

Equilibrium isotherm studies for the biosorption of Cu (II) and Zn (II) from aqueous solution by unmodified lignocellulosic fibrous layer of palm tree trunk- Single component system.

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ABSTRACT: The unmodified lignocellulosic fibrous layer of palm tree trunk (ULFPT), an agricultural waste residue from oilpalm/palmwine was investigated to ascertain its suitability as a low cost adsorbent for Cu and Zn removal from aqueous solutions. Batch biosorption technique was used to investigate the effect of pH, initial metal ion concentration and contact time. The experimental data were analysed using Langmuir, freundlich, redlich-peterson and tempkin isotherm models. The Redlich- Peterson model gave the best fit for Cu and Zn biosorption with regression values $R^2 > 0.9$ respectively. The Langmuir model also gave a good fit for the experimental data. The percentage removal of Cu and Zn ions decreased with increase in the concentration of metal ions and increased with increase in contact time up to a certain point. Cu (II) removal was highest at pH 5.0(81%) while that of Zn(II) was at pH 6.0(79%). The FT-IR study revealed the involvement of functional groups with lone pairs of electrons for binding with metal ions. The success rate is quite low when compared with other low-cost adsorbents available but ULFPT can still be successfully applied for meeting the condition suggested by most isotherm models applied.

KEYWORDS: *Unmodified lignocellulosic fibrous layer of palm tree trunk (ULFPT), isotherm model, Cu (II), Zn(II), pH.*

I. INTRODUCTION

Technology has brought increased challenges to the environment. With the advent of industrialization, environmental pollution by toxic substances increased. The problems associated with the presence of these metals in industrial effluents discharged are enormous, due to their toxicity and carcinogenic properties [1]-[4]. Copper is a micro nutrient but at elevated level (over 1.0mg/l in drinking water) can cause anemia, stomach and intestinal disorders, kidney and liver damage [5]-[6]. Zinc, like copper is a micronutrient but at elevated level can cause damage to pancreas, arteriosclerosis and upset of protein metabolism. Consequently, there arises a need to reduce the concentrations of copper and zinc to permissible limits in water/wastewater. Much works and advance development of technologies have been directed towards the remediation and removal of heavy metals from aqueous media as a result of increased concern by environmentalist and governments on effects of heavy metals and in attempt to protect public health [7]. Conventional methods for metal ions removal from industrial effluents include chemical precipitation, coagulation, solvent extraction, electrolytic processes, membrane separation, ion exchange, reverse osmosis, ultra-filtration, biological systems and adsorption[8]-[9]. These techniques are usually expensive or ineffective especially when the concentrations of heavy metal ions are less than 10mg/l [10]. This has made researchers the world over to search for cheaper and more efficient alternatives. Adsorptions using agricultural by-products have been studied as potential inexpensive alternatives. Many examples are available in literature concerning the direct or activated use³ of these materials as adsorbents [11]. Most waste from oilpalm/palmwine processing is usually used as fuel to produce process steam and electricity in palm oil mills [6]. However, a large portion of it is either burnt in open air or dumped in areas adjacent to the mills, which creates environmental and disposal problems [12]. The use of waste to clean up waste is also achieved in this study. The equilibrium isotherm studies for the removal of Cu (II) and Zn (II) from aqueous solution by unmodified lignocellulosic fibrous layer of palm tree trunk(ULFPT)are reported. Four models of adsorption isotherms were evaluated and reported.

II. MATERIALS AND METHODS

2.1 Preparation of biosorbent material

Unmodified lignocellulosic fibrous layer of palm tree trunk (ULFPT). The biosorbent (ULFPT) used in this study was gotten from the Nigerian institute for Oil palm Research (NIFOR), Benin City, edo state, Nigeria. The dark lignin layer was removed to expose the inner dense network of stiff fibres as was previously reported [6]. After cutting and washing with de-ionized water, the sample was sundried and then oven dried at 90°C for seven days. The dried sample was pulverized and sieved using a 100µm sieve to obtain the biomass which was used for the study.

2.2 Preparation of Adsorbate.

Cu²⁺ and zn²⁺ solutions were prepared by dissolving a known quantity of analytical grade Copper Sulphate (CuSO₄.5H₂O) and Zinc Sulphate (ZnSO₄.7H₂O) from their stock solutions in distilled water respectively. The cold vapour AAS (Perkin Elmer, mercury analyzer, MAS 50) was used to determine the metal ions concentration. To get the required concentration and appropriate pH, a dropwise addition of 0.1M NaOH and 0.1M HNO₃ was done using a pH-meter.

III. BATCH EQUILIBRIUM STUDIES.

The study was conducted at the Ceramics research and production Department of Projects research and Development institute (PRODA), Enugu, Nigeria. A room temperature of 29°C was used for the biosorption studies. The Equilibrium adsorption studies were performed for different contact time (10-90 mins), sorbate dose (10-50 mg/l), and pH (1-7). Each study was performed by adding 1.0g of the processed dry sample to 10ml of the given concentrations of Cu and Zn respectively. The solutions were placed in glass flasks and gently agitated on an orbital shaker at 120rpm, 29°C, at given times. During each study, a parameter was varied while others were kept constant. At the end of a given contact time, the residual concentrations of Cu and Zn in the simulated waste water was measured by Atomic Adsorption Spectrophotometer (AAS) (Buck scientific model 210 VGP). Each sample was analyzed in triplicates. The mean values and standard deviations were recorded as given by AAS. Copper and Zinc uptake (q_e) were calculated respectively using equation (1) as shown below:

$$q_e = V (C_o - C_e) / m \quad (1)$$

The percentage removed was calculated using (2) below;

$$R (\%) = 100(C_o - C_e) / C_o \quad (2)$$

Where C_o and C_e is the initial and equilibrium metal ion concentrations in solution in mg/l respectively, q_e is the equilibrium adsorption capacity in mg/g, V is the volume of metal ion solution used in ml, m is mass of biomass in g.

IV. RESULTS AND DISCUSSION

4.1 FTIR Spectral Studies

The FTIR spectrum of the adsorbent is shown in fig 1.0 The spectrum was used to obtain information about the nature of the functional groups responsible for the biosorption of the metal ions on the binding sites of the ULFPT biomass [13]-[15]. The broad band observed around 3422.85cm⁻¹ is due to vibration of structural OH groups from the ULFPT. The peak at 1640.93 is in the region of C=C for conjugated alkenes (1644-1617). The peak can also be assigned to HOH deformation (δ_{H-O-H}) confirming the presence of water [16]. The peak at 2914.28cm⁻¹ is typical of aliphatic C-H stretch (2850-2920). The assignment of functional groups responsible for bands is as shown in table 1.

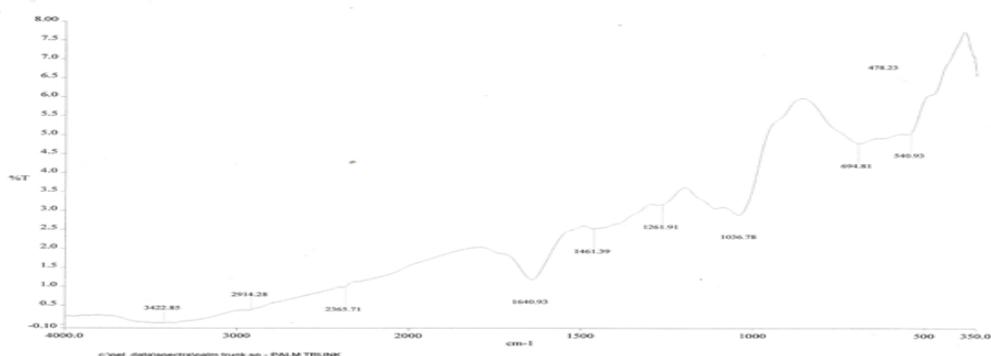


Figure 1: FT-Infrared Spectrum of ULFPT.

From the IR-spectrum, it can be said that the cell wall of the biomass possesses different surface structures and functional groups with lone pair of electrons that are available to bind to the positively divalent metal ions, the reaction involved being the biosorption of metal ion (represented as M^{2+}) and the adsorbent with lone pair of electrons (represented as X) from the liquid phase to the solid phase [15]. The reaction is also considered reversible with equilibrium made between the two phases shown below:

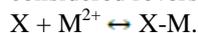


Table 1

Wave number(cm^{-1})	Functional groups
3500-3300 (Broad)	OH, NH- stretch
2920-2850	C-H stretch
2365.71	O-H, esters, aliphatic alcohols, carboxylic acids
1644-1617	C=C, conjugated alkenes, HOH deformation(δ_{H-O-H})
1461.39	C-H, -CH ₂ - bend
1300-1000	C-O, alcohols, ethers, esters, anhydrides, carboxylic acids.
1000-650	=C-H, alkenes (out of plane)

4.2 EFFECTS OF pH

The initial pH is reported to be one of the most critical parameters in the adsorption process which affects surface charge of the adsorbent material and the degree of ionization and specification of adsorbate [17]-[18]. Researchers have shown that different metals require different pH levels for their removal using specific adsorbents. The pH determines the net charge on the biomass and this invariably determines whether the metal ions can bind or not [15]. The effect of pH on the biosorption of Cu^{2+} and Zn^{2+} onto the biomass at pH 1-8 is shown in fig. 2.

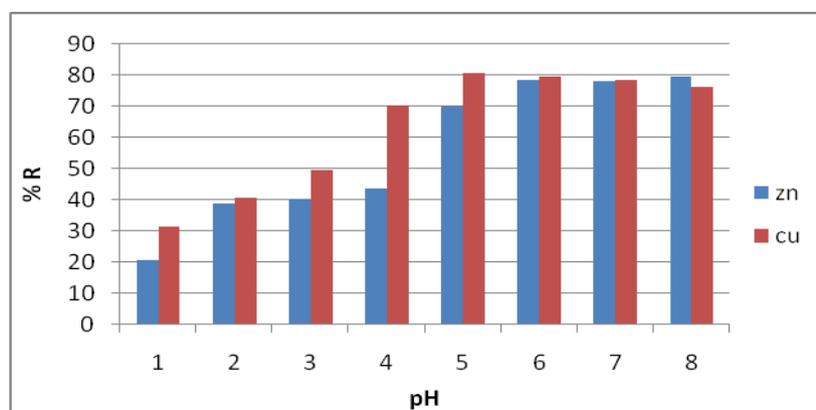


Figure 2: Effect of pH on Zn and cu

From fig. 2 above, the maximum pH for Cu adsorption was 5.0 representing 81% and with a slight reduction at pH 6 (79.70%). Hence, subsequent studies for Cu^{2+} were carried out at pH 5.0 as the optimum pH. For Zn, the % removal increased with increase in pH to 6.0, slight decrease at pH 7.0 and an increase at pH 8.0. Since metals tend to precipitate at high pH levels, it was suspected that the further increase in Zinc removal may have been a result of Zinc Precipitation. pH 6.0 was chosen as the optimum pH for Zn adsorption in further studies. Biosorption mechanism on the biomass surface is a reflection of the phytochemical interaction of the species in solution and the biosorptive sites of the sorbent [19]-[21] At high acidity, the low pH makes the active sites positive. Consequently, metal ions compete with H^+ ions for the available active sites present in the cell wall of the biomass. The result is the reduction in metal ions uptake by the sorbent [21]. Protonating the available active sites on the biomass cell wall also reduces the negatively charge sites required by the metal ions to bind. At low acidity of solution, the functional groups on the biomass surface are deprotonated, making the negative charge density on the cell wall of the biomass to increase. Consequently, competition between metal ions and H^+ ions is reduced leading to increase in biosorption. The increase in Zinc removal at high pH can also be attributed to the reduction of H^+ ions which compete with metal ions at lower pH [18], [22].

4.3 EFFECT OF INITIAL METAL IONS CONCENTRATION

The initial concentration of metal ions in solution determines the amount of metal ions biosorbed by the biomass in the presence of available active sites.

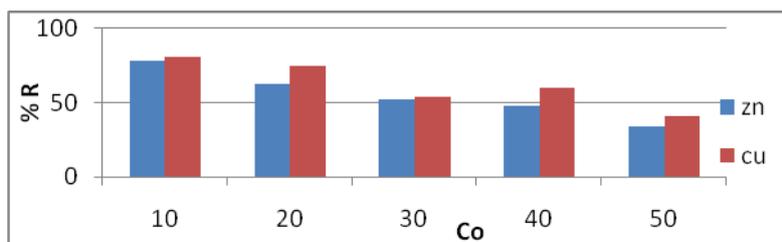


Figure 3.0: Effect of concentration of Zn and Cu on biosorption, expressed as percentage removed (% R)

As observed from fig 3.0 above, the percentage removal (%R) for Cu and Zn decreased with increase in initial Cu (II) and Zn (II) ions concentration. This is because at lower concentrations, almost all the ions are adsorbed due to availability of active sites, which becomes saturated at higher concentrations [10]

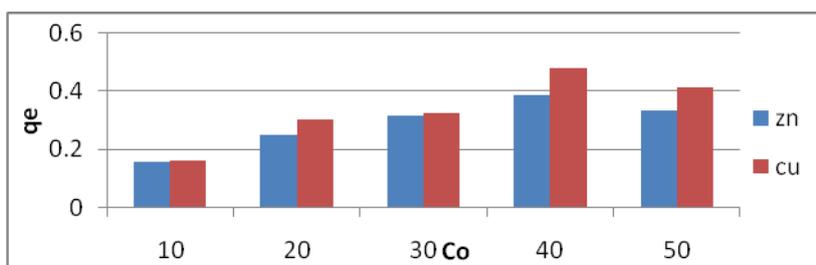


Figure 4.0: Effect of concentration plot for Zn and Cu biosorption, expressed as quantity adsorbed q_e (mg/g).

Fig 4.0 above shows an increase in uptake capacity with increase in the concentration of Cu and Zn. This is due to higher availability of metal ions for sorption [23]. The increase in metal ions concentration leads to increase in collision between the metal ions and the sorbent. The higher concentration results in higher driving force generated which makes utilization of active sites effective. The fall in metal uptake capacity with increasing metal ions concentration as seen in fig 4.0 above is observed when the equilibrium adsorption is exceeded, the metal ions in solution are more than the available active sites in the biomass surface.

4.4 ADSORPTION ISOTHERMS

Data obtained from equilibrium isotherms helps to understand adsorption mechanisms and in developing mathematical models that could be used for the quantitative description of the results. The Langmuir, Freundlich, Temkin, and Redlich-peterson isotherms were tested in this study. Linear regression is often used to determine the best-fitting isotherm, the applicability of the isotherm equation compared by judging the correlation coefficients.

Table 2.0

isotherms	constants	C_0	Zn	Cu	
Langmuir	q_{max}		0.379	0.466	
	b		0.363	0.15	
	R^2		0.978	0.955	
	R_L	10		0.216	0.4
		20		0.12	0.25
		30		0.084	0.18
40			0.064	0.143	
50			0.052	0.12	
Freundlich	n		3.19	2.854	
	Kf		7.67	0.145	
	R2		0.906	0.828	
	$\Delta q(\%)$				
Temkin	A		0.924	0.944	
	B		220.25	315.33	
	R2		0.879	0.782	
	$\Delta q(\%)$				
Redlich-Peterson	Kr		0.1	0.1	
	a_r		0.172	0.085	
	β		1.123	1.276	
	R^2		0.987	0.981	
Scatchard plot	q_{max}		0.407	0.540	
	b		0.263	0.202	
	r^2		0.857	0.699	

4.4.1 Langmuir isotherm model:

The Langmuir isotherm model was used to describe sorption phenomena and suggest that uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules [18]. The linearized form of the Langmuir equation is given in equation (3) below.

$$C_e/q_e = c_e/q_{max} + 1/q_{max}b \dots \dots \dots (3)$$

Where q_e (mg/g) and c_e (mg/l) is amount of metal ion adsorbed per specific amount of adsorbent and equilibrium concentration respectively, q_{max} is the maximum adsorption capacity for a complete monolayer coverage. b is the Langmuir isotherm constant which expresses affinity between adsorbent and adsorbate. The Langmuir plot for copper and zinc are shown in fig 5 and fig 6 below respectively, from where the constants b and q_{max} is determined.

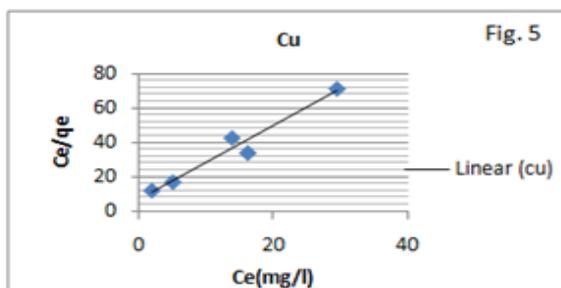


Figure 5: Langmuir isotherm model for the biosorption of Cu (II) by ULFPT (pH of 5.0, time 2hrs, 302°k)

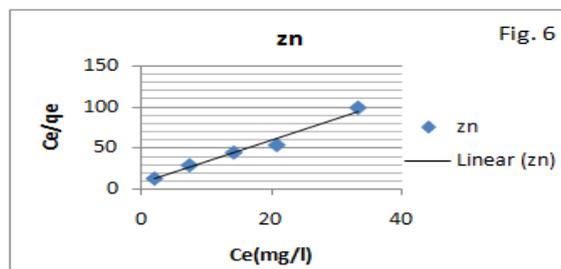


Figure 6: Langmuir isotherm plot for the biosorption of Zn (II) by ULFPT (pH of 6.0, time 2hrs, 302°k).

The values of the linear regression equation R^2 , q_{max} and b are shown in table 2.0 above. Since $0.9 < R^2 < 1.0$ for both Cu (II) and Zn (II), it means that the Langmuir isotherm provided a good fit for the experimental data. An important feature of the isotherm is expressed in terms of a dimensionless constant separation factor (R_L) defined by (4) [24].

$$R_L = 1 / (1 + bC_o) \dots \dots \dots (4)$$

R_L values indicate the type of isotherm to be either favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$) [25]. The R_L values for both copper and zinc biosorption at all initial concentrations lie between 0 and 1. This fulfils the condition $0 < R_L < 1$ needed for favourable adsorption. This suggest the applicability of the lignocellulosic fibrous layer of palm tree trunk as good absorbent for copper and zinc biosorption from waste water.

4.4.2. Freundlich isotherm

This isotherm assumes that the removal of metal ions occurs on a heterogenous surface, involving a multilayer adsorption of metal ions. It is often criticized for lacking a fundamental thermodynamic basis since it does not reduce to Henry’s law at low concentrations [4]. The linearized form of the isotherm is presented in (5).

$$\log q_e = \log K_F + 1/n \log C_e \dots \dots \dots (5)$$

Where K_F and n is freundlich constants, describing the adsorption capacity and intensity respectively. The freundlich parameters are shown in table 2 above. The plot from which these variables were obtained is as shown in fig 7 and 8. The K_F value was higher in Zinc than Copper. The magnitude of the exponent, n , gives an indication of the favourability and capacity of the adsorbent/adsorbate system [26]. n values between 1 and 10 represent favourable adsorption conditions [9]. From table 2 above, the exponent n for copper and Zinc was in the range $1 < n < 4$ and within the range of $1 < n < 10$ for favourable adsorption. The regression values R^2 where not

so close to unity except for zinc. This means that when compared with the Langmuir model, the freundlich model did not provide a good fit for the experimental data

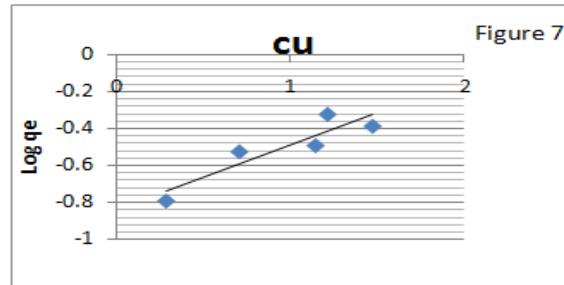


Figure 7: freundlich isotherm plot for the biosorption of Cu (II) by ULFPT (pH of 5.0,time 2hrs, 302^ok)

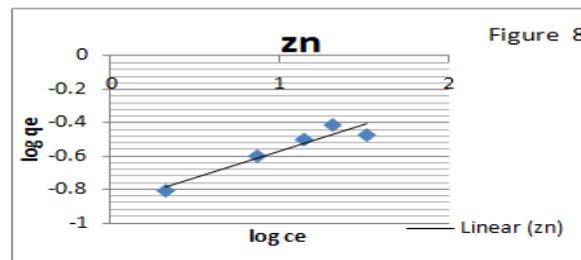


Figure 8: freundlich isotherm plot for the biosorption of Zn (II) by ULFPT (pH of 6.0,time 2hrs, 302^ok).
Figure

4.4.3. Temkin isotherm

This isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the freundlich equation [27]. It takes into account, the interaction between adsorbents and metal ions to be adsorbed. The linearized form of the equation is shown in (6).

$$q_e = B \ln A + B \ln C_e \quad (6)$$

Where B ($B=RT/b$) and A is temkin constant.

The temkin isotherm parameters are shown in table 2. The temkin isotherm plots for copper and zinc biosorption are also shown in fig 9 and 10 respectively. Zinc had a higher R^2 values than copper (see TABLE 2). The constants B which is related to the heat of adsorption was higher for copper than zinc. A (L/min), which is the equilibrium binding constant corresponding to the maximum binding energy was also higher for copper than zinc (table 2).

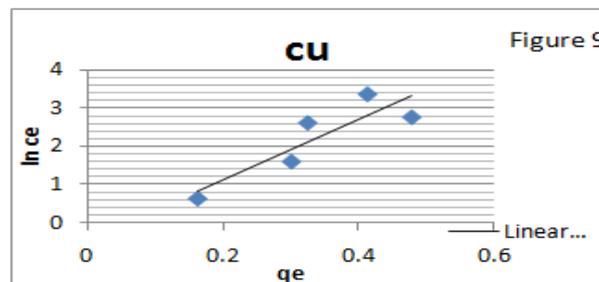


Figure 9: Temkin isotherm plot for the biosorption of Cu (II) by ULFPT (pH of 5.0, time 2hrs, 302^ok)

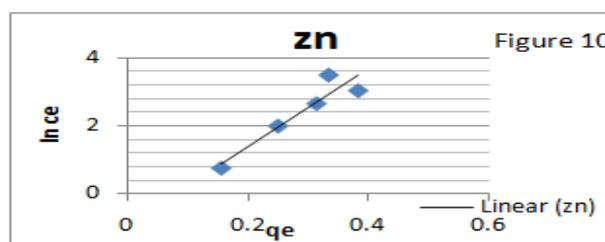


Figure 10: Temkin isotherm plot for the biosorption of Zn (II) by ULFPT (pH of 6.0, time 2hrs, 302^ok).

4.4.4. Redlich-peterson isotherm model.

This equation incorporates three parameters into an empirical isotherm and therefore can be applied either in homogenous or heterogenous systems due to its high versatility [28]. Incorporating the features of Langmuir and freundlich, at low concentrations, the isotherm approximates to Henry’s law and at high concentrations, it behaves like freundlich isotherm. The linearized form of the equation is shown below.

$$\ln ((K_R C_e/q_e)-1) = \ln a_R + \beta \ln C_e \quad (7)$$

The parameter K_R is varied to obtain the maximum value of the correlation coefficient for the regression of $\ln(K_R C_e/q_e - 1)$ versus $\ln C_e$. The values of the constants are shown in table 2. The R-P isotherm plots for copper and Zinc are also shown in fig 11 and 12 respectively.

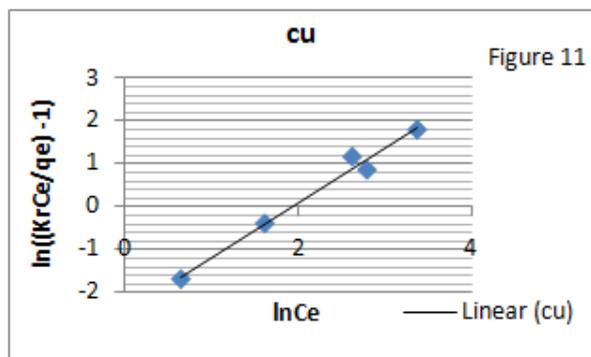


Figure 11: R-P plot for the biosorption of Cu (II) by ULFPT (pH of 5.0, time 2hrs, 302⁰k)

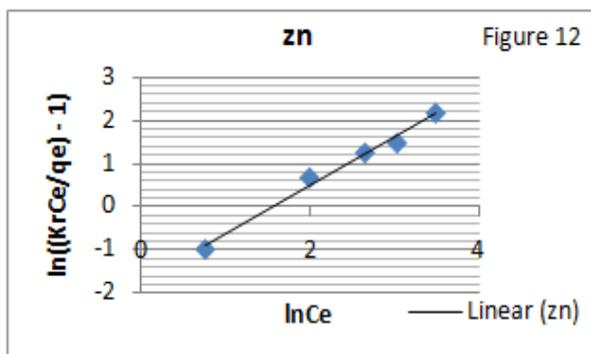


Figure 12: R-P plot for the biosorption of Zn (II) by ULFPT (pH of 6.0, time 2hrs, 302⁰k)

The highest value for the regression R^2 was obtained at K_r value of 0.1. The R^2 value for the biosorption unto ULFPT was higher for Zinc than copper, likewise the a_r value. The closeness of the R^2 values to unity shows that this model provided the best fit for the experimental data. Copper however had a higher β value than zinc.

4.4.5. Scatchard plot analysis

Also called the independent site-oriented model, gives more comprehensive information about the affinity of binding sites [16]. This analysis was applied to the experimental data and the expression is shown in (8).

$$q_e/c_e = q_{max}b - q_e b \quad (8)$$

a plot of q_e/c_e against q_e allows other constants (q_{max} and b) to be determined. The shape of the plot relates the adsorbate/adsorbent interaction. If the plot of q_e/c_e against c_e gives a straight line, then only one type of binding site is present in the adsorbent but if the plot shows deviation from linearity, the adsorbent presents more than one type of binding sites [30]. The scatchard plot constants are shown in table 2. The scatchard plots for copper and zinc are also shown in fig 13 and 14 respectively.

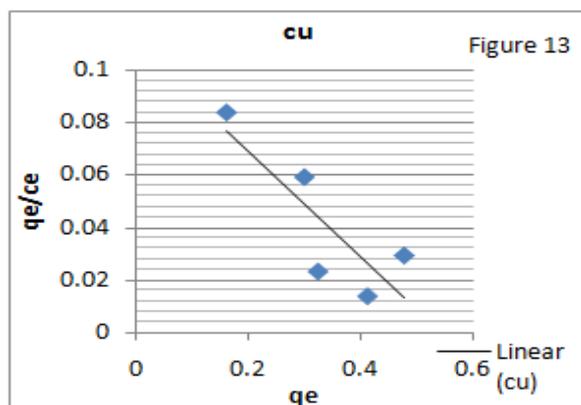


Figure 13: Scatchard plot for the biosorption of Cu (II) by ULFPPT (pH of 5.0, time 2hrs, 302^ok)

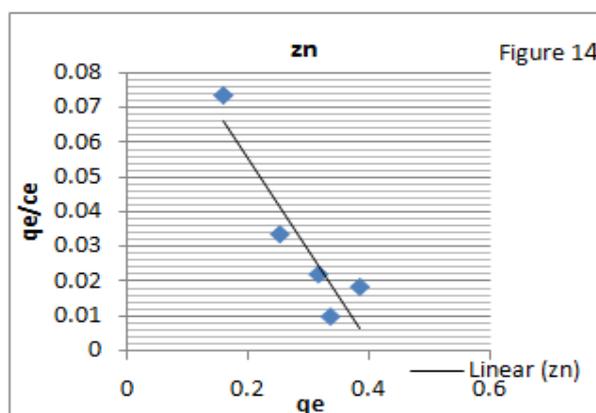


Figure 14: Scatchard plot for the biosorption of Zn (II) by ULFPPT (pH of 6.0, time 2hrs, 302^ok)

From table 2, the calculated values of b and q_{max} from Langmuir isotherm were close to those calculated from the scatchard analysis and this corresponds to the low affinity binding sites ($R^2 < 1.0$). It can then be assumed that the biosorption of copper and zinc by the adsorbate is mainly attributed to low affinity binding sites. The plots show deviation from linearity (see fig 13 and fig 14). It can also be assumed that the adsorbent presented more than one binding sites.

V. CONCLUSION

The study was carried out on unmodified ligno-cellulosic fibrous layer of palm tree trunk to see its potentials for removal of metal ions from simulated waste water using batch sorption techniques. The percentage removal of Cu and Zn ions decreased with increase in the concentration of the metal ions and increased with increase in contact time up to a certain level. Cu ion removal was highest at pH 5.0 while that of Zn was at pH 6.0

The non-linearity of scatchard plots in this study reveals different affinity binding sites of ULFPPT towards metal ions.

These results suggest that ULFPPT can be applied as a low-cost adsorbent for copper and zinc ions removal from waste water.

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