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Studies on the Effect pH on the Sorption of Pb(II) and Cu(II) ions from Aqueous Media by Nipa Palm (*Nypa fruticans Wurmb*)

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ABSTRACT: The effect of pH on the sorption of Pb^{2+} and Cu^{2+} ion onto Nypa f*ruticans Wurmb* biomass was investigated. Initial pH value of 2, 5, 7, 9, and 12 were used for this study with varying initial concentrations of metal ions. The experimental results were analyzed in terms of Langmuir, Freundlich and Flory-Huggins isotherms. The data showed that the maximum pH (pH_{max}) for the efficient sorption of Pb^{2+} and Cu^{2+} is 5.0. Evaluation using the Langmuir equation gave the monolayer sorption capacity as 91.0mg/g for Pb^{2+} and about 61.0mg/g for Cu^{2+}. The sorption of Pb^{2+} and Cu^{2+} ion is pH dependent and the data showed that Nypa *fruticans wurmb* biomass is a successful biosorbent for treating heavy metal contaminated wastewater. The thermodynamic assessment of the metal ions on Nypa *fruticans wurmb* gave negative ΔG^0 values, which confirms the feasibility of the process and the spontaneous nature of the sorption. @JASEM

The presence of toxic metals such as Pb^{2+} and Cu^{2+} in the environment has become a major threat to plants, animals and human life due to their bioaccumulating tendencies. It is an established fact that metals are also toxic to aquatic organisms, consequently, a number of projects objective for metal concentration in aquatic environment need to be proposed to protect the organisms. In light of the above, there has been an abundance of interest in removal of heavy metals from contaminated waste streams (Basta 1992, Godfredsen 1994, Horsfall et al 2004 and Jewel 1994).

The conventional methods in existence for the removal of metals from waste streams such as precipitation, flocculation, reverse osmosis, etc are expensive and not economically feasible for small and medium scale industries prevalent in developing countries (Cheng 1994). There is the need therefore to develop alternative methods of sorption of metals using natural plant products as adsorbents, which are inexpensive and always available. Some natural materials that have been used for similar study include clay (Vinod and Anirudhan, 2001), Cassava waste (Abia et al 2003) and Medicago Sativa- Alfalfa (Gardea- Torresday et al 1998). Presently no information is available on the use of Nypa Fruitcans wurmb biomass as a biosorbent for toxic metals from wastewater.
Nypa fruitcans wurmb commonly called Nipa Palm, considered one of the most common palms in South-East Asia and now ravaging the mangroves of the Niger Delta Area of Nigeria is a swamp specie, which belongs to the PALMAE FAMILY (Gonzales, 1979). Nypa fruitcans wurmb possess chemical functional groups that are most likely responsible for metal binding and are inexpensive, easily obtained and is presently a nuisance and colonizing the mangroves of the Niger Delta Region. It may be a potential bioresource for extraction and recovery of toxic metals from contaminated waters.

The principal aim of the present study is to investigate the effect of pH on the potential use of the biomass of *Nypa fruitcans wurmb* as novel biosorbent for toxic metals from aqueous media.

MATERIALS AND METHODS

Preparation and Activation of Biomass: The shoots of Nipa plant were obtained from the brackish waterfronts of the Niger Delta Area of Nigeria. The samples were cut into smaller sizes and washed with deionized water and then dried. Dried samples were ground and passed through the 100-mesh, screens using a Wiley mill.

Determination of Pb^{2+} and Cu^{2+} Sorption as a Function of pH: 1.0 $\pm$ 0.01g Nypa *fruticans* biomass was weighed into several flasks. Standard solutions of initial metal ion concentrations ranging from 2 to 10mg/l of Pb^{2+} and Cu^{2+} were prepared from stock solutions of $PbSO_4$ and $CuSO_4$ respectively. 50ml of the metal ion solutions in triplicate were added to the biomass. The pH of these suspensions were adjusted to 2.0, 5.0, 7.0, 9.0 12.0. The pH adjustments were made either by adding 2M HCl or 2M NaOH solution and the pH recorded as initial pH (pH_{in}). The flasks were tightly stopped and the mixtures gently agitated on a Stuart shaker for 1 hour at 30^0C. At the end of shaking, the pH of the suspension was measured and recorded as the final pH (pH_f) of each solution. The suspension was then filtered through Whatman No 45 filter paper and centrifuged at 2800 x g for 5 minutes. The metal content at each pH_f was determined using flame atomic absorption Spectroscopy.

Metal Content Analysis: The Pb^{2+} and Cu^{2+} content at each pH were determined with a Buck Scientific Flame Atomic Absorption Spectrometer (FAAS) model 300A. Analytical grade standards were used to calibrate the instrument, which was checked

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periodically throughout the analysis for instrument's response. The batch experiments were performed in triplicates and the averages were computed for each set of values.

Data Analysis: The amount of Pb^{2+} and Cu^{2+} sorbed by the biomass during the series of batch investigation were determined using a mass balance equation (Chu and Hashim, 2001) expressed as: $q_e = \frac{V}{M}(C_o - C_e)$ ……….1

Where q_e = metal concentration on the biomass (mg/g biomass) at equilibrium, C_e = metal concentration in solution (mg/dm^3) at equilibrium; C_o = initial metal concentration in solution (mg/dm^3); V = Volume of initial metal solution used (dm^3); M = mass of biomass used (g).
The sorption data was tested against Langmuir, Freundlich, and Flory Huggins adsorption isotherm models. The linear form of the Langmuir model as shown below was used.

$$\frac{C_e}{q_e} = \frac{1}{X_m k} + \frac{C_e}{X_m} \quad ……….2$$

where X_m (mg/g) is the maximum sorption upon complete saturation of the biomass surface and K (dm^{3}g^{-1}) is a constant related to the adsorption/desorption energy. The constants were obtained from the slope and intercepts of the plots of C_e/q_e against C_e.

Plotting In C_e against Inq_e using the linear equation (eq. 3) tested the Freundlich model:

$$\ln q_e = \ln K_f + \frac{1}{n}\ln C_e \quad ………. 3$$

Where: q_e = the adsorption density (mg/g): C_e = concentration of metal ion in solution at equilibrium (mg/dm^3); K_f and n are the Freundlich constants determined from the slope and intercept. The value of n indicates the affinity of the sorbent towards the biomass.

The Flory-Huggins model is represented by 4

$$\log\frac{\theta}{C} = \log Ka + n\log(1-\theta) \quad ……….4$$

Where θ is the degree of surface coverage, n is the number of metal ions occupying sorption sites, k_a is the equilibrium constant of adsorption and C is equilibrium metal ion concentration. A plot of log θ/^{c} against log (1 - θ) yielding a straight line was made to confirm the model.

The θ in 4 was calculated from the relation below:

$$\theta = 1 - \frac{C_e}{C_o} \quad ………. 5$$

The apparent Gibbs free energy of sorption ΔG^0, which is a fundamental criterion of spontaneity, was evaluated using the following equation: (eq. 6)

$$\Delta G^o = RT\ln C_a \quad ……….6$$

Where R is the universal gas constant, 8.314 J/molk and T is absolute temperature. Ca is obtained from the Flory-Huggins isotherms in equation 4.

RESULTS AND DISCUSSION

The effects of pH treatment on the Nypa *fruticans wurmb* biomass basic properties were determined to assess the extent of incorporation of surface charges on the biomass matrix and its resultant effect on the sorption of metal ions. The initial pH of the reaction mixture controls the efficiency of metal ion sorption by the biomass. Table 1 shows that as the initial metal ion concentration (C_o) increases, the resultant equilibrium final pH (pH_{fin}) decreases for all concentrations

The dependence of sorption of Pb^{2+} and Cu^{2+} onto Nypa fruitcans wurmb biomass on pH is shown in figures 1 and 2 respectively. Using up to 10.0mg/l initial metal ion concentration, the data revealed that at pH 2, no significant sorption of both Pb^{2+} and Cu^{2+} was observed. Less than 20.0% of the metal ions were sorbed by the biomass.

Table 1: Mean equilibrum pH (pH_{fin}) at various initial metal ion concentration (C_0mg/l)

Initial	Final pH (pH_{fin})									
pH	Pb^{2+}					Cu^{2+}				
	2mg/l	4mg/l	6mg/l	8mg/l	10mg/l	2mg/l	4mg/l	6mg/l	8mg/l	10mg/l
2	1.96	1.94	1.94	1.90	1.86	1.92	1.80	1.79	1.75	1.73
5	3.45	3.42	3.40	3.35	3.20	3.65	3.61	3.56	3.39	3.20
7	5.99	5.97	5.98	5.80	5.77	5.96	5.89	5.87	5.80	5.72
9	7.36	7.85	7.75	7.72	7.58	7.54	7.52	7.49	7.45	7.42
12	10.53	10.50	10.45	10.41	10.37	10.90	10.83	10.81	10.77	10.73

As the pH increased to 5, the sorption of Pb^{2+} and Cu^{2+} also increased to about 50%. There was a slight differential in the metal ion removal as the pH increased beyond 5. The sharpest increase in removal efficiency with pH_{in} was noticed as the pH_{in} was raised from 7 to 12. This trend in pH –

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dependence suggests that the removal of both metal ions is favoured by high pH values and metal ions bound to the Nypa *frutican* biomass could be desorbed and the spent biomass regenerated.

This binding behaviour suggests that to some extent carboxyl groups (-COOH) may be responsible for the binding of Pb^{2+} and Cu^{2+}, since ionization constants for a number of carboxyl groups range between 4 and 5. At lower pH carboxyl groups retain their protons reducing the probability of binding to any positively charged ions. Whereas at higher pH, the carboxylate ($-OO^-$) ligands attract the positively charged Pb^{2+} and Cu^{2+} and binding occurs, indicating that the binding process is an ion-exchange mechanism. According to Low et al (1995), at low pH value the surface of the adsorbent, would be closely associated with hydronium ions (H_3O^+) which hinder the access of the metal ions to the surface functional group. Consequently the percentage of metal ion removal may decrease at low pH.

SORPTION EQUILIBRIUM

Isotherm models were used to evaluate the sorption processes. The equilibrium sorption data obtained were analyzed in terms of the Langmuir, Freudlich and Flory-Huggins equation as explained in the data analysis. Figures 3 and 4 are the data linearised to fit the Langmuir equation and Table 3 represents the constants derived by regression analysis for the equation.

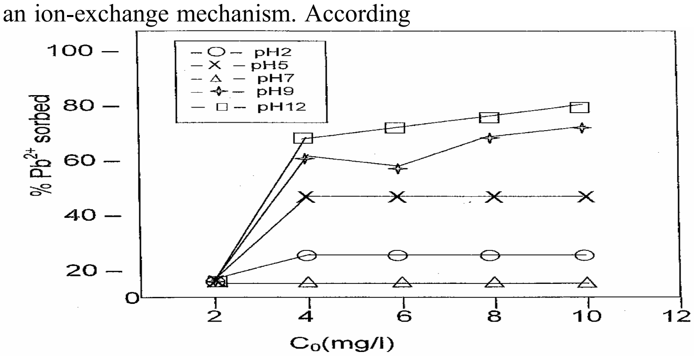

Fig. 1. Effect of initial pH (pH_{in}) on the sorption of Pb^{2+} ions by Nypa *fruticans* biomass

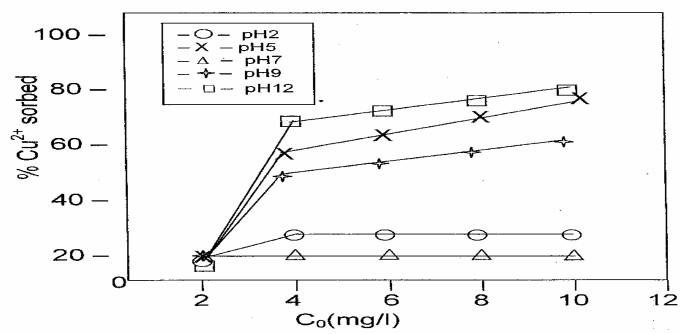

Fig. 2. Effect of initial pH (pH_{in}) on the sorption of Cu^{2+} ions by Nypa *fruticans* biomass

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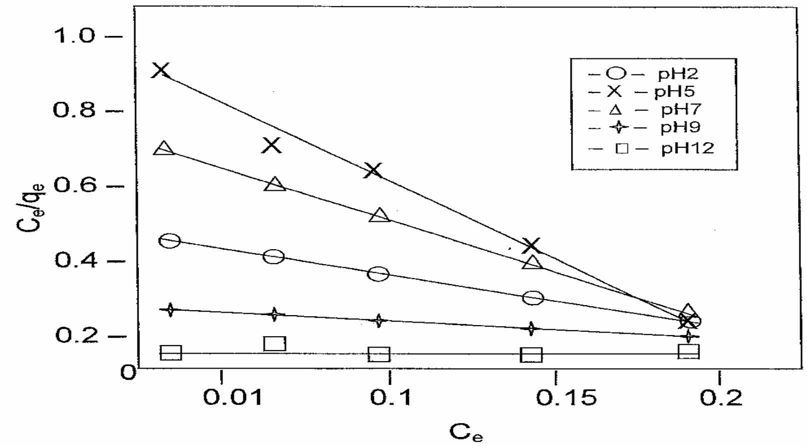

Fig. 3. Langmuir isotherm plot for the sorption of Pb^{2+} ions on Nypa *fruticans* biomass

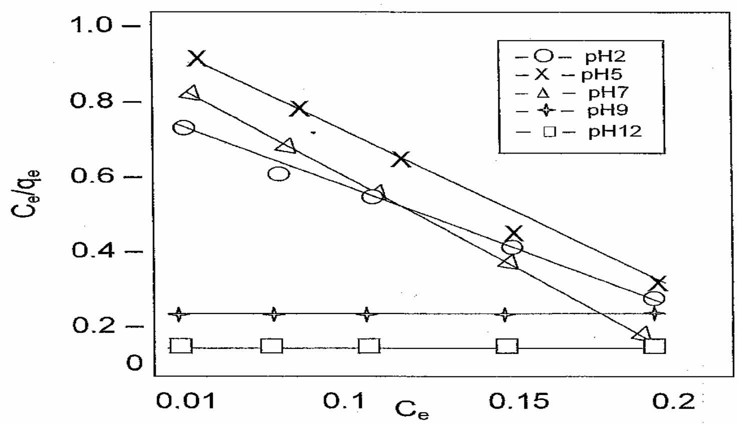

Fig. 4. Langmuir isotherm plot for the sorption of Cu^{2+} ions on Nypa *fruticans* biomass

Table 3: Langmuir isotherm parameters

pH	Pb^{2+}			Cu^{2+}		
	q_{max} (mg/g)	K1(l/g)	R^2	q_{max} (mg/g)	K1(l/g)	R^2
2	50.5	0.091	0.752	3.00	0.084	0.877
5	57.90	8.79	0.972	45.8	3.05	0.971
7	89.72	16.00	0.991	58.3	1.89	0.934
9	90.73	15.59	0.984	60.47	1.81	0.957
12	93.41	15.11	0.990	61.03	1.79	0.973

A comparison of the Langmuir monolayer sorption capacity at various initial pH was made by plotting q_{max} (mg/g) against pH_{in} as shown in figure 5. The results confirmed that at pH 2 and 3, the sorption of Pb^{2+} and Cu^{2+} on Nypa *frutican* biomass was less than at pH 4 and above, indicating that the biomass is a less effective sorbent at low pH values. Hence, lowering the pH may aid the regeneration and recycling of spent biomass. The R^2 values suggested that the Langmuir isotherms provides a good model of the sorption system. The sorption coefficient, KL, which is related to the apparent energy of sorption, was greater for Pb^{2+} than Cu^{2+} at all pH_{in}.

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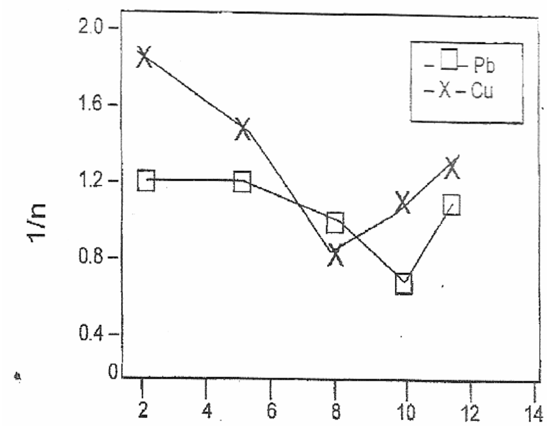

Fig. 6. Variation in the Freundlich sorption constant 1/n with initial pH

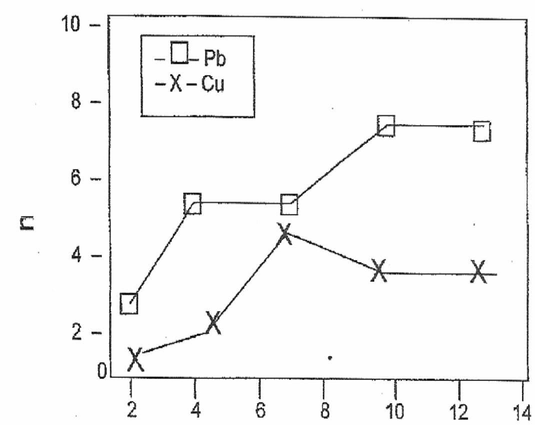

Fig 7. Variation in the Flory-Huggins sorption constant n with initial pH

The linear Freundlich isotherm plots for the sorption of the metal ions (Pb^{2+} and Cu^{2+}) onto the Nypa fruticans biomass are presented in Figures 8 and 9. The plots show that the Freundlich isotherm is also an appropriate model for the sorption study of Pb^{2+} and Cu^{2+}. Table 4 shows the linear Freundlich sorption isotherm constants and the coefficient of determination (R^2). Values of 1/n for Pb^{2+} and Cu^{2+} were found to be less than unity at initial pH of 5, 7, 9 and 12 indicating that significant sorption could take place at these initial pH values. Confirmation of the pH_{max} was made by plotting the Freundlich equation parameter 1/n, which is a measure of the coefficient of determinations (R^2) values as shown in Table 4, the sorption intensity against pH in [figure 6]. Based on the linear form of the Freundlich isotherm appears to produce a reasonable model for the sorption of the two metals. The K-values suggest that Pb^{2+} has a greater sorption tendency towards the biomass in neutral solution.

To account for the sorption surface behaviour of the metal ions on the biomass, the fraction of biomass surface covered by the metal ion was also studied at different pH values using the Flory-Huggins isotherm.

The plots of $0/C_0$ against log (1-0) were made as shown in Figures 10 and 11 and the regression lines were obtained. The data shows that Flory-Huggins adsorption is obeyed at higher pH. The Flory-Huggins model was chosen to estimate the degree of surface coverage on the biomass. The number of metal ions occupying sorption sites, n, was plotted against pH_{in} (Figure 7). The overall coverage process indicates that increase initial pH increases the surface coverage on the biomass until is nearly fully covered with a monomolecular layer at pH 5 and 7.

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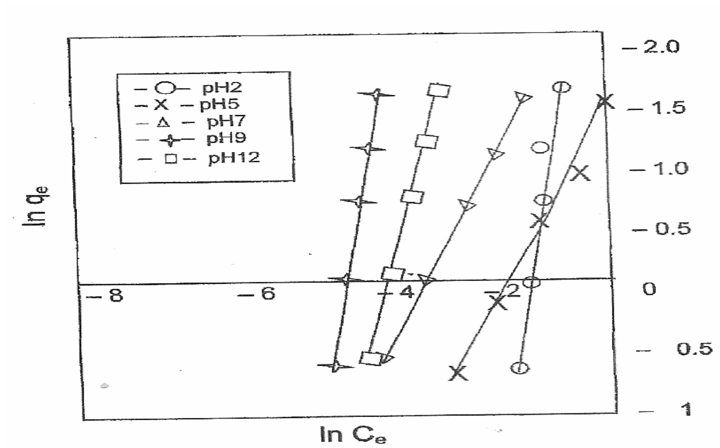

Fig. 8. Freundlich plot for the sorption of Pb^{2+} ions on Nypa *fruticans* biomass.

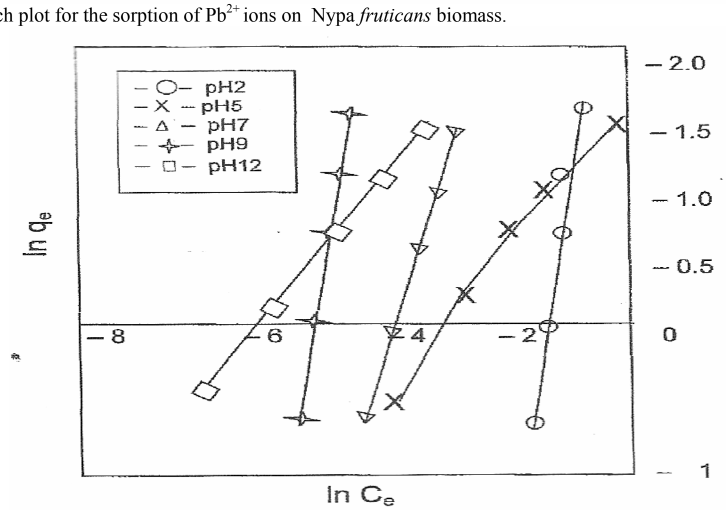

Fig. 9 Freundlich isotherm plot for the sorption of Cu^{2+} ions on Nypa *Fruticans* biomass

Table 4. Linear Freundlich isotherm parameters

pH	Pb^{2+}			Cu^{2+}		
	1/n	K_f	R^2	1/n	K_f	R^2
2	1.16	0.05	0.636	1.65	0.57	0.937
5	0.97	1.84	0.691	0.99	1.65	0.959
7	0.58	2.17	0.998	1.09	0.58	0.967
9	0.98	1.94	0.985	1.61	0.75	0.943
12	0.99	1.19	0.975	1.71	0.77	0.933

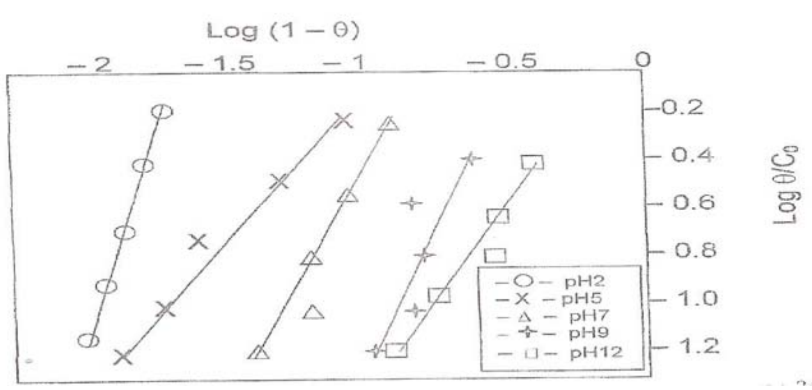

Fig. 10 Flory Huggins isotherm plot for the sorption of Pb^{2+} ions on Nypa *fruticans* biomass.

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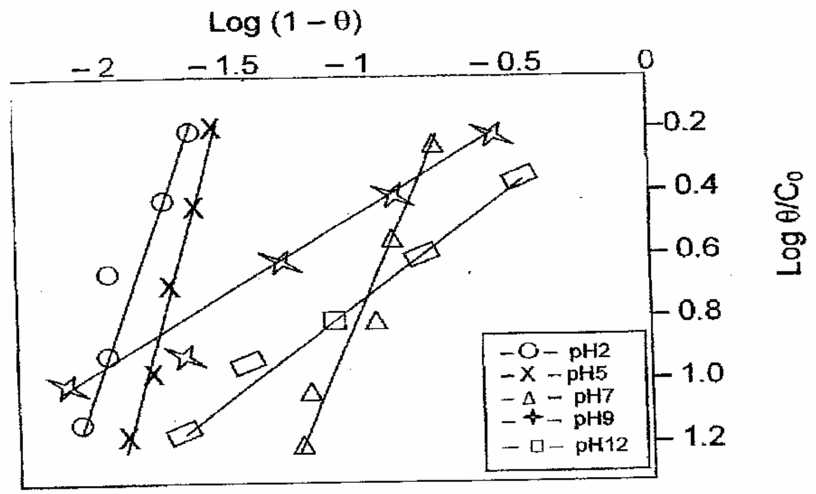

Fig 11. Flory-Huggins isotherm plot for the sorption of Cu^{2+} ions on Nypa *fruticans* biomass

Table 5. Flory-Huggins isotherm parameters for the Pb^{2+} and Cu^{2+} on Nypa biomass.

pH	Pb^{2+}		Cu^{2+}	
	K_a	ΔG^0(Kjmol^{-1}K^{-1})	K_a	ΔG^0(Kjmol^{-1}K^{-1})
2	0.733	-0.785	0.465	-0472
5	0.545	-1.518	0.582	-1.931
7	0.541	-1.539	0.551	-1.490
9	0.557	-1.496	0.654	-1.098
12	0.577	-1.501	0.690	-1.098

Furthermore, the equilibrium constant, k_a obtained from the Flory-Huggins isotherm was used to compute the apparent Gibbs free energy of change. The apparent Gibbs free energy of sorption. ΔG^0 is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG^0 is negative quantity. The negative values of ΔG^0 in Table 5 confirm the feasibility of the process and the spontaneous nature of the sorption.

Conclusion: The data from the results has revealed that the sorption process of Pb^{2+} and Cu^{2+} ions on to the Nypa *fruticans wurmb* biomass is feasible and spontaneous in nature. From the studies, the equilibrium data fitted the Langmuir, Freundlich and Flory-Huggins isotherm very well. The sorption of Pb^{2+} and Cu^{2+} ions is confirmed to be pH dependent. The data showed that Nypa *fruticans wurmb* biomass is a successful biosorbent for treating heavy metal contaminated wastewater and may serve as an alternative adsorbent to conventional means. This may provide an affordable technology for small and medium scale industries. This pH study gives indication of the possible regeneration of the biomass for reuse.

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