

## Removal of Copper from Aqueous Solution Using Raw Cowpea Husk, And Cowpea Husk Coated With Zinc Oxide Nanoparticle Adsorbent

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### Abstract

Raw Cowpea husk(CPH), and Cowpea husk coated (CPHC) with nano Zinc oxide (ZnO) were used as adsorption media to remove Copper ( $\text{Cu}^{2+}$ ) from aqueous solutions. Functional groups, morphology, structure, and percentages of surfactants before and after adsorption were characterized through Fourier-transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive spectroscopy (EDS). Several variables, including pH, connection time, dosage, initial concentrations, and temperature, were controlled to obtain the optimum condition. Thermodynamic studies, adsorption isotherm, and kinetics models were examined to describe and recognize the type of interactions involved. Resultantly, the best operation conditions were at pH 5, contact time of 210 min, 1 g/100ml of dosage, initial concentration of 30 mg/L, and a temperature of 45 °C. The removal percentage of  $\text{Cu}^{2+}$  under the optimum condition was 77% for CPH and 96% for CPHC. Thermodynamic analysis indicated that the removal efficiency was slightly increased with temperature depending on the positive value of  $\Delta H^\circ$ , thus indicating that the adsorption phenomenon was endothermic. The Langmuir model fitted the study ( $R^2 = 0.987$ ) for CPH and( $R^2 = 0.967$ ) for CPHC, demonstrating that the adsorption sites were homogenous. The experimental results were best matched with the second-order kinetic model, implying that chemisorption was the primary process during the adsorption process.

**Keywords** Adsorption · Cooper · ZnO nanoparticles · cowpea . kinetic

### Introduction

Heavy metal removal from Wastewater is a significant issue. Several chemical industries, like electroplating, petrochemical processing, battery manufacture, etc., emit highly harmful metal ions and pollutants, Metals detected in industrial wastewater today are beyond the allowable limit, which may be related to faulty treatment methods[1]. These metals are non-degradable and cause disposal issues. That is a significant global concern[2]. Waste water frequently contains toxic metals or metalloids like heavy metals chrome, bronze, silver, gold, arsenic, arsenic, argent, cadmium, antimony, mercury, thallium, lead, ferric and copper[3].

One of the main dangerous contaminants in wastewater is copper[4]. Humans need copper because it plays a crucial part in the creation of enzymes, the growth of tissues, and the formation of

bones[5]. However, divalent copper ( $\text{Cu}^{2+}$ ), when ingested in excess is poisonous and can cause cancer. Consuming too much  $\text{Cu}^{2+}$  causes it to accumulate in the liver, which then causes vomiting, headaches, nausea, respiratory issues, abdominal discomfort, liver failure, renal failure, and finally gastrointestinal[6]. It harms numerous plant species and has recognized negative impacts on the soil organisms[7].

In order to remove heavy metals from wastewater, conventional procedures, i.e. Coagulation and flocculation[7], chemical precipitation[9], ion-exchange [9], ion flotation[10], and adsorption[11] .are examples of processes that occur in the body. But these techniques have a number of drawbacks, such as high operating costs, the production of harmful byproducts, and high energy[12]. Of all these methods, adsorption seems effective, low operating costs, simple in design, quick in nature, and efficient at lower doses[13], which are found in nature in a variety of forms, including plant waste and forest waste, offer promise for use in wastewater treatment procedures. Adsorption is superior to traditional treatment options in a number of ways, including Reusable materials, effectiveness at low concentrations, and relatively inexpensive in nature are all advantages of metal regeneration[14]. It consists of a liquid state (solvent) that contains the material or other species acting as the biosorbent, as well as a solid phase (sorbent).

Graphite, clays, bentonite, zeolites, activated carbon, and aerogels are some of the most frequently utilized adsorbents [15].These adsorbents provide excellent laboratory results, but they are expensive to set up and maintain. Therefore, the creation and application of inexpensive adsorbents is essential. A natural adsorbent that is readily accessible and inexpensive is agricultural waste. Numerous studies confirm the heavy metals' effective elimination[16] .

Vegetable and fruit peels, sawdust, leaves, husks, shells, bran, straw[16], sawdust[17], and agriculture are some of the major agricultural waste materials utilized as sorbent materials for waste water treatment. Compared to standard treatment procedures, organic fertilizers or biosorption materials have a number of benefits, such as cheap cost, the ability to regenerate, high adsorption efficacy, minimal toxic or liquid waste, and the potential for metal recovery[18]. Agricultural goods in general and cellulosic materials in particular display a high potential biosorption capability due to their structural makeup including lignocellulosic materials, phenol, organic components, triglycerides, peptides, simple sugars, aqueous hydrocarbons, and carbohydrates[19].

The development of new categories of nanoparticles for the purification of water is the result of efforts to identify low-cost alternatives to current materials and recent advancements in nanotechnology. Due to their unusual features and possible uses, nanoparticles—often distinguished

by enormous specific surface areas—have drawn a lot of attention[20]. Multiple adsorption experiments were conducted on zinc oxide nanoparticles (ZnO), and after they successfully passed the tests, they were chosen as sorbent materials and catalysis in the processing[21]. ZnO is simple to make, inexpensive, adaptable in morphology, environmentally friendly, and unaffected by changes in the environment[22].

In this study, cowpea husk (CPH) coated with ZnO was employed as a low-cost, efficient, and environmentally acceptable adsorbent. Its adsorption ability for heavy metals contained in aqueous solution was examined using the batch approach; it was possible to assess how various factors, including initial concentration and adsorbent mass, affected the effectiveness of heavy metal adsorption. Adsorption kinetics models, Elovitch kinetic models, and "pseudo-second order kinetic" modeling techniques were all employed to analyze the kinematics of metal adsorption on cowpea husk. The "Langmuir and Freundlich, " equations were fitted to the experimental equilibrium data to determine which isotherm equation best matched the data.

This work aims to investigate the removal efficiency of  $\text{Cu}^{2+}$  via adsorption by using cowpea husk (CPH) coated with zinc oxide nanoparticles (ZnO NPs). There are no previous studies on using CPH coated with ZnO NPs as catalyst for  $\text{Cu}^{2+}$  removal from aqueous solution.

## Materials and Methods

### Materials

Copper (Chemical Formula : $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ; Molecular weight (g/mole):241.60) were obtained from Hi Media -INDIA . The pH was maintained throughout the experiment by adding 0.1 mol/L hydrochloric acid (HCl) and/or 0.1 mol/L sodium hydroxide (NaOH). Acetonitrile purchased from Sigma-Aldrich (Milan, Italy) was employed without further purification[23].

### Adsorbent preparation

The cowpea husk coated (CPHC) adsorbent in the current investigation was made using the following fundamental process. Locally gathered cowpea peel was hand-cleaned, properly washed thoroughly with distilled water, soaked for a couple of hours, and then dried in a suitable oven at 105 °C for twenty-four hours. The prepared dried peels were ground and sieved to distinct particle sizes: 125  $\mu\text{m}$ . Small samples of the produced (CPH) were analyzed, and the ZnO nanoparticles coated the surface of the remaining samples. A appropriate dispersion (acetone) was combined with ZnO nanoparticles obtained from manufactured ZnO nanoparticles and then stirred in a magnetic stirrer for 30 minutes. The ZnO nanoparticles were then rapidly agitated while various masses of

CP were introduced in proportions of 5:1 (CPHC: ZnO) (g/g). After that, the liquid was decanted, and the coated cowpea peel with ZnO nanoparticles (CPHC) that had formed as a result was filtered before being dried completely in an oven at 70°C. Finally, stoppered flasks were utilized to preserve the dried (CPHC) so that it could be employed in the necessary studies. Figure (1) showing the (CPHC) preparation [23]–[25].



**. Figure (1) The cowpea husk collection(a), The cowpea husk ground(b), ZnO nanoparticles(c), The cowpea husk after coating with ZnO nanoparticles(d)**

### **Characterization of CPHC**

The following analyses were performed to investigate the adsorbent's characteristics: At a 10 KV potential and a 6-mA fluorescence, SEM (NOVASEM, FEL450L) examination was utilized to look at the surface properties of the adsorbent. This experiment demonstrates how the adsorbent's structural properties change both before and after the  $\text{Cu}^{2+}$  is withdrawn. It was carried out at the University of Tehran's College of Science. "Energy dispersive X-ray analysis" "(EDX)" is a system that combines "scanning electron microscopy" with chemical microanalysis (SEM). It is used to ascertain the elemental makeup of a material. This examination took place at the University of

Tehran's College of Science. "Fourier transform infrared spectroscopy" (FTIR): it studies presents a method to recognize functional groups on the surfaces that are available on the material and permits spectrophotometric monitoring. The spectra analysis was done in the range of forty hundards to forty thousand  $\text{cm}^{-1}$  region consuming a "Bruker Tensor 27 spectrophotometer and the KBr pellet" technique. It is obtained from the College of Science at the University of Tehran's College of Science. The specific surface area of was determined using Brunauer–Emmett–Teller (BET) analysis. It is obtained from the College of Science at the University of Tehran's College of Science.

### Adsorption experiments

Each experiment involved shaking 100 ml of solution in a 250 ml flask using an orbital shaker for a predetermined amount of time. Following this, the sample was filtered and its heavy metal concentration was determined using an atomic absorption spectrophotometer. The following equations were used to compute the removal effectiveness (%) and the equilibrium adsorption capacity ( $q_e$ , mg/g) equation (1,2) [25].

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

$$\text{Removal Efficiency \%} = 100 \frac{(C_o - C_e)}{C_o} \quad (2)$$

Where V is the sample volume (in L),  $C_o$  and  $C_e$  are the heavy metal's starting and optimum levels (in mg/L and mg/L, respectively), and W is the amount of the adsorbed that was used (g).

The determination of pHpzc adsorbent was carried out according to the conventional method[26],[27] . Thus, nine flasks filled with 50 mL of 0.1 M NaCl solution were adjusted to the initial pH of 3.0 to 11 using 0.1 M NaOH or HCl solutions, followed by addition of 0.5 g of dried powdered Raw Cowpea husk(CPH), and Cowpea husk coated (CPHC) with nano Zinc oxide (ZnO) to each flask. To further equilibrate the condition, the mixture obtained undergoes vigorous shaking to for 24 h at 25 °C and speed of 150 rpm. The final pH was noted and plotted versus initial pH, where the intersection point of the two curves determines the pHpzc of the biomass.

### Adsorption Equilibrium Models

#### Thermodynamic study

The analysis of thermodynamic parameters is an important step in evaluating thermodynamic feasibility, process spontaneity and adsorption mechanism . The thermodynamic parameters such as

Gibbs free energy change ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) were calculated using the following equations (3,4) .

$$\Delta G^0 = -RT \ln K_C \quad (3)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (4)$$

where  $K_C$  is the distribution coefficient for adsorption and is determined as:

$$K_C = q_a / C_e$$

where  $C_a$  is the equilibrium heavy metal concentration on the adsorbent (mg/ L) and  $C_e$  is the equilibrium dye concentration in solution (mg/ L).  $R$  – represents the universal gas constant ( $8.314 \times 10^{-3}$  kJ /mol.K); Where:  $\Delta G^0$  standard free energy change (kJ/mol);  $\Delta H^0$  standard enthalpy change (kJ/mol),  $\Delta S^0$  standard entropy change (kJ/mol.K),  $T$  the temperature,  $K_c$  the equilibrium constants ( $q_e/C_e$ ),  $\Delta S^0$  values in the adsorption process were determined from the intercept and slope of the plot of  $\ln K_c$  versus  $1/T$ , respectively

### isotherm model

The isotherm models are followed to describe the distribution of the adsorbate among the adsorbent surface. A set of isotherm model assumptions are made in relation to the heterogeneity or homogeneity, coverages, and possibility of interaction. Langmuir isotherm and Freundlich Isotherm were examined for the equilibrium data to describe how the adsorbate molecules interaction with adsorbent surface. The following equation (5,6) expresses the Langmuir model isotherm [28].

$$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e} \quad (5)$$

$$q_e = k_f C_e^{1/n} \quad (6)$$

$q_{\max}$ : maximum adsorption capacity at complete monolayer coverage (mg/g);  $q_e$ : equilibrium adsorbate uptake (mg/g);  $C_e$ : equilibrium (final) concentrations of the sorbate (mg/L);  $K_L$  is defined as the affinity parameter related to the bonding energy of the sorbate;  $k_f$ : Freundlich isotherm constant (mg/g). $n$ : adsorption intensity[29].

### Kinetic Study

Kinetic tests rate of adsorption process and adsorption potential rate-limiting steps. provide crucially important details for the time needed to reach equilibrium. If an adsorbent is intended to be used in wastewater treatment facilities on industrial scales, in addition to its high adsorption

capability and removal performance, a high adsorption rate is also a critical character necessary. Predicting adsorption kinetics in a wastewater treatment process is an important aspect as it offers valuable information into the adsorption mechanism process and is a rate-limiting step. Commonly accepted kinetic models including: pseudo-first-order, pseudo-second-order and intraparticle diffusion. For diffusion rate limiting analysis, the third model is based.

For the pseudo-first order model of Lagrange, it can be generally expressed as follows equation (7,8) [23]:

$$\frac{dq_t}{dt} = K(q_e - q_t) \quad (5)$$

The integral form of this equation is given as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where  $q_e$  is the equilibrium adsorption capacity of the adsorbent (mg / g),  $q_t$  is the adsorption capacity (mg / g) when the contact time is  $t$ ,  $K$  and  $k_1$  are the rate constants of the pseudo first-order adsorption model.

The pseudo-second-order kinetic model is known to be successfully applied in systems where the rate controlling step is chemisorption. The pseudo-second-order model can be expressed as follows equation (9,10) [30]:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (9)$$

The integral form of this equation is given as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (10)$$

where  $q_e$  is the equilibrium adsorption capacity of the adsorbent (mg /g),  $q_t$  is the adsorption capacity (mg / g) when the contact time is  $t$ ,  $k_2$  is the rate constant of the pseudo second-order adsorption model.

The Intraparticle diffusion model can be expressed as follows equation (11) [31]:

$$q_t = k_d t^{\frac{1}{2}} + C \quad (11)$$

Where  $q_t$  (mg / g) is the adsorption capacity at time  $t$  (min),  $k_d$  (mg / g.min<sup>-0.5</sup>) is the intraparticle diffusion rate constant, and  $C$  (mg / g) is the intercept which represents the boundary layer

thickness.

## RESULTS AND DISCUSSION

### FTIR Analysis of Adsorbent Characters (Raw and chemically modified Cowpea Husk)

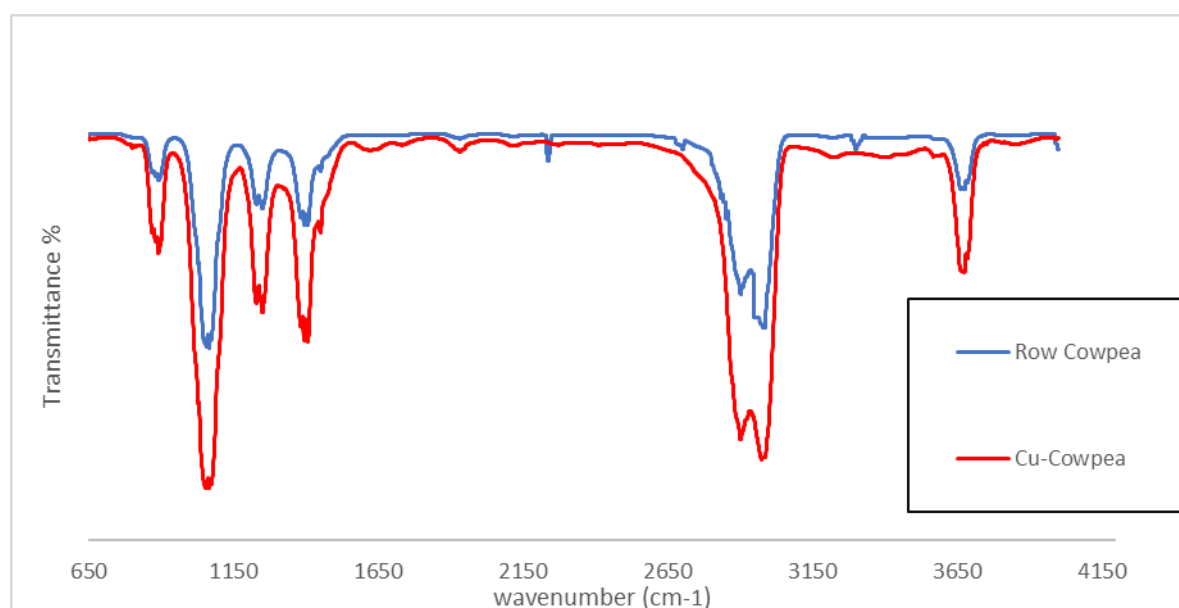
This method of analysis, known as FTIR spectroscopy, is an analytical test method used to identify organic, polymeric, and, in some cases, inorganic materials. FTIR technology uses infrared light to scan test samples and monitor chemical properties. The device used for analysis sends infrared radiation to the sample particles; The absorbed radiation is converted into rotational or vibrational energy. The signal generated in the detector represents the molecular mark (i.e fingerprint) of the sample, and each chemical molecule or structure generates a unique spectral fingerprint, making it a great tool for chemical identification. FTIR spectra were recorded in the region of  $4000\text{ cm}^{-1}$  to  $450\text{ cm}^{-1}$  for non-modified adsorbent (Cowpea husk) before and after adsorption are plotted in Figure (2) to specify the main functional groups that enhanced the removal Heavy metals (Jose et al., 2019; Özsin et al., 2019).

In the range of the high wavenumbers, we see a high-intensity absorption band at  $3848.82 - 3666.61\text{ cm}^{-1}$  which is due to stretching vibrations of hydroxyl groups (O-H) (Beddiaf, Chihi, and Leghrieb, 2015). Also, the stretching vibrations at  $3359.4\text{ cm}^{-1}$  is due to the activation of (C-H). A less strong band, caused by the bending of H-O-H, has been seen at  $1793.16 - 1650.27\text{ cm}^{-1}$  [35]. C=O stretching can be recognized in the present samples of cowpea husk due to doubly degenerate asymmetric stretching vibration at a wavenumber of  $1423.59\text{ cm}^{-1}$  and also at  $875.08 - 711.30\text{ cm}^{-1}$  [36]. The Si-O-Si bond occurred at a sharp adsorption band of  $1196.52$  and  $1082.92\text{ cm}^{-1}$ . The existence of O-Si-O vibrations at  $669.55$  and  $670.1\text{ cm}^{-1}$  confirms the presence of quartz; however, this quartz considers crystalline due to the band at  $472.2\text{ cm}^{-1}$ . After adsorption, the intensity of the sharp adsorption band and the extent of their vibration is different as a result of their as a result of the interaction of the adsorbent active site with the heavy metals molecules. Noted that there was a displacement in intensity in the wavenumber of  $(3800 - 3600)$ ,  $(2900 - 2800)$ ,  $(1000 - 1200)$ , and  $(800 - 700)\text{ cm}^{-1}$  which means that the active groups that fall within these wavelengths are

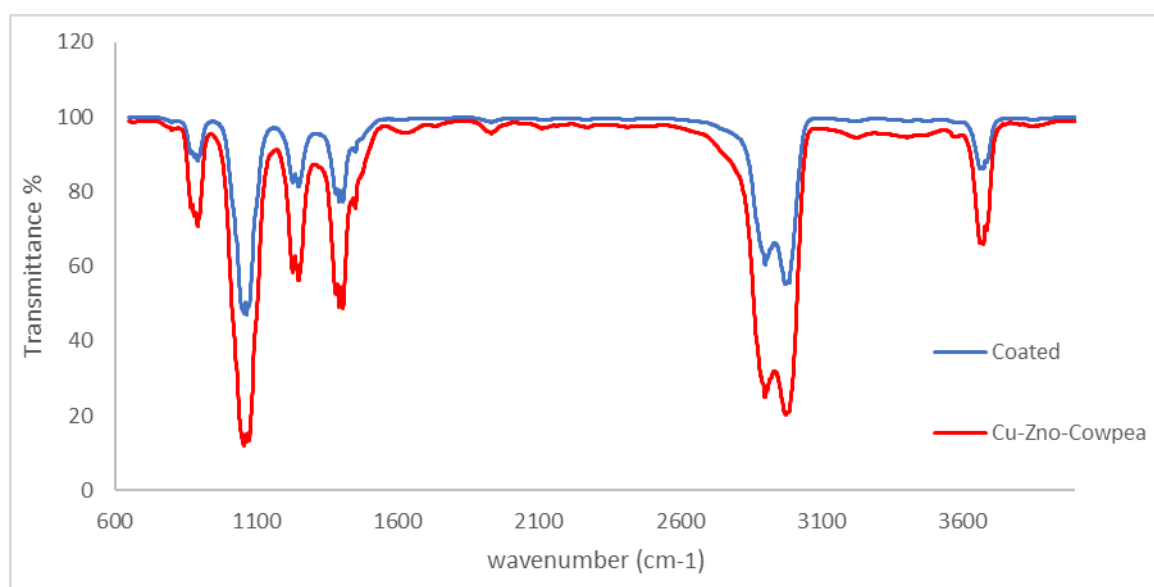


responsible of adsorption process [37].

FTIR spectrum of coated adsorbent before and after adsorption is presented in figure (3). The peak shown between 916 and 1104  $\text{cm}^{-1}$  are considered as a finger print region for carbohydrates [38], the stretching vibrations at 916  $\text{cm}^{-1}$  is due to the activation of C-N group. The peaks at 1400 and 1491  $\text{cm}^{-1}$  with nearly equal intensity were assigned to C-H group. The absorbance 1730 and 1760  $\text{cm}^{-1}$  are due to C=O and carboxyl group. Broad transmission band at around 2968  $\text{cm}^{-1}$  can be attributed to C-O stretching vibration due to present of carbonate and the weak band at 2972  $\text{cm}^{-1}$  is attributed to C=O bonds from carbonate [39]. The observed peak at 3704  $\text{cm}^{-1}$  is related to the stretching vibration of O-H groups. Also, the peaks at 1650  $\text{cm}^{-1}$  are all corresponding to stretching and bending vibration of N-H groups [40]. The FTIR spectra show some functional groups such as carboxyl, hydroxyl, O-H, C-H, COOH, C=O, C=C, CH<sub>2</sub> and C-O-C are various functional groups present in the raw and chemically modified Cowpea husk. The results show that the bands of hydroxyl and carbonyl groups shifted to lower displacement and therefore it plays the major role in adsorption process.



**Figure (2): FTIR Analysis spectrums for row cowpea husk before and after sorption of metal ions**



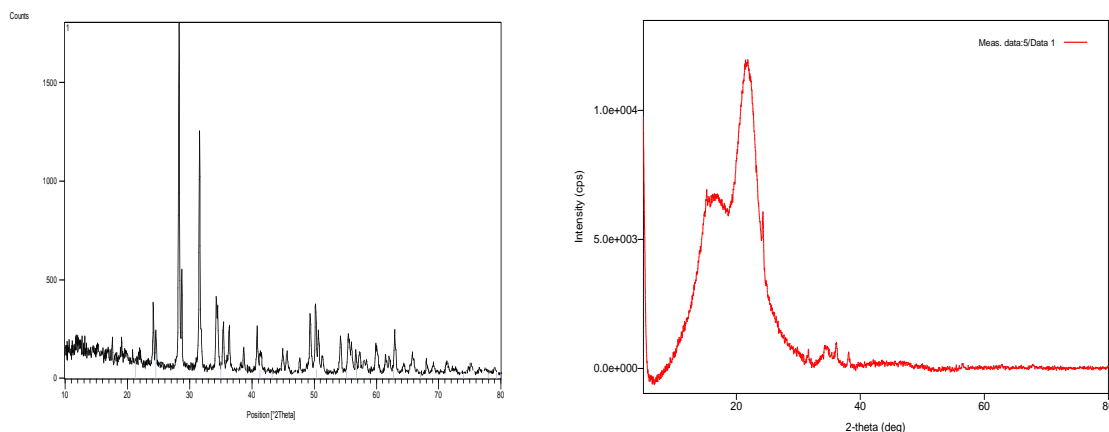
**Figure (3): FTIR Analysis spectrums for coated cowpea husk before and after sorption of metal ions**

### **The X-ray Diffraction of Row and Chemically Modified Cowpea Husk**

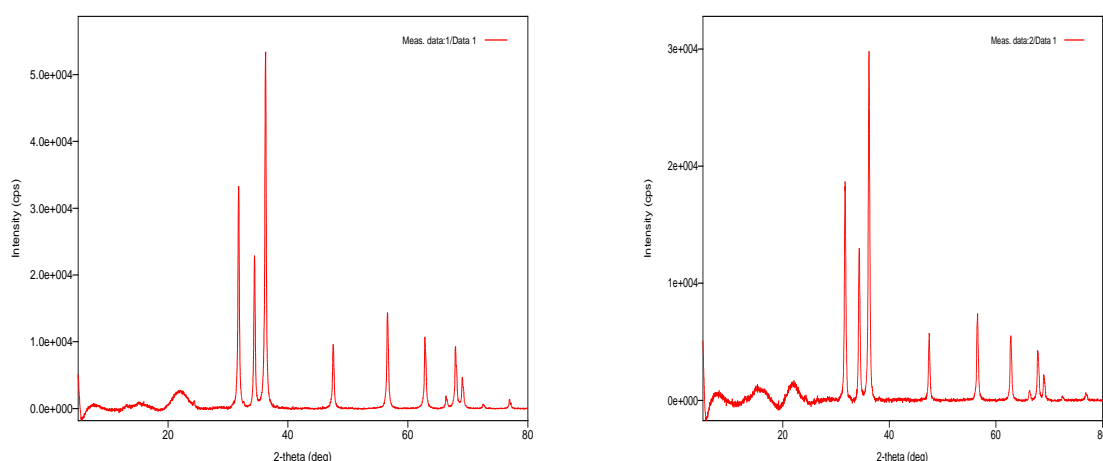
X-ray diffraction, or XRD, is a technique for analyzing the atomic or molecular structure of materials. It is non-destructive and works most effectively with materials that are wholly, or part, crystalline. The X-ray diffraction test results of adsorbent give data in the form of  $2\theta$  diffraction angle and intensity. The X-Ray diffraction pattern of row cowpea husk before and after adsorption has shown in Figure (4). The diffraction pattern shows the existence of 37 diffraction peaks. The main peaks were at the position of ( $2\theta$ ) 17.5, 19, 24.13, 28.2, 31.5, 35.4, 40.8, 49.3, 51.3, 57.3, and 63. The main chemical composition is zirconia and Potassium Aqua Molybdenum Oxide, Zinc Oxide, Vanadium Zirconium Fluoride that have a chemical formula of  $\text{ZrO}_2$ ,  $\text{K}_{0.23}(\text{H}_2\text{O})_{0.27}\text{MoO}_3$ ,  $\text{ZnO}$ , and  $\text{VZrF}_6$  respectively. The references code of these compound according to Joint Committee on Powder Diffraction Standards (JCPDS) are 00-013-0307, 00-052-0178, 01-075-0576, and 01-081-1939. There's no obvious difference between the result of the row adsorbent and metals-adsorbent (i.e. after adsorption) XRD tests. That means there is no change in the chemical composition of the adsorbent, suggested that physical adsorption is the mechanical control of the removal process.

Figure (5) displays the XRD profiles of Coated Cowpea husk before and after adsorption. Though the natural, the chemically modified adsorbent and adsorbate-adsorbent pattern of analysis have similar diffraction peaks. The diffraction pattern shows the existence of 14 diffraction peaks. The main peaks were at the position of ( $2\theta$ ) 15.78, 21.89, 24.39, 31.7, 34.4, 47.5, 66.3, and 76. The adsorbent major peaks between  $21^\circ$  and  $47.5^\circ$  were representing the raw sample which have quartz

and cristobalite phases. All the test of XRD analysis indicated that in general the composition and structural characters has no significant changes. Hence, it is concluded that the removal of heavy metals is only surface treatment [41].



**Figure (4): The XRD pattern of row cowpea husk before and after sorption of metal ions: a) row Cowpea husk adsorbent, b) Cu-Cowpea husk adsorbent.**



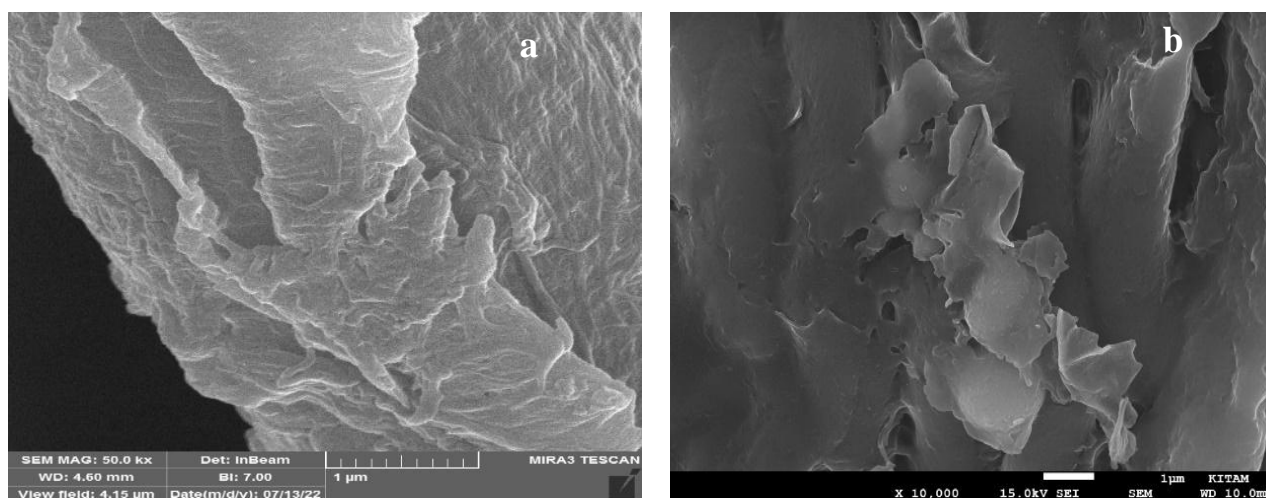
**Figure (5): The XRD pattern of row cowpea husk before and after sorption of metal ions: a) coated Cowpea husk adsorbent, b) Cu-Cowpea husk adsorbent.**

### Scanning Electron Microscope of Row and Chemically Modified Cowpea Husk

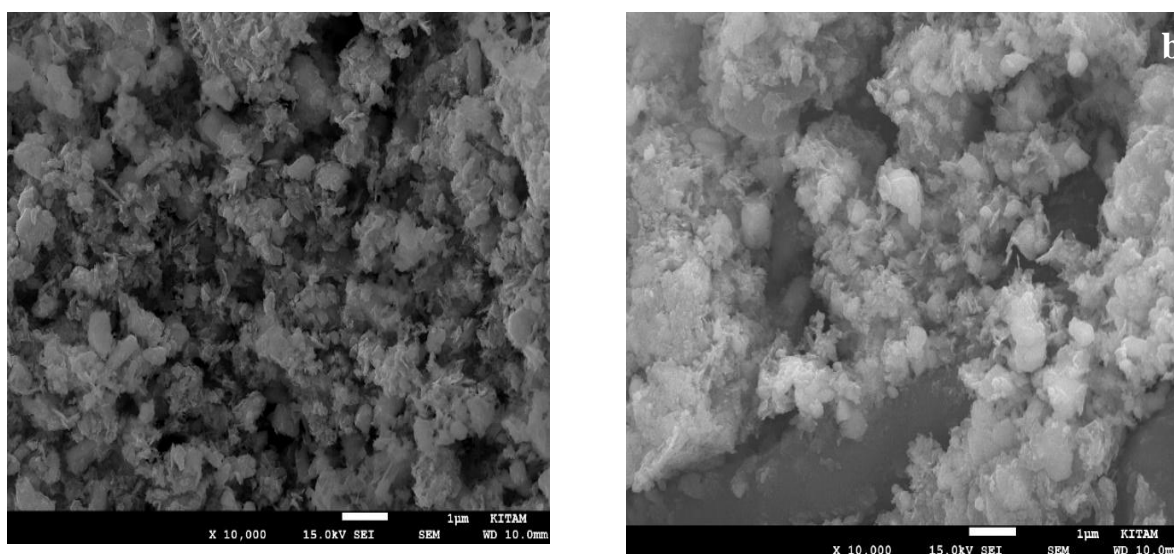
Scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. To understand more about the surface morphology, microstructures and crystalline phases of row and chemically coated Cowpea husk before and after adsorption, SEM investigation of row cowpea husk before and after adsorption shows a wide variety of irregular sizes and shapes of grains as showed in figure (6). intragranular pores come in a variety of sizes and shapes. The relatively high porosity of these

adsorbents is due to a combination of irregular grain size and shape, as well as a high amount of intragranular porosity, indicating high surface areas. The surface shape after adsorption is more uniform and consistent compared to cowpea husk, which could be attributed to the contaminants that filled these holes and grooves.

Figure (7) depicts the SEM images that provided visual and direct internal structure of the coated adsorbent before and after treatment. In addition to the micropore structure, the coated adsorbent exhibited porous morphology, indicating a larger specific surface area. When compared to row adsorbent, the morphology of the surface after adsorption is nonuniform and inconsistent; this could be due to impurities that scatter the surface.



**Figure (6): The SEM pattern of row cowpea husk before and after sorption of metal ions: a) row Cowpea husk adsorbent, b) Cu-Cowpea husk adsorbent.**

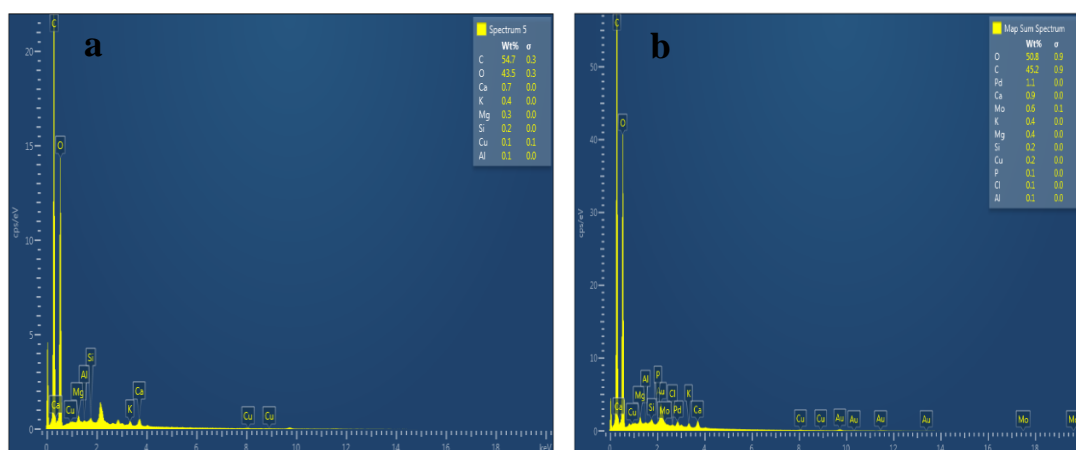


**Figure (7): The SEM pattern of coated cowpea husk before and after sorption of metal ions: a) coated Cowpea husk adsorbent, b) Cu-Cowpea husk adsorbent.**

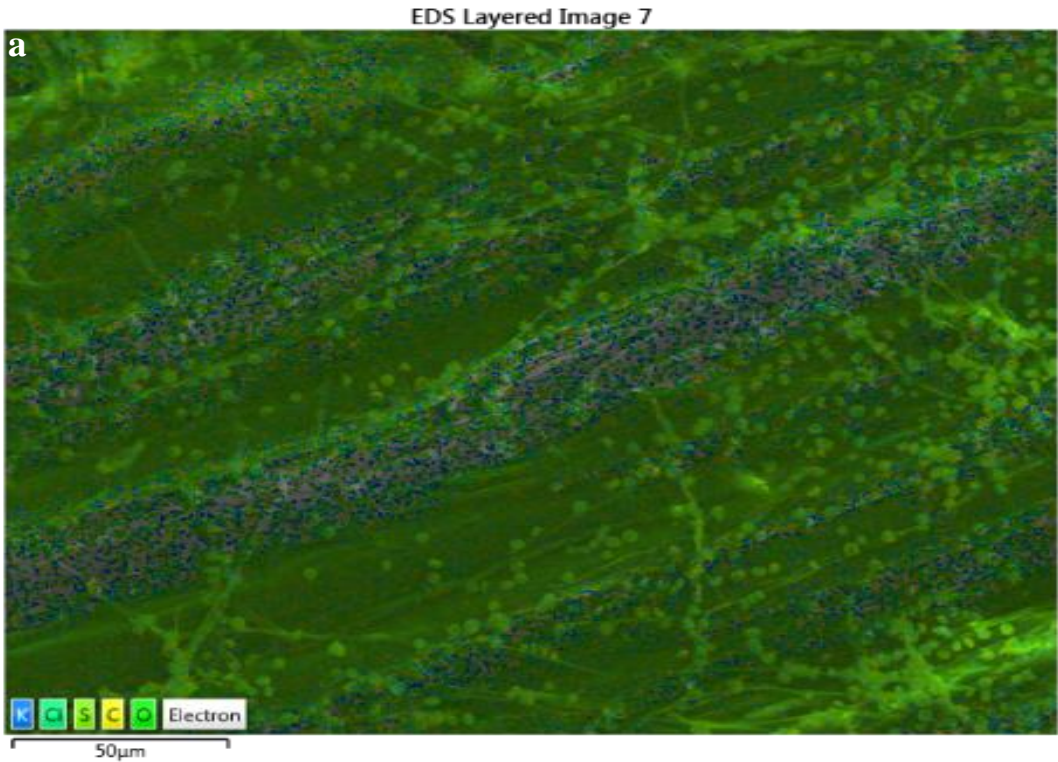
## Energy-dispersive X-ray spectroscopy of Row and Chemically Modified Cowpea Husk

Energy-dispersive X-ray spectroscopy (EDS) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Elemental analysis for the adsorbent and modified adsorbent before and after the removal process of the heavy metal were carried out by EDS. The EDS analysis of row adsorbent before and after adsorption (figure 8) shows the existence of several elements in the surface of adsorbent bed. There are different percentage of elements that consist the CWs bed: Carbon (54.7%), Oxygen (43.5%), Calcium (0.7%), potassium (0.4 %) Mg (0.3%), Aluminum (0.1%), Silicon (0.2%). the existence of these elements and the fact that the surface is rich in Carbon and Oxygen made the EDS analysis compatible with the FTIR (The major functional groups present in the samples were carbonyl and carboxyl groups). The other percent of elements of adsorbent after adsorption are displayed in the figure (9).

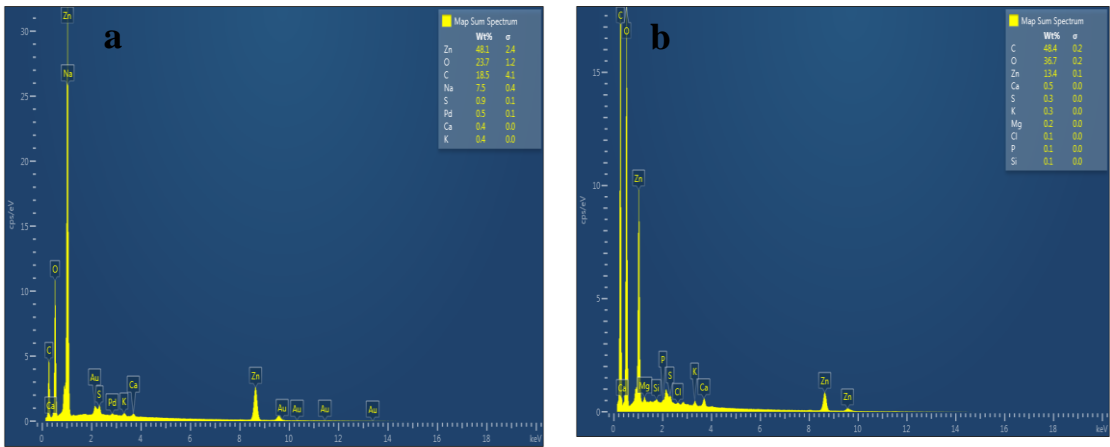
EDS analysis of coated adsorbent before and after adsorption is shown in Figure (10) in which the main peaks were the zinc, oxygen, Carbon, sodium and silicon can be observed with the atomic percentage of 48.1%, 23.7%, 18.5%, 7.5%, and 0.9% respectively. In addition, the other peaks ascribed to Pb, Ca, and K are also presented in different percentage. The high percentage of zinc that appearance in the EDS analysis of coated adsorbent is as a result of chemically modified of adsorbent using nanoparticles of ZnO. the inequality in the amount of the elements that constitute the surface of adsorbent after adsorption .



**Figure (8): The EDS analysis of row cowpea husk before and after sorption of metal ions: a) row Cowpea husk adsorbent, b) Cu-Cowpea husk adsorbent.**



**Figure (9):** The EDS analysis of row cowpea husk after sorption of metal ionsCu-Cowpea husk adsorbent.



**Figure (10):** The EDS analysis of row cowpea husk before and after sorption of metal ions: a) coated Cowpea husk adsorbent, b) Cu-Cowpea husk adsorbent.

**Effects of Experimental Parameter**

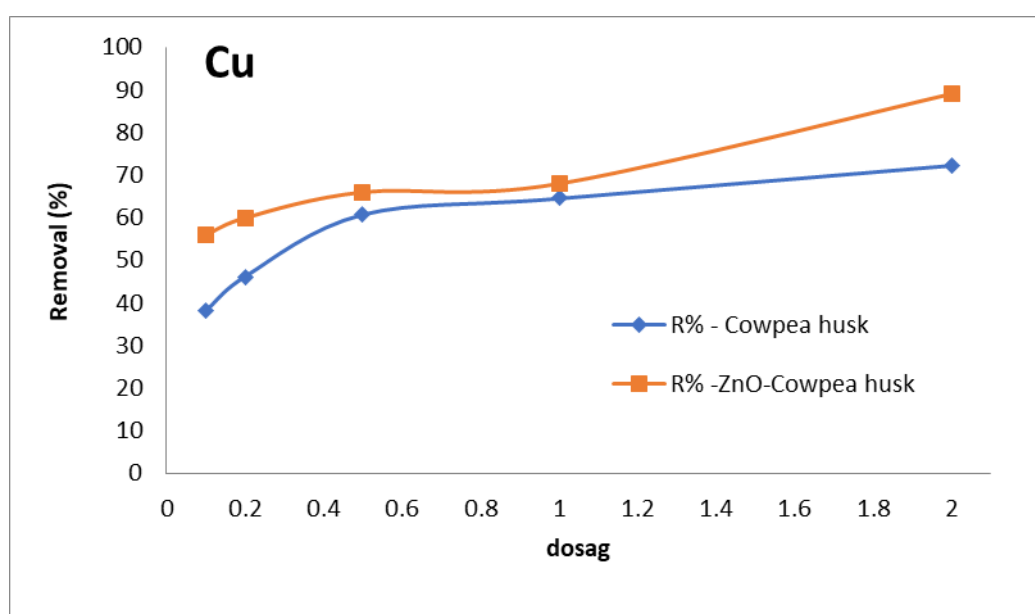
**Effect of Dosage on Removal Efficiency**

The effect of varying the adsorbent dose on the adsorption of heavy metals is shown in Figure (11). the effect of dosage was examined on the removal percent at different dose values ranging from 0.1 to 2 g/100 ml to obtain the best removal efficiencies. It is clearly seen that the removal efficiency



increases as the adsorbent mass increases. That the removal efficiency increases from (38.06%) to (72.32%) for  $\text{Cu}^{2+}$ , on the surface of row cowpea husk. On the other hand, the removal percent on coated adsorbent increase from (56%) to (89%) for  $\text{Cu}^{2+}$ . Also, noted that the coated adsorbent has the higher ability to remove the metals ion from the wastewater since the adsorbent modification process enhance the physical and chemical properties of adsorbent media.

Several studies have found that increasing the adsorbent dosage increases the percentage of metal ions remove [42]. The increase in the adsorbent mass attributed these behaviors to the higher number of available adsorption sites. Similar observations were obtained by [43].

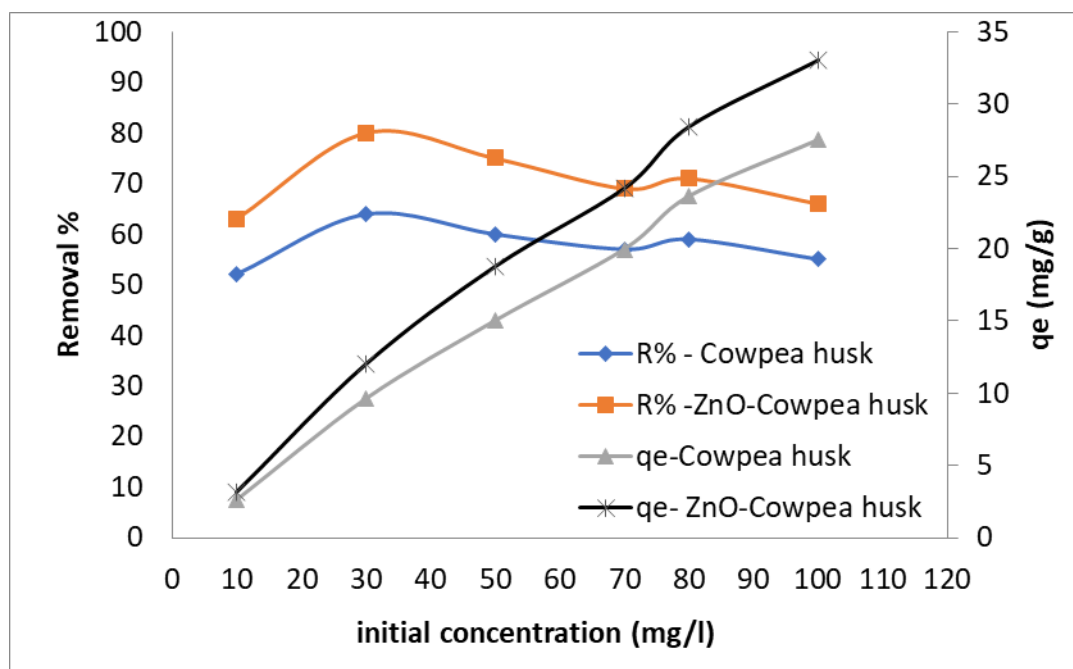


**Figure (11): Effect of dosage on the Adsorption of Cu (II) onto row and modified cowpea husk, (pH=5,  $\text{Co}$ =50 mg/l, time=120min, particle size =125 $\mu\text{m}$ , and 150 rpm)**

#### 4.3.2 Effect of Initial concentration on Removal Efficiency

The experiments were performed at distinct initial  $\text{Cu}^{2+}$ , concentrations ranging from 10 to 100 mg/L. As shown in Figure (12) The results shows that the removal percent of Cu increase from (52% to 64%) and (63% to 80%) as the initial concentration increase from 10 to 30 mg/l on the row and coated adsorbent respectively.. higher concentration implies more metal ions. A possible explanation may be that increasing the concentration of metal metals ions in solution causes an increase in mass transfer due to the increment of driving force for the transportation of ions from solution to the adsorbent surface (Tan et al. 2016). After this point the removal percent start to decline as the initial concentration of heavy metals increase, this is due to the lack of binding sites in the adsorbent sample for the adsorption of metal ions at higher concentrations. The effect of initial metal concentration could be explained as follows: at low adsorbate/adsorbent ratio,

contaminant adsorption involves higher energy binding sites. As the heavy metals /adsorbent ratio increases (i.e., at higher initial concentration), the higher energy binding sites are saturated and adsorption begins on lower energy binding sites, resulting in decrease in the adsorption efficiency [37]. Also, noted that the adsorbate uptake ( $q_e$ ) still increases as the initial concentration increase during detention time.  $q_e$  values depend upon the initial mass of heavy metals in solution, high initial concentration mean rise in metals mass that well trans to adsorbent surface.



**Figure (12): Effect of dosage on the Adsorption of Cu (II) onto row and modified cowpea husk, (pH=5, dose=1 g/100 ml, time=120min, particle size =125 $\mu$ m, and 150 rpm).**

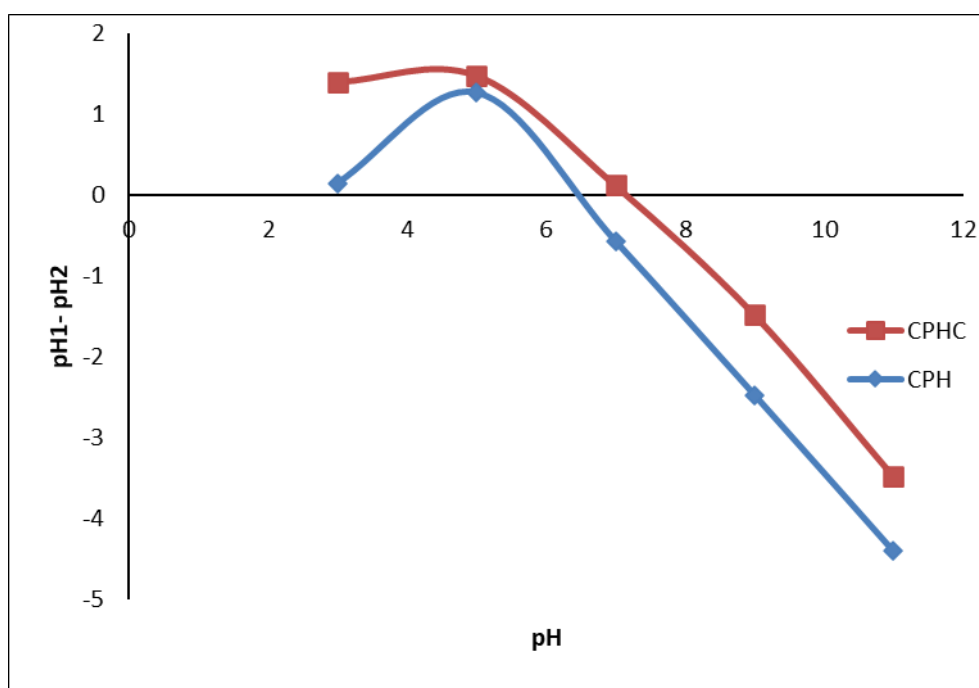
#### 4.3.3 Effect of pH on Removal Efficiency

the effect of pH was examined from solutions at different pH values ranging from 3 to 11 to obtain maximum removal efficiencies. The effect of pH on the adsorption efficiency of row and modified Cowpea husk for the removal of Cu (II) cation was performed by mixing the suitable dose of adsorbent (1 g/100 ml) of 50 mg/l (47.2 mg/L concentration of metal ion solution as the atomic reading). In general, the removal efficiency of any pollutant from aqueous solution in the adsorption system is dependable on pH values of aqueous solution. Changing the pH values in the adsorption process has a double effect: (i) it influences the charge of the adsorbent surface, and (ii) it affects the adsorbate speciation and its degree of ionization [44]. Also, In the adsorption of metal ions, hydrogen ion concentration of the solution is an important factor that should be considered. pH affects the solubility of the metal ions in the solution and replaces some of the positive ions found in the active sites and the degree of ionization of the adsorbate [33]. The point of zero charge (pzc)

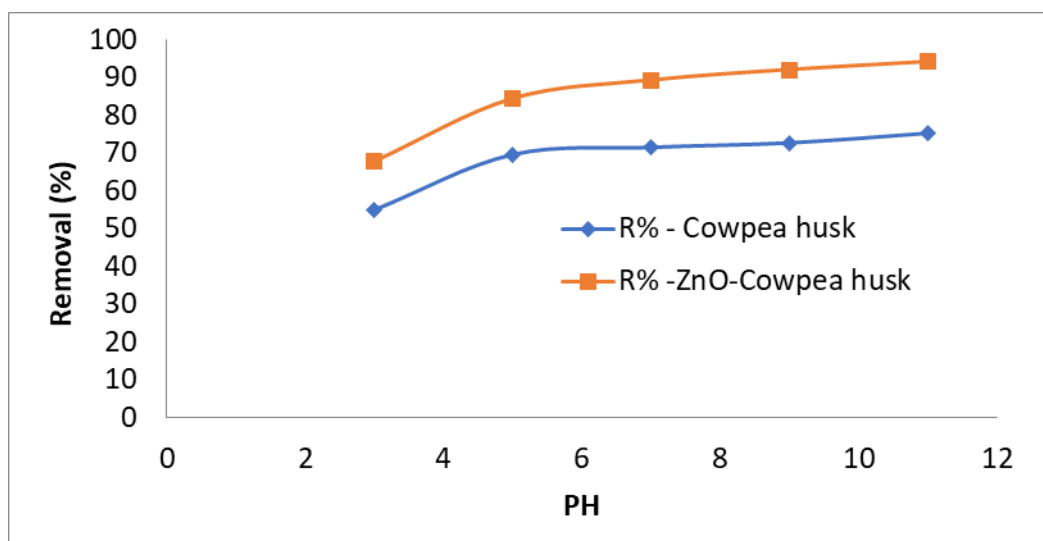


is generally described as the pH at which the net charge of total adsorbent's surface is equal to zero. So as, the surface charge of the adsorbent is negative when the pH values are higher than  $pH_{pzc}$  and vice versa [45]. The adsorption of cations, such as (Cu), is favored at  $pH > pH_{pzc}$ , while the adsorption of anions is favored  $pH < pH_{pzc}$ , due to electrostatic repulsion [46]. In this direction, the analysis of  $pH_{pzc}$  Figure (13) is very important to indicate the pH value at which the surface of adsorbent is being neutral charge. According to analysis, the  $pH_{pzc}$  of the Cowpea husk and Cowpea husk coated was determined to be 6.5 and 7.2, respectively. Also, it is important to note that the surface of ZnO nanoparticle typically comprises hydroxyl (OH) groups of neutral charge. The charge of this group may vary according to the pH value [47]. At  $pH > pH_{pzc}$ , the  $H^+$  ions leave the adsorbent surface owing to cause a negative charge of ZnO. Oppositely at  $pH < pH_{pzc}$ , ions of  $H^+$  are transferred to the adsorbent surface and combined with  $OH^-$  groups leading to a positive charge of ZnO surface due to formation  $ZnOH_2^+$  groups [48].

clearly noted that the removal efficacy of metal ions were increased with pH increasing as displayed in figures (14). It was noted that heavy metals agglomerate and precipitate in alkaline solutions, so the high removal efficiency when the pH values is or above 6 the copper started precipitating as  $Cu(OH)_2$  could be due to the deposition of these metals not as a result of adsorbent effectiveness. So as, it was considered that the best pH value is 5.



**Figure (13):  $pH_{pzc}$  of Adsorbent**



**Figure (14): Effect of dosage on the Adsorption of Cu (II) onto row and modified cowpea husk, (dose= 1 g/100ml, Co=30 mg/l, time=120min, particle size =125 $\mu$ m, and 150 rpm).**

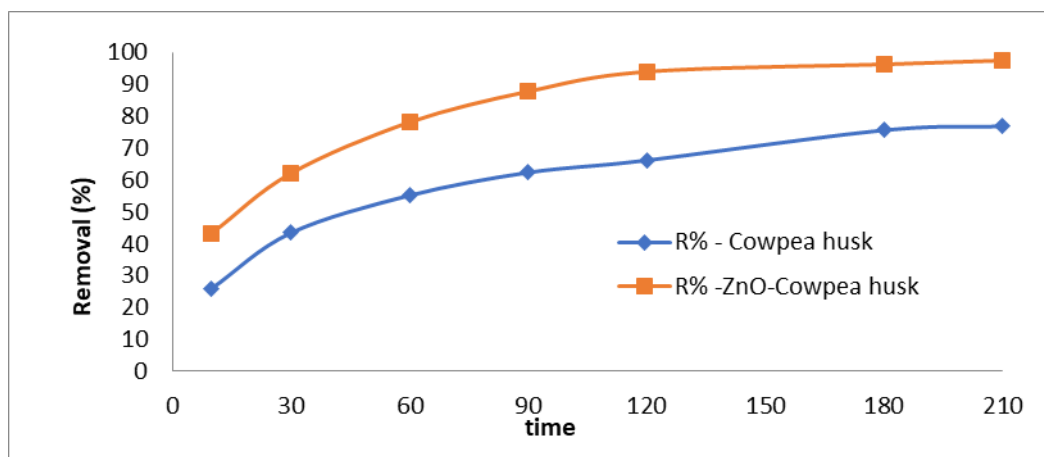
#### 4.3.4 Effect of Detention time on Removal Efficiency

The adsorption of heavy metals was studied as a function of contact time in order to determine the necessary adsorption equilibrium time. The results showed that the removal rate of Cu (II) on row adsorbent increases from 25.9% to 76.87 when the contact time is extended from 10 to 210 min. also, the removal percent on the coated adsorbent increase from 43.3% to 97.44%. As displayed in figures (15) - (4.23) the adsorption process of heavy metals was quick at the beginning, This Rapid adsorption at the earlier contact time often be attributed to the hollow active sites existence on the adsorbent, in another hand, slow adsorption rate is likely due to the adsorbate slow diffusion molecule into the adsorbent bulk [48]

It is observed that adsorption was fast when the surface of adsorbent was not saturated with metal ions. an equilibrium time between adsorbate and adsorbent surface was established at 120 min for Cu (II) ions. It is revealed that there was no considerable change after these periods for all initial concentrations.

Hence adsorption rate was fast initially and then slowed down gradually due to saturation. the fast-phase sorption may be explained as the passive uptake through physical adsorption, or the biosorbent surface ion exchange [49]. Because the adsorption phenomenon tends to achieve instantaneous equilibrium and many agricultural wastes act as natural ion exchange agents [49]. It is also relevant to point out that since active sorption sites in a system is a fixed number and each active site can adsorb only one ion in a monolayer [27], the metal uptake by the sorbent surface will be rapid initially and then slowing down because of the competition for decreasing availability of

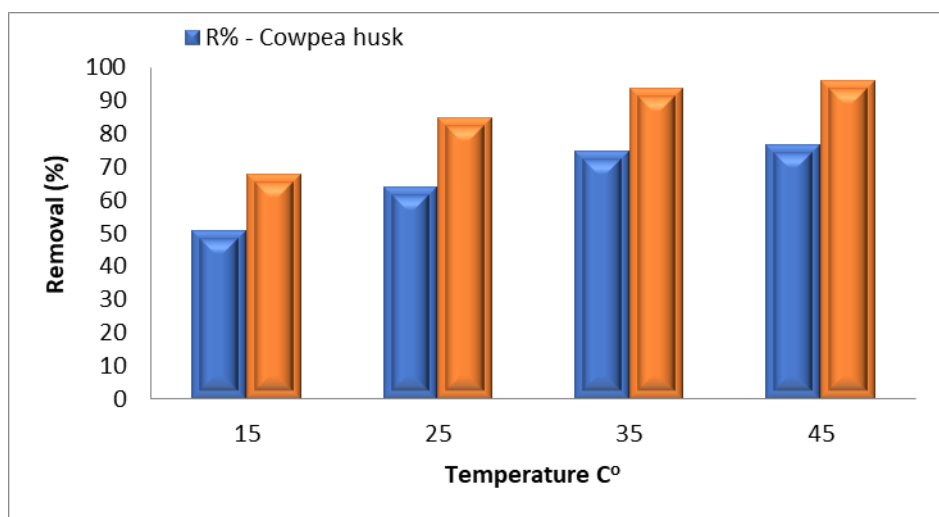
active sites intensifies by the metal ions remaining in solution [50].



**Figure (15): Effect of dosage on the Adsorption of Cu (II) onto raw and modified cowpea husk, (dose= 1 g/ 100ml, Co=30 mg/l, pH= 5, particle size =125 $\mu$ m, and 150 rpm)**

#### 4.3.5 Effect of Temperature on the Removal Efficiency

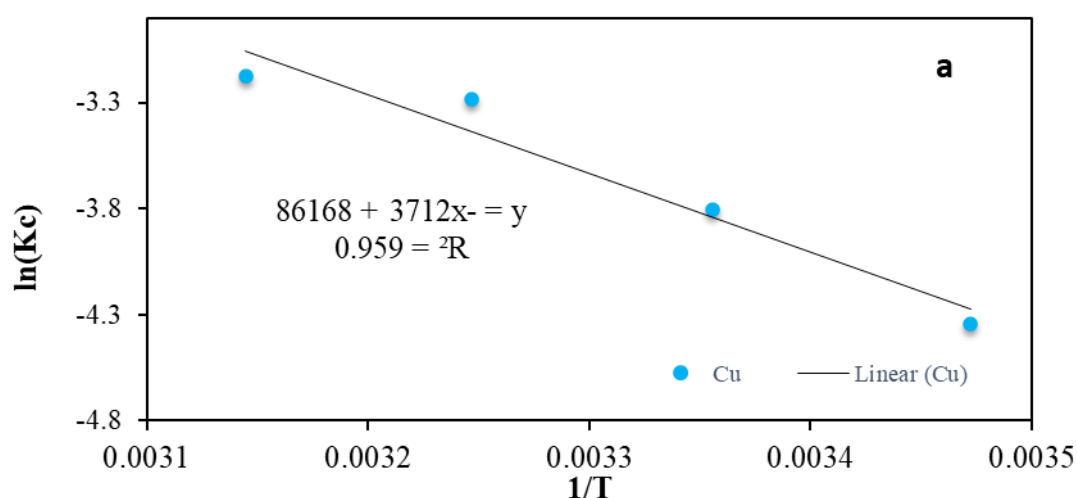
Temperature has been recognized in recent years as an important factor governing the sorption of trace and heavy metals [51]. Analyses of the collected data revealed that temperature variations between the studies were mostly only a few degrees Celsius, and most of the experiments were conducted at room temperature [52]. Temperature is a significance parameter on sorption process. Since the higher temperature contributes to an increase in the rate of diffusion of adsorbed molecules through the outer boundary layer and the internal pores of the adsorbent particles. Figure (16) . illustrates the influence of various temperatures (15, 25, 35 and 45) C°. noted that the removal percent of Cu (II) increase from (51%) to (77%), on the non-modified cowpea husk. On the other hand, the removal percent increase from (68%) to (% , 94%) of Cu (II), on the modified adsorbent. This finding revealed that the removal efficiency improves through increasing the temperature, which means that the metals removal process is endothermic [53]. In boating enough energy (i.e., high temperature) the number of molecules is increased to undergo interaction with active site on the surface [54]. At high temperature the adsorption capacity is increased because of the internal-diffusion controlled adsorption process [55].

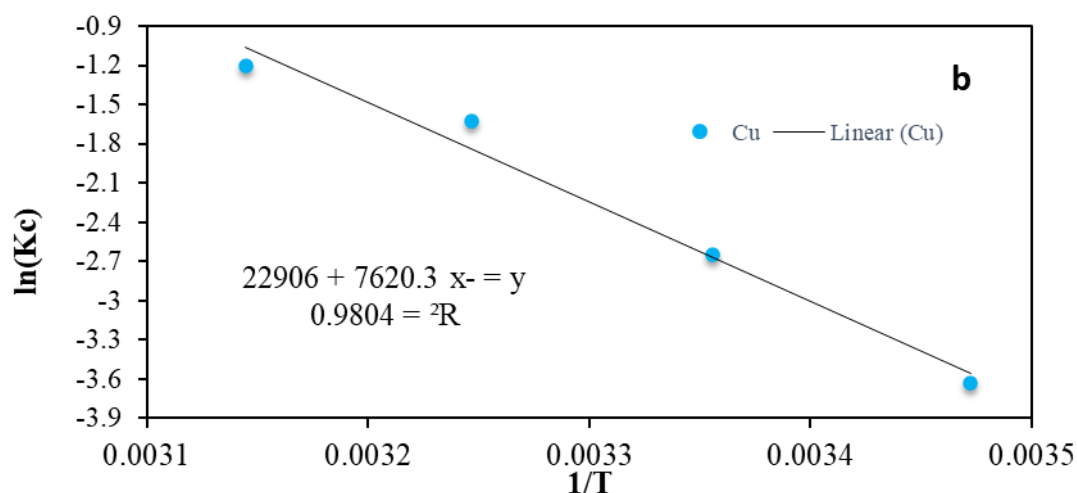


**Figure (16): Effect of dosage on the Adsorption of Cu (II) onto row and modified cowpea husk, (pH=5, Co=30 mg/l, time= 120min, particle size =125µm, dose = 1 g/ 100ml, and 150 rpm**

#### 4.4 Thermodynamic Study

The thermodynamic parameters of adsorption provide in depth information about the nature of the process. The thermodynamic of adsorption investigation for the sorption of Cu (II) onto row and coated cowpea husk at different temperatures are shown in Figures (17). The change in Gibbs free energy ( $\Delta G^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and entropy ( $\Delta S^\circ$ ) values of Cu (II) adsorption is given in Table (1). The negative value of  $\Delta G$  is an indicator of the viability and spontaneity of the adsorption process. Positive value of  $\Delta H$  indicated that the nature of process is endothermic, while the positive  $\Delta S$  confirm the perfect affinity of adsorbate to adsorbent [56].





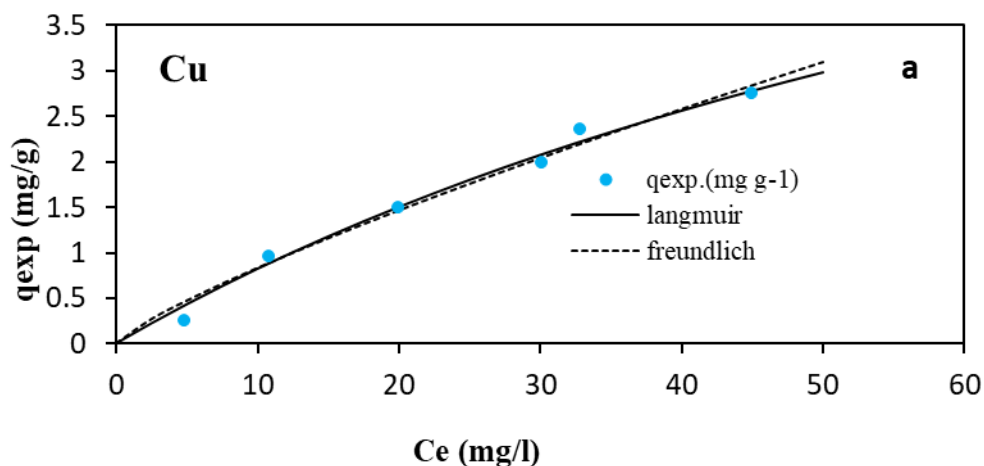
**Figure (17): Relationship between  $\ln K_d$  vs.  $1/T$  for thermodynamic constants determination for Cu (II) onto a) row and b) modified cowpea husk, (pH=5,  $C_0$ =50 mg/l, time=120min, particle size =125 $\mu$ m, and 150 rpm)**

**Table( 1 ): Thermodynamic parameters of Cu(II) adsorption onto row and modified cowpea husk.**

metals	T (C <sup>o</sup> )	Cowpea husk				ZnO- Cowpea husk			
		$\Delta G^\circ$ (kj/mol)	$\Delta H^\circ$ (kj/mol)	$\Delta S^\circ$ (j/mol K)	$R^2$	$\Delta G^\circ$ (kj/mol)	$\Delta H^\circ$ (kj/mol)	$\Delta S^\circ$ (j/mol K)	$R^2$
Cu (II)	15	-0.031	30.86	71.64	0.95	-0.063	63.63	190.4	0.98
	25	-0.055				-0.173			
	35	-0.096				-0.5			
	45	-0.11				-0.793			

### Isotherm Models

Also, to gives a comprehensive understanding of nature of interaction as showed in figure (18) Table (2) shows the values parameters of the isotherm models with correlation coefficient ( $R^2$ ). The maximum adsorption capacity of heavy metals onto row cowpea husk are 8.734mg/ g for  $Cu^{2+}$ . While the maximum capacity of chemically modified adsorbent are 6.566mg/g for  $Cu^{2+}$ . As shown in table (3) the value of the maximum adsorption capacity of heavy metals onto row and modified cowpea husk is large compared to previous studies. From the value of RL ( $0 < RL < 1$ ) which is mean the adsorption is favorable process. Also dependent on the value of n (i.e., Freundlich intensity) ( $n > 1$ ) know that the adsorption is preferential adsorption. Langmuir Model is the more fitted model that has the largest value of  $R^2$ .



**Figure (18): Sorption Isotherm of Langmuir and Freundlich model for the a) Cu (II) adsorption onto row cowpea husk**

**Table (2): Sorption Isotherm for Langmuir and Freundlich model for the heavy metals adsorption onto row and modified cowpea husk**

Model	parameters	Row Cowpea husk	Coated Cowpea husk
		Cu	Cu
<b>Freundlich Model</b>	<b><math>K_f</math></b>	0.126	0.296
	<b><math>n</math></b>	1.223	1.439
	<b><math>R^2</math></b>	0.981	0.953
<b>Langmuir Model</b>	<b><math>q_{max}</math></b>	8.734	6.566
	<b><math>b</math></b>	0.01	0.03
	<b><math>R^2</math></b>	0.987	0.967
	<b><math>R_l</math></b>	0.65	0.426

**Table (3): maximum adsorption capacity of Cu from previous studies**

Adsorbent	Adsorbate	$q_{max}$ (mg/g)	REF.
Tannic acid immobilized AC	Cu	2.23	[57]
rice husk	Cu	11.98	[58]
Coated AC	Cu	35.39	[59]
Fucus serratus	Cu	1.6	[60]
Husk Biomass	Cu	11.05,	[61]

### Kinetic Study

Adsorption has been extensively researched as a cost-effective method for removing a wide range of hazardous materials from aqueous solutions, such as dyes and heavy metals. The majority of adsorption research has focused mainly on kinetic processes. The kinetic data analysis is important for the adsorption process because the kinetics describe the adsorbate uptake rate, which controls the resident time in the adsorbent [62]. The rate at which pollutants are extracted from the aqueous solution is called adsorption kinetics. Also, the kinetics analysis is important to evaluate the effectiveness of adsorption and to explain by which process the adsorption phenomena is takes place, as well as, provide vital evidence for the time required to achieve equilibrium, the rate of adsorption, and the limiting step of the adsorption rate. If an adsorbent is targeted to be used in wastewater treatment facilities; a high adsorption rate is necessarily characteristic in addition to its adsorption ability and the removal efficiency [63].

The adsorption kinetics of the  $\text{Cu}^{2+}$  metal onto adsorbents was investigated using pseudo first order, pseudo second order, and intra-particle diffusion model using the experimental data at various initial concentrations figures (19-21) . The calculated parameters values obtained from the application of these models according to Eqs. (2.4) are tabulated in Tables (4). The favorable model is recognized by comparing  $R^2$  for each applied model and the compatibility between the calculated  $q_e$  and the experimental  $q_e$  values. These kinetic model parameters were determined using nonlinear regression in Microsoft excel 2016. The higher values of  $R^2$  and the values of theoretical  $q_e$  which are near to the experimental  $q_e$ , indicated that the second-order model is appropriate to adsorption behavior of  $\text{Cu}^{2+}$  both row and modified adsorbent as shown in table (4). Furthermore, the  $C$  values were greater than zero confirming that adsorption process rate limiting contribute to the diffusion of the boundary layer, not intra-particle diffusion [64].

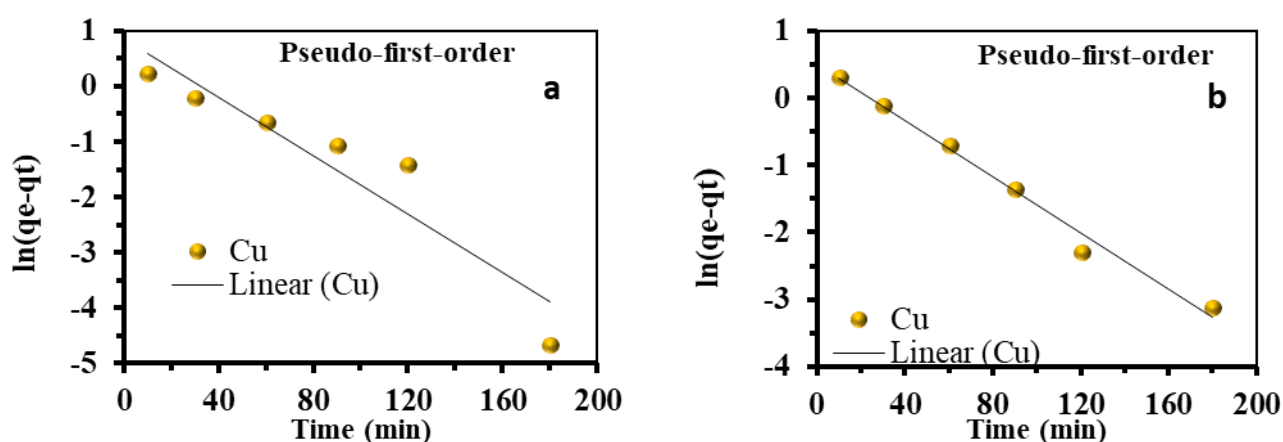


Figure (19): Pseudo-first-order for (a, b) Cu (II) onto row and modified adsorbent .

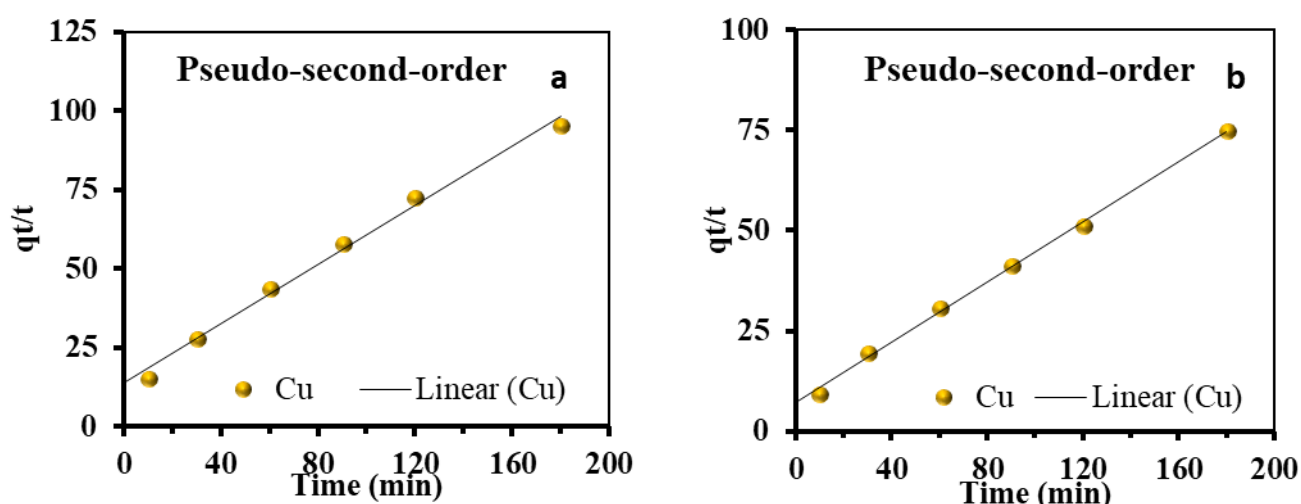


Figure (20): Pseudo-second-order for (a, b) Cu (II) onto row and modified adsorbent .

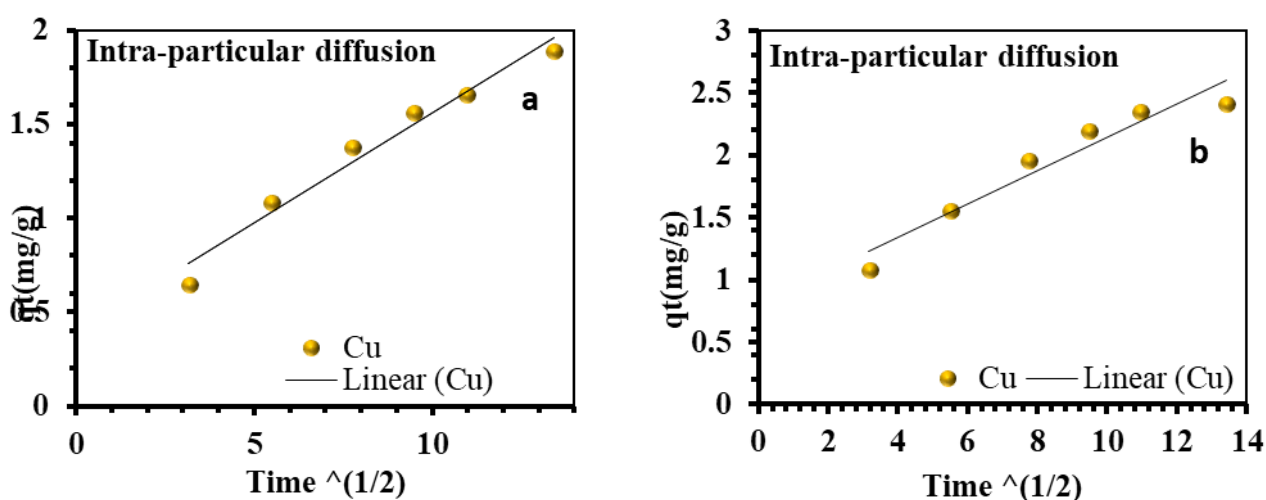


Figure (21): intraparticle- diffusion model for (a, b) Cu (II) onto row and modified adsorbent

Table (4) .: Kinetic parameters of various models fitted for the sorption of heavy metals experimental data.

Model	parameters	Row Cowpea husk	Coated Cowpea husk
		Cu	Cu
Pseudo- first order	$q_e$	2.188	1.884
	$K_1$	0.0257	0.022
	$R^2$	0.899	0.983



<b>Pseudo-second order</b>	<b>q<sub>e</sub></b>	2.13	2.657
	<b>K<sub>2</sub></b>	0.016	0.0202
	<b>R<sup>2</sup></b>	0.993	0.997
<b>Intraparticle diffusion</b>	<b>C</b>	0.3848	0.802
	<b>K<sub>P</sub></b>	0.1176	0.1338
	<b>R<sup>2</sup></b>	0.9691	0.9314

## CONCLUSIONS

In the present study, the capacity of Raw Cowpea husk(CPH), and Cowpea husk coated (CPHC) with nano Zinc oxide (ZnO) to adsorbent and remove Cu<sup>2+</sup> from aqueous solutions. The Raw Cowpea husk(CPH) and Cowpea husk coated (CPHC) with nano Zinc oxide (ZnO) adsorbent was characterized by advanced means of SEM, XRD, and FT-IR. The findings re-Vvealed that the prepared adsorbent was generally more effective when the CPH was coated in Zinc oxide (ZnO) nanoparticles than that without the Raw Cowpea husk(CPH). This improved both the practical utilisation and adsorption capacity. The isotherm analysis showed that heterogeneous and homogeneous adsorption sites were found on the Raw Cowpea husk(CPH), and Cowpea husk coated (CPHC) with nano Zinc oxide (ZnO) surface, all of which were ready to react with Cu<sup>2+</sup>. Moreover, the thermodynamic analysis showed that the adsorption process was both spontaneous and exothermic in nature. The Raw Cowpea husk(CPH), and Cowpea husk coated (CPHC) with nano Zinc oxide (ZnO) maximum adsorption capacity for the Cu<sup>2+</sup> as follows, according to the findings of the Langmuir model:. The pseudo-second-order model adequately models the kinetic data of Cu<sup>2+</sup>, demonstrating that kinetic adsorption is a chemical-based process. Furthermore, the kinetic investigation revealed that the kinetic rate was controlled by multiple processes. The current study found that Cowpea husk coated (CPHC) with nano Zinc oxide (ZnO) is an excellent adsorbent that can be used to sequester Cu<sup>2+</sup> in adsorption treatment systems.

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