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Adsorption Capacity of Maize Biomass Parts in the Remediation of Cu²⁺ Ion Polluted Water

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ABSTRACT

We investigated the efficiency of maize biomass parts - seed chaff, stalk, cob and husk, in the remediation of Cu^{2+} ion polluted water in modeled solutions. The adsorption capacity of these parts followed the order of husk > stalk > cob > seed chaff, with values of 9.65 mg/g, 4.83 mg/g, 3.70 mg/g and 2.48 mg/g, respectively. Maximum adsorption capacity of each part was reached in 45 min. Herein, the husk giving the best removal efficiency of 80.80%. Characterization of the maize husk using PIXE showed that potassium is the main cation on this biomass, with concentration 5.602 g/kg. FTIR scans of the husk before and after adsorption of Cu^{2+} ions gave shifts in adsorption bands on -OH carrying molecules, indicating that complexation is a mechanism in the metal ion removal process. The multi porous structure of the husk, and uniform surface coverage by ions observed from SEM images before and after adsorption, shed more light on the high adsorption efficiency shown by this natural waste material.

Keywords: Remediation, Maize husk, Adsorption capacity, Copper, Removal efficiency

1. INTRODUCTION

The environment has been found to be contaminated with various pollutants which may be found in air, water or soil. One of such pollutants are heavy metals which are released into the environment by industrial and metallurgical processes, and tend to persist indefinitely, circulating and finally accumulating throughout the food chain (Kuppusanily et al., 2004).

Their sources are mostly wastes from industrial discharges (Hasfalina et al., 2012). These metals accumulate in the food chain and once absorbed into body tissues, cannot be easily excreted. The heavy metals of concern to human health are lead, mercury, cadmium, arsenic, chromium, zinc and copper (Jimoh et al., 2012).

Most copper contamination in drinking water occurs in the water delivery system, as a result of corrosion of the copper pipes or fittings. Copper piping and fittings are widely used in household plumbing (Goyer, 1991; Noggue et al., 2000). Immediate effects from drinking water which contains high concentration of copper include vomiting, diarrhea, stomach cramps and nausea (Wisconsin Department of Natural Resource, 2003). High copper levels in human liver has been reported to cause Wilson's disease, thalassemia, hemachromatosis, yellow atrophy of liver, tuberculosis and carcinomas. Women have more tendency of accumulating copper than men, and show symptoms like premenstrual syndrome, miscarriages, infertility, low libido, etc all related to copper imbalance (Eck and Wilson 1989).

The available conventional treatment methods such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange and membrane technologies have been widely used to remove heavy metal ions from water (Sciban and Klasnja 2004). These processes may be ineffective or expensive, especially when the heavy metal ions are at low concentrations (< 100 mg/L) (Barros et al., 2006). Biological methods such as biosorption which are more ecofriendly may provide an attractive alternative to physicochemical methods (Geay et al., 2000).

Various metal-binding mechanisms have been postulated to be active in biosorption. These include chemisorption by ion exchange, complexation, coordination and/or chelation, physical adsorption, microprecipitation and oxidation/reduction. These mechanisms can also act simultaneously (Kumar, 1992). Agrowastes are now being used as adsorbents because of their abundant availability and low cost owing to their relatively high fixed carbon content and the presence of porous structure. These agricultural by-products are composed of lignin and cellulose as major constituents and may also include other polar functional groups found in lignin, which includes alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups. These groups have the ability to bind heavy metals by donating an electron pair to form complexes with the metal ions in solution (Demirbas, 2008).

Maize husk is a major waste generated during maize harvest within cities in the South Eastern part of Nigeria and some other countries. Improper disposal of this waste biomass in the cities has resulted in environmental pollution arising from blocking of drainages and other water channels. Recycling of this waste and its use in the remediation of heavy metal polluted water, would not only be economical but also help to stabilize the environment.

Though reports on the use of maize parts like cob (Opeolu et al., 2009; Duru and Duru, 2017) stalk (Duru and Duru, 2017; Vafakhah, 2016) and husk (Igwe et al., 2005; Duru and Duru, 2017) in the removal of heavy metal ions from solutions abound in literature, comparison of these parts on their efficiencies in the removal of selected metal ions are scarce (Adiaha 2016, Mazengia 2016, Akwaji et al. 2016, Redi et al. 2016).

This study therefore compares the adsorption capacities and efficiencies of maize parts, to determine the most functional part for the sorption of copper ions in modeled solutions. It would also characterize the most efficient part of the plant and predict the mechanism followed in the sorption of copper ions.

2. MATERIAL AND METHODS

2. 1. Solution preparation

CuCl$_2$·3H$_2$O, HCl and NaOH were supplied by Merck Chemicals Ltd. UK. Stock solution of copper (1000 mg/L Cu^{2+} ions) was prepared by dissolving 2.682 g of CuCl$_2$·3H$_2$O in 1000 mL of distilled water. The stock solution was diluted to specified concentrations. The pH of the working solution was adjusted to desired values with 0.1 M HCl and 0.1 M NaOH solutions. All chemicals used were of analytical grade and purchased from Finlab, Nigeria Ltd, Owerri, Nigeria.

2. 2. Collection and preparation of biosorbent

Maize parts from white corn were collected from a farm in Eziobodo in Ihiagwa, Owerri West, Imo State, Nigeria. They were washed repeatedly with distilled water to remove dust and soluble impurities then dried for 5 hr in a convection oven at a temperature of 100 °C. The dried parts were crushed with a mechanical grinder to a fine powder which was passed through a sieve of 30 mesh size and stored in plastic bottles for further use.

2. 3. Biosorption Studies

Batch adsorption tests were conducted in triplicates to determine the adsorption capacities and efficiencies of the different biomass materials from maize plant. All experiments were carried out at pH 5 in a thermostated water-bath set at 30 °C. The concentrations of Cu^{2+} ions in the different solutions were determined using HI 83200 Multiparameter Bench Photometer by HANNA Instruments.

2. 3. 1. Determination of adsorption capacity of biomass materials

Cob, husk, stalk and seed chaff each of weight 0.2 g were added to 50 mL of 50 mg/L Cu^{2+} solutions in separate glass reactors all at pH 5. They were covered with aluminum foils and agitated on a Thermo Scientific^{TM} Precision ^{TM} Reciprocating Shaker Bath, at 150 rpm. After 120 min, the suspensions were filtered and the concentrations of Cu^{2+} ions in the filtrates were measured. The adsorption capacity of each biomass material was calculated using the Equation:

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (1)$$

where: q$_e$ is adsorption capacity of biomass material, (mg g^{-1}); V, the volume of the solution (L); C$_o$, the initial concentration of Cu^{2+} ions in solution (mg L^{-1}); C$_e$, the equilibrium Cu^{2+} ions in solution (mg L^{-1}) and m, is mass of adsorbent (g).

2. 3. 2. Determination of equilibrium adsorption time of biomass materials

The time dependence of metal ion uptake by biosorbents was determined at pH 5. Five reactors, each containing 50 mL of 50 mg/L Cu^{2+} solution were prepared. To each reactor, 0.2 g of a given biomass material was added. They were covered with aluminum foils and agitated at 150 rpm. A reactor was removed from the water bath every 15 min for a period of 75 min and the suspensions were filtered and concentrations of Cu^{2+} ions in the filtrate were

measured. This process was repeated using the other biomass parts. The removal efficiencies (γ) of the biomass materials were determined using Equation 2:

$$\gamma = \frac{C_0 - C_t}{C_0} \cdot 100 \tag{2}$$

where: C_o is the initial concentration of Cu^{2+} ions in the solutions (mg/L) and C_t is the concentrations of Cu^{2+} ions in the solutions at time t.

2. 4. Characterization of most efficient biomass material

The concentrations of exchangeable cations in the most efficient biomass were determined using Particle Induced X-ray Emission technique. A proton beam of 3 MeV energy generated by a 3 MV Pelletron Accelerator was used to excite the sample. The sample was placed at an angle of 45° and the characteristic x-ray emitted were recorded with a high resolution Si(Li) detector. Shifts in adsorption bands of functional groups on the biomass before and after adsorption were determined using Fourier Transform infrared spectrophotometer (Agilent Cary 630 FTIR). Surface morphology of the biomass before and after adsorption was visualized by a scanning electron microscope SEM.

3. RESULTS AND DISCUSSION

3. 1. Adsorption capacity studies

The adsorption capacities of the biomass parts in the study solutions are compared in Figure 1.
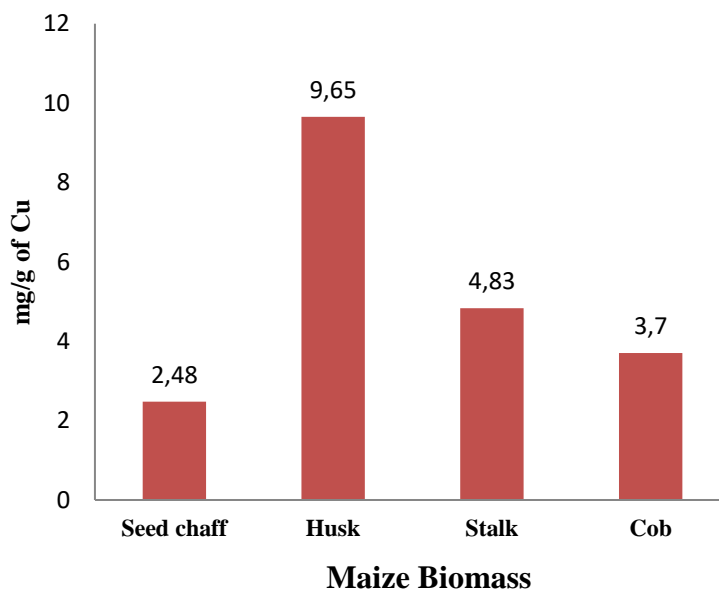

Figure 1. Adsorption capacity values of maize biomass parts

The capacities followed the order husk > stalk > cob > seed chaff. The adsorption capacity values indicate that the affinity of Cu^{2+} ions by maize husk is about twice greater than that of stalk, three times more than the cob and four times more than the seed chaff. This suggests that the maize husk has more available and greater number of adsorption sites for Cu^{2+} uptake than the other biomass parts.

The time dependence of percentage removal of Cu^{2+} ions from solution for each biomass part is shown in Figure 2.
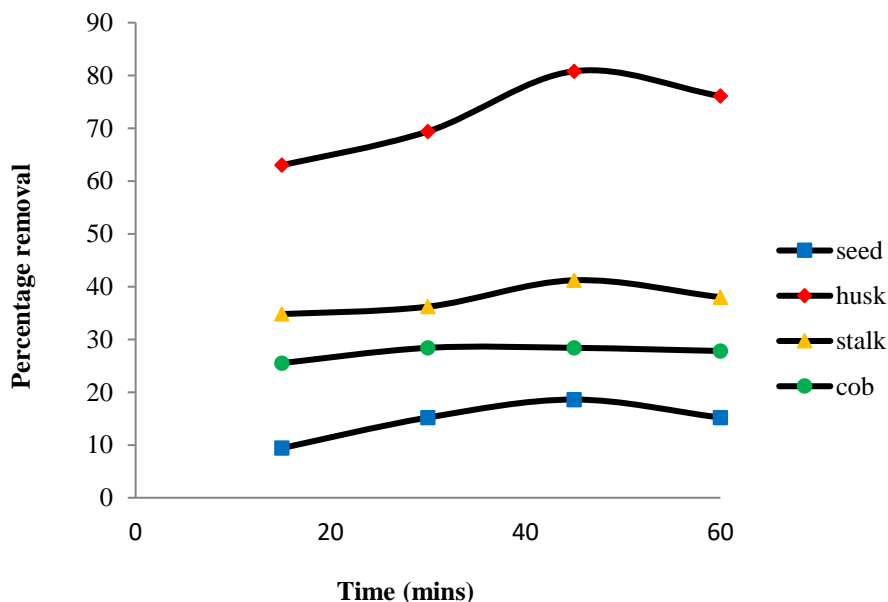

Figure 2. Time dependence of percentage removal of Cu^{2+} ions by different maize parts

The rate of adsorption of each part increased over time reaching maximum in about 45 min. The percentage removal of the husk increased geometrically in the order 2, 3, and 4 over the stalk, cob and seed chaff respectively. These values are clear indications that the husk is the most efficient part of the maize plant in the removal of Cu^{2+} ions from aqueous solutions.

3. 2. Characterization of the most efficient biomass part

Kalembasa, (2006) and Piekarczyk et al., (2011) independently analyzed the elemental composition of straw ash and hay ash respectively. Their results showed that the main elements in these biomass materials were potassium, calcium, phosphorus and magnesium. Other elements like iron, manganese zinc and copper were also present. The presence and concentrations of different elements on the maize husk from this study are shown in Table 1.

The concentrations of the metallic elements found in this biomass were in the order K > Fe > Mg > Ca > Al > Mn. Sulaiman and Garba (2014), in the study of the adsorption of Cu^{2+} ions from aqueous solutions using Neem leaf powder, Energy Dispersive X-ray (EDX) of the adsorbate showed that magnesium and potassium in the biomass were exchanged with Cu^{2+} ions from the solution. This observation indicated the involvement of ion-exchange in Cu^{2+}

adsorption. The relatively high concentration of potassium on the maize husk is suggestive of a similar mechanism in Cu^{2+} ion uptake in the study solutions.

Table 1. Elemental Analysis Results of Maize Husk Adsorbent

| Element	Concentration (g/kg)
Mg	0.839
Al	0.022
Si	0.582
P	0.944
S	0.421
Cl	2.525
K	5.602
Ca	0.628
Mn	0.021
Fe	2.302

Fourier Transform infrared Spectroscopy (FTIR) scan of the maize husk was used to identify the functional groups present in this adsorbent. The adsorption capacity of adsorbent depends on the porosity and chemical reactivity of functional groups on the adsorbent surface (Kumar et al., 2010).

The infrared spectra of the maize husk before adsorption is shown in Figure 3i. The major bands were observed at 3325 cm^{-1}, 2922 cm^{-1}, 1730 cm^{-1}, 1636 cm^{-1} and 1368 cm^{-1}and were assigned to O-H, OCH$_3$, HO-C=O, C=O and O-H-Ar respectively. Shifts in adsorption bands of functional groups to lower or higher energies show metal binding process taking place at the surface of the adsorbents (Srivastava et al., 2006; Pravasnt et al., 2006). Figure 3ii shows the infrared spectra of the maize husk after adsorption. Clear shifts in adsorption bands to 3288 cm^{-1}, 1710 cm^{-1} and 1364 cm^{-1} were observed for the O-H, HO-C=O and O-H-Ar, functional groups respectively. This is an indication that the –OH function group on the maize husk was the site majorly responsible for Cu^{2+} ion biosorption from the solution.

The surface morphology of the adsorbent before and after metal ion adsorption was observed using SEM analysis. The SEM image of maize husk before adsorption is shown in Figure 4i. This image shows that this biomass has a rough structure, dense, highly porous and non-compact. The implication therefore is that considerable numbers of pore spaces would exist for Cu^{2+} ions to be trapped and adsorbed into these pores. With these features, the adsorptive capacity of this biomass should be high as has been observed earlier.
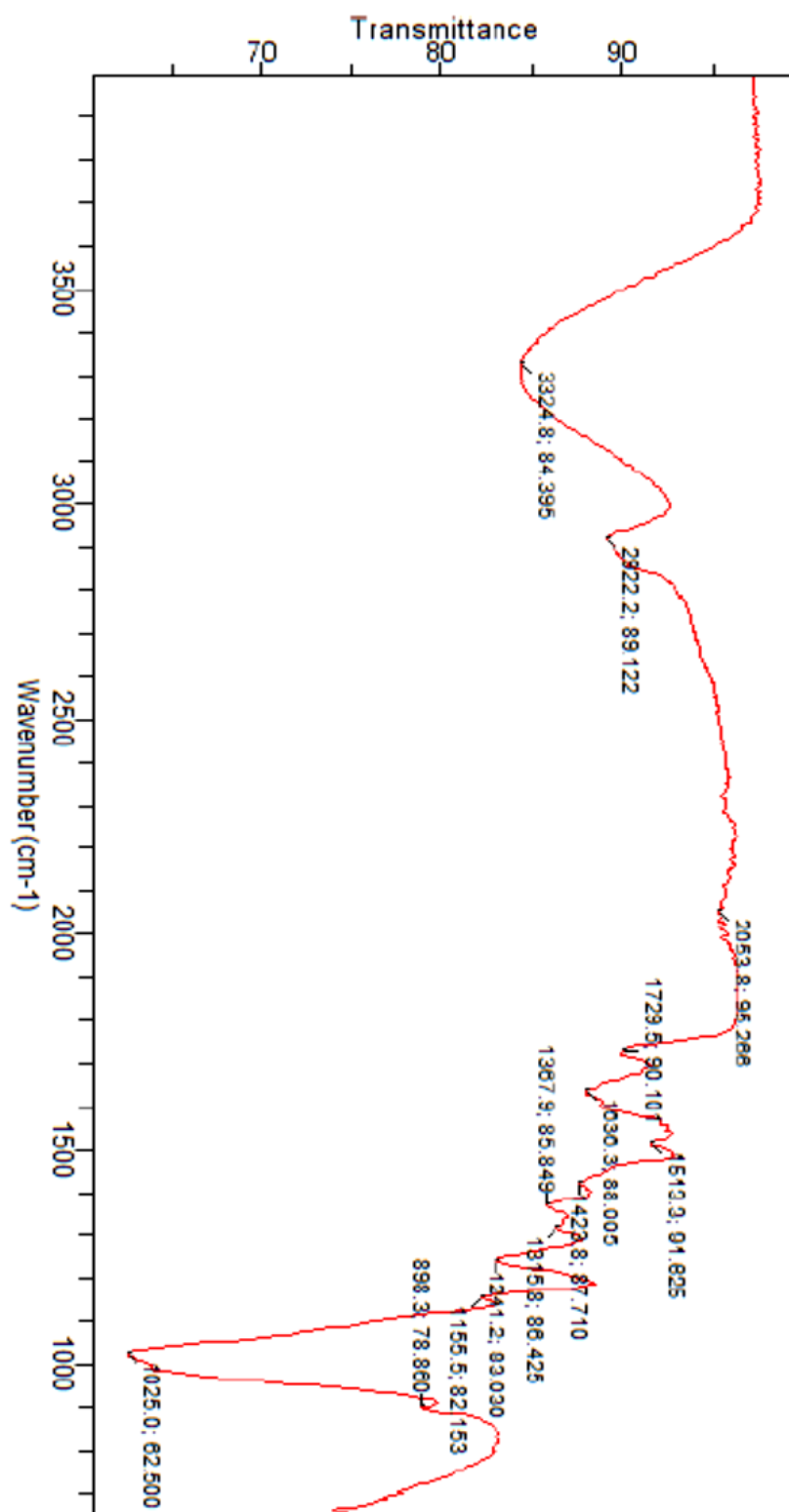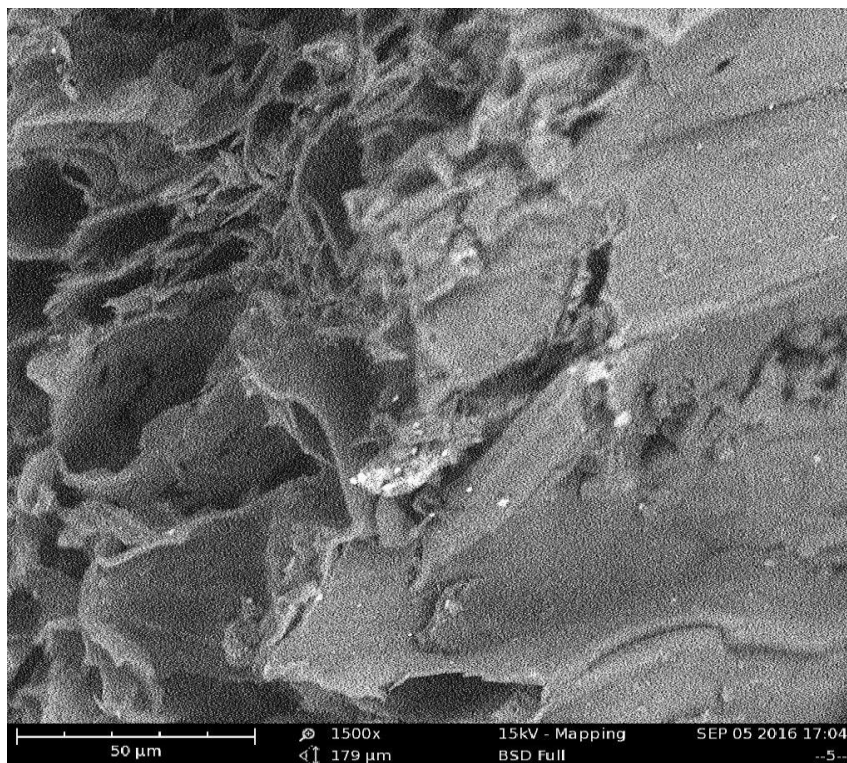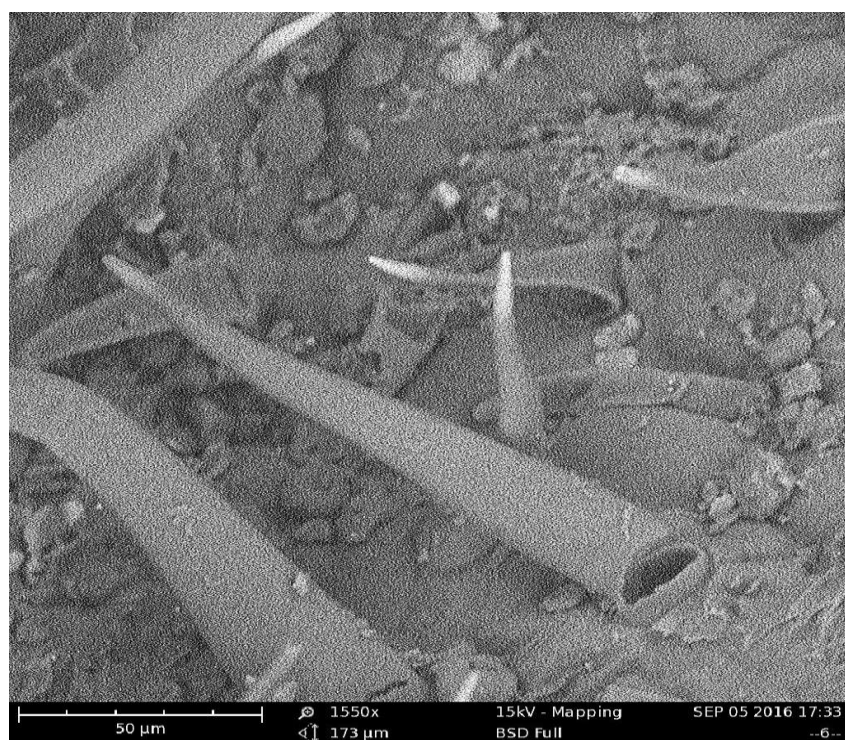
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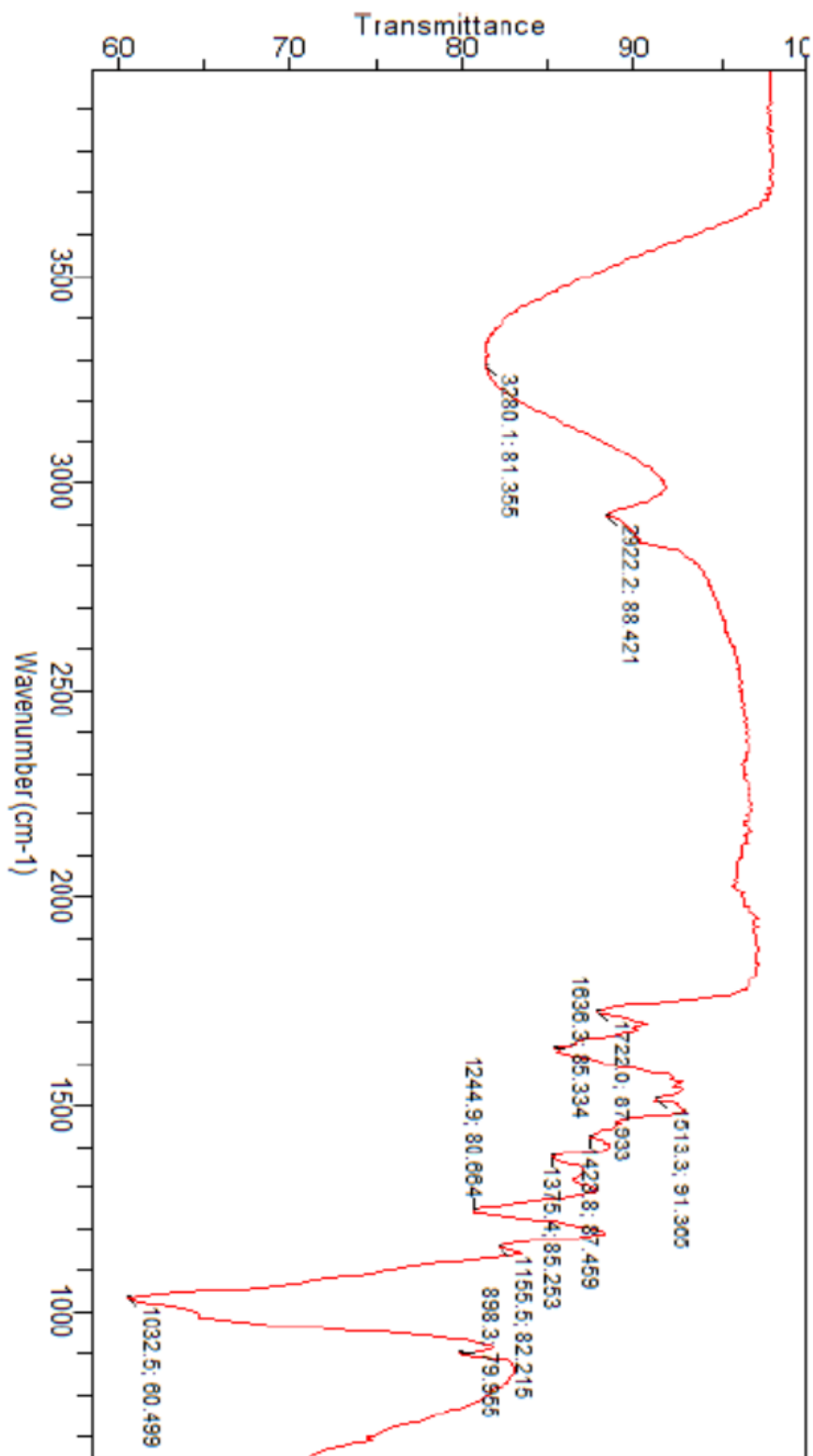
(ii)

Figure 3. FTIR spectra of maize husk before (i) and after (ii) adsorption

(i)

(ii)

Figure 4. SEM of maize husk before (i) and after (ii) adsorption

The image of the maize husk biomass after adsorption is shown in Figure 4ii. The porous structure of the biomass was no more visible after it was used in the adsorption of Cu^{2+} ions. The smooth and almost uniform coverage of the biomass by the adsorbate, is an indication that the functional groups which are distributed over the entire biomass were responsible for the adsorption process. Also the appearance of whisker-like deposits on the smoothly covered surface of the biomass suggests a multilayered packing of metal ions on the surface of the biomass. These observations are clear indications of the effectiveness of maize husk in the removal of Cu^{2+} ions from aqueous solutions.

4. CONCLUSIONS

Pollution of drinking water by Cu^{2+} ions can significantly affect the health and wellbeing of infants and nursing mothers. Different parts of maize biomass have been shown to possess active sites that can bind to the ions of this metal in water. The husk showed the highest capacity and very good efficiency in the removal of these ions from solution. The presence of exchangeable cations, complex forming functional groups and highly porous surface structure of this maize part are plausible reasons for the observed efficiency.

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