



Adsorption of Cu onto Maize Husk Lignocellulose in Single and Binary Cu-Zn Solution Systems: Equilibrium, Isotherm, Kinetic, Thermodynamic and Mechanistic Studies



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Adsorption of Cu onto maize husk in single and Cu-Zn binary aqueous solutions was compared. Equilibrium adsorption studies showed that Cu in the single solution system packed vertically on the surface of the adsorbent but penetrated into the porous network of the adsorbent in the binary solution system. Data from the isotherm studies in the single and binary systems were well fitted in the Freundlich model, with linear regression correlation coefficient values (R^2) 0.764 and 0.994 respectively. The n values from this model indicated that Cu ions were chemisorbed on the adsorbent in the two solution systems but formed stronger bonds in the binary solution. Adsorption capacity of the adsorbent for Cu in the single solution was 1.21 mg/g but increased to 1.63 mg/g, 1.67 mg/g and 1.84 mg/g in the 2:1, 2:2 and 1:2 Cu:Zn binary solutions respectively. Adsorption of Cu in all the solution systems were spontaneous, with the 1:2 binary solution been the most energy efficient system. Selectivity of Cu ions in the equimolar Cu:Zn binary solution was synergistic. The marked reduction in the percentage content of calcium and potassium on the adsorbent when it was contacted with the Zn and Cu-Zn solutions showed that these elements were exchanged with Cu and Zn on the adsorbent matrix. Shift in absorption band at the R-OH functional group on the adsorbents in all the studied solution systems showed that complexation of metal ions occurred at these points. The disappearance of the carboxylic acid -OH absorption band on the husk in the Cu ion solution system was an indication that an additional adsorption site was involved in the complexation of Cu on the adsorbent. The findings from this study showed that using maize husk as adsorbent, copper adsorption is more enhanced in the presence of zinc ions in binary solutions of the two heavy metals.

Keywords: Maize husk, Isotherm, Chemisorption, Synergistic, Complexation, Ion exchange

Introduction

The presence of inorganic pollutants such as heavy metals in the ecosystem has over the years been a major environmental problem. Toxic heavy metals not only contaminate earth's waters, but also underground water in trace amounts [1]. The metals with significant toxicity to humans and the environment include: chromium (Cr), copper (Cu), lead (Pb), cadmium (Cd), mercury (Hg), zinc (Zn), manganese (Mn) and nickel (Ni) [2]. These heavy metals are reported as priority pollutants because they are not biodegradable and are highly persistent in the environment [3]. Heavy metal

toxicity can result in damage or reduced mental and central nervous function, lower energy levels and damage to blood composition, lungs, kidneys, liver and other vital organs [4]. Although copper and zinc are essential trace elements, high levels can cause harmful health effects. Copper is also toxic to a variety of aquatic organisms, even at very low concentrations [5].

Many physicochemical methods have been developed for the removal of toxic heavy metals from aqueous solutions [6]. The successes of most of these methods in heavy metal removal notwithstanding, their application is often limited

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due to high capital investment and operational costs. Consequently there is a growing search for novel technologies that are generally affordable, eco-friendly and more efficient.

Biosorption has proven to be an efficient and relatively inexpensive option for the removal of heavy metals from wastewater in the past few decades. This method uses inexpensive biomaterials like microorganisms and plant waste biomass to sequester environmental pollutants from aqueous solutions by a wide range of physiochemical mechanisms including ion exchange, chelation, surface complexation, physical adsorption and precipitation [7]. Some of these biosorption mechanisms can take place simultaneously [8-10]. These processes however are not yet fully understood and therefore, the mechanism of metal ion uptake is at present a complicated process.

Lignocellulose contains a series of organic functional groups such as acetamido groups, carbonyl, phenolic, structural polysaccharides, amido, amino, sulphhydryl carboxyl groups, alcohols, esters and mineral elements [11]. The complex structure of raw biomass implies that there are many ways, by which they remove various pollutants. Numerous studies on the adsorption of heavy metals by plant biomass in single metal ion systems have been reported [12-16]. Duru and Duru [17] have shown that maize husk has good removal efficient for Cu in aqueous solution.

In recent times, the interactions of different metal ions during adsorption by different types of biomass have been studied by researchers. Sheng *et al.* [5] studied the adsorption of lead, copper, cadmium, zinc, and nickel by different marine algal biomass. Their results showed that the affinity of the metal ions to the biomass materials were different for the biomass types. The general affinity sequence for *Padina sp.* was $Pb > Cu > Cd > Zn > Ni$, while that for *Sargassum sp.* was $Pb > Zn > Cd > Cu > Ni$. Jain *et al.* [18] reported the competitive adsorption of Ni(II), Cd(II) and Cr(VI) onto sunflower waste biomass carbons, viz. sunflower head carbon and sunflower stem carbon from multimetal aqueous solution. They observed that the adsorption capacity of the adsorbents was highest in mono-metal system but decreased with increase in the number of co-ions. Juang and Shao [19] reported the sorption of copper, nickel and zinc ions in binary solutions using glutaraldehyde cross-linked chitosan beads obtained from lobster

shell wastes. The study revealed a preferential sorption of copper ions on chitosan beads. Copper sorption appeared to be preferred in the binary systems Cu-Ni and Cu-Zn, while the removal of zinc was favored in the Ni-Zn system.

Actual wastewater systems often have mixtures of heavy metals. Copper and zinc are two important and essential elements for plants, animals and man. Because of their regular use and application, they are often times found together in wastewater solutions. The interactions of the component metals in these solutions have been shown to affect the uptake of a select metal ion by a given biosorbent. Research is still ongoing in this area to fully understand the nature of these interactions. This study therefore compared the changes in the adsorption of copper in single and binary Cu-Zn aqueous solutions and also predicted the mechanism of adsorption of copper in the two solution systems onto maize husk adsorbent.

Materials and Methods

Reagents

Metal solutions were prepared by dissolving appropriate amounts of Copper (II) nitrate trihydrate, $Cu(NO_3)_2 \cdot 3H_2O$ (MW: 241.60 g/mol; Assay: 99 %) and Zinc (II) nitrate hexahydrate, $Zn(NO_3)_2 \cdot 6H_2O$ (MW: 297.49 g/mol; Assay: 98 %) from Sigma-Aldrich, Germany, in 1000 mL of distilled water.

Biomass Collection and Preparation

Corn seeds of genus *Oba super II*, were collected from the National Agriculture Food Council, Umudike, Abia State Nigeria, and planted by the researchers. At maturity, the husks (leafy outer covering of the maize ear) were collected and thoroughly washed with tap water and then rewashed with deionized water to remove fugitive mineral elements from the tap water. They were oven dried at 100 °C for 4 hr and ground into powder using an electric grinder. The ground maize husk was sieved to particle size of 30 mesh using American Society for Testing and Materials (ASTM) standard sieves. The powdered husk was then stored in a moisture free and air tight plastic container and used as adsorbent in all adsorption studies [2].

Equilibrium and isotherm studies

Batch adsorption tests were performed in triplicates for all adsorption experiments at pH 5.5. Adsorbent of weight 0.5 g was placed in separate 100 mL conical flasks with 50 mL of Cu ion solution at different initial concentrations 10, 20, 30, 40 and 50 mg/L. The flasks and their

contents were agitated on an orbital shaker at 120 rpm for 30 minutes. Aliquots from each flask were removed and the copper concentration in the solution determined using Agilent 240 AA atomic absorption spectrophotometer. This procedure was repeated with 50 mL of equimolar solution of Cu and Zn ions containing 10, 20, 30, 40 and 50 mg/L of each ion [2].

Kinetic studies

Batch adsorption studies were conducted in triplicates using 50 mL Cu-Zn solutions with concentrations of Cu:Zn in the ratio 20:0, 20:10, 20:20 and 10:20 mg/L of solution. Five of each of the solution systems was prepared and 0.5 g of the adsorbent introduced simultaneously in each reactor set. The systems were agitated on a shaker water bath at 30 °C. The reactors were withdrawn at contact time of 2, 4, 6, 8 and 10 minutes. The content of each vessel was filtered and the concentration of Cu in the filtrate determined [14, 15].

Mechanistic studies

Four reactors containing 50 mL deionized water, 50 mL of 50 mg/L Cu ions, 50 mL of 50 mg/L Zn ions and 50 mL of a mixture of Cu and Zn ions containing 50 mg/L of each ion. The solutions were adjusted to pH 5.5 using 0.5 mol/L HCl and 0.5 mol/L NaOH. Adsorbent of weight 0.5 g was added into the solution in each of the reactors and stirred for few seconds. The mixtures were then agitated for 10 minutes at 120 rpm using an orbital shaker. The content of each reactor was filtered and the maize husk residue washed with 100 mL of deionized water. They were spread on filter papers and left to dry at room conditions [5, 9].

Maize Husk Characterization

The mineral element composition of the adsorbents was determined using EDX3600B X-ray fluorescence (EDXRF) spectrophotometer (Precision- 0.01– 0.05 % deviation; Detection limit- 0.0001 % – 99.9999 %) by Skyray Instrument. The energy dispersive X-ray spectra were obtained by pulverizing a given adsorbent sample to fine homogenous size and pelletizing the resulting powder. The fluorescence spectrophotometer was calibrated using pure silver standard and the working curve for the sample selected before the sample analysis.

Shifts in absorption bands at the functional group points on the adsorbent surfaces were detected using Agilent Cary 630 Fourier transform infrared (FTIR) spectrophotometer. A spatula full of KBr was added in an agate mortar and ground to

fine powder using a pestle. A 2 % w/w equivalent of the adsorbent sample was mixed with the KBr powder in the mortar and the mixture was ground for about 5 minutes. The final mixture was placed on a collar and covered with the die and the assembly was inserted in a Handi-Press. The powder was pressed for about 2 minutes to form thin transparent pellets. The collar together with the pellet was placed on the sample holder and the Fourier transform infrared spectrum of the adsorbent was taken.

The surface morphology of the adsorbent from different metal systems were viewed with Thermo Fisher (FEI) Q250 scanning electron microscope. The adsorbent to be viewed was bonded to a sample stub using a carbon tape and placed in a gold sputtering system for 30 s at ~ 70 mTorr pressure. The SEM chamber was vented and allowed to reach nominal pressure. The SEM sample compartment was opened and the sample stub containing the sample was placed onto the stage and tightened into place. The sample compartment was closed and the system was allowed to reach vacuum. An operating voltage of 10 kV and magnification of 1000× was selected for sample image capturing.

Results and Discussion

Equilibrium studies

The amount of Cu ions adsorbed per unit weight of adsorbent in the single and binary solutions were determined using Eq. 1 [15].

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

Where q_e is adsorption capacity of biomass material, (mg/g), V is the volume of the solution (L), C_o is the initial concentration of the heavy metal in solution (mg/L), C_e is the equilibrium concentration of Cu ions in solution (mg/L) and m is the mass of adsorbent (g). The plots of adsorption capacity versus concentration at equilibrium are shown in Fig. 1.

The curves obtained in the single and binary solution systems belonged to the S-type and C-type isotherm classes respectively [20]. The S-type isotherm class which is concave at the midpoint indicated that the Cu ions in the single solution system had moderate interionic attractions, causing them to pack vertically in regular array on the surface of the adsorbent. The linear C-type isotherm class observed in the binary solution system indicated that the Cu ions penetrated into the porous spaces in the adsorbent.

Isotherm studies

The experimental data for the uptake of Cu by maize husk in the single and binary solutions showed negative linear regression correlation coefficients when fitted in the Langmuir isotherm model. It however fitted well into the Freundlich isotherm model given in Eq. 2, and the linearized form given in Eq. 3 [15].

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

Where K_F is a constant indicative of the relative adsorption capacity of the adsorbent ($\text{mg}^{1-\frac{1}{n}} \text{L}^{\frac{1}{n}} \text{g}^{-1}$), and the magnitude of n gives an indication of the favorability of the adsorption given as follows: $n = 1$ (linear); $n < 1$ (chemical process) and $n > 1$ (physical process) [21, 22]. The linear plot of $\ln q_e$ versus C_e for Cu in the single and binary solution systems are shown in Fig. 2 and 3.

The Freundlich parameters for the two systems are summarized in Table 1.

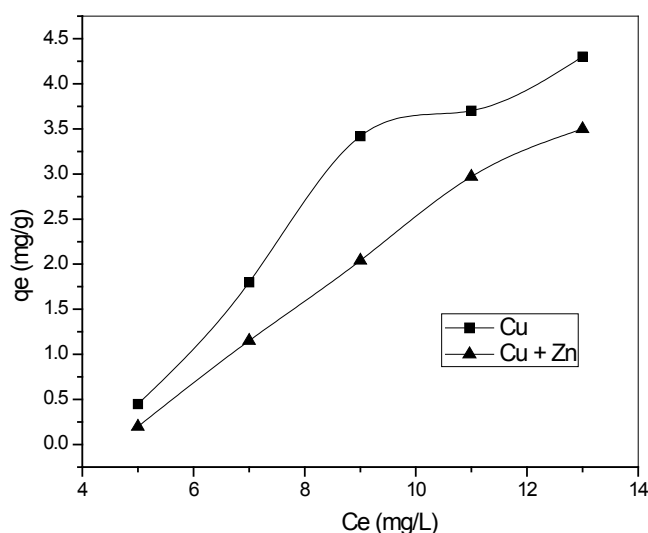


Fig.1. Equilibrium plot for the single and binary metal solution systems.

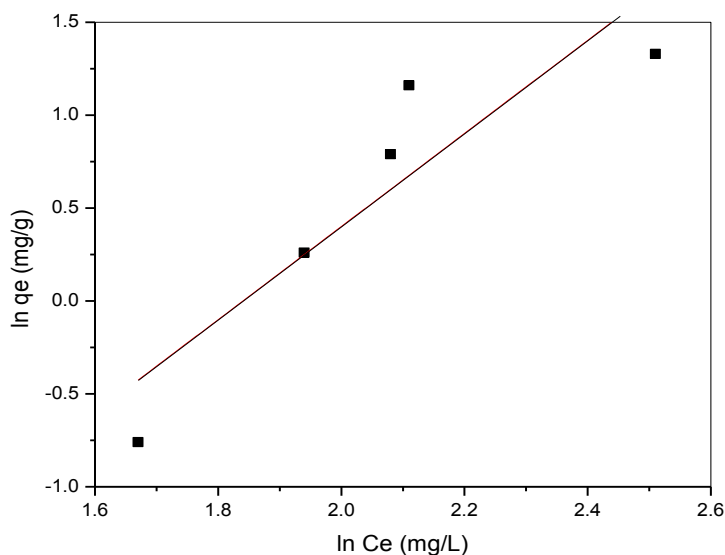


Fig. 2. Freundlich isotherm plot for Cu ions in the single solution system.

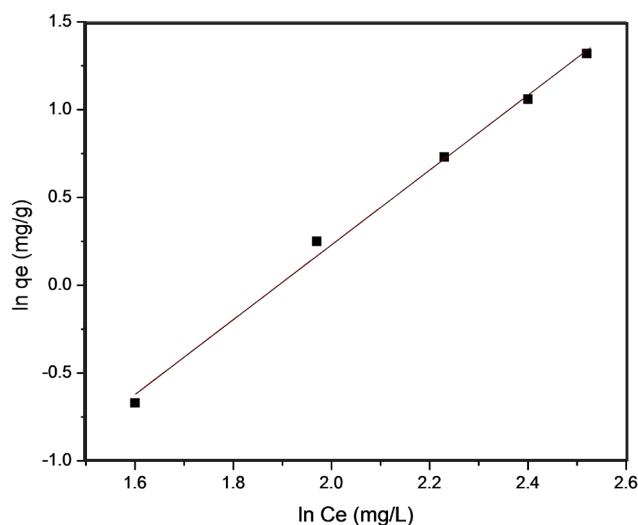


Fig. 3. Freundlich isotherm plot for Cu-Zn binary solution system.

TABLE 1. Freundlich parameters for Cu(II) and equimolar Cu:Zn binary solution systems.

Metal System	Cu	Cu:Zn
K_f ($\text{mg}^{1-\frac{1}{n}} \text{L}^{\frac{1}{n}} \text{g}^{-1}$)	2.45×10^{-5}	9.33×10^{-5}
n	0.3990	0.4695
R^2	0.764	0.994

The linear regression correlation coefficient R^2 for the Cu and Cu:Zn systems indicated that the adsorption of Cu in the two systems followed Freundlich isotherm model. However, the binary solution gave a better fit than the single ion system implying that the Freundlich isotherm model better explained the adsorption process in the binary solution system. The K_f value in the binary solution system suggested that maize husk had a higher capacity to adsorb Cu in this system. The n values for both systems were less than one, implying that Cu ions were chemisorbed on the adsorbent with the Cu ions in the binary system forming stronger chemical bonds on the adsorbent surface.

Kinetic studies

The rate of adsorption of Cu in the different Cu:Zn solution systems were fitted in the pseudo-first order and pseudo-second order kinetic models. The pseudo-second order model gave a better fit with $R^2 > 0.980$ in all the solution systems. The linearized form of the pseudo-second order kinetic model is given in Eq. 4 [14].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

Where q_t and q_e (mg/g) are the adsorption capacity of the adsorbent at time t and at equilibrium respectively and k_2 (min g/mg) is pseudo-second order rate constant. The linear plot of t/q_t versus t is shown in Fig. 4.

The pseudo-second order parameters are summarized in Table 2.

The R^2 values for the adsorption of Cu in the different solutions were all very high and increased with increase in Zn concentration. A similar increase was observed in the values of the pseudo-second order rate constant in the solution systems.

The capacity of the adsorbent to take up Cu also increased with increase in the concentration of Zn in solution. This supports the earlier observation in the equilibrium studies that adsorption of Cu in the Cu-Zn binary solution follows the C-type isotherm class indicating the penetration of Cu ions into the porous adsorbent [20] probably in the search for sites to accommodate more ions.

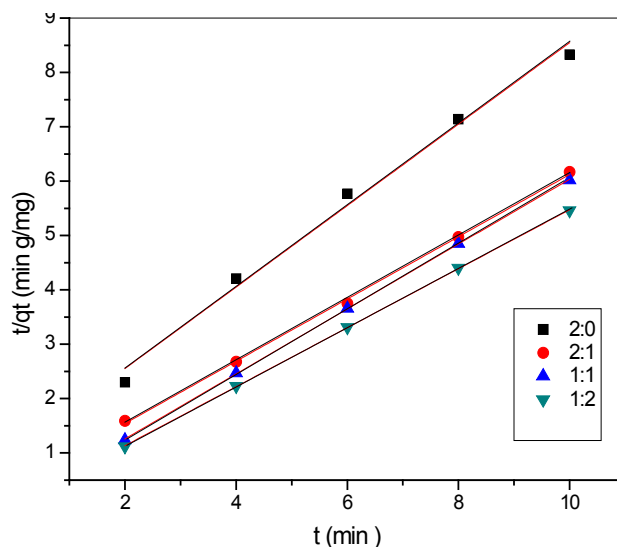


Fig. 4. Pseudo-second order kinetic plot of different Cu:Zn solution systems.

TABLE 2. Pseudo-second order kinetic parameters for different Cu:Zn solution systems

(Cu:Zn)	R ²	k ₂ (min g/mg)	q _e (mg/g)
2:0	0.988	0.537	1.21
2:1	0.999	0.822	1.63
1:1	1.000	5.368	1.67
1:2	1.000	6.028	1.84

Thermodynamic studies

The free energies (ΔG) of adsorption of Cu onto the adsorbent in the different binary solution systems were calculated using Eq. 5 [15].

$$\Delta G = -RT \ln K_D \quad (5)$$

$$K_D = \frac{C_o - C_e}{C_e} \quad (6)$$

Where R is the universal gas constant (8.314 Jmol⁻¹K⁻¹), T is the absolute temperature (K), K_D is the equilibrium constant.

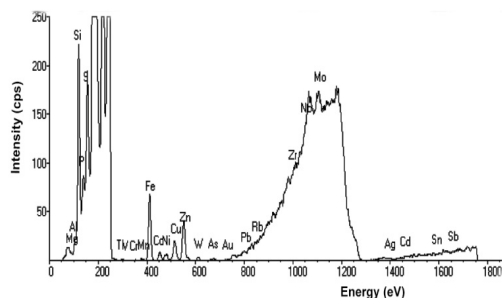
The negative ΔG values suggested that Cu adsorption on the adsorbent in the single and different binary solution systems were spontaneous. The values of ΔG decreased with increase in the concentration of Zn ions in the binary solution systems indicating the favorability of adsorption as zinc concentration increased.

Competitive adsorption of metal ions

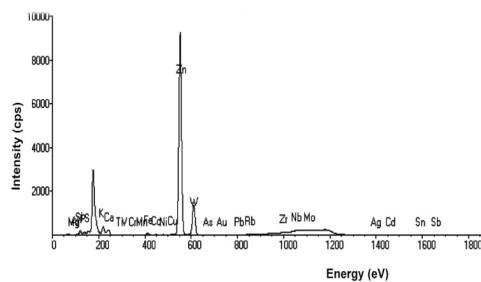
The selectivity of Cu ions in the equimolar binary solution system was evaluated in terms of the relative metal adsorption (R_i %) given in Eq. 7 [23]. The percentage R_i predicts whether the interaction of Cu ions i and Zn ions j in the binary system are antagonistic, synergistic or non-interactive in nature.

$$R_i = \frac{\text{metal } i \text{ adsorption capacity with coexistence of metal } j}{\text{metal } i \text{ adsorption capacity without coexistence of metal } j} \times 100 \quad (7)$$

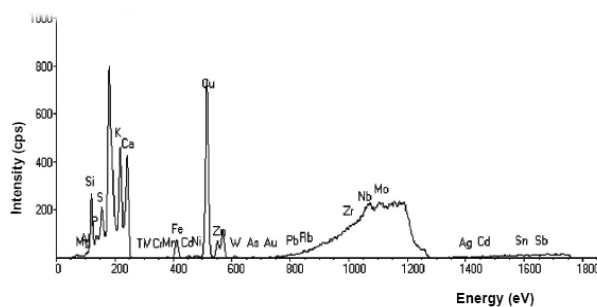
If $R_i > 100$ %, it indicates that the interactive effect of the mixture of metals is synergistic, $R_i < 100$ % indicates antagonistic behaviour and $R_i = 100$ % indicates non-interactive behavior [18]. The value of R_i (%) in the equimolar ionic solution was 138 %, suggesting that the interaction between the ions in the binary solution system was synergistic [18].



(a)



(b)



(c)

Fig. 5. EDXRF scans of (a) maize husk (b) maize husk after immersion in Zn solution (c) maize husk after immersion in equimolar Cu-Zn binary solution

TABLE 3. Free energy of Cu adsorption in the single and different binary solution systems.

Binary Solutions	ΔG° (kJmol ⁻¹)
2:0	-1.12
2:1	-3.86
2:2	-4.23
1:2	-6.48

TABLE 4. Percentage content of mineral elements on maize husk in Cu-Zn binary solution.

Element	Percentage of Element		
	Husk	Husk-Zn	Husk-Cu-Zn
Al	0.883	0.351	0.722
K	3.114	0.740	2.263
Ca	6.174	0.179	2.940
Fe	0.939	0.467	0.839
Cu	0.078	0.058	7.582
Zn	0.211	39.391	0.270
Pb	0.008	0.000	0.008

Mechanistic studies

The energy dispersive X-ray spectra of the adsorbents in the studied solution systems are shown in Fig. 5.

The percentage mineral element composition of the adsorbent and their changes in content following adsorption of Cu and Zn ions in the different solutions are shown in Table 4.

The exchangeable mineral elements found on the adsorbent were Al, K, Ca, Fe, Cu, Zn and Pb. In the Zn ion solution system, very significant reduction in the initial concentration of the elements with almost a complete disappearance of Ca and K ions on the adsorbent were observed. This observation indicated that Zn adsorption onto the adsorbent followed ion exchange mechanism. In the equimolar Zn:Cu solution, there was rapid increase in Cu concentration on the adsorbent followed by significant reduction in concentration of Zn and all the other mineral elements on the adsorbent. This strongly suggested that the up-take of Cu onto the adsorbent followed ion exchange mechanism and did not compete with Zn ions in the solution.

The superimposed FTIR spectra of the adsorbent in the different solution systems are shown in Figure 6.

The prominent absorption peaks on the adsorbent were at wavenumbers 3456.55 cm^{-1} corresponding to alcohol –OH groups [24,25,26], 2360.95 cm^{-1} , corresponding to carboxylic acid –OH vibration [27], 1643.41 cm^{-1} corresponding to C=O stretching vibration [28,29,30] and 1149.61

cm^{-1} corresponding to C-O stretching [31]. Changes in absorption bands either by shifts in wavenumbers or disappearance of absorption peaks after adsorption indicated that those functional groups were involved in the adsorption of metal ions. These shifts were observed at the alcohol –OH and carboxylic acid –OH functional groups.

At the alcohol –OH band, shifts in wavenumbers to 3425.69 cm^{-1} and 3433.44 cm^{-1} were observed in the Cu and Zn solution systems respectively. This showed that this functional group was involved in the uptake of Cu and Zn ions from the solution. The greater difference in wavenumber between the scans from the Cu-ion system and that from the Zn-ion system inferred a greater preference for Cu ions than Zn ions at this functional group.

At the carboxylic acid –OH band (COOH), no shift in wavenumber was observed in the Zn ion system. In the Cu ion system however, the disappearance of the carboxylic –OH peak showed that this functional group was involved in the adsorption of Cu ions. This suggested that Cu have more adsorption sites than Zn on the adsorbent.

The SEM images of the adsorbent surfaces from the different solutions are shown in Figure 7.

In the Cu ion system, the occupation of the porous husk surface by Cu deposits was apparent and gave an even coverage over the adsorbent surface. In the Cu-Zn binary ion system however, the deposition was much thicker and suggested greater uptake of the Cu from solution onto the adsorbent as was observed in the EDXRF analyses.

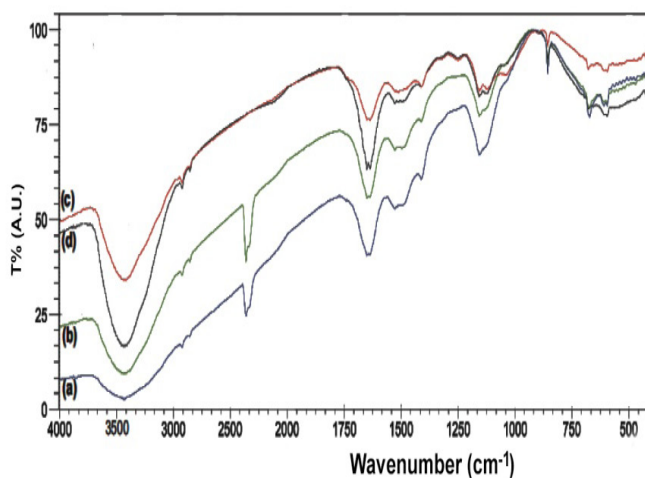


Fig. 6. FTIR spectra of (a) maize husk (b) maize husk after immersion in Zn solution (c) maize husk after immersion in Cu solution (d) maize husk after immersion in equimolar solution of Cu-Zn ions

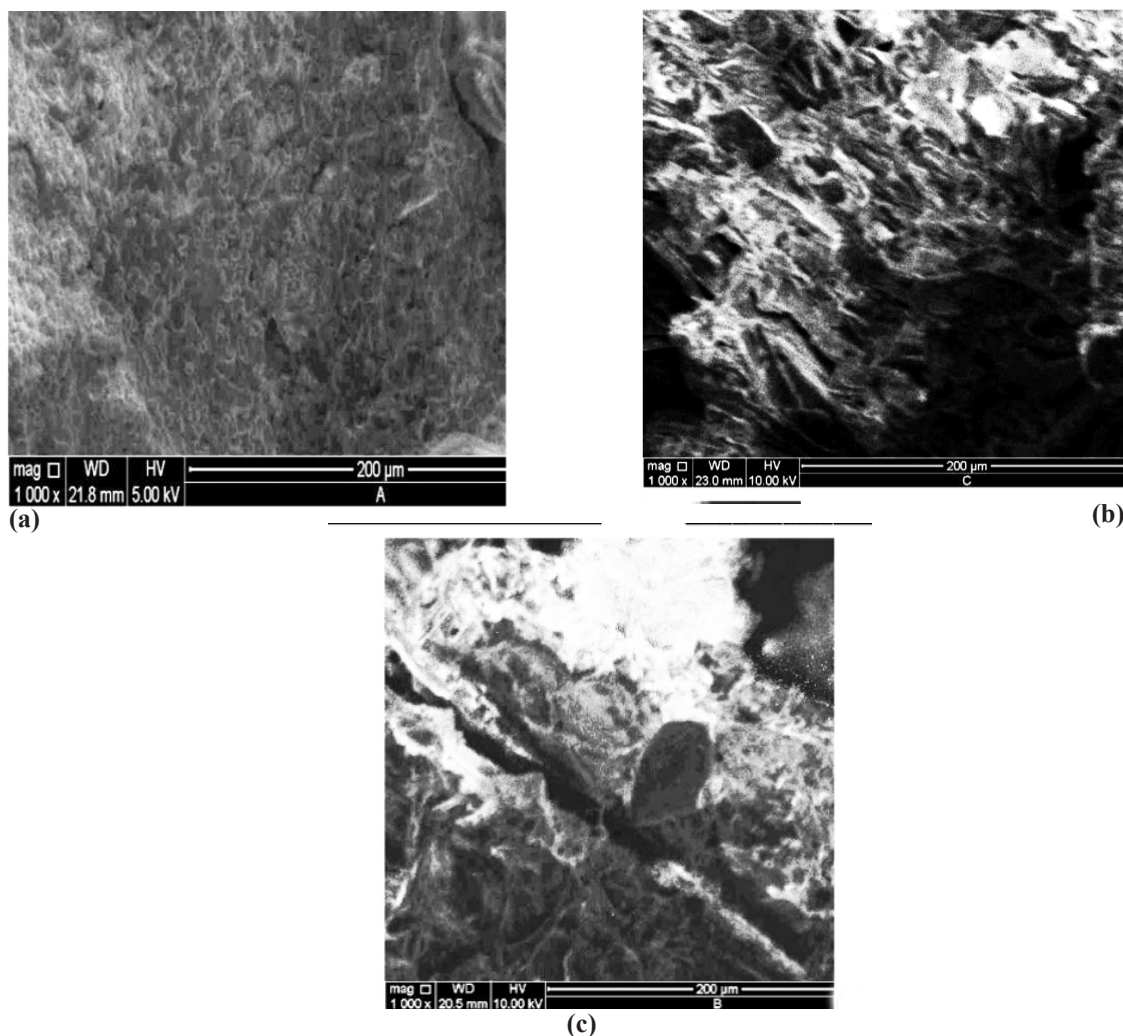


Fig. 7. SEM images of (a) maize husk (b) maize husk after immersion in Cu solution (c) maize husk after immersion in Cu-Zn solution

Conclusions

The adsorption of Cu in the two solution systems followed the Freundlich isotherm model with the indication that the adsorption process was by chemisorption with the bonds been stronger in the binary solution system. Equilibrium adsorption study showed that Cu adsorption onto the adsorbent in the single solution system was on the surface but penetrated the porous structure in the binary solution system.

The pseudo-second order kinetic model better explained the adsorption kinetics of Cu in the single and binary solutions. The rates of Cu adsorption and adsorption capacities of the adsorbent increased as the concentration of the Zn increased in the binary solutions, with the indication that the interaction of Cu and Zn ions in the binary solutions was synergistic in nature.

The free energy of adsorption in the single and binary solutions was spontaneous and decreased as the concentration of Zn increased.

Mineral elements and functional groups on maize husk were both actively involved in the adsorption of Cu and Zn from solution. Ion exchange and complexation mechanisms were the driving forces responsible for the adsorption of Cu onto the maize husk lignocellulose.

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