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Maize Waste Biomass as an Adsorbent for the Removal of Pb^{2+}, Zn^{2+} and Cu^{2+} from Aqueous Solution

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Abstract In order to search for cheaper, eco-friendly, Adsorption of lead, zinc and copper ions from aqueous solution by maize waste was studied using the batch adsorption process. The results obtained from the study, indicated that maize waste biomass is an excellent adsorbent for the removal of Pb^{2+}, $Zn^{2+}$and Cu^{2+} from aqueous solution. The extent of adsorption of the metal ions tends to increase with increase in the initial ion concentration, the adsorbent dose and with the period of contact. The adsorbent functions best for lead ion and least for zinc ion, a trend that correlated with ionic radii of the metal ions and charge to mass ratios. Functional groups linked to the adsorbent of the metal ions were identified through FTIR analysis and they were found to differ for the different metal ions studied. Adsorption characteristics of maize waste biomas for $Pb^{2+,}$ Zn^{2+} and Cu^{2+} fitted the Freundlich, Temkin and Dubinin-Radushkevich adsorption models. From the Freundlich and Temkin models, the extent of interaction was established through the values of their respective adsorption constant. The application of Dubinin-Radushkevich isotherm to the adsorption of the studied metal ions confirmed the mechanism of physical adsorption characterized with adsorption energies that were less than 8kJ/mol at all concentrations. Kinetic modelling also confirmed that the adsorption of the metal ions unto maize waste surface best suited the pseudo first order kinetic model.

Keywords Water pollution, Pb^{2+}, $Zn^{2+}$and Cu^{2+}, remediation, adsorption

1. Introduction

Quality water is a major requirement for the success of numerous sectors in the world. Apart from been a universal solvent, domestic and industrial applications have high demand for quality water. Globally, numerous problems are associated with contaminated or unclean water [1]. Literature reveals that about 1.2 billion people lack access to safe drinking water while 2.6 billion have little or no sanitation and millions of people die annually, including about 3,900 children resulting from water burned diseases [1].

Several anthropogenic and industrial activities are responsible for contamination of most water bodies (including surface and underground water system). Water contamination majorly arises from introduction of pollutant (at concentration that is injurious to the environment) into the water bodies [2]. Some of these pollutants are insoluble (mostly undissolved particles) and can easily be removed by filtration process. However, most of them (For example heavy metal ions, some microorganism, some chemical pollutants) are soluble and cannot be removed through filtration or other simple processes. Therefore, there is need to source for a low cost, effective, eco-friendly and robust methods of disinfecting and decontaminating water for its useful applications [3]. Adsorption is an established and one of the best options available for the removal of pollutants from water [4].

The applications of low-cost adsorbents obtained from plant wastes (including maize waste biomass) as a replacement for costly conventional methods of removing heavy metal ions from wastewater have been reviewed by several authors [6]. However, the use of maize wastes as adsorbent for heavy metals and other pollutants has not been fully explored. Opeolu *et al*. [6] investigated the use of maize cob to removed lead ion from aqueous solutions and effluents from battery and paint industries using batch adsorption method and found that the maize cob exhibited high efficiency for the removal of lead ion through adsorption. Alves *et al*. [7] found that maize waste (among other agricultural waste) is a good adsorbent for the removal of tyrosine and phenylalanine from aqueous solution. Elizades-Gonzalez *et al*, [8] characterized the adsorption properties of maize waste using thermogravimety, porosimetry and elemental analysis. The characterized maize waste was found to be a good adsorbent for the removal of some dyes from aqueous solution. The adsorption behavior of the adsorbent responded favourably to Henry, Langmuir and Freundlich adsorption models. According to Zvinowanda *et* al. [9], maize waste such as maize tassel is a novel adsorbent that is mesopourous with BET specific surface area, total pore volume and average pore width of 2.52 m^2/g, 0.0045 cm^3g and 7.2 nm respectively. Particle size obtained from laser diffraction pattern analysis gave particle size distributions in the range of 45-50, 50-150 and 150 to 300 μm fractions. Analysis of micrograph obtained for the waste materials reveals predominance of flattish, rodlike particles while stability to thermal decomposition was sustained upto 230 °C. Therefore the present study is aimed at utilizing waste obtained from maize cob for the adsorption of lead, copper and zinc ions from aqueous solution.

Lead (Pb) and its compounds are widely used in several industries and are commonly found in air, water, soil and food [10]. Lead ion may be introduce to an aquatic environment through smelters, industrial effluents from battery, paint, plastic, textiles, microelectronics and other activities [11]. The target organs for lead toxicity in human is the blood and bones and are commonly associated with the replacement of major divalent element (such as calcium) by lead. Copper toxicity, often called copperiedus explains the consequences of excess copper in the human system. Acute symptoms of copper poisoning by ingestion include vomiting, hematemesis (vomiting of blood), hypotension (low blood pressure), melena (black "tarry" feces), coma, jaundice (yellowish pigmentation of the skin), and gastrointestinal distress. Individuals with glucose-6-phosphate deficiency may be at increased risk of hematologic effects of copper [12]. Although the toxicity of zinc ion is not as severe as those of copper and lead ions, health problems such as stomach cramps, vomiting, skin irritations, anemia, and nausea have been linked to high concentration of zinc in the human body [13].

In view of the above, the present study is aimed at investigating the potential of maize biomass as an effective adsorbent for the removal of lead, copper and zinc ions from aqueous solution. The adsorption study shall be carried out using batch adsorption process while the functional groups associated with the adsorption shall be analysed through FTIR spectroscopy.

Materials and Method

All reagents used for the study were of analar grade while the Maize waste sample was gotten from Ikot Ekpene Main Market, Akwa Ibom State, Nigeria. The sample was sundried to a constant weight. The dried sample was crush to powder form using laboratory mortar and pestle. 400 g of the sample was treated with phosphoric acid, heated to a temperature of 120 ˚C. The activated sample was repeatedly washed with ionised water until the pH of the filtrate falls between 6.0-6.5.

Standard solutions of Pb^{2+},Zn^{2+} and Cu^{2+} ions were prepared from lead nitrate, Zinc tetraoxosulphate and chromium heptaoxodichromate and from there, serially diluted concentrations of their respective solutions (20, 40, 60, 80, and 100 ppm) were prepared for batch adsorption Experiment.

Adsorption Experiment

Equilibrium adsorption of Cu (II), Pd (ll) and Zn (ll) ions on the maize waste biomas was carried out using 100ml of various concentrations of the adsorbent, different contact time, different metal ion sizes and different concentration of the adsorbate through a batch experimental process. In each case, the concentration of the metal ion adsorbed were determined using AAS (model no AA-6800-SHIMADZU) and the equilibrium amount of metal adsorbed was calculated using the following equation.

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

where q_e is the amount of adsorbate 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.

FTIR Analysis

FTIR analysis of the sample before and after adsorption of the respective heavy metal ion was carried out using Scimadzu FTIR-8400S Fourier transform infra-red spectrophotometer. The sample were smeared on the sample holder and placed in the sample compartment of the machine. 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.

Results and Discussions

Effect of metal ion concentration

Fig. 1 is a plot showing the variation of equilibrium concentration with time for the adsorption of zinc, copper and lead ions from aqueous solution by maize waste. The pattern of the plots generally reveals that the concentrations of lead, copper and zinc ions adsorbed by maize waste vary linearly with concentration and increases with increase in concentration. The observed trend may be due to progressive occupation of the available adsorption sites on the surface of the maize with increasing concentration. Since the plots for the respective metal ion are not parallel, it follows that the adsorption mechanism depends on the metal ion. Lead ion was the most adsorbed ion, followed by copper and lastly by zinc. Since all the metal on are divalent, it is evident that the adsorption does not depend on the charge of the ion but on the ionic radius. The ionic radii of Zn^{2+}, Cu^{2+} and Pb^{2+} are 74, 73 and 86 ppm. Generally, the extent of adsorption is expected to increase with decreasing ionic radius as displayed by the studied metal ions. The observation agrees with those reported by Cheng *et al*. [14], Lin *et al*. [15] and Bohli *et al*. [16] for the adsorption of some heavy metal ions from aqueous solution.

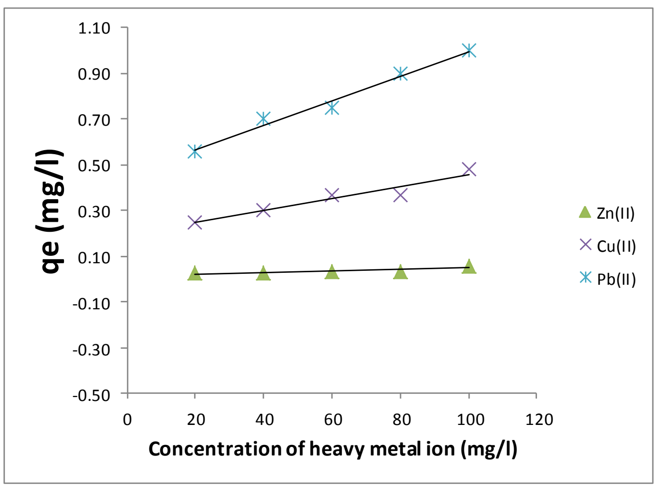

Figure 1: Variation of lead, copper and zinc ions adsorbed (by maize waste) with concentration

Effect of adsorbent dose

Fig. 2 is a plot depicting the pattern of relationship exhibited between the amount of metal ion adsorbed and the amount of the adsorbent. Zinc ion was the least adsorbed ion while lead was the highest adsorbed metal ion. Zinc ion adsorption was observed to experience a sharp increase in the beginning followed by a slight decrease and a progressive rise. In the case of lead and copper ions, the adsorption was almost steady. This indicate that the amount of adsorbent has significant effect on the adsorption of zinc ions than lead and copper ions

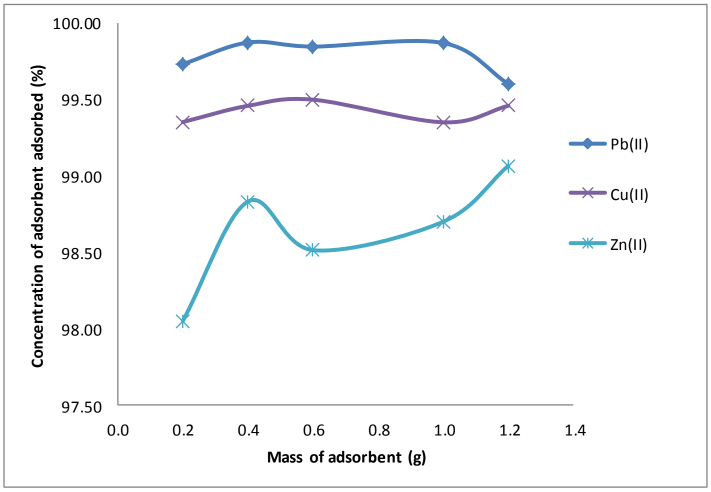

Figure 2: Variation of the concentration of lead, copper and zinc ions adsorbed with mass of the adsorbent

Effect of contact time

Fig. 3 is a plot illustrating the variation of the amount of heavy metals adsorbed unto a unit biomass (maize wastes) with time. The Figure reveals that the adsorption of zinc, lead and copper ions increases with time. However, the adsorption of zinc ion first decreases with time upto 20 minutes before increasing. It has been found that the period of contact of an adsorbates and adsorbents is of great importance in adsorption study because it depends on the nature of the system used. Adsorption of heavy metals unto a non-living cell is generally considered as a rapid process that occurs within a few minutes. According to Baysal *et al*. [17], metal ion adsorption reaches equilibrium, within 5–20 min. From Fig. 3, it can be seen that Pb^{2+}-maize waste, Cu^{2+}-maize waste and Zn^{2+}-maize waste equillibra were attained within 20 minutes.

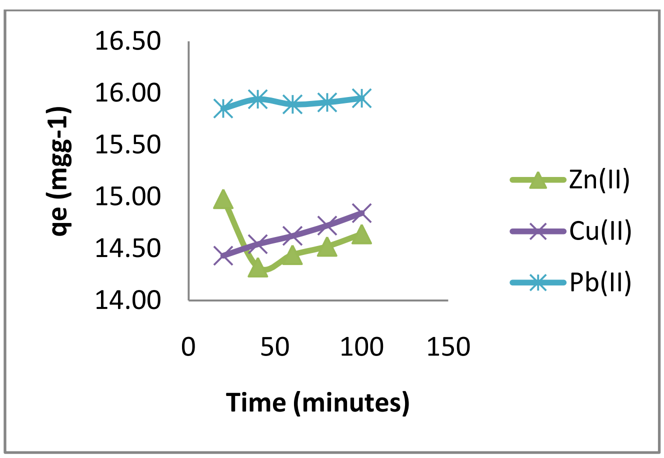

Figure 3: Variation of the amount of lead, copper and zinc ions adsorbed with time

Adsorption kinetic

In other to investigate the adsorption mechanism, several kinetics models were employed. These included the solid capacity (a pseudo first-order equation of Lagergren) and solid phase adsorption (a pseudo second-order equation) models. According to Eddy and Ekop [18], the Lagergren equation for a pseudo first order kinetics can be written as

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

where q_e and q_t are the amount of metal ion adsorbed (mgg^{-1}) at equilibrium and at any time, t (minutes) respectively. $k_1(min^{-1})$ is the equilibrium rate constant of pseudo first-order sorption. The mathematical implication of equation 2 is that plotting of $\log(q_e - q_t)$ versus t should be linear with slope and intercept equal to $k_1/2.303$ and $\log(q_e)$ respectively. The Lagergreen pseudo first order plots for the adsorption of lead, copper and zinc ions by maize waste are shown in Fig. 4. Values of, k_1, q_e, and R^2, deduced from the plots are presented in Table 1. The closeness of calculated values of degree of linearity (R^2) to unity confirmed that the adsorption of lead, copper and zinc ions onto maize waste is consistent with the Lager-green pseudo first order kinetic.

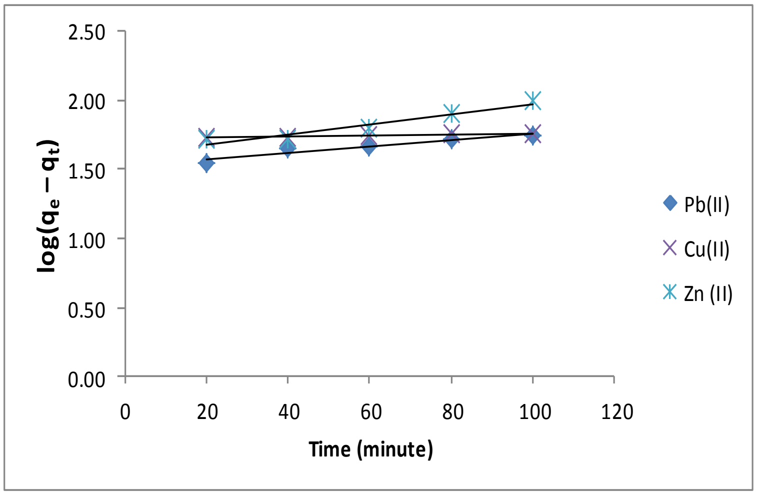

Figure 4: Variation of $\log(q_e - q_t)$ with t for the adsorption of lead, copper and zinc ions by maize waste biomass

Table 1: Pseudo first and second order kinetic constants for the adsorption of lead, copper and zinc ions by maize waste

Metal ion	q_e (mg/g)	k_1 (min^{-1})	R^2	q_e (mg/g)	K_2 ($gmg^{-1}min^{-1}$)	R^2
Pb(II)	1.0055	0.0055	0.9278	78.1250	0.0002	0.9644
Cu(II)	1.0009	0.0009	0.9753	84.0336	0.0009	0.9485
Zn(II)	1.0086	0.0085	0.9423	64.9351	-0.0079	0.9970

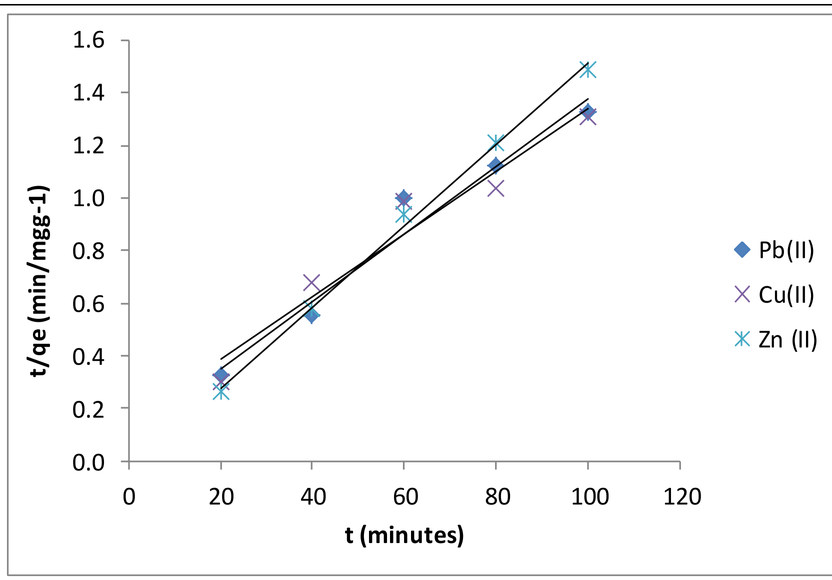

Figure 5: Variation of $\frac{t}{q_e}$ with t for the adsorption of lead, copper and zinc ions by maize waste

The differential form of pseudo second order kinetic model can be written as [19]

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

Mathematical interpretation of equation 3 implies that a linear plot of $\frac{t}{q_e}$ versus t should give slope and intercept values numerically equal to $\frac{1}{q_e}$ *and* $\frac{1}{k_2 q_e^2}$ respectively, provided the model is obeyed. Fig. 5 presents a pseudo second order plots for the adsorption of lead, copper and zinc ions unto maize waste. Kinetic parameters deduced from the slope and intercept of the plots are also recorded in Table 1. R^2 values obtained for the pseudo second order model pointed towards excellent degree of linearity, hence the adsorption the studied ions by maize waste also supports pseudo second order kinetics.

Adsorption isotherm

In order to optimized the adsorption characteristics of the metal ions on maize waste biomass, adsorption characteristics of the adsorbates (lead, zinc and copper ions) were investigated by fitting data into different adsorption models. The test indicated that the data best fitted Freundlich and Temkin adsorption models, The Freundlich adsorption model can be expressed according to equation 4.

$$q_e = kC_e^{\frac{1}{n}} \qquad 4$$

Where *k* and *n* are the Freundlich constants that characterized the system. They are related to the adsorption capacity and adsorption intensity of the adsorbent and they characterized the system. Linearization of equation 4 through logarithm expression yielded equation 5

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

The 5 indicates that *k* and *n* can be determined from intercept and slope of the linear plot of log q_e against log C_e (Fig. 6) while 1/*n* can be estimated from the slope of the plot. 1/nis an index for the adsorption intensity of the heavy metal ion onto the sorbent. It is related to surface heterogeneity.

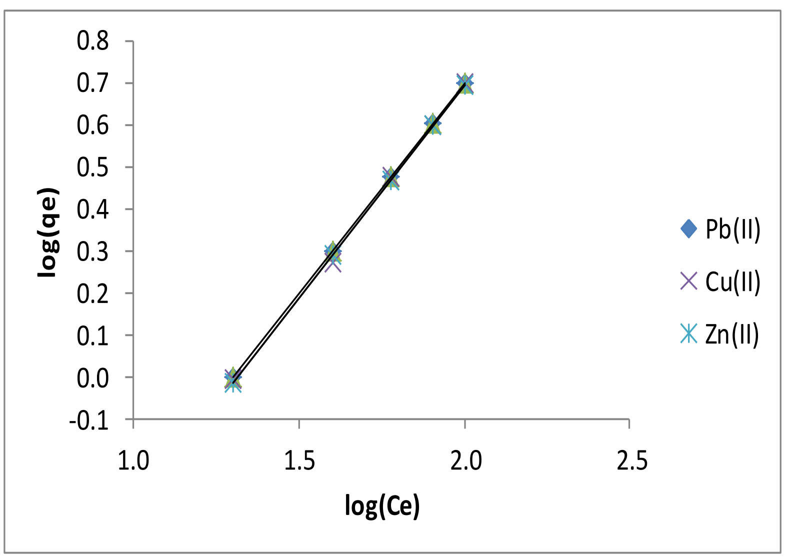

Figure 6: Variation of log(q_e) with log(C_e) for the adsorption of lead, copper and zinc metals by maize waste

The surface becomes more heterogeneous as the ratio (1/n), gets closer to zero. 1/n values less than unity suggest adsorption behavior that is similar to the Langmuir isotherm (which assumes that the surface is homogenous) while values of 1/*n* above unity is indicative of cooperative adsorption. The Freundlich adsorption constants evaluated from the isotherms (Fig. 6) are presented in Table 2. The closeness of R^2 values to unity confirms that the Freundlich model fitted the experimental data. Since values of 1/n are closer to unity, it suggests that the adsorbent surface is homogenous towards the adsorption behavior of lead, zinc and copper ions unto maize cob [20-21]. The observed isotherms for lead, zinc and copper ions are parallel to each which suggests that their adsorption behaviour follows similar mechanism.

Table 2: Freundlich and Temkin parameters for the adsorption of lead, copper and zinc ions by maize waste biomass

Metal ion	Freundlich parameters			Temkin parameters		
	n	logk	R^2	B	A	R^2
Pb(II)	0.1793	-6.5819	0.9472	1.3402	1.018	1.0000
Cu(II)	0.1779	-6.6862	0.9904	1.3412	1.0186	0.9987
Zn(II)	0.1793	-6.6148	0.9551	1.3402	1.0182	1.0000

The Temkin adsorption isotherm for the adsorption of lead, copper and zinc ions can be expressed according to equation 6 [21],

$$q_e = A + BlnC_e \qquad 6$$

where *A* is the Temkin adsorption potential, and *B* is the Temkin constant that is related to the heat of sorption while q_e (mg/g) and C_e(mg/l) are equilibrium adsorbate concentrations in the solid and aqueous phases respectively. Equation 6 implies that a plots of q_e versus lnC_e should be linear with slope and intercept equal to B and A respectively. Fig. 7 shows the Temkin isotherms for the adsorption of lead zinc and copper ions unto the surface of maize waste. Also, the closeness of R^2 values to unity confirms the application of the Temkin model to the adsorption of the studied heavy metals. Adsorption parameters deduced from the plots are also presented in Table 2. The results obtained indicated that values of Temkin constants were relatively high, suggesting the existent of strong interactions between the adsorbates and the adsorbent. These interactions maybe consistent with ion-exchange mechanism or chemical interface between the metal ions and maize cob surfaces [22].

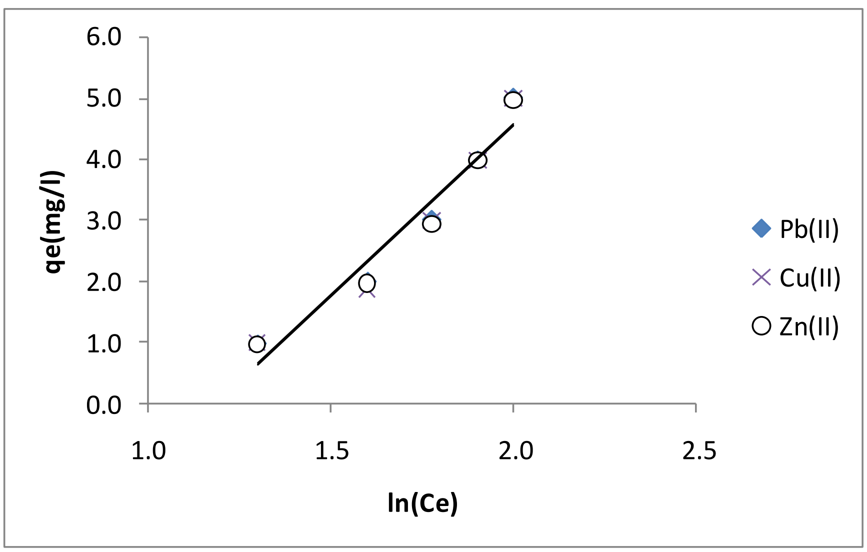

Figure 7: Variation of q_e with $ln(C_e)$ for the adsorption of lead, copper and zincions by maize waste

Dubinin-Radushkevich (D-R) adsorption model is unique in predicting the mechanism of adsorption of metal ion unto adsorbent, the characteristic porosity of the adsorbent and the apparent energy of adsorption. The Dubinin-Radushkevich (D-R) adsorption model can be expressed according to equation 7 [19].

$$lnq_e = lnX_m - \beta\left(RTln\left(1 + \frac{1}{C_e}\right)\right)^2 \qquad 7$$

Where q_e (mgl/g) is the concentration of the adsorbate adsorbed in the adsorbent, X_m(mg/g) is the maximum sorption capacity, β (mg^2/kJ^2) is a constant 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 7 represents the polanyl potential while the constant, β is related to the mean adsorption energy (E), which can be expressed as,

$$E = \frac{1}{(2\beta)^{\frac{1}{2}}} \quad 8$$

Application of equation 7 to the adsorption of lead, copper and zinc ions unto maize waste surface reveals that plotting of lnq_e versus $\left(RTln\left(1+\frac{1}{C_e}\right)\right)^2$ were linear with slope and intercept equal to β and lnX_m respectively. This is shown in Fig. 8. Calculated Dubinin-Radushkevich adsorption parameters are presented in Table 3. The results confirmed that the energies of adsorption of lead, zinc and copper ions are less than the threshold value of 8 kJ/mol. Therefore, the adsorption of these ions onto maize waste is consistent with the mechanism of physical adsorption.

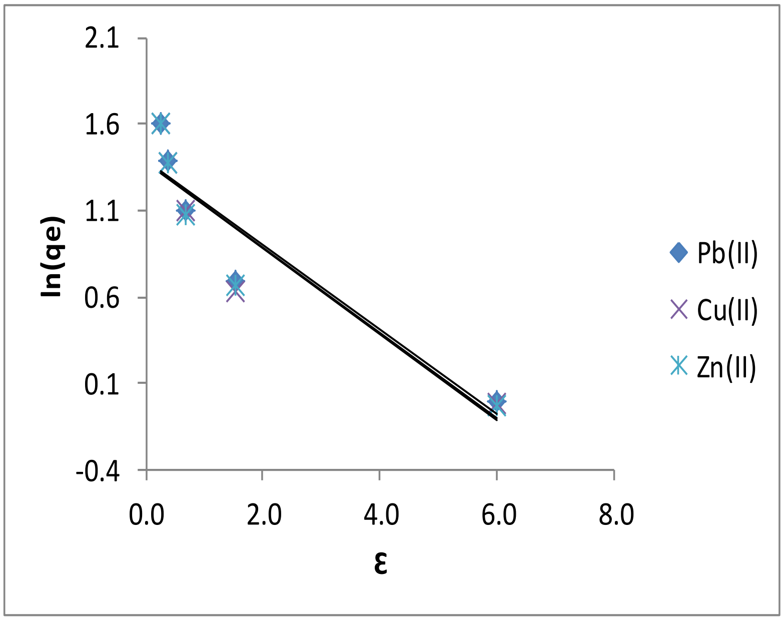

Figure 8: Variation of log(q_e) with ε for the adsorption of lead, copper and zincions by maize waste

Table 3: D-R parameters for the adsorption of lead, copper and zinc ions by maize waste

Metal ion	β(mg²/kJ²)	ln(Xm)	E (kJ/mol)	R²
Pb(II)	0.2458	1.3914	1.4262	0.8688
Cu(II)	0.2475	1.3772	1.4213	0.8507
Zn(II)	0.2498	1.3813	1.4150	0.8686

FTIR study

Functional groups identified in the FTIR spectrum of maize waste are recorded in Table 4. The spectrum revealed the presence of C –X stretch due to alkyl halide at 705 cm^{-1}, C=N stretch due to amide or amine at 2220 cm^{-1}, N-H stretch due to amine at 3388 cm^{-1}, O-H and C-H stretches due to hydroxyl group and alkyl at 3900 and 1366 cm^{-1} respectively . However, when maize waste biomass was used as an adsorbent for Pb ion, the resultant spectrum gave some adsorption frequencies and peaks, which are recorded in Table 4. The C-X stretch due to alkyl group was shifted from 705 to 646.17 cm^{-1}, the C-N stretch due to amine and amides acid was shifted from 1034 to 1030.02 cm^{-1}, the C≡C stretch due to triple bonded carbon was shifted from 2220 to 2353.23 cm^{-1}, the O-H stretch due to alcohol was shifted from 3900 to 3428.58 cm^{-1} while the C-H stretch due to ethane at 1366 was shifted to 2928.04 cm^{-1}. These shifts in frequencies of IR adsorption imply that there is interaction between Pb and the maize waste surfaces. On the other hand, the C-H stretch due to C-C bond, the -C≡N stretch due to carbon-amide triple bond were missing in the spectrum suggesting that these functional groups were used in the adsorption of Pb (II) ions [22].

Table 4: Peaks and intensity of IR absorption by maize waste

Peak (cm^{-1})	intensity	Assignment
705	19.88	C-X stretch
845	19.45	C-H"oop"
1034	22.31	C-N stretch
1366	21.88	C-H rock
2220	20.76	-C≡N stretch
2358	21.88	-C≡C- stretch
3388	23.67	N-H stretch
3900	20.56	OH stretch

Data obtained from the FTIR spectrum of maize waste after adsorption of copper ions are presented in Table 5. The results indicated that the C-N stretch in maize waste shifted from 1034 to 1400 cm^{-1}, C≡N stretch shifted from 2220 to 2166 cm^{-1}, -C≡C- stretch shifted from 2358 to 2357 cm^{-1}, NH stretch shifted from 3388 to 3325 cm^{-1} and OH stretch shifted from 3100 cm^{-1} to 3429 cm^{-1}. These shifts revealed that there was interaction between the adsorbent and the adsorbate. On the other hand, new bonds were formed (OH stretch at 2925 $cm^{-1}$and CN stretch at 1044 cm^{-1}) while C-X stretch were missing in the new spectrum. These bonds might have been used for bonding. Similarly, functional groups associated with maize waste after adsorption of zinc ion are recorded in Table 7. It is evident from the data that the C-X rock vibration at 705 cm^{-1} was shifted to 701cm^{-1}, the C-Hoop at 845 was shifted to 841 cm^{-1}, the C-N stretch at 1034 was shifted to 1038 cm^{-1}, the C-H rock at 1366 was shifted to 1385 cm^{-1}, the -C≡N stretch at 2220 was shifted to 2122 cm^{-1}, the -C≡C- shift at 2358 was shifted to 2354 cm^{-1} and the NH stretch at 3388 was shifted to 3383 cm^{-1}. These shifts are indication of interaction between the Zn(VI) ions and the maize waste while the appearance of a new bond (OH stretch at 2972 cm^{-1}) suggest that the adsorption appear via this bond.

Table 5: Peaks and intensity of IR absorption by maize waste after adsorption of Pb^{2+}

Peak (cm^{-1})	intensity	Assignment
646.17	20.529	C-X stretch
1030.02	19.502	C-N stretch
1428.34	19.842	C-C stretch
1641.48	19.989	-C=C stretch
2353.23	18.787	-C≡C- stretch
2928.04	18.377	C-H stretch
3428.58	16.259	OH stretch

Table 6: Peaks and intensity of IR absorption by maize waste after adsorption of Cu^{2+}

Peak (cm^{-1})	intensity	Assignment
1044.49	15.444	C-N stretch
1400.37	18.806	C-H rock
1624.12	18.317	-C=C- stretch
2166.13	24.729	C≡N stretch
2357.09	23.859	-C≡C-
2925.15	18.599	OH stretch
3325.39	14.692	N-H stretch
3419.9	14.759	OH stretch

Table 7: Peaks and intensity of IR absorption by maize waste after adsorption of Zn^{2+}

Peak (cm^{-1})	intensity	Assignment
700.18	21.291	C-X stretch
840.99	20.455	C-H"oop"
1038.7	16.504	C-N stretch
1385.9	13.763	C-H rock
2121.77	26.619	-C≡N stretch
2354.2	25.309	-C≡C-
2927.08	18.743	OH stretch
3383.26	11.157	N-H stretch

Conclusions

Maize waste (cob) is an effective adsorbent that is suitable for the removal of lead, copper and zinc ions from aqueous solution. The adsorption capacity of the adsorbent depends on the charge to mass ratio of the ion, the period of contact, adsorbent doze and on the initial metal ion concentration. The adsorption of lead, copper and zinc ions unto maize waste favours the pseudo first order kinetic model better the pseudo second order kinetic model. Its adsorption characteristic is consistent with the Freundlich and Temkin adsorption models and supports the mechanism of physical adsorption.

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