



Adsorption of Copper (II) Ions from Aqueous Solution onto Synthetic Goethite and Two Naturally Available Red Soils from Yaoundé –Cameroon

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Authors' contributions

This work was carried out in collaboration between all authors. Author KJM designed the study, author TGM performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Author NJN managed the analyses of the study and managed the literature searches. All authors read and approved the final manuscript.

Research Article

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ABSTRACT

The present investigation deals with the utilization of synthetic goethite and two red soils obtained from AHALA-NSAM and NKOLOFANE as adsorbent for the removal of copper from waste water. The synthetic goethite was characterized by IR, XRD and BET where the red soils were characterized by XRD, Chemical Analysis and BET. A series of experiments were conducted in a batch system to evaluate the effect of system variables. The effect of contact time, pH and the initial concentration of copper (II) solution were considered. The results show that the contact time of 180 minutes, 20 minutes and 15 minutes are sufficient to fit the equilibrium for GEO, E1-B1 and NSAM-B2 respectively. The optimal adsorption pH for the adsorption of copper (II) ions is 4.6 ± 1 . The maximal quantities adsorbed by every adsorbent were 78.2 mg/g for GEO, 41.2mg/g for E1-B1 and 32.2mg/g for NSAM-B2. The experimental results obtained have been correlated to four kinetic models including the first order, the second order, Elovich and intra particle diffusion models. The kinetic model that gave the value of the linear correlation coefficient which best fits is that of second order. Three isotherms models amongst which are Langmuir, Freundlich and Tempkin's have been applied to the experimental data. The

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Langmuir model best described the adsorption of copper (II) ions in aqueous solution by the three adsorbents.

Keywords: Adsorption; goethite; red soils; kinetic models; models of isotherms.

ABBREVIATION

GEO – Goethite; E1-B1 - red soil from Nkolofane in Yaoundé (Cameroon); NSAM - B2 - red soil from Ahala –Nsam in Yaoundé (Cameroon).

1. INTRODUCTION

Heavy metal pollution of wastewater is a common environmental hazard, since the toxic metal ions dissolved can ultimately reach the top of the food chain and thus become a risk factor for human health. One of such heavy metal of concern is copper. It is present in the waste water of several industries, such as metal cleaning and plating baths, refineries, paper and pulp, fertilizer, and wood preservatives [1-2]. The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney [3]. Effective methods for copper ion removal that have been used include ion exchange, reverse osmosis, electrochemical treatment, evaporative recovery, and adsorption. The application of such processes is often limited because of technical or economic constraints [4]. Adsorption is an economical, simple, effective and environmental friendly method [5-6]. The high cost of activated carbon has motivated scientists into the search for new low cost adsorption means. In recent years, considerable attention has been focused on the removal of copper from aqueous solution using adsorbents derived from low-cost materials. Several adsorbents, such as sawdust [4], wheatshell [7], bagasse fly ash [8], spent activated clay [9-10], and modified goethite [11] have been used for the treatment of copper (II) rich effluents at the solid–liquid interface.

Goethite, a crystalline iron hydroxide (α -FeOOH), is the most widespread iron hydroxide in natural systems and has been used extensively in various adsorption studies [11].

Natural red soil comes from disintegration of laterite rock which is a heterogeneous, anisotropic rock consisting of hard ferruginous skeletal framework impregnated with soft clayey materials [12]. Red soil (Laterites) are product of intense sub aerial weathering whose iron and/or aluminium content is higher and silicon content are lower than in merely kaolinized parent rocks [12]. In the present investigation synthetic goethite (GEO) and two natural red soils (E1-B1); (NSAM-B2) has been used as adsorbents for the removal of copper (II). The effect of such factors as contact time, initial pH and initial concentration was investigated. The kinetics of Copper (II) adsorption on both adsorbents was analyzed by various kinetic models. Experimental equilibrium data were fitted to the Langmuir, Freundlich and Tempkin.

2. MATERIALS AND METHODS

2.1 Adsorbent

Red soil was collected from AHALA-NSAM and NKOLOFANE, the Red soil crushed, then washed several times with clean water until its particles detached. These detached particles were dried in a hot-air oven at 110°C for 24 hours. Screened material was stored in capped bottle.

The Powder goethite was prepared according to the following procedure 180 mL KOH solution (5M) was added to 100mL solution of ferric chloride (1M) under vigorous shaking, and then the obtained solution was immediately diluted with 2L of distilled water and aged at 70°C for 60hours. The obtained precipitate was washed by centrifugation twice using distilled water, and then dried at 110°C for 24hours. The obtained solid was broken and ground into fine powder using a mortar and was then allowed to pass through an 80 µm mesh opening size sieve. The sieved powder was kept in an oven at 110°C for 24 hours, removed and cooled in a desiccator containing CaCl₂ (drying agent) for 1 hour. The adsorbent was removed from the desiccator, the required mass weighed and stored in an airtight plastic bag for use.

2.2 Adsorbent Characterization

Difrap+d8 model bruker and Philips equipment were used to obtain the X-ray diffraction (XRD) pattern of synthesized goethite and the red soil samples respectively, to identify the crystalline compounds. Infrared spectra of the synthesized samples were measured from 400 to 4000 cm⁻¹ using a brukeralpha-p spectrometer with ethanol as solvent. The BET specific area, total pore volume and average pore diameters of goethite were determined by standard multipoint techniques of nitrogen adsorption, using TriStar 3000 V6.05A equipment. The chemical analysis of red soils is obtained by Harrison method and X fluorescence. The Specific area of the red soils is obtained by volumetric equipment as described by Haul and Dumbgen.

2.3 Prepaton of Copper Solution

All reagents used in this study were of analytical grade. A stock solution of copper (II) ion of concentration 5ppm (5000mg/L) was prepared by dissolving 13.3658g of CuCl₂.2H₂O in a 500ml volumetric flask. This was swirled until all the salt dissolved, transferred into a 1-L volumetric flask and completed with distilled water up to the mark. This solution was stirred on a magnetic stirrer for one hour to obtain homogeneity. All experimental solutions were prepared by diluting the stock solution to the required concentration

2.4 Kinetic Adsorption Experiments

Kinetic adsorption experiments were conducted using a series of 20 mL solutions containing fixed amount of adsorbent and copper ions (800mg/L). The solutions were vigorously agitated with a magnetic stirrer for increasing time intervals. At the end of each run, the solution is filtered and the copper (II) concentration in the filtrate is determined. Copper (II) ionstiration was carried out by using UV-visible spectrophotometer model CORNING 259at the wavelength 830 nm.

2.5 Batch Adsorption Equilibrium Studies

For each run the adsorbent is mixed with 20 mL solution of copper (II) at different initial concentrations (200-1000 mg/L). The suspensions were stirred for 180 minutes with GEO, 20 minutes with E1-B1 and 15 minutes with NSAM-B₂ by using a magnetic stirrer. The amount of copper (II) adsorbed at equilibrium, Q_e (mg/g) was calculated using equation 1:

$$Q_e = \frac{(C_0 - C_e)}{m} \times V \quad (1)$$

where,

C_0 (mg/l) and C (mg/L) are copper (II) ions concentrations initially and at equilibrium respectively, V the volume of the solution (L) and m the adsorbent mass (g).

2.6 Error Analysis

The optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the equation to the experimental data [13]. Apart from the correlation coefficient (R^2), the residual root mean square error (RMSE) and the chi-square test were also used to measure the goodness-of-fit. RMSE can be defined as:

$$RMSE = \sqrt{\frac{1}{n-2} \sum_{i=1}^n (q_{e,exp} - q_{e,calc})^2} \quad (2)$$

The subscripts "exp" and "calc" show the experimental and calculated values and n is the number of observations in the experimental isotherm. The Smaller RMSE value indicates the better curve fitting [14]. The chi-square test can be defined as:

$$\chi^2 = \sum_{i=1}^n \frac{(q_{e,exp} - q_{e,calc})^2}{q_{e,exp}} \quad (3)$$

If data from model are similar to the experimental data, χ^2 will be a small number [15].

3. RESULTS AND DISCUSSIONS

3.1 Characterization of Adsorbents

The XRD pattern of the synthetic material (Fig.1.) showed a well-defined crystalline structure when their diffractogram with goethite (JC17-536 card) which was the principal component found [16]. The formation of pure goethite phase is also supported by IR studies. A very strong and broad band at 3127 cm^{-1} (Fig. 2.) corresponds to OH stretching mode in the sample [17]. The 1627 cm^{-1} sharp band can be ascribed to the bending mode of H_2O molecules [18]. The characteristic sharp bands at 799 cm^{-1} and 890 cm^{-1} can be assigned to the Fe-O-H bending vibration of goethite. Specific area of the goethite sample was

67.3629m²/g, the pore volume was 0.4192cm³/g and the average diameter was 24.8977nm. In general the result is within the range in the literature for goethite [19].

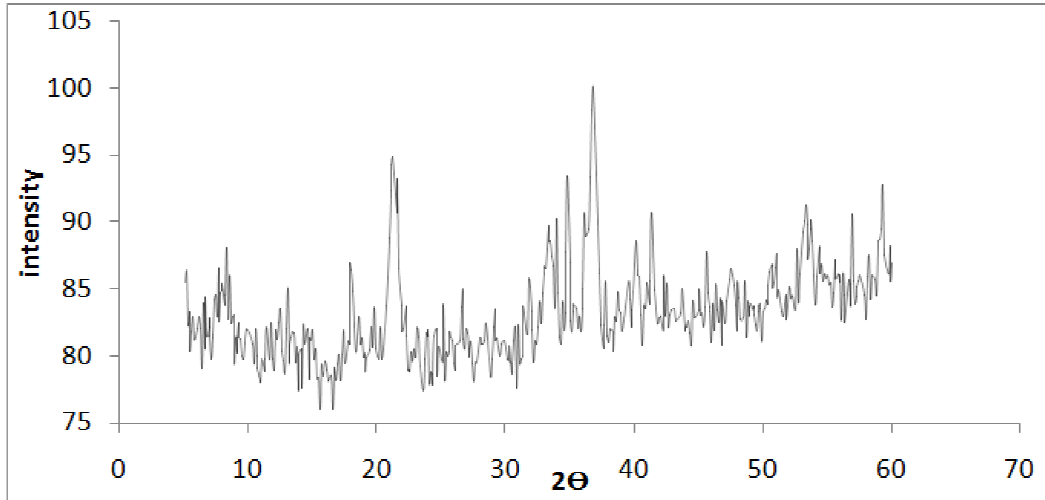


Fig.1. XRD patterns of Synthetic Goethite sample

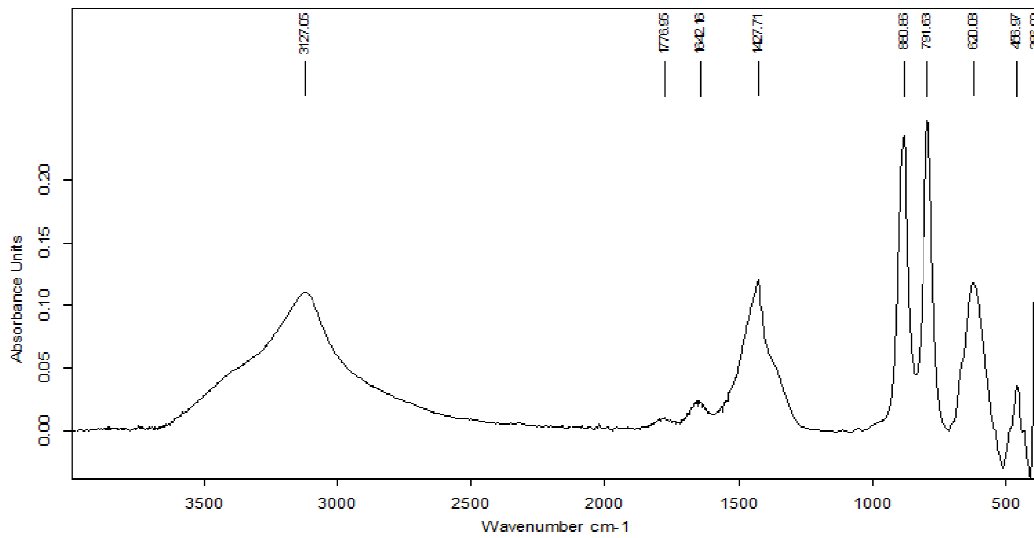


Fig. 2. FT IR spectra of Goethite sample

The XRD of the red soils (Fig.3.) shows that the major constituents of the red soils are hematite, quartz, kaolinite, and goethite. The chemical analysis (Table 1) shows that the major elements are SiO₂, Al₂O₃ and Fe₂O₃. The Specific area of the red soils is 42m²/g and 26m²/g respectively for E1-B1 and NSAM-B2.

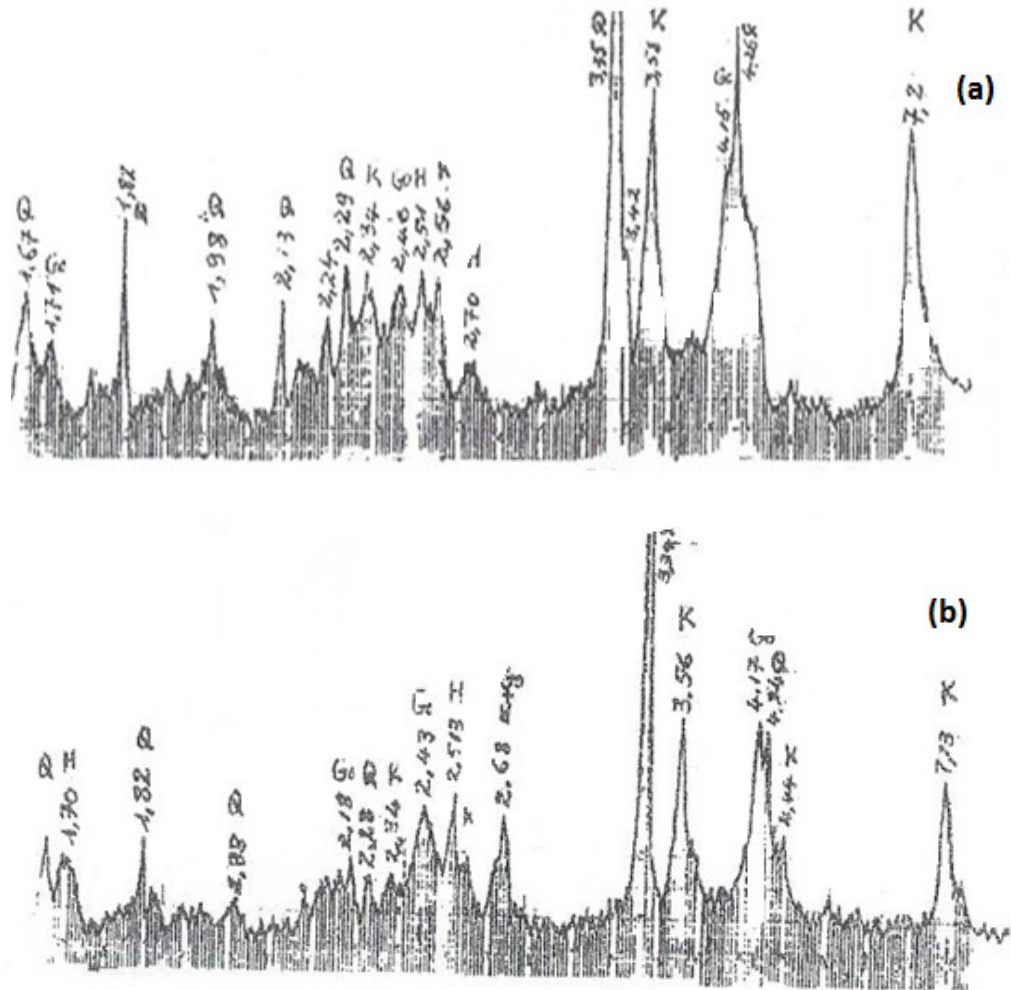


Fig.3. XRD Patterns of Red Soils Sample (a) E1-B1; (b) NSAM-B2
H = Hematite; Q=Quartz; K = Kaollinite; Go=Goethite

Table 1. Chemical composition of the red soils

Oxide (%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	I.i	Total
E1-B1	52.3	23.6	9.3	0.02	0.14	0.04	0.2	0.24	1.6	0.24	11.5	99.18
NSAM-B2	25.5	20.4	38.6	0.05	0.08	0.05		0.04	0.9	0.25	12.3	98.17

3.2 Effect of Contact Time

In order to determine the effect of the agitation time, 0.1 g of the adsorbent was stirred with a 20 mL solution of copper (II) ions of initial concentration 800 mg/L for a time interval between 30 to 360 minutes for GEO, 5 to 35 minutes for E1-B1 and 5 to 60minutes for NSAM-B2 with pH=4, 6 The experimental results obtained for the adsorption of copper ions during varying contact times are show in (Fig.4a, 4b, 4c). It is clear from the graph that amount of uptake qt

(mg gm⁻¹) increased with increased contact time and after certain period of time; it reached to a constant value beyond which no further adsorption took place. The results showed that, the adsorption was fast at initial stage of contact period and after that near the equilibrium it became slower. With the lapse of time, the surface adsorption sites were exhausted. The remaining vacant sites were difficult to be occupied by the cation due to repulsive forces between adsorbate present in solid and bulk phases [20]. Adsorptions reach equilibrium within 180, 20 and 15min for GEO, E1-B1 and NSAM-B2 respectively as represented by Figs. 4a, 4b and 4c.

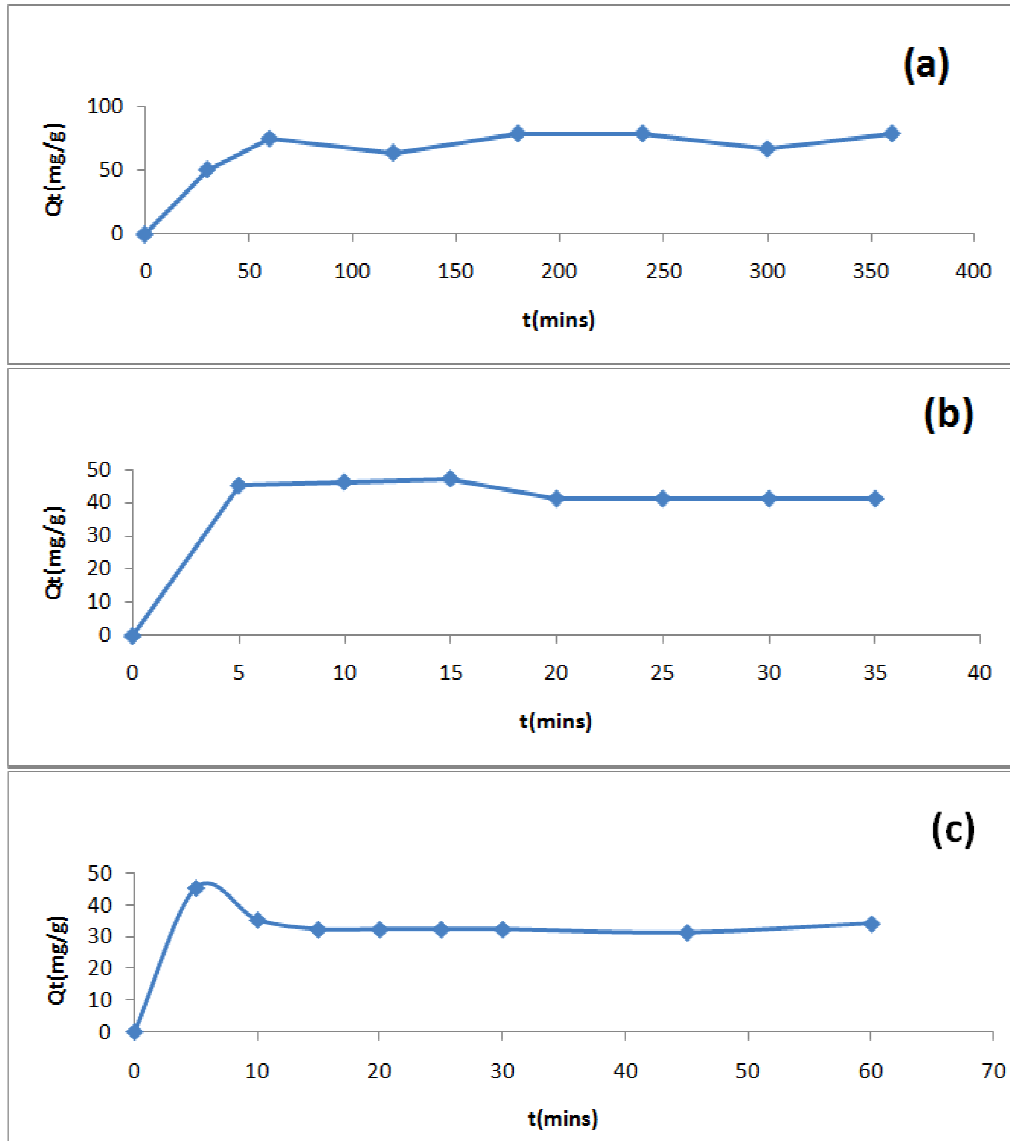


Fig.4. Effect of agitation time on the adsorption of copper (II) ions on (a) Goethite (b) E1-B1 (c) NSAM-B2

3.3 Effect of Initial Ph on Copper (II) Adsorption

pH is an important parameter influencing heavy metal adsorption from aqueous solutions. It affects both the surface charge of adsorbent and the degree of ionization of the heavy metal in solution [21]. (Fig. 5.) represents the effect of initial pH of the solution on the adsorption of copper(II) onto GEO, E1-B1 and NSAM-B2 using 800 mg/L initial copper (II) concentration and 0.1g of adsorbent, in the present study the pH was varied between 2 and 5.

The lower adsorption at pH less than 3 this may be attributed to the competition between the hydrogen and copper ions on the sorption sites [2]. At pH values higher than 5.0 insoluble copper hydroxide starts precipitating from the solutions making true sorption studies impossible [22]. According to the Fig. 5 we saw that the optimum adsorption pH was between 3.5 and 4.6 for GEO, E1-B1 and NSAM-B2. Consequently, the working pH value for copper removal onto GEO, E1-B1 and NSAM-B2 was chosen as 4.6 and the other adsorption experiments were performed at this pH value.

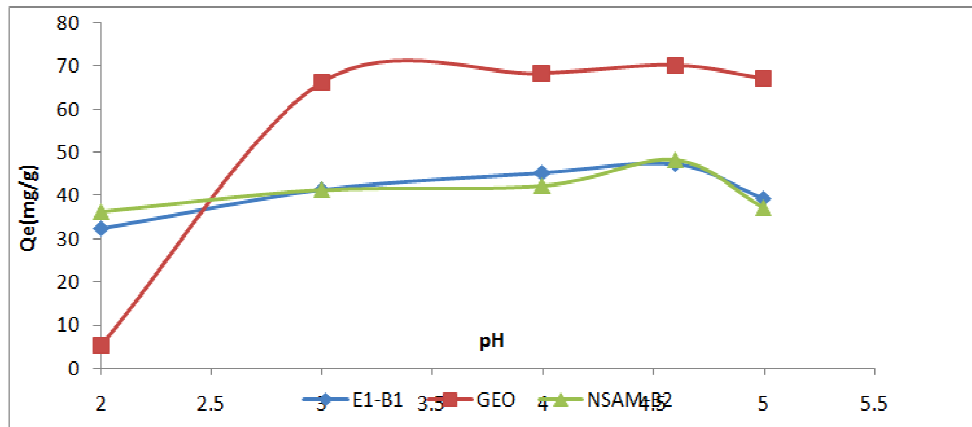


Fig.5. Effect of pH on copper(II) ion adsorption on GEO, E1-B1 and NSAM-B2

3.4 Kinetic Modeling of Copper(II) Ions Adsorption

The kinetics of the adsorption of copper (II) ions has been studied to elucidate the mechanism by which copper (II) ions are adsorbed using four kinetics equations, that is, pseudo first-order, pseudo second-order, Elovich and intra particle diffusion equations were considered to interpret the experimental data [23-26].

The pseudo first-order kinetic model equation is represented in an integral form as given in equation (2) [23]:

$$\ln(Q_e - Q_t) = \ln(Q_e) - K_1 t \text{ or } \ln C_t = -K_1 t + \ln C_0 \text{ after reduction} \quad (4)$$

where,

K_1 is the rate constant of pseudo first order adsorption ($\text{mg}^{-1} \text{min}^{-1}$).

The pseudo second-order kinetic model is expressed as given in equation (3) [24]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \quad (5)$$

where,

Q_e and Q_t are the sorption capacity at equilibrium and at time t respectively (mg/g) and k_2 is the rate constant of pseudo-second order sorption (g.mg⁻¹.min⁻¹).

The Elovich equation is generally expressed as presented in equation (10) [25]:

$$\frac{dQ_t}{dt} = \alpha \exp(-\beta Q_t) \quad (6)$$

where,

α is the initial sorption rate (mg⁻¹.g.min⁻¹) and β is the desorption constant (g.mg⁻¹) during any one experiment. The integrated and simplified equation is:

$$Q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (7)$$

The intraparticle diffusion kinetic model can be written in the linear form as presented in equation (6) [26]:

$$\ln P = \ln k_{id} + a \ln t \quad (8)$$

where,

P is the percent removal of copper (II) ions at time t , K_{id} is the intraparticle diffusion rate constant and a is a gradient whose value depends on the adsorption mechanism.

In order to obtain parameters related to each kinetic model, experimental data have been tested with linear forms of these models. Parameters are given in (Table 2). These results show that the adsorption of copper ion on both adsorbents is better described by the pseudo – second order model with a correlation coefficient 0.9733, 0.9968, 0.9947 for GEO, E1-B1 and NSAM-B2 respectively. This implies that copper (II) ions adsorption on both adsorbent may occur through a chemical process involving the valence forces of the shared or exchanged electrons [27]. The resulting copper (II) adsorption values obtained from this model is almost the same as compared to the maximum adsorption capacity experimentally obtained. This means that the chemisorption reaction or an activated process becomes more predominant in the rate-controlling step for the copper system [28].

3.5 Adsorption Isotherms Studies

The equilibrium adsorption isotherm is of fundamental importance in the design of adsorption system [29]. Adsorption equilibrium data can conveniently be characterized by adsorption isotherms which are helpful in determining the adsorption capacity of an adsorbent material. In order to analyse an adsorption isotherm, it is fundamental to develop an equation which accurately represents the results and which may be used for design purposes. Classical adsorption models are used to describe the equilibrium established between adsorbed component on the adsorbent and unadsorbed component in solution (represented by adsorption isotherms). Langmuir, Freundlich and Temkin adsorption models were used to analyse the equilibrium data for adsorption and copper (II) ion by both adsorbents.

Langmuir adsorption isotherm: The Langmuir adsorption equation is one of the most common isotherm equations for modelling equilibrium data in solid – liquid systems. This equation is valid for monolayer adsorption onto a surface with a finite number of identical sites which are homogeneously distributed over the adsorbent surface. The general form of the Langmuir equation is [30];

Table 2. Kinetic models parameters of adsorption

Models	Parameter	Adsorbent		
		GEO	E1-B1	NSAM-B2
Pseudo-first order	R^2	0.3113	0.6262	0.2281
	K_1	0.0005	0.0010	0.0017
	$RMSE$	0.27	0.13	0.10
	X^2	0.49	0.20	0.17
	R^2	0.9733	0.9968	0.9947
Pseudo-second order	h (mg/g min)	7.3961	5.8016	3.7361
	K_2 ($\times 10^{-3}$ g/mg. min)	1.203	20.401	246.55
	Q_e (mg/g)	76.92	39.68	32.67
	$RMSE$	0.078	0.038	0.032
	X^2	0.045	0.016	0.053
	R^2	0.4656	0.5333	0.555
Elovich	β (g/mg)	0.125	0.342	0.236
	α (mg/g min)	368.02	6.22×10^{-5}	6.24×10^{-5}
	$RMSE$	0.078	0.020	0.031
	X^2	0.053	0.004	0.013
	R^2	0.6291	0.5854	0.5543
Intra-particle Diffusion	K_{id} (min^{-1})	21,404	33.090	29.984
	a (mg/g) $\times 10^{-2}$	14.5	7.14	11.35
	$RMSE$	0.089	0.0207	0.031
	X^2	0.059	0.00004	0.014
	R^2	0.6291	0.5854	0.5543

$$Q_e = \frac{Q_m K_L C_e}{(1 + K_L C_e)} \quad (9)$$

Where C_e is the equilibrium concentration of copper (II) ions (mg/L), Q_e is the amount of copper (II) ions adsorbed per unit mass of the adsorbent, K_L is the Langmuir adsorption constant (L/mg) and Q_m is the maximum amount of per unit mass of adsorbent to form a complete monolayer on the surface (mg/L). The linear form of this equation is as follows

$$\frac{1}{Q_e} = \frac{1}{Q_m K_L C_e} + \frac{1}{Q_m} \quad (10)$$

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

$$R_L = \frac{1}{1 + K C_0} \quad (11)$$

The R_L value indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) as shown in Table 3 in this work [31].

Freundlich Adsorption Isotherm: Freundlich equation is an empirical equation based on the adsorption on a heterogeneous surface [32]. It suggests that binding sites are not equivalent and/or independent. The Freundlich isotherm is represented by the equation:

$$Q_e = K_f C_e^{1/n} \quad (12)$$

where,

Q_e is the quantity of solute adsorbed at equilibrium (adsorption density: mg of adsorbate per g of adsorbent). C_e is the concentration of adsorbate at equilibrium (mg/L). K_f (mg/g) and n (g/L) are Freundlich constants related to adsorption capacity and adsorption intensity of the adsorbent respectively. This equation is conveniently used in linear form by taking the logarithm of both sides as:

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (13)$$

Tempkin Adsorption isotherm: Tempkin isotherm assumes that the heat of adsorption decreases linearly with the coverage due to adsorbent - adsorbate interaction [33]. The Tempkin isotherm has generally been applied in the following linear form:

$$Q_e = \frac{RT}{B_T} \cdot (\ln A_T + \ln C_e) \quad (14)$$

where,

A_T (L/g) is Tempkin isotherm constant, B_T (J/mol) is a constant related to heat of sorption, R is the gas constant (8.314 J/mol K) and T the absolute temperature (K).

Adsorption isotherms on NSAM-B2 is type I adsorption isotherm, characteristic of microporous adsorbent, chemical adsorption or physical adsorption limited to monolayer coverage. While adsorption process reaches equilibrium, the curve is not parallel to the concentrations-axis; this reveals that mesopores are also involved in the adsorption process [34]. Adsorption isotherm on GEO and E1-B1 is type IV characteristic for most mesoporous adsorbents [35]. Fig. 6 also shows that, the amount of copper (II) ion adsorbed by samples was in the order of GEO > E1-B1 > NSAM-B2 which is in the same order like the surface capacity each adsorbent.

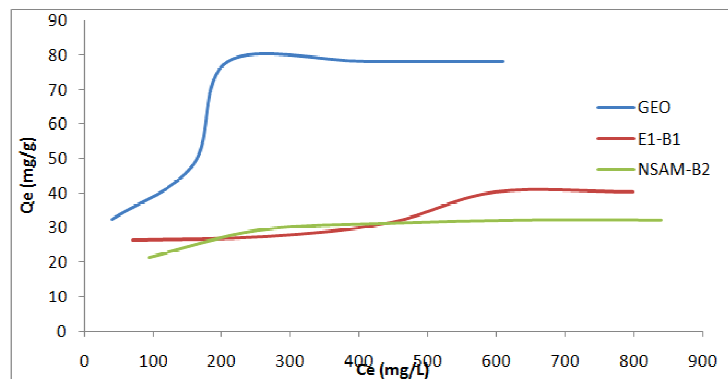


Fig.6. Adsorption isotherms

Data obtained from these studies have been tested with the Langmuir, Freundlich and Tempkin linearized equations. These results are summarized in (Table 3). The Langmuir model effectively describes the sorption data with a correlation coefficient 0.9701, 0.9728, 0.9993, the residual root mean square error 0.103, 0.06, 0.05 and the chi-square test 0.05, 0.04, 0.02 for GEO, E1-B1 and NSAM-B2 respectively. Thus, the isotherm follows the sorption process in the entire concentration range studied. The separation factor (R_L) Table 4) value indicates that Cu (II) ion adsorption on both adsorbent is favourable [31]. The good value of correlation coefficient for Tempkin isotherm with the adsorbent NSAM-B2 allowed to said that it describe well the nature of the adsorption of copper (II) ion by NSAM-B2. The positive value of sorption energy ($B_T=0.484\text{kJ/mol}$) indicate that the adsorption of copper (II) ion by NSAM-B2 is endothermic and the value is less than 8 kJ/mol this also indicates the weak interaction between the adsorbent NSAM-B2 and the copper (II) ions [36]. The Q_m values obtained for the present system in comparison with those reported earlier for sorption of copper (II) onto various adsorbents (Table 5) revealed that GEO, E1-B1 and NSAM-B2 were effective adsorbent in removing copper.

Table 3. Isotherm models parameters of adsorption

Models	Parameter	Adsorbent		
		GEO	E1-B1	NSAM-B2
Langmuir Isotherm	R^2	0.9701	0.9728	0.9993
	Q_{max} (mg/g)	90.09	44.84	39.84
	$K(L/mg) \times 10^{-3}$	12.7	8.64	17.21
	$RMSE$	0.103	0.06	0.05
	χ^2	0.05	0.04	0.02
Freundlich Isotherm	R^2	0.8464	0.6197	0.8958
	$1/n$	0.345	1.043	0.1927
	$K_F(L/g)$	9.322	0.177	9.302
	$RMSE$	0.125	1.13	0.02
	χ^2	0.06	10.09	0.003
Tempkin Isotherm	R^2	0.8112	0.7552	0.9177
	$A_T(L/g)$	0.154	0.721	0.844
	$B_T(KJ/mol)$	0.135	0.409	0.484
	$RMSE$	0.108	0.043	0.015
	χ^2	0.05	0.018	0.002

Please mention Table 4 in the text

Table 4. Langmuir isotherm with separation factor (R_L)

Concentration (ppm)	200	400	600	800	1000
Adsorbant	R_L				
GEO.	0.282	0.164	0.116	0.089	0.072
E1-B1	0.366	0.224	0.161	0.126	0.103
NSAM-B2	0.225	0.126	0.088	0.067	0.054

Table 5. Comparison of adsorption capacity of Copper(II) with other Adsorbents

Adsorbent	Q_m (mg/g)	Reference
Rice bran	33.58	[37]
Carrot residue	32.74	[38]
Wheat shell	18	[39]
Activated rubber wood sawdust	148	[40]
Bagasse fly ash	10.84	[41]
Goethite GEO	90.09	Present Study
Red soils E1-B1	44.84	Present Study
Red soils NSAM-B2	39.84	Present Study

4. CONCLUSION

Goethite (GEO), Red soil (E1-B1) and Red soil (NSAM-B2) have been used as adsorbents for the removal of copper (II) ions from solutions. Adsorption was influenced by various parameters such as initial pH and initial copper (II) ion concentration. The maximum uptake of copper (II) ions occurred at an initial pH of 4.6. Adsorption was increase with increasing initial copper (II) concentration 200-1000 mg/L. The maximum copper (II) ion uptake capacity was 90.09, 44.84 and 39.84 mg/g for GEO, E1-B1 and NSAM-B2, respectively. The kinetics of copper (II) ion adsorption nicely followed pseudo second-order for both adsorbents. Langmuir isotherm could be used to describe adsorption copper (II) by both adsorbents. Kinetic and isotherm studies revealed that GEO, E1-B1 and NSAM-B2 can be effectively employed for the adsorption of copper (II) ions.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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