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Adsorption studies on heavy metal removal using raw /zinc oxide nano composite of grape fruit peels

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Abstract

Water pollution by heavy metal is a serious environmental problem that affects the ecosystem and living beings, hence, calls for serious global attention, in the area of remediation. Adsorption is one of the best technologies for the removal of heavy metals and attention has been focused on agricultural waste materials. Agricultural waste materials are emerging as low-cost adsorbents for these pollutants from aqueous solutions. The application of Nano technology has provided efficient adsorbents for the removal of heavy metals from aqueous solution because of the unique properties they display such as large surface area, enhanced active sites and the functional groups that are present on their surface. This research explored the potentials in grape fruit peels (Citrus paradise) in the raw, activated carbon /zinc oxide Nano composite forms(G(raw), G(NC) for the removal of copper from aqueous solutions. Batch adsorption studies were carried out to determine the adsorption capacities of the different adsorbents and the influence of varying conditions such as (temperature of the system, time of contact and concentration of the metal ion) were studied. From the experimental data, different kinetic and equilibrium models were sampled and the results showed that the sorption process best fitted into the pseudo second order kinetic model than the pseudo first order model with high regression values (0.999 &0.998 for G(raw) and G(NC) respectively), indicating a chemisorption process. The experimental data also showed best fit to the intra particle diffusion model against the liquid film model for G(NC)indicating pore penetration mechanism while G(raw) yielded more to liquid film diffusion model indicating surface penetration of the adsorbate onto the adsorbent. The thermodynamic studies conducted in this study revealed the sorption process is chemisorption in nature, spontaneous and with increased randomness or disorderliness of the system. From the obtained results, it is possible to affirm that all adsorbents used are good alternatives to the synthetic materials, with adsorption capacities being greater with G(NC).

Keywords: heavy metals, adsorption, Nano technology

Introduction

Safe water is very important for public health, whether it is for drinking, domestic use, production or recreational purposes. water pollution has given rise to increasing concerns around the world. The human population has increased tremendously and as such the agricultural and industrial sectors have also intensified their production to meet the demands of the growing populace hence their activities have continued to introduce contaminants / pollutants into the environment (water bodies).

Among these pollutants in the environment, Heavy metal pollution is the most worrisome (Yesilada, 2001) [29] because not only are some of them harmful even at low concentration, they are also non-biodegradable and non –thermo degradable. This non –biodegradability and non-thermo degradability nature of heavy metals make them to persist in the environment. Over a long time, they accumulate and get to toxic, non-tolerant (non-permissible) levels which when they enter into the water or food chain causes health issues (Ajah *et al*, 2022).

In recent decades, different agricultural wastes has been examined in terms of their capacity to remove heavy metals in aqueous solution. A good number of studies have been carried out to evaluate the efficiency and effectiveness of agricultural wastes as adsorbents in metal removal, including nut shells (Altun and Pehlivan, 2007) [4], fruit shells (Hamza *et al*, 2016, Mallam-pati *et al*, 2015) [11, 17], seeds (Okparaeke *et al*, 2016), peels (Ahnadurai *et al*, 2003), roots (Mukaratiwa-Muchanyereyi *et al*, 2015) [20], and leaves (Fadzil *et al*., 2016) [10].

Most recently, the application of Nano-materials has gained weight in the removal of heavy metals because of the enhanced properties they possess as compared to their large-scale counter parts. Zinc oxide nanoparticles constitute one of the important metal oxides materials that have been widely applied in materials science due to its unique physical, chemical, and biological properties such as biocompatible, environmentally friendly, low cost and non-toxic nature (Alwan *et al*. 2015) [5]. Owing to its exceptional properties, ZnO nanoparticles have been applied as a functional advanced material to solve different problems especially in the field of catalysis for wastewater treatment and also as cosmetics and antimicrobial additives (Ruszkiewicz *et al*. 2017) [24]. Zinc oxide nanoparticles display some properties such as high chemical and thermal stability, unsaturated surfaces, and excellent adsorption behavior towards organic and inorganic pollutants in aqueous matrix (Ray and Shipley, 2015) [23].

This study presents the first outcoming results about the possible use of grape fruit peels in its activated carbon /zinc oxide Nano composite form as heavy metal bio sorbents. This material was chosen considering its availability and cost effectiveness.

The aim of the present work was to study the adsorption capacity of the agricultural waste (grape fruit peels) for heavy metal (Copper) removal from aqueous solution under different experimental conditions. The effect of various operating parameters on biosorption such as contacts time. Dosage of the adsorbents, initial metal ion concentration was studied and optimal experimental conditions were decided.

Materials and methods

1. Adsorbent preparation

The adsorbent (grape fruit peel) was thoroughly washed to remove dusts and dirt. They were dried under sunlight for 16 hours I.e. (4 hours for 4 days) and was allowed to dry in the oven at 60^0C for 4 hours to remove moisture before being ground to powdered form and was sieved to achieve the desired size of less than 300µm using British standard sieve (BSS)

2. Metal stock solution

A portion 0.5ml of 100mg/l Copper stock solution was carefully measured into a 100ml volumetric flask and made up to mark with distilled water to get 5mg/l. A working solution of 0.158, 0.315, 0.630,1.250,2.50 and 5.0mg/l was prepared by diluting 0.0158,0.0315,0.0630,0.125 and 0.250ml stock solution to mark in a 100ml volumetric flask by using the equation

$$M_1V_1 = M_2V_2 \tag{1}$$

3. Preparation of activated carbon

3.1 Carbonization and activated process

The powdered raw sample (grape fruit peel) was activated by impregnating with 20% $Zncl_2$ in the ratio of 1:2 for 24 hours, after which was drained and dried in the oven at 80^0C. Then transferred to a crucible and placed in the furnace at a temperature of 300^0C for 15 minutes. The resulting carbon was washed until the pH is neutralized. It was then allowed to dry in the oven for 105^0C for 4 hours.

3.2 Preparation of activated carbon / Zinc oxide Nano composite (Madha *et al,* 2018)

A portion (2g) of the activated carbon was carefully measured in a 200ml of 10%(V/V) HCl solution in order to remove impurities for 24hours and filtered. The residue was transferred into a 250ml beaker and 100mL of 0.9M Zinc acetate solution was carefully measured into it and allowed to stand for 12h and then filtered. The final product was dried at 80^0c for 18hr and then calcined in a furnace at 400^0c for 4h. The resulting product was transferred into a nylon bag and stored prior to use.

4. Adsorption Studies

4.1 Adsorption experiment

The batch adsorption experiment was carried out in 100ml Erlenmeyer flasks where 0.1g of the adsorbents and 20 ml of the metal stock solution of (100-300mg/L) concentrations. This was added at a pH of 6 for the solution. The flasks were placed on a shaker at 120rpm at 30^0C for 60 minutes, After the equilibrium was attained, each sample was filtered to obtain solution containing un-adsorbed Cu^{2+} that is free from adsorbent and the concentration of the metal ions was analyzed by Atomic Absorption Spectrophotometer (AAS) model AA500 at the specific wavelength of the metal (Copper). The amount of adsorption at equilibrium q_e (mg/g), then calculated by

$$q_e = \frac{(C_O - C_e)\,v}{W} \tag{2}$$

Where C_0= initial concentration, C_e= concentration at equilibrium, V= volume of solution in L, W=weight of dry adsorbent in g, q_e= adsorption capacity

$$\text{and \% Removal} = \frac{Co - Ce}{Ce}\, X100 \tag{3}$$

To study the effect of Concentration, temperature (30^0c), time (60 mins), dosage (0.1g) and pH(6) were kept constant and the experiments were carried by varying concentration between 100-300mg/L. In the same way, the effect of time, dosage and temperature were studied by varying time between (30-180 mins), dosage between (0.1-0.5g) and temperature (30-50^o c) respectively while leaving other variables constant.

Results and discussion

1. Study of variables

1.1 Effect of contact time

The investigation of contact time is an important aspect to consider when designing an industrial reactor because of the economy of operation and for gaining insights into the kinetics involved during the sorption process. At initial stages, adsorbent surface sites are available for rapid adsorption of metal ions (Saini *et al*., 2019) [25]. At equilibration time, the active sites become exhausted limiting the number of metal ions that can be adsorbed (El-Araby *et al*., 2019) [9]. Fig. 3.1.1 shows the effect of contact time on the adsorption capacities (qe). As shown, the adsorption capacities increased as the sorption time increased from 30 -180 mins. 180 mins resulted in maximum adsorption capacities (28.23), (30.00) for G(raw) and G(NC) respectively. The initial fast adsorption may be due to the initial adsorption onto the surface of the material (Dawodu and Akpomie, 2014) [8] and the slow uptake in the later stages may be as a result of less available active sites for adsorption. However, G(NC) adsorbed more than G(raw). This is due to the enhanced surface area/porosity brought about by chemical modification.

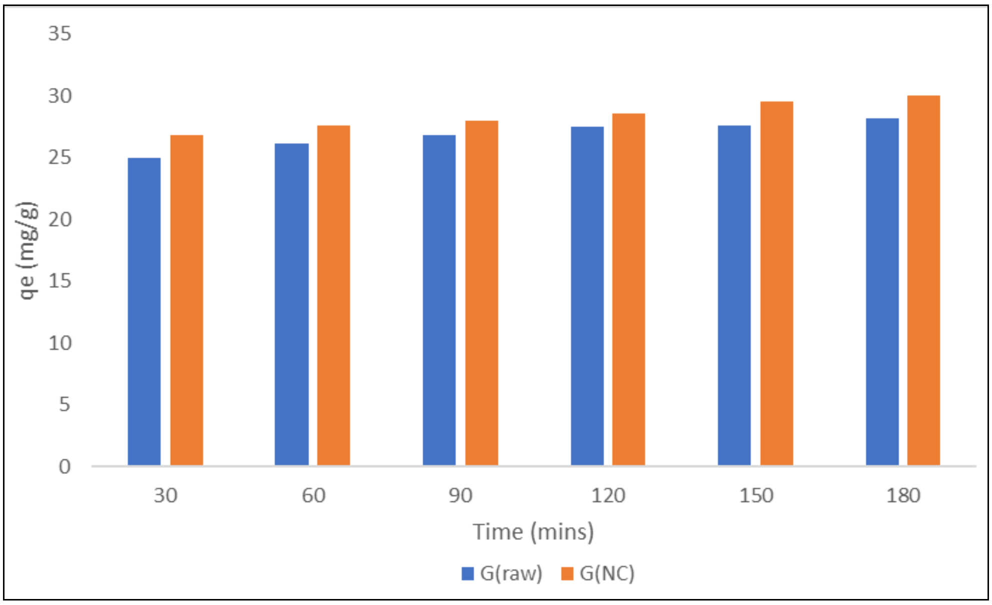

Fig 1: Effect of contact time on adsorption capacity

1.2 Effect of temperature

Temperature is an important factor to be considered in a sorption process being that Biomass contains more than one type of sites for metal binding. The effect of temperature on each site is different and contributes to overall metal uptake. In this study, the adsorption capacity; qe increased as temperature increased from 30ºc up to 45ºc and decreased at 50^0C as shown in figs 3.1.2. The temperature higher than 45ºC caused a change in the texture of the biomass and thus reduced its sorption capacity. Increasing the temperature increases the velocity of adsorbate species towards the interior of the adsorbent. As a result, the adsorbate molecule diffuses greatly across the exterior of the boundary layer as well as into the pores of the adsorbent.

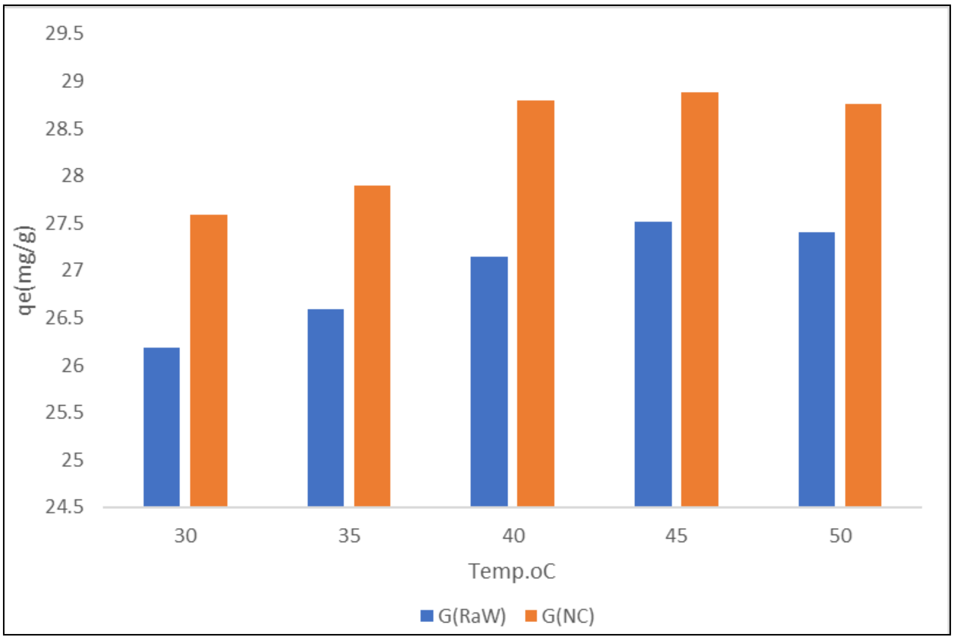

Fig 2: Effect of temperature on adsorption capacity

1.3 Effect of initial solution pH

The pH of a solution is a vital factor in adsorption studies as it affects the surface functional groups of the biomass and the solubility of the ions in aqueous solution. The initial pH of a solution affects the magnitude of negative charge on adsorbent surface and the adsorbent capacities (Abdel-Ghani and Elchaghaby, 2007) [1]. Increase in solution pH increases the adsorption capacity of an adsorbent. In acidic medium, low adsorption capacities observed for metal ions may be due to hydrogen ions competing strongly with adsorbate for negatively charged sites on the adsorbent and consequently makes it more difficult for the metal ions to access binding sites, thus, a lower uptake is observed. As solution pH increases, the hydrogen ion concentration of the solution is lowered thereby reducing the competition for binding sites by hydrogen ions.

Figs 3.1.3 shows there was general increase in uptake of copper by all samples from pH 2-8 with G(NC) performing best at pH 8 with maximum adsorption capacity (30.00mg/g) than G(raw) (29.82mg/g). However, at pH 10 a general decline in adsorption capacity and %removal was recorded (G(NC) 29.90 and G(raw) 29.67. These also confirmed pH 8 as optimum pH for copper adsorption in the study.

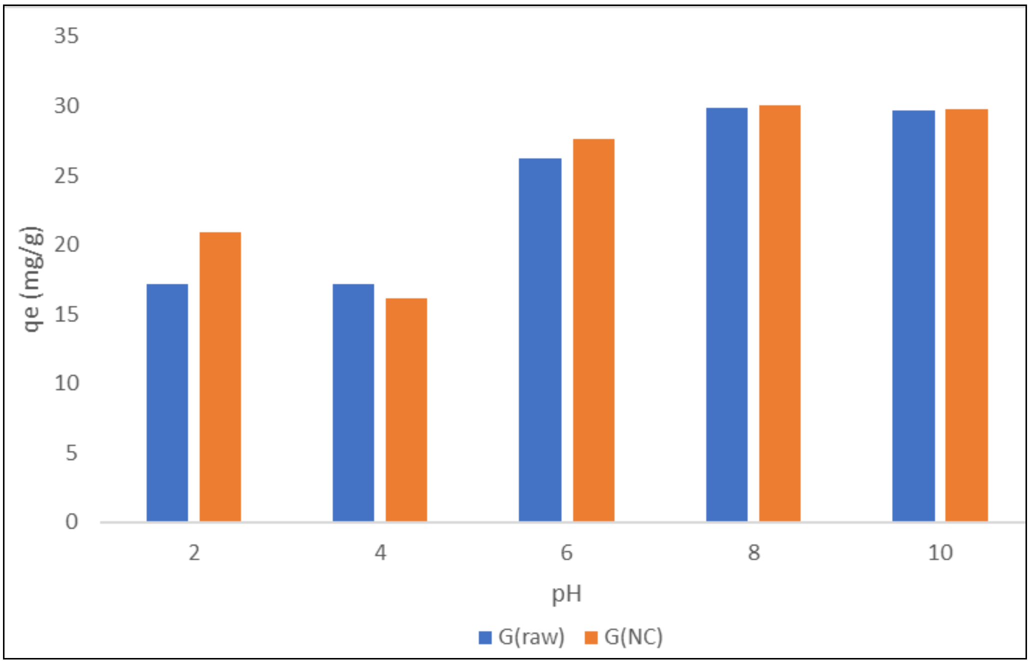

Fig 3: Effect of pH on adsorption capacity

1.4 Effect of initial metal ion concentration

The result of the effect of varying the initial concentration of the metal ions while other factors are kept constant during the adsorption experiment are represented in fig 4.1.4. It showed that there was general increase in adsorption capacities of all the adsorbents as the initial concentration the metal ion in solution increased from 100 to 300mg/g. (G(NC), however, had the higher adsorption capacity than G(raw).

This increase in adsorption capacity with increasing initial cation concentrations is because at higher initial concentration, the driving force for mass transfer becomes larger and as such there will be more equilibrium uptake (Barka *et al*., 2013) [6].

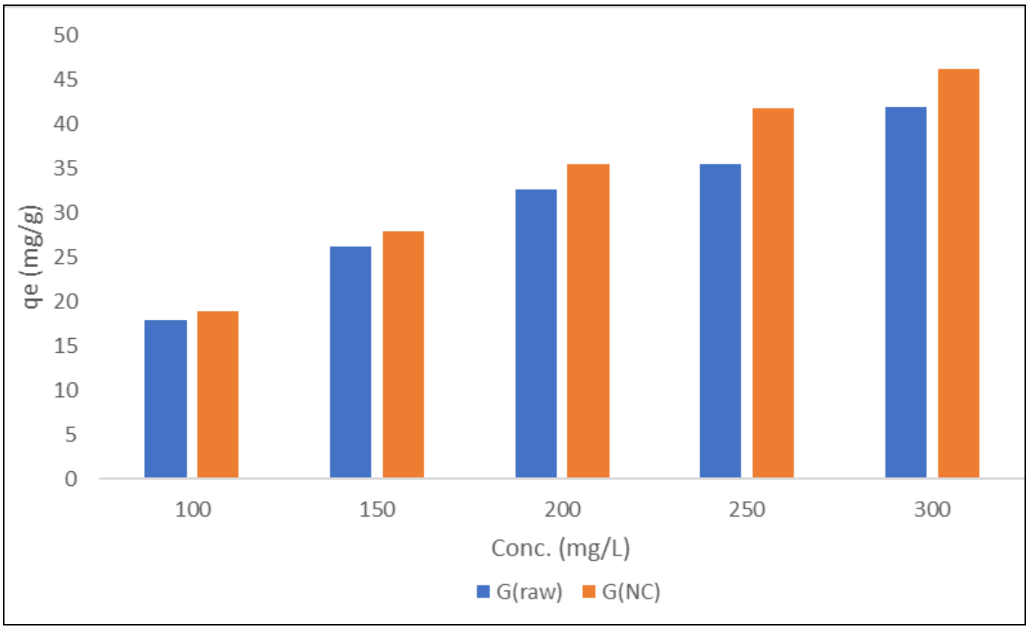

Fig 4: Effect of concentration on adsorption capacity

2. Adsorption isotherms

Adsorption isotherm is the most common representation of the adsorbate concentration and quantity of material adsorbed; graph of the amount adsorbed against the equilibrium concentration, at a specific temperature. In this study, the Langmuir and Freundlich isotherm models were tested to analyze the equilibrium data and the results are shown in Table 1

Table 1: Comparison of Langmuir and Freundlich isotherm model constants for the adsorption of copper onto G(raw)and G(NC)

Isotherm models	G(raw)	G(NC)	Isotherm models	G(raw)
LANGMUIR Qmax	2.2989	5.5556		
KL	21.7495	9.4736		
RL	0.0003	0.0007		

R^2	0.969	0.998		
FREUNDLINCH KF	8.3813	11.8343		
1/n	0.357	0.336		
R^2	0.993	0.962		

2.1 Langmuir Isotherm

This model is applicable where only one molecular layer of adsorbate is formed at the adsorbent surface. which remains constant even at higher concentrations of the adsorbate. The model assumes monolayer adsorption onto a surface containing a finite number of adsorption sites. Monolayer adsorption is distinguished by the fact that the amount adsorbed reaches a maximum value at a moderate concentration; this corresponds to complete coverage of the adsorbent surface by a monomolecular layer of adsorbate (Nwadiogbu *et al*, 2016) [20].

The Langmuir equation can be presented by (Malik, 2004) [16]:

$$\frac{Ce}{qe} = \frac{1}{qe\ \max.k} + Ce/qmax \qquad (4)$$

Where qmax is the monolayer adsorption capacity of the adsorbent (mg/g) it is the maximum amount adsorbed, kLis the Langmuir adsorption constant (L/mg), Ce is the equilibrium metal ion concentration in the solution (mg/L) and qe is the equilibrium metal ion concentration on the adsorbent (mg/g). Values of qmax and KL are calculated respectively from the slope and the intercept of plot of Ce/qe vs. Ce. Value of Langmuir parameters and R^2 were summarized in table 1. From Table 1, very high correlation coefficients (R^2) of 0.969 for G(raw) and 0.998 for (GNC) were seen indicating a good fit of the Langmuir isotherm model in the sorption process. This indicated that the surface of the adsorbent is homogenous in nature and involves a monolayer sorption of Cu(II). The essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (RL) defined by the relationship:

$$RL = 1/[1 + KLCo] \qquad (5)$$

Where Co is the initial metal ion concentration in (mg/L) and KL is the Langmuir equilibrium constant (L/mg). The separation factor (RL) gives information about the nature of the adsorption process. The adsorption is said to be irreversible (RL= 0), favorable (0 < RL< 1), linear (RL= 1) or unfavorable (RL> 1). in this study, the values of RL ranged from 0.0003 to 0.0007; indicating a favorable adsorption of Cu (II) onto G(raw) and G(NC).

2.2 Freundlich Isotherm

The Freundlinch model assumes a multilayer coverage of metal ions associated with different adsorption energies (Ali *et al*., 2016) [3]. The Freundlich isotherm linearized equation is expressed by the equation

$$\ln qe = \ln KF + 1/n\ ln\ Ce \qquad (6)$$

Where Ce: concentration of metal ions (mg/L) at equilibrium, qe: amount of metal ions removed (mg/g) at equilibrium. KF is adsorption capacity and 1/*n* is the adsorption intensity or surface heterogeneity. The values of KF and 1/*n* are calculated by plotting a graph of lnqe against lnce (Moyo *et al*., 2013) [19]. When 0 < 1/*n* < 1, adsorption is considered favorable. Unfavorable adsorption occurs when 1/*n* > 1 and is irreversible at 1/*n* = 1.

As seen from Table 1, the values of the correlation coefficient (R^2) for the adsorbents (0.933 and 0.962 for G(raw) and G(NC) respectively for Freundlich model were lower than those of the Langmuir isotherm model. Furthermore, the value of 1/*n* obtained, indicates a favorable adsorption process.

3. Kinetic studies

Kinetics of adsorption is an important characteristic in defining the efficiency of adsorption. For an effective sorption system to be designed, investigations should be carried out to determine the rate of sorption by implementing the experimental data on several kinetic models.

Table 2: Summary of the kinetic model parameters for the sorption of copper onto G(raw) and G(NC)

Kinetic model	G(raw)	G(NC)
qe_{max} exp (mg/g)	28.23	30.00
Pseudo first order qe_{cal} (mg/g)	4.92	6.32
$K_{1\,=}$ (min^{-1})	0.014	0.015
R^2	0.966	0.837
Pseudo second order qe_{cal} (mg/g)	29.41	31.25
$K_{2\,=}$ (min^{-1})	0.00006	0.00005
R^2	0.999	0.998
Intra particle diffusion Kd (meg g^{-1} min^{-1})	0.605	0.648
R^2	0.933	0.987
C (intercept)	24.77	26.15
Liquid Film diffusion K_{ed}	0.443	0.328
R^2	0.971	0.234

3.1 Pseudo-first order kinetic model

The pseudo-first order (Lagergren's rate) model is the one most widely used for the adsorption of a solute from a liquid solution (Lagergren, 1898). The linear form of the pseudo-first order equation is given by:

$$\log (qe-qt) = \log qe\ K1\ \frac{t}{2.303} \qquad (7)$$

Where k is the pseudo-first order rate constant. The slope and intercepts of the plot of log (qe-qt) against t were used to determine the value of k and qe respectively and the value are listed in Table 2. As shown in Table 2, pseudo-first order equation provided a poor fit to the experimental data of the adsorbents. This is indicated by the low values of their linear regression (R^2) not close to 1. However, the values of qecal were way too lower than the experimental values obtained.

3.2 Pseudo-second order kinetic model

The pseudo-second order kinetic model assumes that chemisorption is the rate determining step and is given as (Li *et al*, 2013) [14]:

$$\frac{1}{qt} = \frac{1}{K2qe2} + \frac{1}{qe}t \qquad (8)$$

where K2 is the equilibrium rate constant of pseudo-second order adsorption (g/mg min). The values of qe and K2 were calculated from the slope and intercept of the linear plot of t/qt against t and the values are recorded in Table 2.

The pseudo-second order model provided a good fit to the experimental data as can be seen from the high regression coefficient (R^2) values of 0.999 and 0.9998 for G(raw) and G(NC) respectively. Furthermore, the qe calculated values are close to the qe experimental values. The pseudo-second order model provided a better fit than the pseudo first order model and is in line with most adsorption studies (Badmus *et al*., 2007). However, the best fit presented by the pseudo-second order models indicated chemisorption as the major process for the adsorption of copper ion onto the adsorbents.

3.3 intra particle diffusion model

The intra particle diffusion model can be expressed as (Weber and Morris, 1963) [28]

$$qt = K_{id}t^{1/2} + C \qquad (9)$$

Where K_{id} (mg/g min), the intraparticle diffusion rate constant is obtained from the slope of straight line of qt versus $t^{1/2}$, C gives an idea about the thickness of boundary layer i.e. the larger the intercept, the greater the boundary layer effect (Tan *et al*, 2008) [26]. If the plot of qt versus t1/2 gives a straight line passing through the origin, then the sorption process was controlled by intra-particle diffusion only and the slope gives the rate constant, Kid. However, if the data exhibit multilinear plots, then two or more steps influence the sorption process, also a very large intercept would suggest that surface sorption contributes more to the rate determining step (Nwadiogbu *et al*, 2015) [21]. From the results in Table 1, a high regression coefficient (R^2) and a non-zero intercept were obtained. The deviation from the origin may be due to the difference in mass transfer between the initial and final stages of the sorption process (Das and Mondal, 2011) [7]. The high regression coefficient indicates the existence of an intra particle diffusion mechanism for the sorption of Copper ion onto G(raw) and G(NC).Furthermore, the presence of the boundary layer effect confirmed the existence of surface sorption, indicating that intra particle diffusion mechanism was not the only rate -determining step. However, with the moderate value of intercept, penetration of the adsorbate into the pores of the adsorbent(G(NC) was more predominant than surface sorption.

3.4 Liquid film diffusion model

Liquid film diffusion model was also used in this study to investigate if transport of metal ions from the liquid phase up to the solid phase boundary also played a role in the adsorption process. (Issabayeva *et al*, 2007) [12]

$$\ln(1-F) = -Kfd.t \qquad (10)$$

where F is the fractional attainment of equilibrium (F = qt/qe), Kfd is liquid film diffusion constant. A linear plot of ln (1−F) versus t with zero intercept would suggest that the kinetics of the sorption process was controlled by diffusion through the liquid film surface surrounding the solid sorbent. qe is the adsorption capacity of the sorbent at equilibrium (mg g-1).In this study, the liquid film diffusion model produced a good regression (R^2) value for G(raw) indicating that surface sorption also played a role in the rate determining step. This result indicates that G(raw) can be reused because minimal energy will be required for desorption since it was surface sorption that took place.

4. Thermodynamic study

The thermodynamics for Copper ion removal by G(raw) and G(NC) was investigated in temperature range of 303-323 K, and the influence of temperature on the adsorption capacity is shown in Fig. 3.1.2. It can be found that adsorption capacity increased with increase in temperature**.**

The thermodynamic functions can be expressed as:

$$\boldsymbol{InK} = -\boldsymbol{\Delta H}^{0/}\ \boldsymbol{RT} \qquad (11)$$

Thermodynamic parameters such as change in enthalpy (ΔH) and entropy (ΔS) were calculated respectively from the slope and intercept of the plot of ln K versus 1/T, where KL (l/mg) is the Langmuir isotherm constant and T is absolute temperature in Kelvin. The change in Gibb's free energy determined using the following equation (Mohammed *et al*, 2016) [11]

$$\Delta G = -RT \ln k \qquad (12)$$

$$\Delta G = \Delta H - T\Delta S \qquad (13)$$

where: R= Universal gas constant (8.314J/mol) T= Temperature, K = Distribution coefficient, ΔG= Change in Gibb's free energy (kj/mol), ΔH = change in enthalpy, ΔS=entropy change = degree of randomness or disorderliness of a system

Table 3: Thermodynamic parameters

Adsorbents	**Enthalpy Of reaction ΔH (kj/mol)**	**Entropy of Reaction ΔS(Kj/mol)**	**Gibb's free energy ΔG**					
			303K	**308K**	**313 K**	**318K**	**323K**	**R^2**
G(raw)	20.0218	0.0820	-4.8303	-5.2404	-5.6505'	-6.0606	-6.4707	0.8952
G(NC)	29.3958	0.1173	-6.1461	-6.7326	-7.3191	-7.9056	-8.4921	0.8102

The thermodynamic parameters associated with the adsorption process is listed in Table 3. Values of ΔG were calculated from the values of adsorption equilibrium constant (KD) using equations 7&8. The negative values of ΔG at the different temperature ranges (303, 308, 313, 318. 323) K show that the adsorption process is spontaneous and the degree of spontaneity increases with increasing the temperature., The ΔH values obtained for the adsorption of copper onto all the adsorbents showed positive values, this indicates that the adsorption process is endothermic in nature. The ΔH (change in enthalpy) values for all the adsorbates adsorbed onto the adsorbents in this study are greater than 20 kj/mol, meaning that all the sorption process in this study followed chemisorption mechanism. According to Vasu,2008, physisorption is characterized by enthalpy value in the range of 5-20 kJ mol-1 while that of chemisorption is greater and in the region of that of chemical bonding Similar results were reported for the adsorption of methylene blue onto activated carbon (Abechi, 2008) [2]. A positive ΔS imply increased randomness at the solid- solution interface. It also shows the affinity of the adsorbents for the adsorbate in this study.

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