellulose fabrics from Cordia dichotoma, Carbohydr. Polym. 2011, 86(4), 1623-1629.

[32] Han, R.P., Zhang,L.J., Song, C., Zhang, M.M., and Zhu, H. M., Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode, Carbohydr. Polym. 2010, 79(4), 1140-1149.

[33] Kumar, R., Barakat, M.A., Decolourization of hazardous brilliant green from aqueous solution using binary oxidized cactus fruit peel. Chemical Engineering Journal, 2013, 22(6), 377- 383

[34] Ofomaja, A. E., Sorptive removal of methylene blue from aqueous solution using palm kernel fibre : effect of fibre dose. Biochem. Eng. J, 2008, 40, 8-18.

[35] Deng. H., Li. G., Yang. H., Tang. J., and Tang. J., “Preparation of activated carbons from cotton stalk by microwave assisted KOH and K2CO3 activation,” Chemical Engineering Journal, vol. 163, no. 3, pp. 373–381, 2010.

[36] Mitome. T., Uchida. Y., Egashira. Y., Hayashi. K., Nishiura. A., and Nishiyama. N., “Adsorption of indole on KOH-activated mesoporous carbon,” Colloids and Surfaces A: Physicochemical and Engineering Aspects, vol. 424, pp. 89–95, 2013.

[37] Loredo-Cancino. M., Soto-Regalado. E., Cerino-Córdova. F. J., García-Reyes. R. B., García-León. A. M., and Garza-González. M. T., “Determining optimal conditions to produce activated carbon from barley husks using single or dual optimization,” Journal of Environmental Management, vol. 125, pp. 117–125, 2013.

[38] Liu Y, Liu YJ. Biosorption isotherms, kinetics and thermodynamics. Sep Purif Technol 2008; 61:229–42.