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Sorghum Waste as an Efficient Adsorbent for the Removal of Zn^{2+} and Cu^{2+} from Aqueous Medium

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Abstract *In order to offer green solution to the removal of heavy metal ion from aqueous medium, sorghum waste was found to be effective for the removal of Cu^{2+} and Zn^{2+} metal ions from aqueous solutions. The result obtained shows that the extent of metal ion removed increases with increasing contact time, increasing adsorbent doses and increasing metal ion concentrations. Different adsorption models including the Freundlich, Temkin and Dubinin-Radushkevich were used, to described the adsorption characteristics of sorghum waste for Zn^{2+} and Cu^{2+} ions. The extent of interaction was established through the values of their respective adsorption constant. The kinetic of the adsorption process best fitted the pseudo second order kinetic model. Functional groups linked to the adsorbent before and after adsorption experiments were identified through FTIR analysis and they were found to differ for the different metal ions. The adsorption of these metal ions from aqueous solution was consistent with the mechanism of physical adsorption. Sorghum waste was found to be an excellent adsorbent for Cu^{2+} and Zn^{2+} ions in aqueous environment*.

Key words: *Adsorption, Adsorbent, Sorghum waste, Heavy metals, isotherm*

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1.0 Introduction

Heavy metals constitute a serious environmental problem especially in the aquatic environment and can subsequently endangered the larger environment through bio-magnification, bioaccumulation and can be transferred to higher organism through the food chain (Mahdavi *et al*.,2012) Several health risks have been investigated and linked to heavy metal pollution (Fawell *et al*.,2001). The risk of water pollution by heavy metals has attracted global concerns because most of these metal salts are soluble in water (which is a universal solvent) and water is used globally for various domestic and industrial purposes (Chen *et al*.,2010.., Barakat *et al*.,2011; Essien *et al*, 2018) .Heavy metals are those metals whose density is greater than 5 g/cm^3 and they include most of those metals that are associated with numerous industrial processes. For example, lead and cadmium ions may be easily found in acid industrial waste. In most industries, heavy metal wastes are produced in form of sludge or effluent and are often discharge to the water bodies or the environment without adequate treatment. Such discharge may endanger the normal utilization of water by man or other members of the eco-system. Consequently, several technologies have been developed for decontamination of heavy metal polluted water. Some of them include ion exchange, membrane technology, electrolysis, adsorption, reduction, precipitation, coagulation and floatation (Odoemelam *et al*., 2018). Most of these technologies can be expensive to operate for optimum heavy metal removal while some produces other non-biodegradable wastes that will even requires stringent environmental requirements for further disposal. Adsorption is one of the simplest, less expensive and relatively effective method for the removal of heavy metals from contaminated water. The use of plant materials as an adsorbent for water decontamination has given hope on meeting ecofriendly operations during decontamination processes because they are biodegradable, unlike most inorganic adsorbents.

Several conditions affect adsorption process. For example, Rahman *et al*. (2016) *u*sed synthetic polymer ligand to remove some heavy metals including copper from wastewater and this process was reported to be pH, time, concentration and adsorbent dosage dependent, Ajmal *et at*. (2000) used *Citrus reticulata* (fruit peel of orange) as an adsorbent for the removal of Zn, Ni, Cu, Pb and Cr ions from electroplating wastewater. Their results indicated that the removal efficiency was highest for Ni (II) ions and it was in the order Ni(II) > Cu(II) > Pb(II) >Zn(II) > Cr(II).The extent of removal was found to be dependent on initial adsorbent dose, temperature, pH and concentration of different metal ions, however, orange fruit is seasonal and so it would be costly to have its availability all year round. *Gupta et al*., (2006) had demonstrated that spirogyra (green algae) can be used as adsorbent for the removal of copper (II) ions from aqueous medium and the adsorption studies were done using the batch adsorption process which indicated great dependence on pH and algae dose. Naseem *et al*., (2018) and Essien *et al*. (2015) used sorghum waste to remove some heavy metal ions from aqueous solution and found that optimum adsorption efficiency was a function of pH, concentration, period of contact and adsorbent dosages. In spite of the large volume of work done on the use of plant materials to remove heavy metal ions from aqueous solution, literature is scanty on the use of sorghum waste and yet this waste has given some hopes as effective adsorbent for the removal of heavy metals from aqueous solution. Besides, sorghum waste is normally discarded carelessly by the brewery and other industries indicating that their utilization for useful purposes can address the global goals of environmental management through resource recovery. Therefore, the present study is aimed at investigating the adsorption efficiency of sorghum waste for the removal of zinc and copper ions from aqueous solution.

2.0 Experimental

2.1 Material preparation

Sorghum waste used for the study was collected from Champion Breweries Limited, Uyo in Akwa Ibom State, Nigeria. The sample was oven dried for 24 hours at a constant temperature of 60˚C, It was grounded in a mortar and sieve into 180 µm particle sizes. All reagent used were analar grade. The sieved sample was sundried to a constant weight and later crushed to a powder form using laboratory mortar and pestle. The sample was treated with phosphoric acid and heated to a temperature of 120 ºC in order to activate it. The activated sample was repeatedly washed with deionized water until the pH of the filtrate falls between 6.0-6.5. Copper tetraoxosulphate (VI) and zinc tetraoxosulphate (VI) were used for the preparation of standard solution of copper and zinc ions and the prepared standards were serially diluted to obtain various stock solutions (20, 40, 60, 80 and 100 ppm).

2.2`Adsorption experiment

Equilibrium adsorption of Zn (ll) and Cu (II) ions on the sorghum was carried out using the batch adsorption experiment (Odoemelam *et* al., 2018). 20 g of the adsorbent was added to a beaker containing 100 ml of the test solution. The set up was allowed to stand for respective time interval and the two phases (solid and liquid phases were separated from each other. (*Baysal et* al.,*2009)*. Concentration of heavy metal ion in the filtrate was determined using atomic absorption spectrophotometer (model no AA-6800-SHIMADZU) while the equilibrium amount of metal adsorbed was calculated using equation 1 (Ekope and Edy, 2009),

$$q_e = \frac{MV(C_0 - C_e)}{1000} \quad (1)$$

where q_e is the mass of metal ion adsorbed in milligram per gram of the adsorbent, C_0 is the initial concentration of the metal ion before adsorption process, C_e is the equilibrium concentration of the metal ion in the filtrate after adsorption process and M is the mass in gram of the adsorbent, V is the volume of the solution in ml.

2.3 FTIR analysis

FTIR analysis of the sorghum sample before and after adsorption of heavy metal ion was carried out using Scimadzu FTIR-8400S. Each sample was prepared in KBr and the analysis was carried out by scanning the sample through a wave number range of 400 to 4000 cm^{-1}, the resulting spectrum was printed directly from the attached computer and printer.

2.4 Scanning electron microscope

Scanning electron microscopy was done for the crude sorghum waste before and after adsorption of heavy metal ion**.**

3.0 Results and Discussions

Figs. 1 to 3 shows the scanning electron micrographs of sorghum waste before and after the adsorption of Zn and Cu ions. From the micrographs, it can be seen that the sorghum waste (Fig 1) is a heterogeneous material consisting largely of small spheres, irregular and porous cell wall of plant cells. The surface seems to be rough and rich in protrusions. The micrographs of the sorghum waste loaded with metal ions (Figs 2 and 3) are seen to have numerous covered pores which suggest that adsorption has filled the available sites that were found in the unloaded sorghum waste This shows that Zn^{2+} and Cu^{2+} adsorption was effective to create well developed pores with uniform distribution on the surface of the precursor

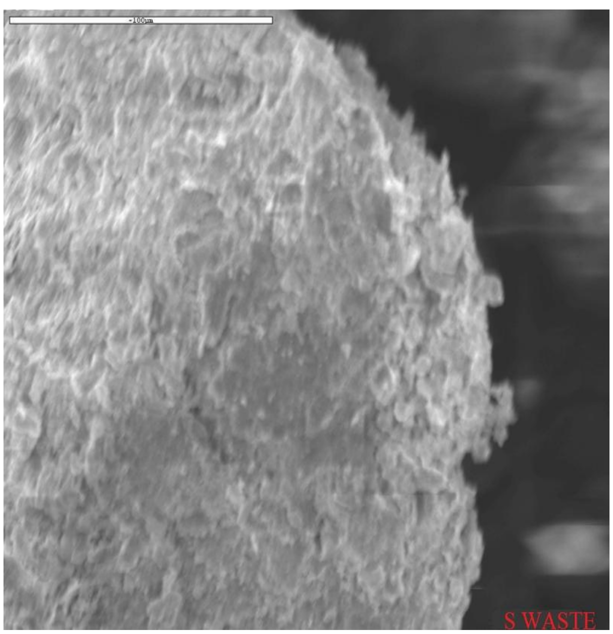

Fig 1: SEM Images of Untreated Sorghum.

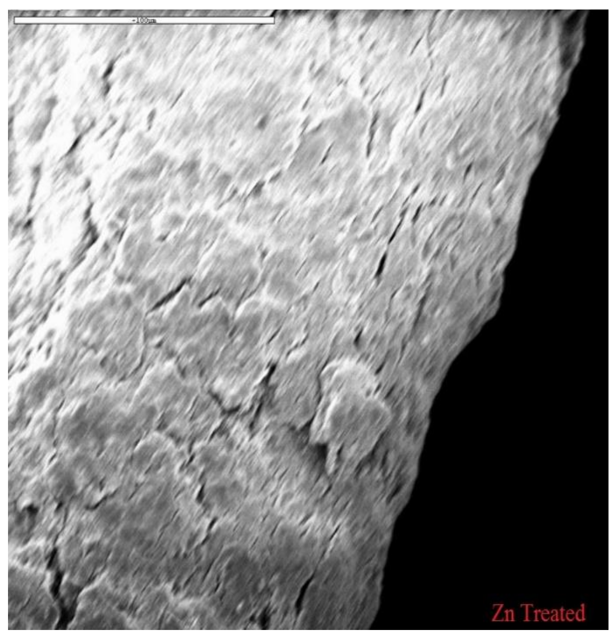

Fig 2: SEM Images of Sorghum treated with Zinc

3.1 Effect of contact time

Fig.4 shows plots for the variation of the amount of heavy metals adsorbed per unit biomass (i.e. sorghum) with time, it can also be seen from the figure that the adsorption of copper ion is less dependent on time while the adsorption of zinc ions is more sensitive to time. According to Baysal *et al*. (2009), metal ion adsorption reaches equilibrium, within 5 to15 minutes. However, Cu(II)-sorghum waste and Zn(II)-sorghum waste equilibria were attained within 20 minutes, which is relatively out of range expected by Baysak *et al*. (2009)

The adsorption capacity of the sorghum waste for copper was better than its capacity for zinc. Both metals are divalent indicating that the difference may not be associated with valency or charge on the metal. However, the ionic radii of the metal ions are 139 pm and 140 pm for Zn^{2+} and Cu^{2+} respectively, This suggests that better adsorption of copper ion compared to zinc ion may be partly attributed to large ionic radii of the metal ion, which is relatively diffuse to probably accommodate more adsorbate compare to the less diffuse zinc ion

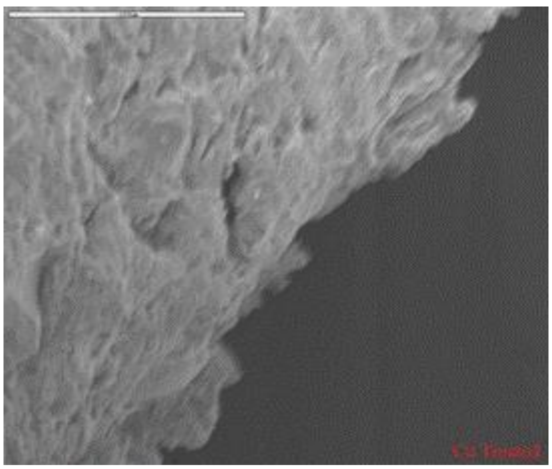

Fig. 3: Sem micrograph of Sorghum waste after adsorption of copper ion

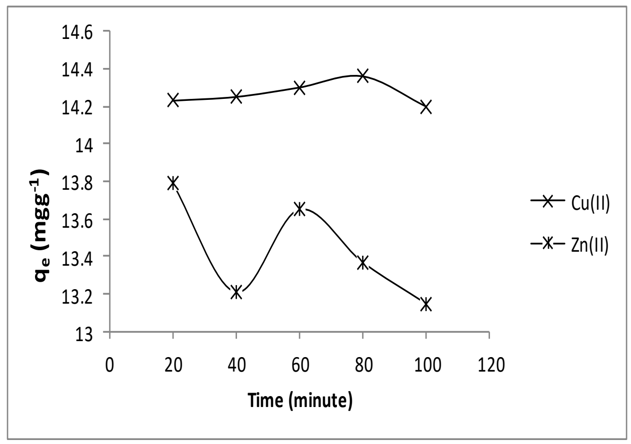

Fig. 4: Variation of amount of copper and zinc ions adsorbed by sorghum waste \with time

3.2 Effect of adsorbent dose

The amount of adsorbent dose that comes in contact with the metal ions was studied using different doses of 0.2 to 1.0 g of the adsorbent while the concentration of the metal ions was maintained at 600 mg/L and at room temperature. Fig.5 shows the variation of extent of adsorption with adsorbent dosage. There was little difference between the impact of adsorption of zinc and copper ions by the sorghum waste (especially after the initial adsorption state) even as the two plots converged. However, zinc ion was the least adsorbed metal ion, displaying a sharp increase in adsorption between 0.2 and 0.4 g. increase in adsorbent mass. The trend was closely succeeded by slight decrease in adsorption as the mass increase from 0.5 and 0.6 g. The rate of rising (or increase in adsorption) for the adsorption of copper was much slower than that of zinc. The adsorption of copper slowly progresses steadily. Several researchers have reported that the increase in the efficiency of removal of metal ion (from aqueous solution through adsorption) with an increase in the adsorbent dosage is due to the increase in the number of adsorption sites. This indicates that active adsorption sites available for copper seems to be greater than that of zinc. This however does not translate to the fact that the sorghum waste does not has fixed number of adsorption sites but because different metal ions have different ionic radius, different affinities for a given adsorbent, then a given adsorption site may preferentially favoured one metal ion over the other

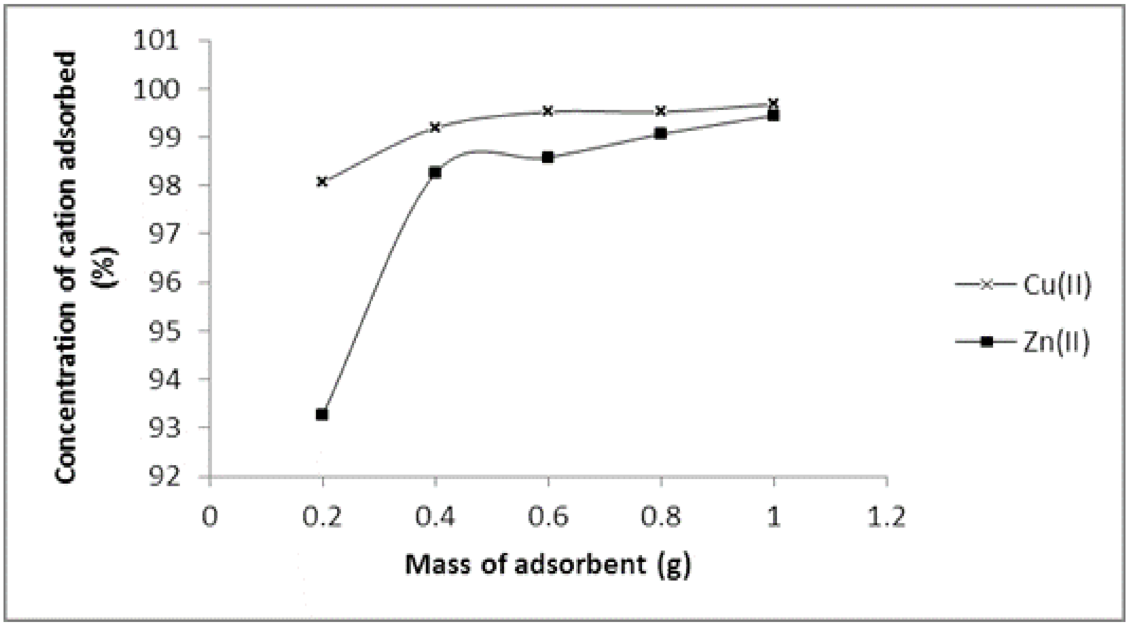

Fig. 5: Variation of the concentration of adsorbed heavy metal ions with mass of the adsorbent for the adsorption of some heavy metal ions by sorghum waste.

3.3 Effect of heavy metal ions on adsorption

Fig.6 shows plots for the variation of amount of metal ions(Cu(II) and Zn(II) ions) adsorbed per unit adsorbent with concentration.

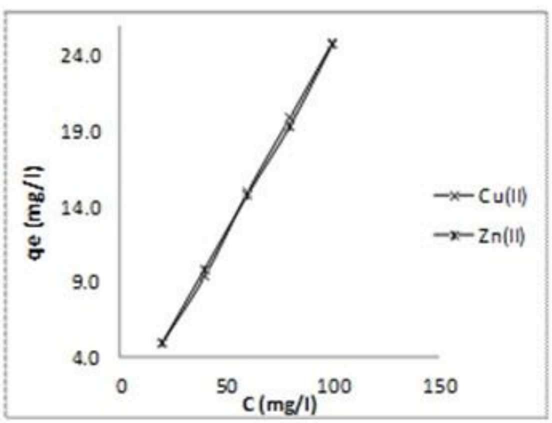

Fig. 6: Variation of amount of heavy metal ion adsorbed (by sorghum waste) with concentration of the metal ion in solution

The adsorbent shows a linear dependency with concentration indicating that the amount of copper and zinc ions adsorbed increases with increase in concentration. According to Odoemelam *et al*., (2009) increase in adsorption with concentration of the adsorbate dose is due to increase in the number of molecules of the adsorbate diffusing to the fixed number of vacant sites in the adsorbent.

3.4 Adsorption kinetics

The Lagergren pseudo first order kinetics can be written according to equation 2 (Yahaya *et al*.,2009).

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2.303}\right)t \qquad (2)$$

From the above equation, q_e and q_t are the amount of metal ion adsorbed (mgg^{-1}) at equilibrium and at time, t respectively while k_1 (min^{-1}) is the equilibrium rate constant of pseudo first-order sorption. Therefore, a plot of $\log(q_e - q_t)$ versus t is a linear model representing a pseudo first order kinetics for adsorption of copper and zinc ions unto sorghum surface (as shown in Fig. 7)..Calculated rate constant, equilibrium adsorption capacities and degrees of linearity are presented in Table 1.R^2 values are relatively low but from the data presented, the estimated adsorption capacity confirmed that copper ion is better adsorbed than zinc ion. On the other hand, a differential form of the pseudo second order kinetic can be written as follows (Ji *et al*., 2009)

$$\frac{t}{q_e} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) t \qquad (3)$$

The mathematical consequence of equation 3 is that a plot of $\frac{t}{q_e}$ versus t should yield a straight line with slope and intercept equal to $\frac{1}{q_e}$ *and* $\frac{1}{k_2 q_e^2}$ respectively. Fig. 8 shows kinetic plots for a Pseudo second order model involving the adsorption of copper and zinc ions.

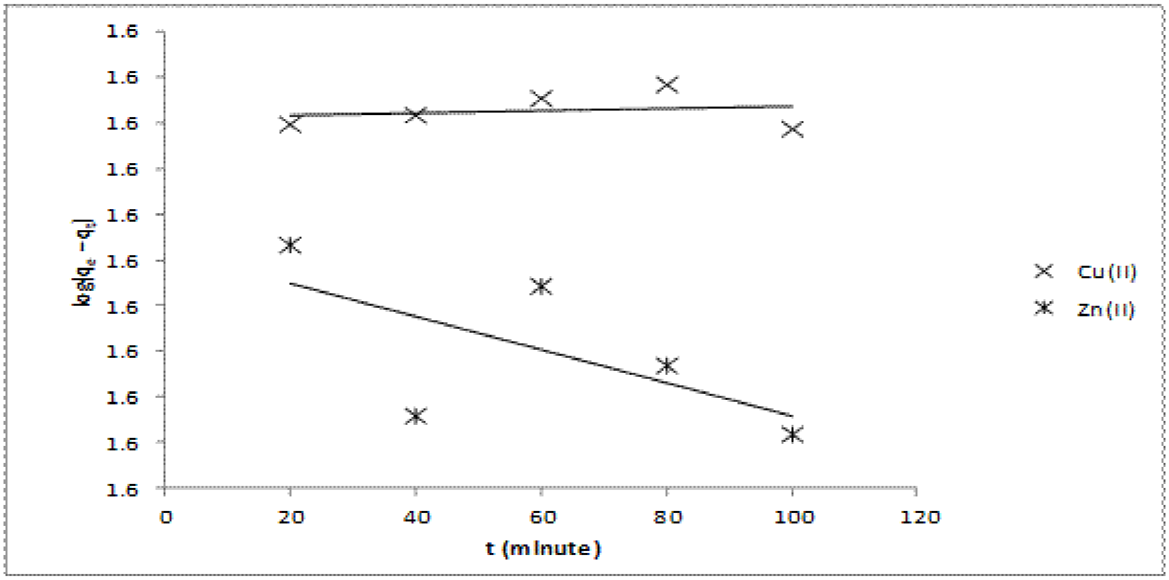

Fig 7: Variation of log qe – qt) with t for the adsorption of some heavy metal ions by sorghum waste.

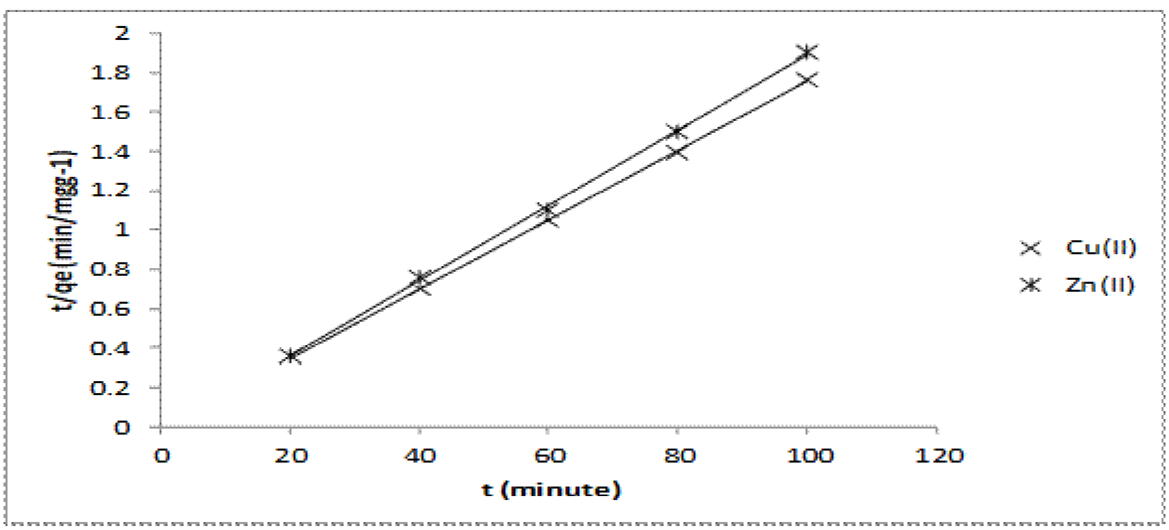

Fig 8: Variation of $\frac{t}{q_e}$ with t for the adsorption of some heavy metal ions by sorghum wast

Kinetic parameters calculated from the slope and intercept of the plots are also recorded in Table 1. The results obtained reflect high degree of linearity as indicated in recorded R^2 values, which confirms the fitness of this model.

Also, adsorption of copper ion is associated with favourable adsorption data than that of zin ions. The adsorption of zinc and copper ions unto sorghum waste surface best fitted the pseudo second order kinetics more than pseudo first order kinetics.

3.5 Adsorption isotherm

The adsorption of copper and zinc ions unto sorghum waste displayed adsorption behavior that best fitted Freundlich, Temkin and Dubinin Raduskevich isotherms. However, the Langmuir isotherm did not fit the adsorption which suggest the existent of interaction between the adsorbed species. The assumptions of the Freundlich isotherm can be expressed in exponential form according to equation 4 (Odoemelam *et al*., 2009)

$$q_e = kC_e^{\frac{1}{n}} \quad (4)$$

n denote the number of water molecule that must be replaced by the adsorbate, q_e represent the fraction of surface of the adsorbent covered by the adsorbate, C_e is the equilibrium concentration of the adsorbed specie and k is the adsorption-desorption constant. Transformation of equation 4 to a linear model, leads to equation 5,

$$log(q_e) = logk + \frac{1}{n}logC_e \quad (5)$$

Fig. 9 shows the Freundlich isotherm for the adsorption of copper and zinc ions on the surface of sorghum waste. Excellent degree of linearity was observed. The equilibrium constant as well as 1/n for Cu (II) ions adsorption were better than those of Zn (II) ions adsorption. Hence, sorghum waste has better adsorption capacity for copper ion than zinc ion.

Table 1: Pseudo first and second order rate constants for the adsorption of Cu^{2+} and Zn^{2+} metal ions by sorghum

Cation	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	K_2 ($gmg^{-1}min^{-1}$)	R^2
Cu(II)	1.6303	2.30×10^{-5}	0.6327	56.81818	-5.49	0.9999
Zn(II)	1.616	46.06×10^{-5}	0.7056	52.35602	-59.76	0.9992

Table 2: Freundlich and Temkin parameters for the adsorption of some heavy metals by sorghum and maize waste biomass

Metal ion	**Freundlich parameters**				**Temkin parameters**		
	n	**logk**	R^2	ΔG^0_{ads} (J/mol)	**B**	**A**	R^2
Cu(II)	0.9811	-0.6436	0.9985	-21.08	28.12	33.47	0.9397
Zn (II)	0.9903	-0.6292	0.9998	-21.360	27.52	32.56	0.9431

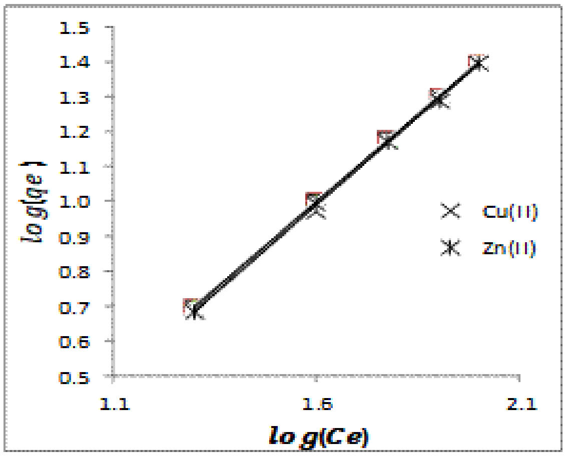

Fig 9: Variation of log (q_e) with log (C_e) for the adsorption of some heavy metals by sorghum waste

The adsorption of Cu(II) and Zn(II) ions by sorghum waste was also found to obey the Temkin adsorption isotherm, which can be written according to equation 7 (Eddy *et al.*, 2015)

$$q_e = A + BlnC_e \quad (7)$$

where A and B are both Temkin's constant, B can also be written as RT/b while q_e (mg/g) and C_e(mg/l) are equilibrium adsorbate concentrations in the solid and aqueous phases, respectively. It was found that plots of q_e versus lnC_e (Fig. 10) were linear with excellent correlation coefficients (R^2) as recorded in Table 2. The relatively high values, obtained for the Temkin constants in this study suggest a strong interaction between the adsorbate and adsorbent consistent (Wambu *et al.*,2011).

To determine the mechanism and energy of adsorption for Cu(II) and Zn(II) ions, adsorption data were fitted into the Dubinin-Radushkevich (D-R) adsorption model which is expressed in equation 8 (El Nerm *et al.*, 2009).

$$lnq_e = lnX_m - \beta\left(RTln\left(1+\frac{1}{C_e}\right)\right)^2 \quad (8)$$

From equation 8 q_e(mgl/g) is the concentration of metal ions adsorbed by the adsorbent, X_m(mg/g) is the maximum sorption capacity, β (mg^2/kJ^2) is a constant that is related to the mean adsorption energy R (kJ/mol/K) is the gas constant and T (K) is the temperature. The bracketed terms in equation 8 represents the Polanyi potential while the constant, β is related to the mean adsorption energy (E) according to the following equation, From equation 8, a plot of lnq_e versus $\left(RTln\left(1+\frac{1}{C_e}\right)\right)^2$ should give a straight line with intercept and slope equal to β and lnX_m respectively.

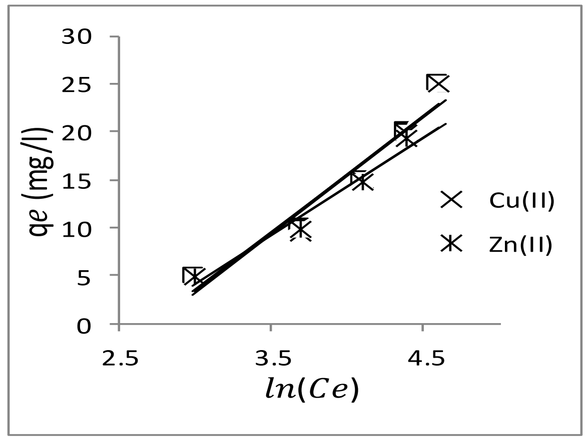

Fig 10: Variation of qe with ln (Ce) for the adsorption of some heavy metal ions by sorghum

Fig. 11 shows the D-R isotherms for the adsorption of Cu(II) and Zn(II) ions by sorghum wastes.

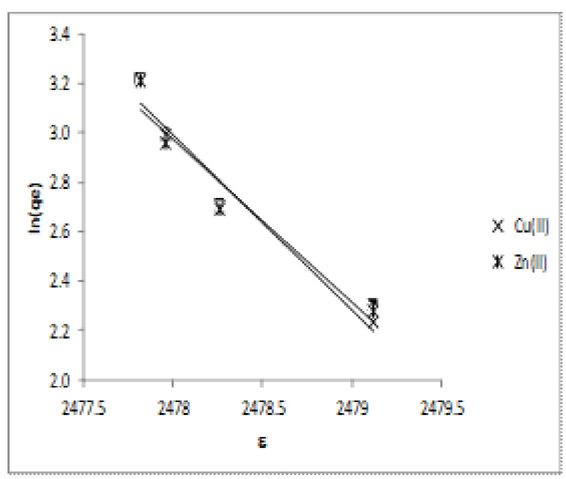

Fig 11: Variation of log (q_e) with ε for the adsorption of some heavy metal ion by sorghum

From the results obtained, the adsorption energy for the metal ions are less than the threshold value of 8 kJ/mol/ therefore, the adsorption of Cu (II) and Zn(II) ions by sorghum waste is consistent with the mechanism of physical adsorption

Table 3: D-R parameters for the adsorption of some heavy metals by sorghum waste

Metal ion	β (mg^2/kJ^2)	$\ln(X_m)$	E (kJ/mol)	R^2
Cu(II)	0.71	1764.4	1.19	0.9587
Zn(II)	0.66	1639.5	1.23	0.9360

3.6 FTIR study

Peaks and frequencies of IR absorption deduced from FTIR spectrum of sorghum waste (graph not shown) are presented in Table 4.

Table 4: Peaks and frequencies of IR absorption by sorghum waste

Peak (cm^{-1})	Intensity	Assignment
692	68.26	C-Cl stretch due to alkyl halide
1052	49.48	C-O stretch due to alcohol or acid
1158	50.10	C-N stretch due to amine
1268	49.13	C-O stretch due to carboxylic acid
1655	33.49	C=O stretch due to carboxylic acid
2925	24.04	C-H stretch due to alkane
3306	22.30	N-H stretch due to amine
3451	22.17	OH stretch due to alcohol
3528	23.46	OH stretch due to alcohol

The spectrum revealed the presence of C –Cl stretch due to alkyl halide at 692 cm^{-1}, C=O stretch due to alcohol or carboxylic acid at 1052, C-N stretch due to amine at 1158 cm^{-1}, C-O and C=O stretches due to carboxylic acid at 1268 and 1655 cm^{-1} respectively, C-H stretch due to alkane at 2925 cm^{-1}, N-H stretch due to amine at 3306 cm^{-1} and OH stretches at 3451 and 3528 cm^{-1} due to alcohol.

The FTIR spectrum of sorghum waste when Cu (II) ions were adsorbed was also obtained (graph not shown) and parameters deduced from the plots are recorded in Table 5. These included peaks and intensities of IR adsorption as well as the assignment of the associated functional groups as recorded in Table 5.

Table 5: Peaks and frequencies of IR absorption by sorghum waste due to adsorption of Cu (II) ions

Peak (cm^{-1})	intensity	Assignment
630	12.88	C-Cl stretch due to alkyl halide
1646	7.03	C=O stretch due to carboxylic acid
2931	4.33	C-H stretch due to alkane
3420	3.15	OH stretch due to alcohol

From the results obtained, it is evident that the C-Cl stretch at 692 due to alkyl halide was shifted to 630 cm^{-1}, the C=O stretch due to carboxylic acid was shifted from 1655 to 1646 cm^{-1}, the C-H stretch due to alkane was shifted from 2925 to 2931 cm^{-1} while the OH stretch due to alcohol was shifted from 3451 to 3420 cm^{-1}. According to Eddy *et al.*, (2010), the difference in frequencies of adsorption confirms the presence of other compounds in the sorghum waste ‘surface and the adsorbate.

Table 6 present peaks, intensities and assignment of functional groups deduced from the FTIR spectrum of sorghum waste after the adsorption of Zn (II) ions. The data, when compared with that of unloaded sorghum wastes, revealed that the C-Cl stretch at 692 was shifted to 626 cm^{-1}, the C-O stretch due to alcohol was shifted from 1052 to 1049 cm^{-1}, the C=O stretch due to carboxylic acid was shifted from 1655 to 1645 cm^{-1}, the OH stretch due to alcohol was shifted from 2925 to 2928 cm^{-1} and the OH stretch due to alcohol was shifted from 3451 to 3407 cm^{-1}. Functional groups that were missing in the new spectrum included C-N stretch at 1158 cm^{-1}, C-O stretch at 1268 cm^{-1}, N-H stretch at 3306 cm^{-1} and OH stretch at 3528 cm^{-1}. According to Eddy *et al*., (2010). The shift in interaction points towards existent of interaction between the adsorbate and adsorbent, formation of new functional groups indicated the formation of new bond while missing functional groups are indication of bonds used for adsorption

Table 6: IR absorption data of sorghum waste due to adsorption of Zn (II) ions

Peak (cm^{-1})	intensity	Assignment
626	9.93	C-Cl stretch due to alkyl halide
1049	8.48	C-O stretch due to alcohol or carboxylic acid
1645	7.46	C=O stretch due to carboxylic acid
2928	6.40	OH stretch
3407	5.98	OH stretch

4.0 Conclusion

The present study reveals that Sorghum is an excellent adsorbent for the removal of zinc and copper ions from aqueous solutions. The adsorbent potential was found to fit into Freundlich and Temkin adsorption models as shown in the article. Its adsorption potential is strongly attributed to the possession of suitable functional groups as potential adsorption sites for cooperative adsorptions as shown from the FTIR analysis. The mechanism of adsorption of zinc and copper ions by Sorghum is a physical adsorption process, characterized by low adsorption energies.

5.0 References

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