

Copper Biosorption by Untreated and Citric Acid Modified *Senna alata* Leaf Biomass in a Batch System: Kinetics, Equilibrium and Thermodynamics Studies

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Abstract Untreated *Senna alata* (USA) and chemically modified *Senna alata* (CAMSA) were evaluated for their effectiveness in the removal of Cu²⁺ from aqueous solution. USA was modified with citric acid and characterized by SEM and FTIR. The parameters determined included pH, point of zero charge and initial concentration. Batched equilibrium, kinetic and thermodynamic experiments were also carried out at 298K and at pH 5. The kinetic data obtained were analyzed using pseudo-first order and pseudo-second order models. The pseudo-second order model was better for describing the adsorption of both USA and CAMSA. The equilibrium data were analyzed using Langmuir, Freundlich and Temkin isotherms. The Sorption isotherm was well fitted to Langmuir for both USA and CAMSA. The maximum monolayer adsorption capacities were 2.44 and 23.8 mg/g for USA and CAMSA respectively. In addition, the specific surface area of CAMSA (3.56m²/g) was higher than that of USA (0.365 m²/g). Thus CAMSA removed more Cu²⁺ than USA. Effect of temperature revealed that the reaction was endothermic and the sorption process was physisorption for both USA and CAMSA.

Keywords *Senna alata*, Kinetics, Equilibrium, Adsorption, Surface area, Thermodynamics, Isotherm

1. Introduction

The presence of heavy metals in our environment is posing serious threat to man and animal. The toxic heavy metals are released from anthropogenic sources such as metallurgical, galvanizing, metal finishing, electroplating, mining, power regeneration, electronic devices manufacturing and tannery industries.

Copper is a common substance that is widely used in many industries as untreated materials or additives, and has been considered a very hazardous pollutant [1, 2]. Some of the sources of copper ion in industrial effluents include metal cleaning, plating bath, paper board, mining, anti-fouling for paint and pigment, fertilizer, wood pulp, etc. [3, 4]. Even though copper as a trace element is essential to human beings, excessive consumption of it can result in liver and brain damages, mucosal irritation, gastrointestinal irritation, hepatic and renal damage, widespread capillary damages, central nervous problems followed by depression, and possible necrotic changes in the liver and kidney [5, 6]. The maximum permissible amount of copper approved by

the World Health Organization in drinking water is 1.5 mg/L [7]. Thus the removal of excessive copper in the water bodies has become very necessary. Some of the different methods of removing heavy metal ions from aqueous solutions include ion exchange, solvent extraction, reverse osmosis, chemical precipitation, membrane filtration, electro deposition. The drawbacks in these methods include the inability to remove low concentrations of heavy metals (10 mg/L), ineffectual removal of toxic sludge, unsuitable for wide range of pollutants, expensive to maintain and mostly involves ex-situ remediation.

The biosorption methods are especially considered in recent decade. The major advantages of the heavy metals adsorption technology by biomass are its efficacious ability to decrease to a reasonable extent the concentration of heavy metal ions to very low levels [8] and the use of cost effective biosorbent materials. Furthermore, biosorption methods often provide better results than activated carbon and natural zeolites and are comparable to synthetic ion-exchange resins [9]. Other undeniable advantages of biosorption include the ability to carry out the remediation in situ and their environmentally benign nature.

Senna alata, also known as Candle bush, is a medicinal tree as well as ornamental flowering plant. It is found in diverse habitat. It grows up to an altitude of 1200 m in the tropics. It has effective fungicidal property and is therefore,

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used for treating ringworms and other fungal skin infections.

In this present study, the adsorption ability of untreated *Senna alata* (USA) and citric acid modified *Senna alata* (CAMSA) containing Cu (II) ions were determined. Both samples were characterized with FTIR and scanning electron microscope, SEM. The effects of some parameters such as initial metal concentration, contact time, temperature, adsorbent dosage and pH on the adsorption efficiency of copper from aqueous solutions onto *Senna alata* were investigated. Additionally, adsorption isotherms, kinetic and thermodynamic parameters were also evaluated.

2. Materials and Methods

2.1. Materials

All reagents employed in these experiments were of analytical grade. Citric acid monohydrate was used in the chemical modification of the biomass. Stock solution of 1000 mgL⁻¹ of Cu(II) from Cu(NO₃)₂ salt was prepared. Series of work solutions with the concentrations ranging from 20 to 100 mgL⁻¹ of Cu(II) were prepared by appropriate dilution of the stock solution immediately prior to their use. The *Senna alata* biomass was obtained from a wetland located in Iwo, Nigeria (7° 38' 01" N, 4° 11' 01" E). After harvest, the biomass was washed several times with deionized water to remove the dust particles, and then dried in an oven at 363K for 24 h. The dried biomass was crushed by a high-speed electric grinder. The particles were sieved with a 500µm mesh size and stored in a plastic bag.

2.2. Citric Acid Modification

Ground untreated *Senna alata* was mixed with 0.2 M CA at the ratio of 1:10 (untreated *Senna alata*: CA, w/v) and stirred for 60 min. The acid/*Senna alata* slurry was initially dried at 60°C for 2.5 hours in the oven after which the temperature was raised to 140°C for 2.5 hours. After cooling, the CA modified *Senna alata* was washed with deionized water. After filtration, the CA modified *Senna alata* was suspended in 0.15 M NaOH at suitable ratio and stirred for 60 min followed by washing thoroughly with deionized water to remove the residual alkali. The wet CA modified *Senna alata* was dried at 105°C until constant weight and preserved in a plastic container as modified sorbent for further use.

NOMENCLATURES

USA	Untreated <i>Senna alata</i> containing Cu (II) ions
CAMSA	Citric acid modified <i>Senna alata</i> containing Cu (II) ions
FTIR	Fourier Transform infra-red spectrometer
SEM	Scanning electron microscopy
q _e	Adsorption capacity at equilibrium (mg/g)
C _o	Initial concentration of copper (II) ions (mg/L)
C _e	Equilibrium concentration of copper (II) ions (mg/L)
C _t	Concentration of adsorbent adsorbed at time t

V	Volume of the copper solution (L)
W	weight of the sample (USA or CAMSA) (g)
PZC	Point of zero charge
SSE	Sum of error square
MPSD	Marquardt's percent standard deviation error function
HYBRID	Hybrid fractional error function
p	Number of data points
j	Number of parameters
A _o	Langmuir maximum adsorption capacity (mg/g)
E _L	Dimensionless equilibrium factor
a	Langmuir constant
D	Specific surface area (m ² /g)
N _A	Avogadro's number
X	Cross sectional area (m ²)
M	Atomic mass of Cu (g)
K _F	Freundlich constant (L/g)
n	Freundlich constant
A	Temkin Equilibrium binding energy constant
B	Temkin constant related to the heat of sorption(Jmol ⁻¹)
R	Gas constant (J mol ⁻¹ K ⁻¹)
T	Absolute temperature (K)
q _t	Biosorption capacity at time t (mg/g)
E	Mean free energy of sorption (kJ/mol)
K _d	Thermodynamic equilibrium constant
ΔG	Free energy change (kJ mol ⁻¹)
ΔH	Enthalpy change (kJ mol ⁻¹)
ΔS	Entropy change (J mol ⁻¹ K ⁻¹)

2.3. Instrumental Characterization of USA and CAMSA

The functional groups on the surfaces of USA and CAMSA containing adsorbed Cu (II) ions were analyzed by Fourier Transform Infrared Spectrophotometer, Agilent Technologies Cary 630FTIR spectrometer. A sample press, which is part of the ATR interface, was used to ensure that the ground USA and CAMSA were in good contact with the sensor surface. Spectral data were collected in the 4,000–650 cm⁻¹ region at 4 cm⁻¹ resolution.

Scanning electron microscope (Zeiss Auriga HRSEM) was applied to analyze the surface morphology of both USA and CAMSA.

2.4. Equilibrium Adsorption

Batch adsorption experiments were performed to examine the effects of different parameters, which included pH and adsorbent dose. In each experiment, 0.5 g of the adsorbent was added to 20 mL copper solution in a 250 mL conical flasks and the pH of the solution was adjusted to the desired value by adding a small quantity of 1.0 mol L⁻¹ HCl or 1.0 mol L⁻¹ NaOH solution, and measured with a pH meter. The conical flasks were then placed in an electric shaker to agitate at a speed of 250 rpm at 298K until the equilibrium was reached. Then the mixture was filtered by using Whatmann's No 1 filter paper. Subsequently, the concentrations of the filtrates were determined using atomic

absorption spectrophotometer (PG 990, PG instruments, Britain). The amount of Cu^{2+} adsorbed q_e (mg/g) which represents the amount of adsorbed metal per amount of adsorbent and the removal percentage (%) can be calculated by the following equations:

$$q_e = \frac{(C_o - C_e)V}{w} \quad (1)$$

$$\% \text{ sorption capacity} = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

Where C_e (mg/L) is the equilibrium concentration of Cu(II) ions in solution while C_o (mg/L) is the initial concentration of Cu(II) ions in solution, V (L) is the volume of the Cu(II) ion in solution and w is the weight(g) of the adsorbent.

2.5. Kinetics and Thermodynamics

2.5.1. Adsorption Kinetic Experiments

0.3 g each of adsorbent was added to 120 mL of 20-100

mg/L copper solutions in 500 mL beakers. The beakers were placed on an electromagnetic stirrer at a constant temperature of 298 K with a speed of 250 rpm. Once the *Senna alata* was added, the timing began. The samples were extracted at a definite interval of time and filtered by Whatmann's No 1 filter paper and the amount of metal adsorbed was determined using AAS. The amount of copper adsorbed q_t (mg/g) which represented the amount of adsorbed copper per amount of adsorbent in a specific time can be calculated by the following equation:

$$q_t = \frac{C_o - C_t}{m} V \quad (3)$$

2.5.2. Adsorption Thermodynamics Experiments

Adsorption was carried out by shaking (at 250 rpm) a fixed mixture with 20 mL of the copper solutions of different concentrations (20-100 mg/L) and 0.1 g of the adsorbent at different temperatures (303, 308, 313 and 318 K) in a batch of conical flasks.

The amount of metal adsorbed was determined by AAS.

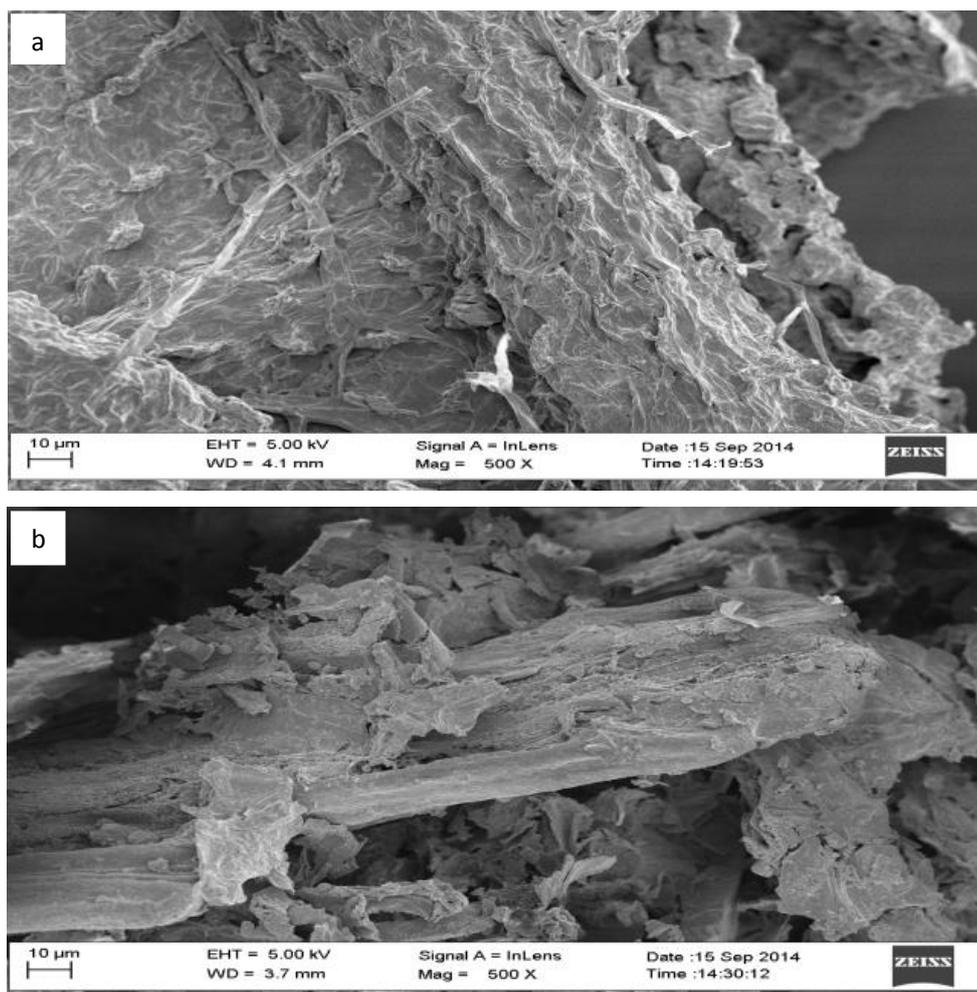


Figure 1. A typical SEM micrograph of (a) USA and (b) CAMSA

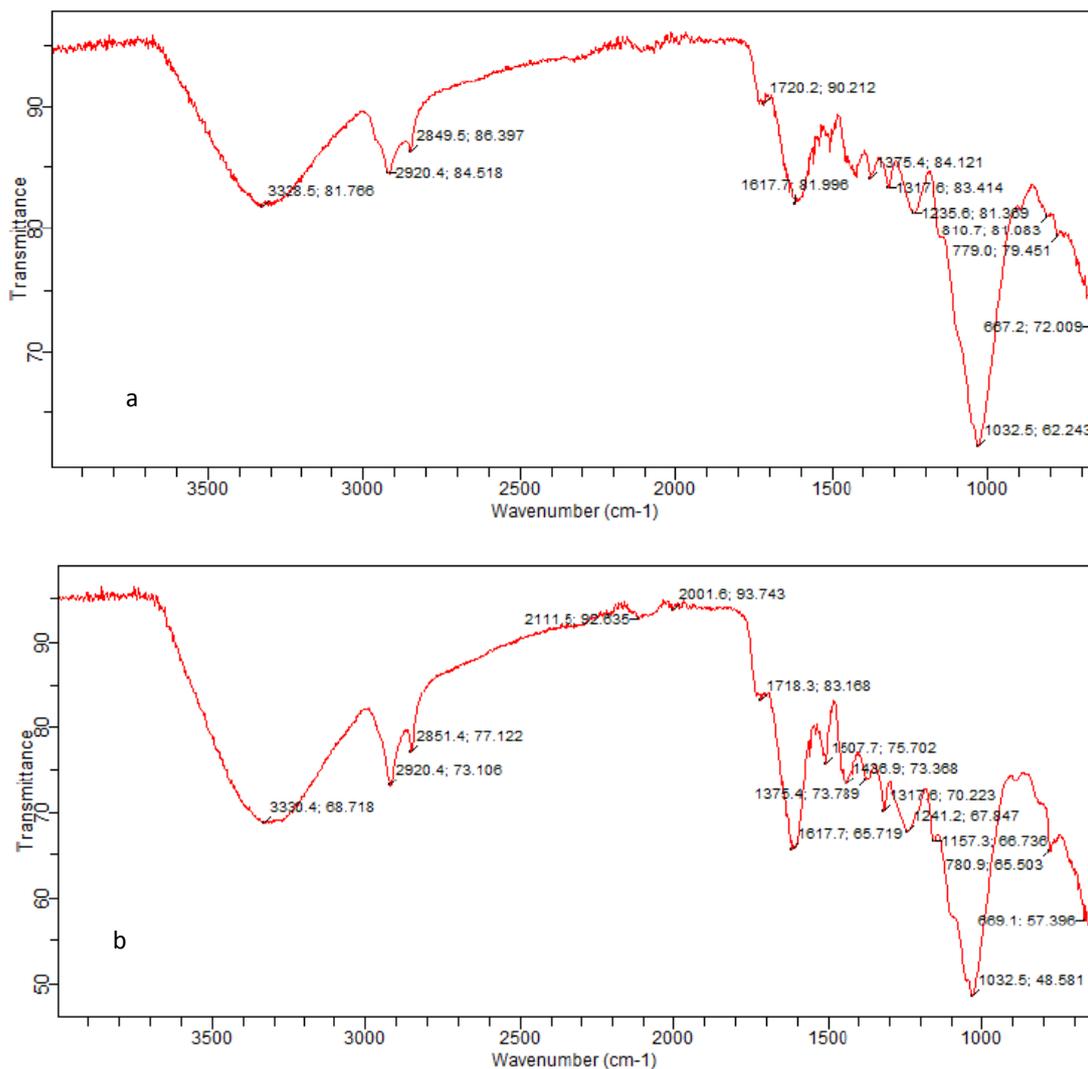


Figure 2. FTIR spectra of (a) USA and (b) CAMSA

3. Results and Discussions

3.1. Biosorbent Characterization

The examination of the textural structure of USA and CAMSA by SEM micrographs at 500x magnification was carried out and are reflected in Figs. 1a and b. Both USA and CAMSA revealed fibrous structures and agglomerates. But USA has more agglomeration than CAMSA. This may be ascribed to the adsorbent weight loss during modification process. Similar observation was obtained by Garcia-Mendeta et al [10] for untreated and formaldehyde modified green tomato husk. In addition, USA and CAMSA have unevenly distributed pores. The FTIR analysis was carried out to show the functional groups present in the USA and CAMSA containing adsorbed Cu (II) ions. Figs. 2a and 2b show the FTIR of USA and CAMSA. The absorption band at 3330.4 cm⁻¹ corresponds to the stretching vibration of the OH group in CAMSA while the absorption band at 3328.5 cm⁻¹ is assigned to the OH group of USA. The absorption

bands at 2920.4 cm⁻¹ corresponds to CH stretch for both CAMSA and USA. Saturated (sp³) C-H stretches were observed at 2851.4 cm⁻¹ and 2849.5 cm⁻¹ for CAMSA and USA respectively. The CO stretch (of saturated carboxylic acid) for USA and CAMSA were observed at 1720.2 cm⁻¹ and 1718.3 cm⁻¹ respectively. The band at 1617.2 cm⁻¹ for both USA and CAMSA was assigned to N-H bend of primary or secondary amine. New absorption bands at 1507.7 cm⁻¹ and 1438.9 cm⁻¹, assigned to C-C stretch and sp³ C-H bend respectively, of CAMSA were absent in USA. 1241 cm⁻¹, 1157.3 cm⁻¹ and 1032.5 cm⁻¹ were assigned to C-O (alcohol or carboxylic acid) stretch for CAMSA while 1235.6 cm⁻¹ and 1032.5 cm⁻¹ were assigned to C-O stretch (alcohol or carboxylic acid) of USA. The vibrational absorption band at 780.9 cm⁻¹ (CAMSA) and 779.0 cm⁻¹ (USA) were assigned to C-Cl. Fig. 2 revealed that most of the functional groups present on USA are also present on CAMSA. Thus the modification of adsorbent resulted in a strong OH of adsorption.

3.2. Effect of pH

The pH is an important parameter in the sorption process optimization. It affects not only the surface charge of the adsorbent, but also the degree of ionization and speciation of the metal ions in solution. Fig.3 presents the effect of pH on the adsorption amounts of Cu^{2+} by the untreated and modified adsorbents. It was found that as pH increased the competition of Cu (II) ions and protons for binding sites decreased and more binding sites are released, which resulted in the increase of adsorption effectiveness [12]. USA showed a sharp increase in adsorption from pH 1-2, the CAMSA showed a sharp increase in adsorption from pH 2-3 while the rate of adsorption gradually increased from pH 3 to 7. The pH at which there was optimum adsorption in untreated and modified *Senna alata* was coincidentally 5.0. The effect of pH can be explained by considering the surface charge on the adsorbent material [13, 14]. The pH value, at which the surface charge is zero, is called the point of zero charge (PZC). The PZCs of the adsorbent were 3 and 7 for CAMSA and USA respectively, which were determined by the method described by Gupta and Nayak [15] as reflected in Fig. 4. Below pH 3 and 7 for both CAMSA and USA, the surfaces were positively charged and under these conditions the uptake of metal ions would be quite low due to electrostatic repulsion. With increasing pH (beyond PZC) the negative charge on the surface of adsorbent increased thereby enhancing the metal adsorption. The positive charges of USA and CAMSA surfaces were primarily due to the next protonation reactions of the hydroxylic sites:



whereas the negatively charged surface was due to the deprotonation of acidic sites depicted by the following reactions:



Where $\approx\text{P}$ represents the surface of USA or CAMSA

Similar results were obtained by Vasconcelos et al [16] and Tong et al. [1] on adsorption of Cu^{2+} on chemically modified chitosan and *Uncaria gambir* respectively.

3.3. Effect of Initial Metal Concentration

The effect of initial metal concentration on the adsorption

of Cu (II) ions is reflected in Fig. 5. The initial Cu (II) ions concentration has significant effect on Cu (II) ions adsorption. Biosorption of Cu(II) ions increased sharply with initial metal concentration where 98.3% of the Cu (II) ions were removed for USA, and 99.6% of the Cu (II) ions were removed for CAMSA.

When low initial but same concentrations are considered for USA removed more metal than CAMSA. This may be due to the fact that Cu^{2+} ions filled up the available sites faster in USA than in CAMSA and that the number of available sites in USA is smaller as compared with that in CAMSA. Consequently, a low initial concentrations USA reached its maximum adsorption faster than CAMSA.

3.4. Adsorption Kinetics

Two kinetic models, Lagergren first-order and pseudo-second order, were used to explain the adsorption of Cu^{2+} on USA and CAMSA. The equations for the Lagergren first-order (eq. 4) and pseudo-second order (eq. 5) are given below

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

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

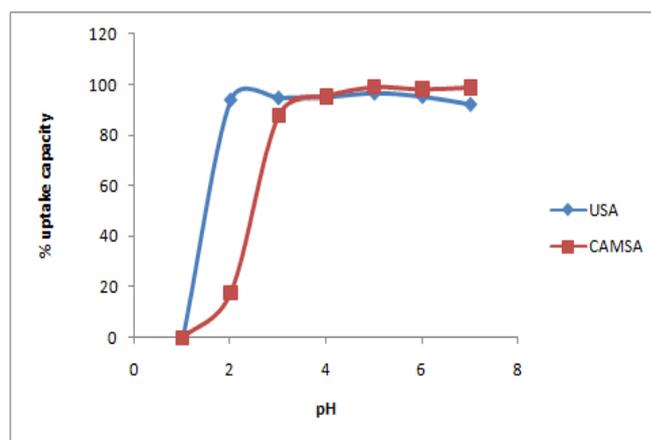


Figure 3. The effect of pH on the adsorption of copper on USA and CAMSA. Conditions: Temp= 298 ± 1 K, C_0 = 20mg/L, agitation speed = 250 rpm

Table 1. The physicochemical characteristics of citric acid

Name	Schematic structure	Physicochemical characteristics
Citric acid (2-hydroxy-1,2,3-propanetricarboxylic acid)		Molecular formula: $\text{C}_6\text{H}_8\text{O}_7$ Molecular weight: 192.12 Appearance: crystalline white solid pH: 1.7 Density: 1.665 g/mL Solubility in H_2O : in any ratio Biodegradability: 100% Melting point: 153°C

In Langergren first order, $\log(q_e - q)$ was plotted against t while in pseudo- second order equation t/q_t was plotted against t as shown in Figs. 6a and 6b. The pseudo first order (not shown) for Cu (II) ions was not suitable for describing the adsorption because the model gave very low $q_{e(cal)}$ compared to the $q_{e(exp)}$. The pseudo- second order equation gave a better fit than the first order equation. The theoretical values of sorption capacity calculated (q_{calc}) for CAMSA (Table 2) showed a very close agreement with the experimental ones (q_{exp}), and the related correlation coefficients were outstanding ($0.995 \leq R^2 \leq 1.000$). The q_{calc} increased both with increase in the initial metal concentration and the experimental sorption capacity. For Cu^{2+} sorption by USA, the pseudo second order rate constant (k_2) to a certain extent, progressively increased with increasing initial metal concentration (C_o) while it decreased for CAMSA except at 60 mg/L (Table 2). Greater variation among k_2 values was observed with USA ($0.116-0.848 \text{ g mg}^{-1} \text{ min}^{-1}$) compared to CAMSA ($0.18-0.39 \text{ g mg}^{-1} \text{ min}^{-1}$). Therefore, pseudo second order model was selected as the better of the two representing metal sorption by USA and CAMSA biomasses. In addition, only the pseudo- second order model, in which the metal binding capacity is assumed proportional to the number of active sites occupied on the sorbents (USA and CAMSA), gave a good representation of the sorption rate [16]. Another point that requires emphasizing is that Cu^{2+} sorption rate on CAMSA was much higher than that on USA as the initial metal concentration increases.

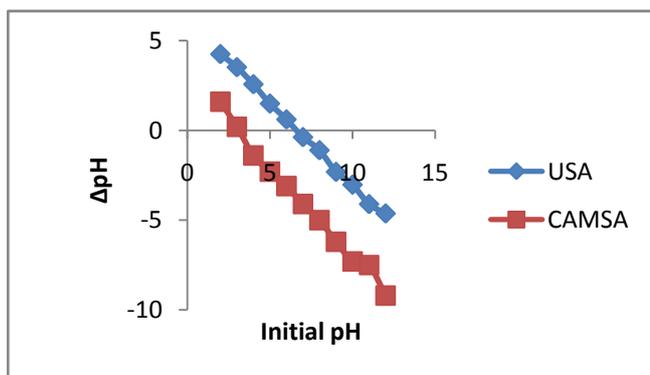


Figure 4. The effect of point of zero charge on the adsorption of copper on USA and CAMSA at $298 \pm 1 \text{ K}$

The appropriateness of the above kinetic models was ascertained through the sum of error squares (SSE), the hybrid fractional error function (HYBRID) and the Marquardt's percent standard deviation (MPSD) error function. The error functions are the following:

$$SSE = \sum_{i=0}^Z \left(q_{e,exp} - q_{e,cal} \right)_i^2 \quad (6)$$

$$MPSD = 100 \left(\sqrt{\frac{1}{z-j} \sum_{i=1}^z \left(\frac{q_{e,exp} - q_{e,cal}}{q_{e,exp}} \right)^2} \right)_i \quad (7)$$

$$HYBRID = \frac{100}{z-j} \sum_{i=j}^z \left[\frac{\left(q_{e,exp} - q_{e,cal} \right)^2}{q_{e,exp}} \right]_i \quad (8)$$

The lower the value of the error, the better will be the kinetic fit. From Table 2, it can be seen that for USA and CAMSA, the SSE, HYBRID and MPSD values were lower for a pseudo- second order kinetic than for pseudo-first order kinetic model. This consequently verified the fact that pseudo second order kinetic model is better for describing the adsorption of Cu (II) ions on USA and CAMSA.

Table 2. Parameters for the sorption kinetics of copper (II) ions on USA and CAMSA leaves powder

	20mg/L	40mg/L	60mg/L	80mg/L
USA				
Pseudo First order				
$q_{e(exp)}$	3.83	7.46	11.3	14.6
$k_1(\text{min}^{-1})$	0.015	0.004	0.42	0.03
$q_{e(cal)}$	1.11	0.95	1.04	1.03
SSE	7.4	32.7	93.3	184
HYBRID	64.4	146	275	421
MSPD	410	443	494	537
Pseudo Second order				
$q_{e(cal)}$	0.84	0.14	0.30	0.13
$k_2(\text{g mg}^{-1} \text{ min}^{-1})$	3.91	7.31	11.6	15.1
R^2	1.00	0.99	0.99	0.95
SSE	5.8×10^{-3}	0.02	0.07	0.28
HYBRID	0.05	0.10	0.19	0.62
MPSD	1.15	1.16	1.13	2.09
CAMSA				
Pseudo First order				
$q_{e(exp)}$	3.89	7.63	11.2	14.9
$k_1(\text{min}^{-1})$	0.014	0.002	0.49	0.03
$q_{e(cal)}$	5.10	1.71	1.64	1.03
SSE	1.47	35.1	91.4	193
HYBRID	12.6	153	272	431
MPSD	1.18	79.2	66.3	104
Pseudo Second order				
$q_{e(cal)}$	3.77	7.89	11.6	0.13
$k_2(\text{g mg}^{-1} \text{ min}^{-1})$	0.39	0.39	0.18	0.30
R^2	0.99	0.99	1.00	0.99
SSE	0.01	0.04	0.14	0.09
HYBRID	0.13	0.18	0.42	0.16
MPSD	1.81	1.52	1.93	1.15

3.5. Adsorption Isotherms

In this study, Freundlich [17], Langmuir [18] and Temkin [19] isotherms were used to explain the equilibrium adsorption data for the adsorption of copper (II) ions by *Senna alata*.

3.5.1. The Langmuir Equation

The assumptions of Langmuir isotherm model are that the removal of the adsorbate takes place on a specific adsorbent surface by uniform monolayer adsorption, all adsorption sites are equivalent and that there is no interaction between adsorbed molecules [20]. The Langmuir equation is given by

$$\frac{C_e}{q_e} = \frac{1}{A_0 b} + \frac{C_e}{A_0} \quad (9)$$

Table 3 shows the Langmuir parameters. The modified sample, CAMSA, removed more Cu (II) ions (23.8 mg/g) than the untreated sample, USA (2.44 mg/g). Moreover, the Langmuir model fitted better for CAMSA ($R^2 = 97.5\%$) than for USA ($R^2 = 94.1\%$). A dimensionless equilibrium factor, E_L , proposed by Weber and Chakkravorti [21] described the favourability of adsorption. It is expressed as

$$E_L = \frac{1}{(1 + aC_o)} \quad (10)$$

E_L value between 0 and 1 implies favourable adsorption while $E_L > 1$, $E_L = 1$ and $E_L = 0$ imply unfavourable adsorption, linear adsorption and irreversible adsorption respectively. Values of E_L for Cu (II) ions removed by USA and CAMSA were 0.019 and 0.049 respectively. This is a reflection of the favourability of Cu (II) ions adsorption.

3.5.2. The Freundlich Isotherm

The Freundlich isotherm model is an empirical and exponential equation. It is used to describe heterogeneous systems and reversible adsorption and is not restricted to the formation of monolayers [22]. It assumes that increase in the adsorbate concentration increases the concentration of adsorbate on the surface of the adsorbent. Freundlich model is given by

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (11)$$

From Fig. 8 it is evident that the experimental data were better fitted for CAMSA ($R^2 = 0.90$) than for USA ($R^2 = 0.80$). Thus, since $R^2 < 0.90$ for USA, it implies that the experimental data of the biosorbent failed to fit the Freundlich isotherm model indicating that a homogeneous type of adsorption exist for USA. This may be due to the unmodification of the surface of USA. Similar result was obtained by [23] for the adsorption of Acid Blue 25 by unmodified and CPC-modified biomass of *Penicillium* YW01. Furthermore, Freundlich parameter, n , denotes the favorability of the adsorption as well as the adsorption intensity. The higher the value of n , the higher will be the affinity between the adsorbate and the adsorbent, and the heterogeneity of the adsorbent sites. The value of n signifies the relative distribution of energy sites and depends on the nature and strength of the adsorption process [24]. From Table 3 it can be said that the value of n for USA is less

than 1 which means that the adsorption of *Senna alata* is unfavourable as compared with that of CAMSA whose n is greater than 1 which indicates favourable adsorption [25].

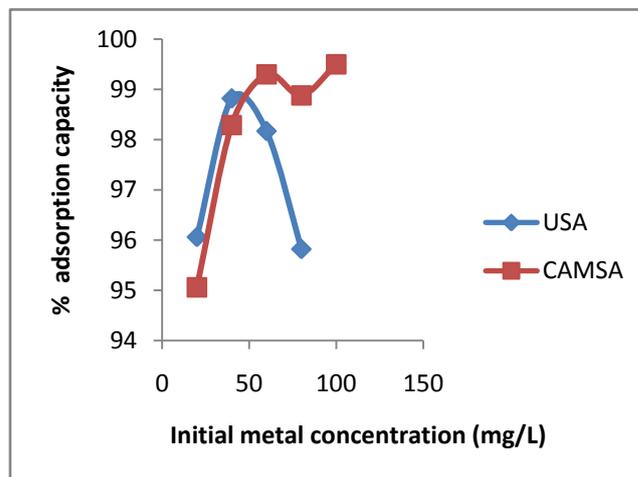


Figure 5. The effect of initial metal concentration on the adsorption of copper on USA and CAMSA Conditions: Temp= 298 ± 1 K, w= 0.5 g, agitation speed = 250 rpm

3.5.3. Temkin Isotherm

The Temkin adsorption isotherm equation assumes that there is a linear decrease in the heat of adsorption of all the molecules as the surface of the adsorbent is covered increasingly as a result of the interactions between the adsorbate and adsorbent, and that the binding energies are uniformly distributed up to some maximum binding energy [26]. Temkin model is given by

$$q_e = \frac{RT}{B} \ln A + \frac{RT}{B} \ln C_e \quad (12)$$

Table 3. Isotherm parameters for the adsorption of Cu (II) ions on USA and CAMSA at 303K

Isotherm models	Parameters	
	USA	CAMSA
Freundlich	$K_F = 4.08$	$K_F = 11.3$
	$n = 0.62$	$n = 2.43$
	$R^2 = 0.80$	$R^2 = 0.91$
Langmuir	$A_0 = 2.44$	$A_0 = 23.8$
	$b = 2.54$ L/mg	$b = 0.98$ L/mg
	$R^2 = 0.94$	$R^2 = 0.98$
	$R_L = 0.019$	$R_L = 0.049$
Temkin	$A = 1.20$ mg/g	$A = 2.70$ mg/g
	$B = 54.0$	$B = 297.4$
	$R^2 = 0.91$	$R^2 = 0.88$

A and B are constants that can be obtained from the intercept and the slope of the linear plot of experimental data of q_e versus $\log C_e$ (Fig. 9). The values of the constants A and B are listed in Table 3.

The A_0 value determined was used to obtain the specific

surface area D of USA and CAMSA. D is given by

$$D = \frac{N_A X A_o}{M} \quad (13)$$

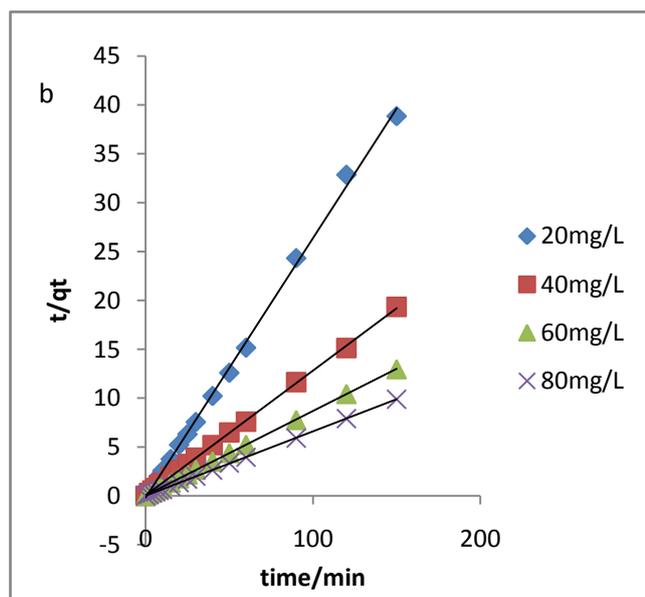
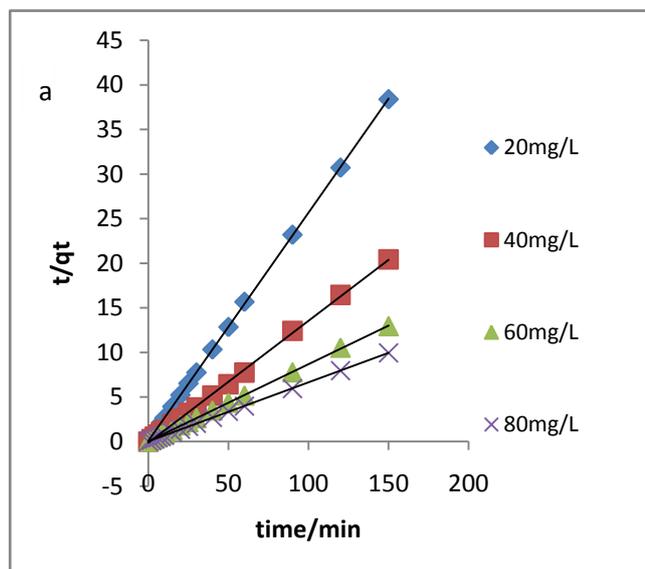


Figure 6. Pseudo second order kinetics for the adsorption of Cu(II) ions on (a) USA and (b) CAMSA leaves powder. Experimental conditions: biosorbent dosage = 0.2 g, contact time = 150 min, shaking speed = 250 rpm, temperature = 298 ± 1K

The specific surface area is calculated on the basis of the A_o value, and it shows the surface area per gram of the material occupied by the metal ions [27]. Copper has an atomic mass of 63.5 g, and the cross sectional area of 1.58 Å² (the radius of Cu(II) ions for close packed monolayer is 0.71 Å). The specific surface area of USA and CAMSA for Cu (II) ion adsorption was found to be 0.365 m²/g and 3.56 m²/g respectively. Thus CAMSA has more surface area than USA which was responsible for its ability to adsorb more Cu²⁺ ions.

3.6. Adsorption Thermodynamics

The effect of temperature on adsorption was investigated at 303°C, 308°C, 313°C and 318°C at optimum pH 6 with different initial Cu(II) concentration. Percentage removal of Cu(II) ions was increased gradually with rise of temperature from 303 to 318°C for both USA and CAMSA.

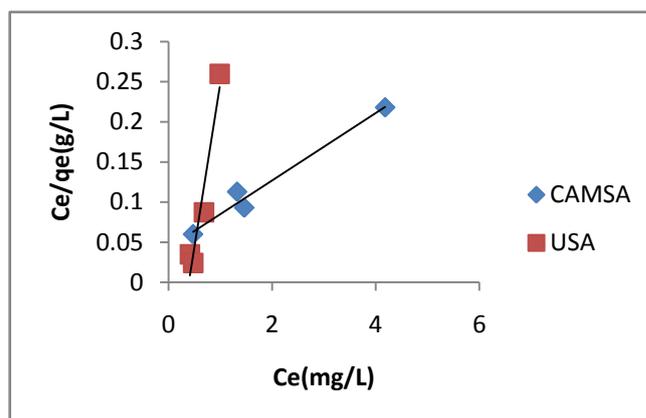


Figure 7. Langmuir sorption isotherm of copper (II) ions on USA and CAMSA. Experimental conditions: pH 6, temperature, 298 ± 1K, shaking speed = 250 rpm

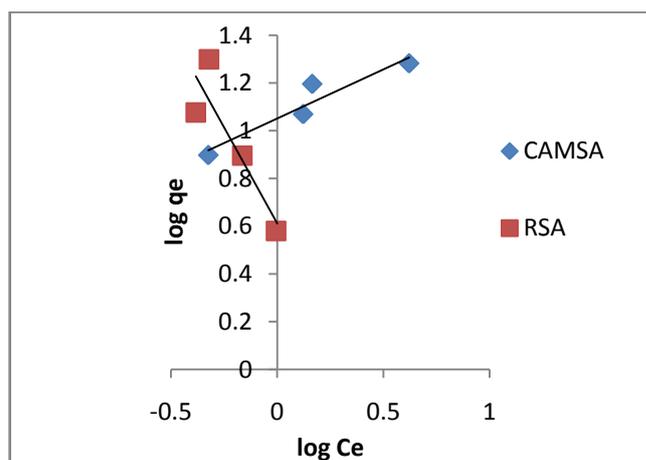


Figure 8. Freundlich sorption isotherm of copper (II) ions on USA and CAMSA. Experimental conditions: pH 6, temperature, 298 ± 1K, shaking speed = 250 rpm

In addition, as reflected in Figs. 10a and b, increase in concentration increases the adsorption of Cu (II) ions at a fixed temperature. The thermodynamic equilibrium constant, K_d , at the respective temperatures was evaluated from the equation

$$\ln K_d = \frac{q_e}{C_e} \quad (14)$$

The Gibbs free energy of adsorption (ΔG°) is related to the equilibrium constant K_d by the following equation [28]:

$$\Delta G^\circ = -RT \ln K_d \quad (15)$$

The thermodynamic parameters such as change in standard free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined by using the following equation [29]:

$$\ln K_d = -\frac{\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (16)$$

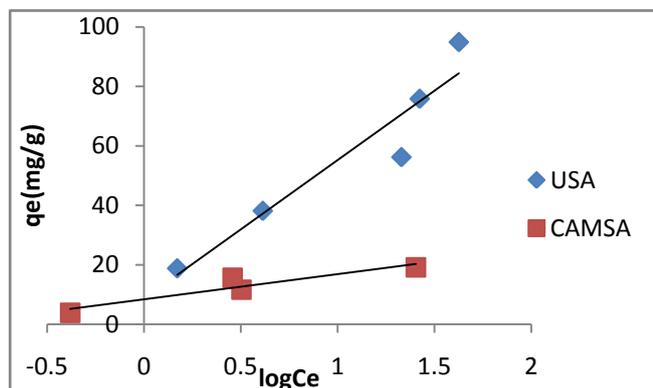


Figure 9. Temkin sorption isotherm of copper (II) ions on USA and CAMSA. Experimental conditions: pH 6, temperature, 298 ± 1 K, shaking speed = 250 rpm

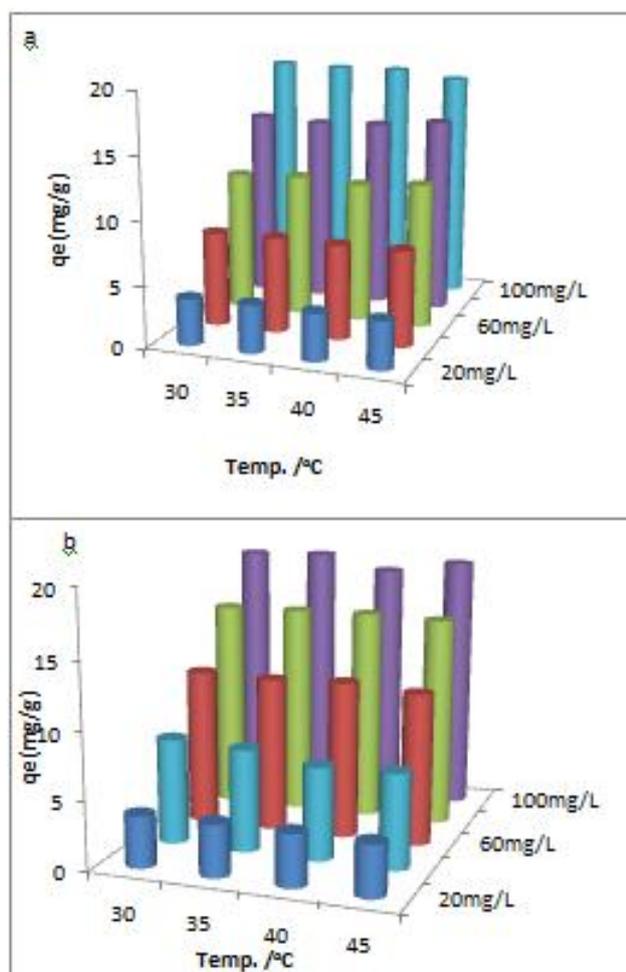


Figure 10. Effect of adsorption capacity and initial concentrations on the temperature for the adsorption of Cu(II) ions on (a)USA and (b)CAMSA

The ΔG values for the metal ions at all temperatures are negative indicating that the adsorption is spontaneous. The change of Gibbs free energy decreased with increasing temperature from 303 to 318K which implied a better adsorption occurred at higher temperatures. The enthalpy

change (ΔH) and entropy change (ΔS) were evaluated following van't Hoff equation (Table 4).

Table 4. Thermodynamic parameters for the adsorption of copper (II) ions on USA and CAMSA

Metal conc. (mg/L)	ΔH (kJ/mol)	ΔS (J/mol)	$-\Delta G$ (kJ/mol)			
			303 K	308 K	313 K	318 K
USA						
20	30.7	111.9	3.02	3.88	4.52	4.66
40	32.4	116.4	3.31	3.65	3.48	4.25
60	32.4	116.4	2.95	3.45	3.90	4.79
80	41.0	144.2	3.18	2.96	4.08	5.24
100	13.3	54.5	3.20	3.14	4.15	3.76
CAMSA						
20	21.8	78.4	1.89	2.50	2.15	2.68
40	3.41	22.4	3.31	3.65	3.48	3.74
60	11.9	45.8	2.14	1.82	1.55	2.61
80	25.6	92.6	2.51	2.90	2.73	3.44
100	9.23	19.7	3.20	3.14	3.26	2.82

Table 5. Adsorption capacities of various adsorbents

Adsorbent	Adsorption capacity (mg/g)	Temperature K	References
<i>Solanium elaeang-Nifolium</i>			
Lentil shell	13.1	-	[32]
Lentil shell	8.98	298	[33]
Lentil shell	9.51	313	[33]
Lentil shell	9.59	338	[33]
Wheat shell	7.39	298	[33]
Wheat shell	16.1	313	[33]
Wheat shell	17.4	338	[33]
Irish peat moss	17.6	-	[34]
<i>Spirulina platensis</i>	67.9	-	[35]
Chemically activated			
pine cone	5.76	-	[36]
<i>Uncaria gambir</i>	9.95	333	[1]
USA	2.44	303	This study
CAMSA	23.8	303	This study

The value of ΔH° is positive for both USA and CAMSA which is an indication that the sorption reaction is endothermic. A probable explanation is that there was the hydration of Cu^{2+} ions and high energy was required to break the hydration covering for adsorption to progress. Thus high temperatures facilitated the dehydration process and consequently, the adsorption process. Similar results were obtained by Chen and Wang [30] and Gupta and Sharma [13]. It can be observed from Table 4 that ΔH° for USA increases as the concentration increases from 20 to 80 mg/L. The sorption process was achieved at less values of enthalpy change for CAMSA (11.9 - 25.6 kJ mol $^{-1}$) than for USA (30.7 - 41.0 kJ mol $^{-1}$). This could be attributed to the presence of more available pores for adsorption in CAMSA than in USA. The values of ΔG° at all temperatures studied for both USA and CAMSA as reflected in Table 4 were

between -20 to 0 kJ mol^{-1} which are indications that the sorption process was physisorption. ΔS° reflected the good affinity of adsorbent for adsorbate and increased randomness during the sorption process. Table 5 presents the comparison of adsorption capacities of different adsorbents. From Table 5, USA has the lowest adsorption capacity. On citric acid modification of the USA to give CAMSA, adsorption increased about ten fold. Thus, CAMSA adsorbed more copper than all the adsorbents except for *Spirulina platensis* (35).

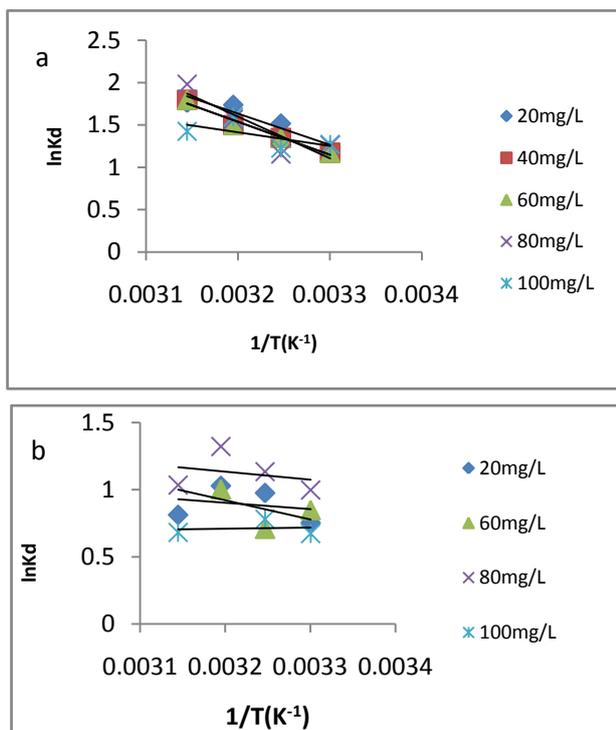


Figure 11. The plot of $\ln K_d$ against T^{-1}/K^{-1} for the adsorption of Cu (II) ions on (a) USA and (b) CAMSA. Experimental conditions; pH6, shaking speed 250 rpm

3.7. Conclusions

Citric acid modified *Senna alata* was a good adsorbent for the removal of copper (II) ions. The optimum pH for the removal of the untreated (USA) and modified *Senna alata* (CAMSA) was coincidentally 5.

The pH, PZC, initial concentration and temperature on the adsorption played significant roles in the Cu (II) ions adsorption capacity of *Senna alata*. The maximum adsorption capability of the adsorption of Cu (II) ions by USA and CAMSA are 2.44 mg/g and 23.8 mg/g respectively. The pseudo-second-order model fitted the experimental data well. Isotherm modeling revealed that the Langmuir equation could better describe the adsorption of Cu on both USA and CAMSA as compared to Freundlich and Temkin models. Negative values of free energy change, ΔG° , indicated that adsorption of Cu by USA and CAMSA was spontaneous.

The thermodynamic study showed that the adsorption processes are random, spontaneous and endothermic.

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