



Competitive modeling for the biosorptive removal of copper and lead ions from aqueous solution by *Mansonia* wood sawdust

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ABSTRACT

Mansonia wood sawdust is applied as a biosorbent for the removal of copper and lead ions from single and binary aqueous solution. The effect of solution pH, electrolyte, metal ion competition and temperature were examined to obtain insight of its application for industrial waste water treatment.

The Langmuir isotherm provided a better fit to experimental data for lead ion sorption with a higher monolayer capacity, while copper ion sorption was best described by the Freundlich and BET isotherms. The combined effect of adsorbing one metal ion in the presence of the other metal ion reduced the adsorption capacity of either metal ion.

In a binary solution, removal of lead ions in the presence of copper ions followed the Langmuir isotherm model while the removal of copper ions in presence of lead ions followed both the Langmuir and BET isotherm models.

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1. Introduction

The quest for cheap and cost effective technology for removal of heavy metals from industrial wastewaters loaded with heavy metal ions has led to the use of materials of biological origin as adsorbents. Biosorption, as this technique is called, is defined as the passive (not metabolically mediated) binding of metals by living or dead biomass. The most popular biosorbents encountered are microbial, bacterial fungal, or algal biomass and lignocellulosic materials (Ho and Ofomaja, 2005, 2006). These materials have been recognized as potential adsorbents for the removal of heavy metal ions from aqueous solution with the view to replacing existing technologies such as precipitation, ion exchange, solvent extraction and liquid membrane for the removal of heavy metal ions from industrial wastewater. This is because all these processes have the limitations in their technical and/or economical viability (Šćiban et al., 2007).

The use of non-living biological materials as biosorbent has been shown to have certain practical advantages over living organisms. For example, microbial growth is inhibited when the concen-

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trations of metal ions are too high or when significant amounts of metal ions are adsorbed by microorganisms (Darnall et al., 1986). Heavy metal ions are known to accumulate on dead cells and agricultural wastes to the same or a greater extent than living cells (Darnall et al., 1986). This is attributed to the changes which occur in the cell structure after cells are dry-killed affect biosorption (Nourbakhsh et al., 1994). Finally maintaining a living biomass during metal ion biosorption is difficult because it requires a continuous supply of nutrients and toxicity of metal towards microorganism may take place (Habib-ur-Rehman et al., 2006).

In living cells, biosorption mechanism could be explained by physical and/or chemical interactions between cell wall ligands and adsorbate by ion exchange, complexation, coordination and microprecipitation (Ofomaja and Ho, 2007). Passive transport mechanisms have been proposed for the diffusion of the metal ion from bulk solution to active sites of the biosorbent (Veglio and Beolchini, 1997), and functional groups such as phosphate, hydroxyl, amino and carboxyl existing on the surface of the adsorbent can bind metals.

Biosorption has been found to be influenced by the presence of other cations present in industrial wastewaters such as sodium and calcium which can produce three possible types of behaviour: synergism, antagonism and non-interaction (Šćiban et al., 2007; Han et al., 2006). It is also common knowledge that industrial waste waters consist of more than one metal ion, therefore, competition of the various metal ions for sorptions sites may occur during biosorption. Therefore, understanding the effect of these

interactions on the biosorption process for a particular biosorbent type under these conditions provides insight to its application for real wastewater treatment.

The potential sources of copper ion in industrial effluents include metal cleaning and plating baths, pulp, paper board mills, wood pulp production, and the fertilizer industry, etc. In wastewater from a copper wire mill, the average concentration of copper ions is about 800 mg/dm^3 (Panday et al., 1985). Lead ion is introduced into natural waters through various industrial activities such as those from the insecticide, storage battery, and metal plating/finishing industries. In industrial wastewaters, lead ion concentration is in the range of $200\text{--}500 \text{ mg/dm}^3$, these values are very high in relation to water quality standards, therefore copper and lead concentrations in wastewaters should be reduced (Ucun et al., 2003).

In Nigeria, about 19,000 ton of *Mansonia* wood is used both by the paper and furniture industry per annum. In this study, *Mansonia* wood sawdust, a readily available wood waste from the paper and furniture industry in West Africa, especially Nigeria, is applied as an adsorbent for the removal of copper and lead ions from aqueous solution of both single and binary metals. The effect of electrolyte (Na^+ and Ca^{2+}) on the metal uptake, metal competition for sites on the sawdust surface and temperature on the equilibrium of sorption was examined. Four isotherm models: Langmuir, Freundlich, Brunner Emmert Teller (BET) and Competitive Langmuir (two competing ions) were applied to describe the equilibrium of sorption in this study. A comparison of the linear regression (r^2) and chi-square (χ^2) analysis of the four forms of the isotherm models have been applied to the experimental sorption data from sorption of copper and lead ions on to *Mansonia* sawdust.

2. Methods

2.1. Materials

Mansonia sawdust used was obtained from a local sawmill in Benin City, Edo State of Nigeria. The sawdust was washed several times with distilled water to remove surface impurities, and this was followed by drying at 100°C for 24 h. The sawdust was ground and sieved. Sawdust particles used was that retained between the set of sieves: $150\text{--}400 \mu\text{m}$. The sieved sawdust was then stored in an airtight container.

Lead nitrate ($\text{Pb}(\text{NO}_3)_2$) and copper nitrate ($\text{Cu}(\text{NO}_3)_2$) salts were used in the preparation of the salt solutions. Stock solutions of 1000 mg/dm^3 were prepared by dissolving the accurately weighed amounts of $\text{Pb}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ in 1000 ml distilled water. Experimental solutions were prepared by diluting the stock solution with distilled water.

2.2. Methods

The proximate composition of *Mansonia* sawdust was determined using methods of the Association of Official Analytical Chemist (Association of Official Analytical Chemists, 1990). The IR spectra of the *Mansonia* sawdust sample was recorded using KBr disk in conjunction with a Perkin–Elmer infrared spectrophotometer.

2.2.1. Determination of active sites

Acidic and basic sites on sawdust were determined by the acid–base titration method proposed by Boehm (1994). The total acid sites matching the carboxylic, phenolic, and lactonic sites (Boehm, 1994) were neutralized using a 0.1 M NaOH solution while the basic sites were neutralized with a 0.1 M HCl solution. The lactonic and carboxylic sites were determined with a 0.05 M Na_2CO_3 solu-

tion and the carboxylic sites were determined with a 0.1 M NaHCO₃ solution. The phenolic sites were estimated by difference.

The acidic and basic sites were determined by adding 50 ml of 0.1 M titrating solution and 1 g of sawdust to a 50 ml volumetric flask. The flask was agitated at 25°C for 24 h. The flask was agitated manually twice a day. Afterward, a sample of 10 ml was titrated with 0.1 M HCl or NaOH solution.

2.3. Effect of solution pH on lead and copper biosorption

Accurately weighed amount (0.25 g) of *Mansonia* sawdust was added to five 250 ml beakers containing 100 ml of 120 mg/dm^3 of lead and copper ion solutions, each adjusted to pH of 2.0, 3.0, 4.0, 5.0, and 6.0 using either 0.1 M HCl or NaOH solutions. The solutions were stirred at 200 rpm for 4 h at 299 K. The mixtures were centrifuged and the clear supernatant liquids were analyzed for the residual concentrations of lead and copper ions by Atomic Absorption Spectrophotometer.

2.4. Equilibrium studies

Equilibrium experiments were carried out by contacting 0.2 g of *Mansonia* sawdust with 100 ml of metal ion solution of different initial concentrations ranging from 60 to 140 mg/dm^3 . A series of such conical flasks were agitated at 200 rpm and temperature was maintained at 299 K. Equilibrium concentrations of lead and copper ions were determined by Atomic Absorption Spectrophotometer.

2.5. Effect of electrolyte solution

The effect of electrolyte concentration on the amount of lead and copper ions biosorbed onto *Mansonia* sawdust from solution containing NaNO_3 and $\text{Ca}(\text{NO}_3)_2$ in the concentration range of $0.001\text{--}0.100 \text{ mol/dm}^3$ was studied at 299 K. Equilibrium concentrations of lead and copper ions were determined by Atomic Absorption Spectrophotometer.

2.6. Biosorption from binary metal solutions

This experiment was divided into two parts: (i) equilibrium studies as carried out above to examine the biosorption of lead ion at equilibrium (lead ion concentration ranging from 60 to 140 mg/dm^3) in the presence of 60 mg/dm^3 of copper ion in solution, and the biosorption of copper ion at equilibrium (copper ion concentration ranging from 60 to 140 mg/dm^3) in the presence of 60 mg/dm^3 of lead ions in solution (ii) a series of binary solution where the concentration of lead ion is fixed at 60 mg/dm^3 and concentration of copper ion is varied from 0 to 60 mg/dm^3 . In another binary system, the initial concentration of copper ion is fixed at 60 mg/dm^3 and the concentration of lead ion is varied from 0 to 60 mg/dm^3 . These binary solutions were agitated at 200 rpm for 4 h. Equilibrium concentrations of lead and copper ions in the various binary solutions were determined by Atomic Absorption Spectrophotometer.

2.7. Effect of temperature

This experiment was carried out by contacting 0.2 g of *Mansonia* sawdust with 100 ml of metal ion solution of different initial concentrations ranging from 60 to 140 mg/dm^3 at 299, 309, 319 and 329 K. The flasks were agitated 200 rpm for 4 h. Equilibrium concentrations of lead and copper ions were determined by Atomic Absorption Spectrophotometer.

3. Results and discussion

3.1. Properties of *Mansonia* sawdust

The physical properties of *Mansonia* wood sawdust are shown in Table 1. The high percentage of carbohydrate in *Mansonia* wood sawdust suggests that the main functional groups present in the adsorbent is the H–C=O and –OH. The wavelength at which the –OH group appears indicates that the sawdust is basic in nature. It is therefore possible that this –OH functional group is that of the phenolics in the adsorbent. The other functional groups present are proposed to be from the protein and lipid portions of the *Mansonia* sawdust adsorbent. The amount of various functional groups in the adsorbent (Table 1) suggests that the acid groups are more than the basic groups and are likely to be the sites for biosorption.

3.2. Effect of pH

Biosorbents usually contains organic functional groups such as alcohol, aldehydes, ketones, carboxylic, phenolic and ether groups on their surface. These groups have been shown to participate in cation binding due to their ability to ionize in aqueous solution (Kapoor et al., 1999; Ofomaja and Ho, 2007). The ability to form electrical charges on the biosorbent surface is dependent on solution pH. For pH values greater than the pK_a of most of these functional groups on biosorbent surfaces, the functional groups or sites are mainly in the dissociated form and can exchange H^+ with metal ions in solution. At pH values lower than the pK_a values of these groups, complexation phenomenon occurs, especially for carboxylic acid groups (Fourest and Volesky, 1996).

In the present investigation, the biosorption of lead and copper ions was studied at a pH range of 2–6. Solution pH greater than pH 6 was not examined in order to avoid metal ion precipitation. The effect of pH on the uptake of lead and copper ions from aqueous solution is shown in Fig. 1. At low solution pH, the amount of lead and copper ions biosorbed were quite low; 3.70 mg/g for copper ion and 8.40 mg/g for lead ion. The presence of positively charged sites on the biosorbent surface may also be responsible for the low metal ion uptake at low solution pH. As solution pH increased, the amount of both metal ions biosorbed increased; suggesting hydrogen ion competition with the metal ions for adsorption sites on the surface of the adsorbent. The increase in the amount of lead ion biosorbed with increasing solution pH was higher than that of cop-

Table 1
Physicochemical characteristics of *Mansonia* wood sawdust.

Characteristics	
Carbohydrate	71.00%
Protein	1.46%
Ash	5.88%
Fibre	6.15%
Lipid	0.49%
Moisture	15.0%
Total acid groups	0.1317 mmol/g
Carboxylic group	0.0298 mmol/g
Phenolic group	0.0482 mmol/g
Lactone group	0.0537 mmol/g
Basic groups	0.0881 mmol/g
pH_{PZC}	6.71
Functional groups	
C=O	(1682.1 cm^{-1})
COOH	(3300–2500, 1111.8 cm^{-1})
–OH	(3426.2 cm^{-1})
C–N	(1030–1237 cm^{-1})
NH ₂	(3400–3500 cm^{-1})

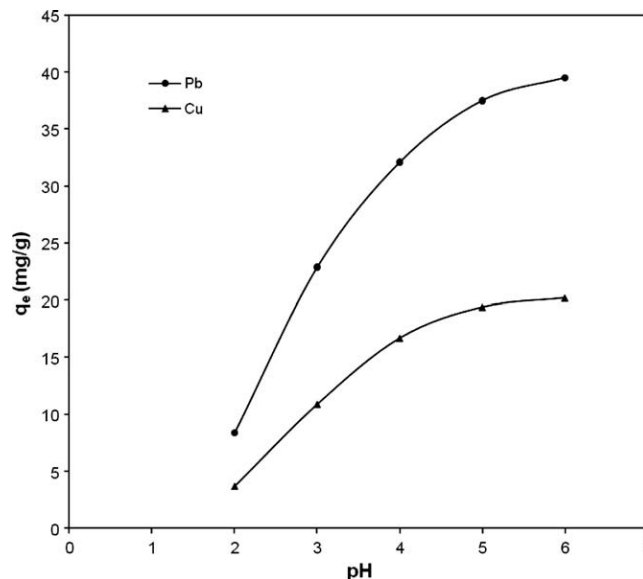


Fig. 1. Effect of solution pH on the uptake of copper and lead onto *Mansonia* sawdust (dose = 2.0; pH 6.0; agitation speed = 200 rpm; temp. = 299 K).

per ion. Between solution pH of 5.0 and 6.0, the rate of increase in metal ion uptake reduces for both lead and copper ions (lead ion 37.5–39.5 mg/g; copper ion 19.4–20.2 mg/g), therefore solution pH 6.0 was chosen for further studies.

3.3. Equilibrium studies

In order to optimize the design of biosorption systems for the removal of metal ions from solution, it is important to establish the most appropriate correlation for the equilibrium curve. Therefore, four isotherm models: the Langmuir, the Freundlich, the BET, and the Competitive Langmuir models were applied in the analyses of the equilibrium data.

3.3.1. Error analysis

The optimization procedure requires an error function to be defined in order to evaluate the fit of the equation to the experimental data. In this study, linear coefficient of determination and non-linear chi-square were examined. The coefficient of determination, r^2 , represents the percentage of variability in the dependent variable that has been explained by the regression line. The value of the coefficient of determination may vary from zero to one. A coefficient of determination of one indicates that 100% of the variation of q_e has been explained by the regression equation. The linear coefficient of determination, r^2 , found from evaluation of data by linear model, was calculated with aid of the equation:

$$r^2 = \frac{S_{xy}^2}{S_{xx}S_{yy}} \quad (1)$$

where S_{xx} is the sum of square of x

$$S_{xx} = \sum_{i=1}^n x_i^2 - \frac{\sum_{i=1}^n X_i}{n} \quad (2)$$

where S_{yy} is the sum of squares of Y

$$S_{yy} = \sum_{i=1}^n y_i^2 - \frac{\sum_{i=1}^n Y_i}{n} \quad (3)$$

where S_{xy} is the sum of squares of X and Y

$$S_{xy} = \sum_{i=1}^n X_i Y_i - \frac{(\sum_{i=1}^n X_i)(\sum_{i=1}^n Y_i)}{n} \quad (4)$$

The chi-square test statistic is basically the sum of the squares of the difference between the experimental data and data obtained by calculation using models, with each squared difference divided by the corresponding data obtained by calculating from models. The equivalent mathematical statement is:

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \quad (5)$$

where $q_{e,m}$ is the equilibrium adsorption capacity obtained by calculation from models (mol/g), q_e is the equilibrium adsorption capacity of experimental data (mol/g). If the data from the model are similar to the experimental data, χ^2 will be a small number and if they are different, χ^2 will be a bigger number. Therefore, it is necessary to also analyze the data set on the non-linear chi-square test to confirm the best isotherm for the adsorption system.

In order to assess the different isotherms and their ability to correlate with experimental results, the theoretical plots from each isotherm have been shown with the experimental data for biosorption of copper and lead ions onto *Mansonia* sawdust at the temperature of 299 K in Fig. 2a and b. The graph is plotted in the form of metal ions biosorbed per unit mass of *Mansonia* sawdust, q_e (mg/

g), against the concentration of metal ions remaining in solution, C_e (mg/dm³). A comparison of the coefficient of determination, r^2 , and the non-linear chi-square, χ^2 , of three isotherms for lead and copper ion biosorption onto *Mansonia* sawdust was made and listed in Table 2. It was observed that the Langmuir isotherm had the highest value for the coefficient of determination, r^2 , for both metal ions and from Fig. 2a and b it is obvious that the Langmuir isotherm model gives the best fit for the biosorption of the metal ions onto *Mansonia* sawdust. The chi-square analysis has also been determined to be best error fitting method for the biosorption of lead onto palm kernel fibre (Ho and Ofomaja, 2005) and cadmium onto coconut copra meal (Ho and Ofomaja, 2006).

At constant temperature, metal ions held onto the biosorbent will be in equilibrium with metal ions in bulk solution. The saturated monolayer isotherm can be represented as

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (6)$$

where C_e is the equilibrium concentration (mg/dm³); q_e is the amount of metal ion biosorbed (mg/g); q_m is q_e for a complete monolayer (mg/g); K_a is biosorption equilibrium constant (dm³/mg) (Ho et al., 2002).

The magnitude of Langmuir constant, K_a , is largely determined by the heat of biosorption. The higher magnitude of Langmuir constant, K_a , the higher heat of biosorption and the stronger the bond formed. The value of q_m (mg/g) is the monolayer capacity of the biosorbent for the metal ion. A good fit of the Langmuir model to the experimental data indicates the homogeneity of the active sites on the biosorbent surface. The Langmuir monolayer capacities of *Mansonia* sawdust for lead and copper ions were obtained as 51.81 and 42.37 mg/g, respectively. The Langmuir constant, K_a , of *Mansonia* sawdust for lead and copper ions were 0.1852 and 0.0196 dm³/mg, respectively. Therefore, the adsorptive ability of *Mansonia* sawdust biosorbent to hold lead ions is larger than for copper ions. Table 3 shows the comparison of the monolayer capacities of lead and copper from this study with results obtained by other authors using sawdust from different sources for lead and copper ion biosorption. The results reveal that *Mansonia* sawdust has a good potential for lead and copper ion removal from waste water.

The Freundlich isotherm constants, $1/n$ and K_F , were calculated for lead and copper ion biosorption according to Eq. (7):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

The Freundlich constant K_F indicate the biosorption capacity of the biosorbent while Freundlich constant n is a measure of the deviation from linearity of the biosorption or the biosorption affinity of the adsorbent for the adsorbate. The values of $1/n$ for copper ions (0.5457) and lead ions (0.2518) biosorption on to *Mansonia* sawdust were between $0.1 < 1/n < 1$, indicating that copper and lead ion biosorption onto *Mansonia* sawdust is favorable at 299 K. The value of K_F for the biosorption of lead ions (18.7234 mg/g) was also found to be higher than for copper ions (2.4706 mg/g). The value K_F is indicative of the biosorption capac-

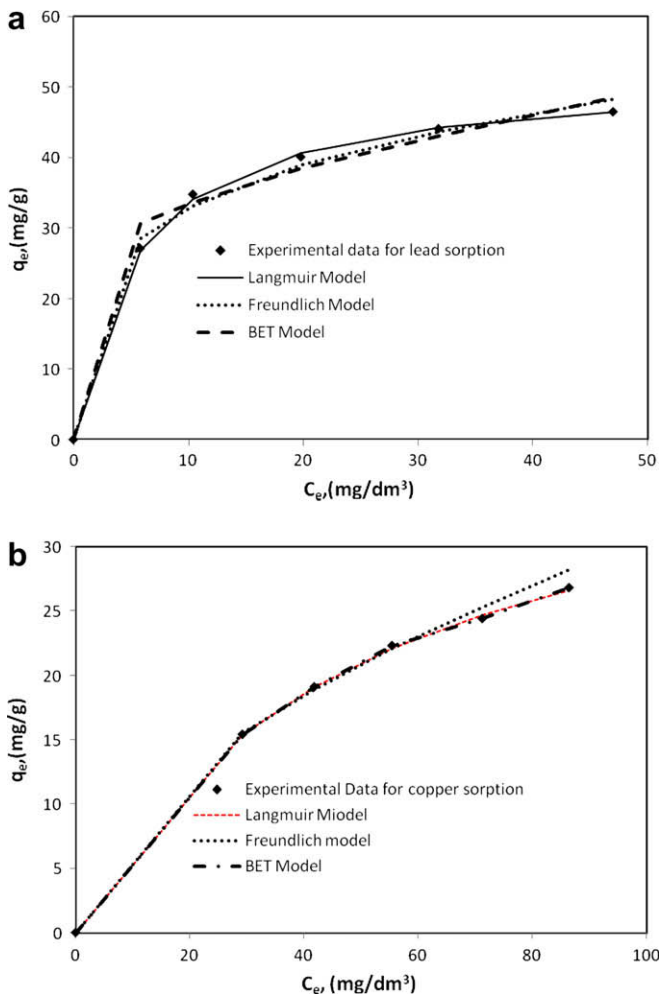


Fig. 2. Isotherm plots of experimental data and three isotherm models for lead and copper sorption onto *Mansonia* sawdust (dose = 2.0; pH 6.0; agitation speed = 200 rpm; temp. = 299 K). (a) Lead sorption on to *Mansonia* sawdust. (b) Copper sorption onto *Mansonia* sawdust.

Table 2

A comparison of chi-square, χ^2 , and coefficient of determination, r^2 , for three isotherm models in the biosorption of lead and copper ions by *Mansonia* wood sawdust.

Metal	Langmuir		Freundlich		BET	
	χ^2	r^2	χ^2	r^2	χ^2	r^2
Pb	0.0050	0.9998	0.0503	0.9585	0.1074	0.9830
Cu	0.0056	0.9992	0.0260	0.9975	0.0059	0.9930

Table 3
Comparison of monolayer capacities of sawdust materials for lead and copper ions.

Metal	Sawdust source	q_m (mg/g)	Reference
Lead	Meranti	34.25	Rafatullah et al. (2009)
	Acacia Arabica	52.38	Meena et al. (2008)
	Poplar	21.05	Li et al. (2007)
	Walnut	6.54	Yasemin and Zek (2007)
	Pinus sylvestris	9.71	Taty-Costodes et al. (2003)
	Mansonia	51.81	This study
Copper	Meranti	32.05	Rafatullah et al. (2009)
	Acacia Arabica	5.64	Meena et al. (2008)
	Poplar	6.59	Li et al. (2007)
	Maple	9.19	Rahmana and Islam (2009)
	Linden	9.90	Bozic et al. (2009)
	Mansonia	42.37	This study

ity, and this result further reveals the higher adsorptive capacity shown by Mansonia sawdust for lead ions than for copper ions (Aksu, 2002; Han et al., 2006).

The BET (Brunauer et al., 1938) isotherm constants, K_B and q_m , were calculated for lead and copper ion sorption according to Eq. (8):

$$\frac{C_e}{(C_s - C_e)q} = \frac{1}{K_B q_m} + \left(\frac{K_B - 1}{K_B q_m} \right) \left(\frac{C_e}{C_s} \right) \quad (8)$$

where C_e is the concentration of solute remaining in solution equilibrium (mg/dm^3), C_s the saturation concentration of solute (mg/dm^3), q the amount of solute adsorbed per unit weight of adsorbent (mg/g), q_m the amount of solute adsorbed per unit weight of adsorbent in forming a complete monolayer on the surface (mg/g) and K_B is the constant expressive of energy of interaction with the surface. A plot of $C_e/(C_s - C_e)q$ against (C_e/C_s) should give a straight line and from the slope and intercept the values of K_B and q_m can be calculated.

The BET model is an extension of the Langmuir model for multilayer biosorption. It is based on the assumption that each adsorbate in the first biosorbed layer serves as biosorption site for the second layer and so on. The values of K_B for copper and lead ion biosorption onto Mansonia sawdust were 8.27 and 43.65 dm^3/mg , respectively, and the q_m values were 10.99 and 33.65 mg/g , respectively, indicating a higher capacity of lead ions by Mansonia sawdust than copper ions.

From the results obtained, it is evident that lead biosorption onto Mansonia sawdust biosorbent is a monolayer coverage of the sawdust surface by lead ions. The Langmuir isotherm was best fitted to the experimental data while the fitting of the Freundlich isotherm which represents a multilayer biosorption and the BET isotherm which is an extension of the Langmuir isotherm multilayer sorption were not as good as the Langmuir model for lead ion biosorption. For copper biosorption, the Langmuir and BET isotherm were both closely fitted to the experimental data as compared with the Freundlich isotherm model, indicating that copper biosorption is a multilayer biosorption in which each adsorbate in the first adsorbed layer serves as an biosorption site for the second layer and so on.

3.4. Effect of electrolyte

The effect of electrolyte on the equilibrium biosorption of copper and lead ions from aqueous solution onto Mansonia sawdust was studied and the Langmuir isotherm parameters are shown in Table 4. At equilibrium, the amount of copper and lead ions biosorbed onto Mansonia sawdust surface is dependent on the electrolyte concentration in solution. Na-electrolyte reduced the equilibrium capacity of copper ions by 5.97% at 0.001 mol/dm^3 concentration of the electrolyte and by 20.53% at 0.10 mol/dm^3

Table 4
Effect of electrolyte concentration on lead and copper ion biosorption onto Mansonia sawdust.

Parameters	NaNO ₃ (mol/dm ³)				Ca(NO ₃) ₂ (mol/dm ³)		
	0	0.001	0.010	0.100	0.001	0.010	0.100
<i>Lead</i>							
q_m (mg/g)	51.81	49.75	46.51	44.05	43.29	41.15	37.31
K_B (dm ³ /mg)	0.1852	0.1844	0.1084	0.1081	0.1373	0.1061	0.1014
r^2	0.9998	0.9995	0.9986	0.9983	0.9970	0.9996	0.9982
χ^2	0.0050	0.0060	0.0234	0.0119	0.0470	0.0047	0.0068
<i>Copper</i>							
q_m (mg/g)	42.37	39.84	36.90	33.67	37.31	35.21	32.79
K_B (dm ³ /mg)	0.0196	0.0177	0.0175	0.0165	0.0166	0.0155	0.0149
r^2	0.9980	0.9991	0.9998	0.9983	0.9983	0.9966	0.9999
χ^2	0.0056	0.0010	0.0003	0.0013	0.0105	0.0136	0.0080

concentration of the electrolyte. For lead ion, the percentage reduction were 3.98% and 15.0% in the presence of 0.001 and 0.10 mol/dm^3 concentrations of Na-electrolyte solution. The presence of Ca-electrolyte in aqueous solution had a stronger effect on the biosorption capacity of Mansonia sawdust for copper and lead ions. Ca-electrolyte reduced the biosorption capacity of Mansonia sawdust for copper ions by 11.9% in the presence of 0.001 mol/dm^3 of the electrolyte and by 22.6% in the presence of 0.10 mol/dm^3 of same electrolyte. For lead ions, biosorption capacity was reduced by 16.4% and 28.0% in the presence of 0.001 and 0.10 mol/dm^3 of Ca-electrolyte. Similar effects have been reported by other authors (Larous et al., 2005; Unuabonah et al., 2007; Han et al., 2006).

Several explanations have been proposed for this phenomenon. Some authors attribute this observation to changes in biosorbent-suspension pH effect on the diffuse double layer (Barrow and Ellis, 1986; Unuabonah et al., 2007). It is believed that increasing the electrolyte concentration of the solution causes a reduction in surface negative charge and reduces metal biosorption. Other authors believe that metal ions form outer-sphere complexes with the active sites, which do not favor the biosorption when the concentration of electrolyte (competing) ions in solution increases (Han et al., 2006). This may indicate that the interaction between the functional groups of the biosorbent and the metal cation is mainly ionic in nature. Again the effect of increasing the ionic strength on the activity coefficient of metal ions, limits their transfer to the solid surface (Corinne et al., 2000; Han et al., 2006).

The stronger effect of the Ca-electrolyte over the Na-electrolyte in the reduction of metal ion biosorption capacity of Mansonia sawdust is attributed to fact that Ca-electrolyte has a stronger ionic strength than the Na-electrolyte. As the concentration of Ca-electrolyte increased, the biosorption capacity decreased to an almost constant value, where further decrease became minimal. This may suggest that ion exchange mechanism may not be the only mechanism of solute uptake by Mansonia sawdust, other biosorption mechanisms such as complexation may be involved in the metal removal.

3.5. Effect of binary metal ion solution

Table 5 shows the amount of metal ion uptake, percentage of metal ion biosorbed and percentage total metal ion biosorbed in single and binary metal ion biosorption of copper and lead ions on to Mansonia sawdust. It will be observed that increasing the initial concentration of metal ions (copper and lead ions), from 40 to 140 mg/dm^3 increased the amount of copper ions biosorbed from 15.4 to 26.8 mg/g and 27.1 to 46.5 mg/g for lead ions. However, percentage metal ion biosorbed was reduced from 51.3% to 38.1% for copper ions and from 90.3% to 66.8% for lead ions. It is possible

Table 5
Effect of competitive biosorption of lead and copper ions onto *Mansonia* sawdust at different metal ion concentrations.

Pb conc. (mg/dm ³)	q _e (Pb) (mg/g)	% Adsorbed	Initial Cu conc. (mg/dm ³)	Total amount adsorbed (%)
60	27.1	90.3	0.0	90.3
80	34.8	87.0	0.0	87.0
100	40.1	80.2	0.0	73.5
120	44.1	73.5	0.0	66.8
140	46.5	66.8	0.0	51.0
0	0.0	0.0	60.0	61.5
60	25.9	86.3	60.0	61.0
80	31.6	79.0	60.0	60.8
100	35.6	71.2	60.0	60.8
120	38.1	63.5	60.0	60.8
140	39.1	55.9	60.0	60.7
Cu conc. (mg/dm ³)	q _e (Cu) (mg/g)	% Adsorbed	Initial PB conc. (mg/dm ³)	Total amount adsorbed (%)
60	15.4	51.3	0.0	51.3
80	19.1	47.8	0.0	47.8
100	22.3	44.6	0.0	44.6
120	24.4	40.7	0.0	40.7
140	26.8	38.3	0.0	38.3
0	0.0	0.0	60.0	90.3
60	25.9	86.3	60.0	61.5
80	31.6	79.0	60.0	61.1
100	35.6	71.2	60.0	61.0
120	38.1	63.5	60.0	60.8
140	39.1	55.9	60.0	60.6

that the initial concentration of the metal ions provides the necessary driving force to overcome the resistances to mass transfer of copper and lead ions between the aqueous phases and the solid phase. The increase in the initial concentration also enhances the interaction between the metal ions in the aqueous phase and the sawdust surface. Therefore, an increase in the initial concentration of metal ions enhances the sorption uptake of copper and lead ions. Similar results were obtained by Han et al. (2006a) in the biosorption of copper and lead by waste beer yeast and Han et al (2006b) in the adsorption of copper and lead ions by manganese oxide coated sand.

The individual and total percentage uptake of lead ions on to *Mansonia* sawdust in the presence of copper ions and copper ion uptake in the presence of lead ions are shown in Table 5. It can be observed that the addition of 60 mg/dm³ of one metal to the increasing concentration (from 60 to 140 mg/dm³) of the other, also lead to a slight increase in the amount of metal ion biosorbed of the metal ion of increasing concentration. To analyze the biosorption interaction of both metal ions, the percentage of the single and binary component systems was compared. From Table 5, it is be expected that the percentage total copper ion biosorbed will be equal to 70.8% for a total metal concentration of 120 mg/dm³ containing equal concentrations (60 mg/dm³) of lead and copper ions. However, the total experimental percentage biosorbed was 61.5% for the total metal ions. Similar results have been obtained by Unuabonah et al. (2007) and Han et al. (2006a,b).

The isotherm data of the binary metal biosorption were modeled using the Langmuir, Freundlich, BET, and Competitive Langmuir isotherm models and the plots shown in Figs. 3a and b.

The competitive Langmuir model for two competing ions was applied in other to express the relationship between the quantity of the first component biosorbed and the concentration of the second component. The equation is written as

$$q_1 = \frac{q_m K_1 C_{e1}}{1 + K_1 C_{e1} + K_2 C_{e2}} \tag{9}$$

$$q_2 = \frac{q_m K_1 C_{e2}}{1 + K_1 C_{e1} + K_2 C_{e2}} \tag{10}$$

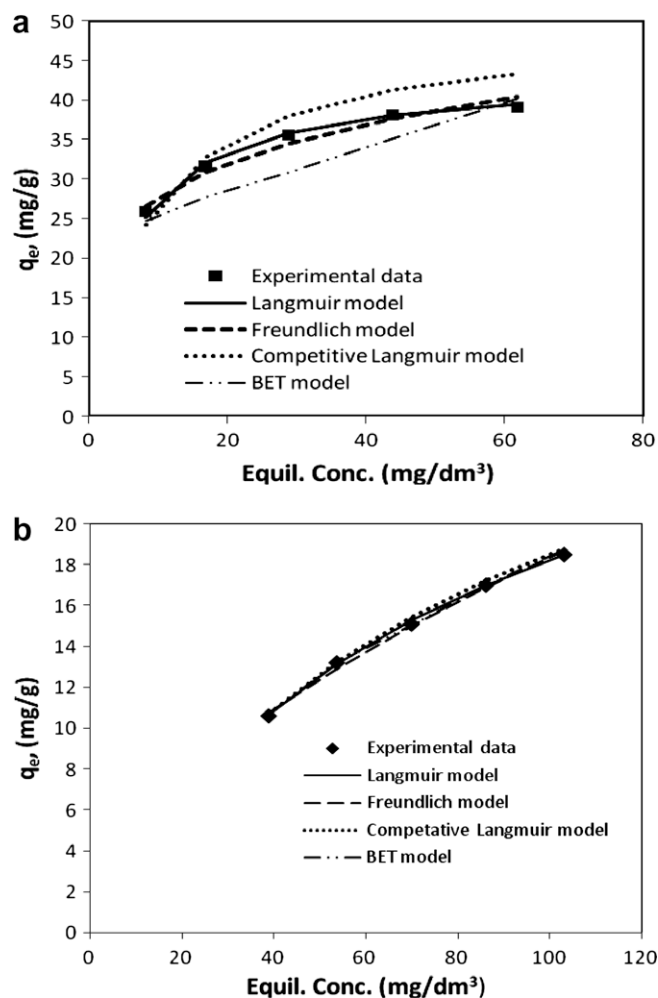


Fig. 3. Isotherm plots of experimental data and four isotherm models for (a) lead in the presence of copper and (b) copper sorption in the presence of lead onto *Mansonia* sawdust (dose = 2.0; pH 6.0; agitation speed = 200 rpm; temp. = 299 K).

where K_1 and K_2 are the individual Langmuir constants of the first and second metal ions (dm^3/mg), and q_{m1} and q_{m2} are the maximum amounts of the first and second heavy metal ions adsorbed (mg/g).

Fig. 3a shows the experimental data along with the isotherm models for the effect of lead ion biosorption in the presence of copper ion. A comparison between the coefficient of correlation, r^2 and the chi-square, χ^2 , error analysis was carried out (Table 6). Both error methods indicated that the Langmuir isotherm gave the best fit to the experimental data. According to the values of coefficient of correlation, r^2 , obtained, the Competitive Langmuir model should give a better fit to the experimental data than the BET and Freundlich model, but this was not so indicated by Fig. 3a. The trend in Fig. 3a was better described by the chi-square error analysis. Therefore, the biosorption of lead ion from a binary metal ion solution of lead and copper ions is best described by the Langmuir isotherm model, indicating that a monolayer of lead ions was formed over Mansonia sawdust particle surface. The comparison between the two methods of error analysis for the biosorption of copper ions in the presence of lead ions indicated that the Langmuir model was the best fitting model. According to the coefficient of correlation values, the Freundlich and BET isotherm should give better fitting than the competitive Langmuir model to the experimental data. The prediction of the chi-square error method showed that BET model had a smaller value than Freundlich and competitive Langmuir, which is similar to the trend in Fig. 3b. The results suggests that the biosorption of copper ions in the presence of lead ions will follow a multilayer biosorption in which the first biosorbed layer forms a biosorption site on which the next layer of ions are biosorbed. The closeness of the Competitive Langmuir model to the experimental data also suggests that metal ion competition for biosorption sites is high for the lead–copper system. It can also be concluded that the chi-square error analysis gives a better prediction of the closeness of the isotherm models to the experimental data.

The equilibrium data for binary biosorption of copper and lead ions may also be analyzed in the form of biosorption capacity of one metal ion in the presence of the other metal ion, Q^m , to the biosorption capacity for the same metal ion when it is present alone in the solution, Q^o , so that for:

$$\frac{Q^{\text{mix}}}{Q^o} > 1 \quad (11)$$

The biosorption is promoted by the presence of the other metal ion

$$\frac{Q^{\text{mix}}}{Q^o} = 1 \quad (12)$$

There is no observable net interaction

$$\frac{Q^{\text{mix}}}{Q^o} < 1 \quad (13)$$

Biosorption is suppressed by the presence of the other metal ion.

The values of Q^{mix}/Q^o for both copper ions (0.8676) and lead ions (0.8356) were found to be less than unity, suggesting that the simultaneous presence of both metal ions reduce biosorption

through competition for biosorption sites on Mansonia sawdust. This can be further confirmed by the ratio of $Q_{\text{Pb}}^o/Q_{\text{Cu}}^o$ (1.22) which is lower than the ratio $Q_{\text{Pb}}^{\text{mix}}/Q_{\text{Cu}}^{\text{mix}}$ (1.29). The ratio $Q_{\text{Pb}}^{\text{mix}}/Q_{\text{Pb}}^o > Q_{\text{Cu}}^{\text{mix}}/Q_{\text{Cu}}^o$ suggests that copper biosorption onto Mansonia sawdust is more affected by the simultaneous presence of a competing metal ion than for lead ions.

The parameter, K_a , of the Langmuir isotherm, describes the binding energy coefficient or affinity constant is related to the free energy change of biosorption of different metal ion species (Van Rieemsdijk et al., 1986). It has been shown that high K_a values are attributed to biosorption of metal ion species on high-energy surfaces with low dissociation constants. However, low K_a values have been related to biosorption on low energy surfaces with high dissociation constants (Adhikari and Singh, 2003).

In the present study it was observed that K_a for lead ions in single solution ($0.1852 \text{ dm}^3/\text{mg}$) was higher than for the binary solution ($0.1696 \text{ dm}^3/\text{mg}$) indicating that the tendency for biosorbed lead ion to dissociate increased in binary solution. The K_a values for lead ions biosorption onto Mansonia sawdust were higher than for copper ions for both single (lead: $0.1852 \text{ dm}^3/\text{mg}$ and copper: $0.0196 \text{ dm}^3/\text{mg}$) and binary (lead: $0.1696 \text{ dm}^3/\text{mg}$ and copper: $0.0107 \text{ dm}^3/\text{mg}$) metal ion solutions. This may account for the higher biosorption capacity of Mansonia sawdust for lead ions than for copper ions. Therefore the simultaneous presence of copper and lead ions in solution will suppress both the biosorption of copper and lead ions onto Mansonia sawdust.

The effect of biosorption of lead ions in the presence of increasing concentration of copper ions and the biosorption of copper in the presence of increasing concentration of lead ions are shown in Fig. 4. It is revealed that as the concentration of copper ion increased in solution, the amount of lead ion biosorbed per unit mass of sawdust, reduced. The amount of lead ions biosorbed reduced from 46.5 to 39.1 mg/g , when copper ion concentration increased from 0 to 60 mg/dm^3 . Similarly, the amount of copper ions biosorbed reduced from 26.8 to 19.2 mg/g when lead ion concentration was increased from 0 to 60 mg/dm^3 . Therefore, when both metal ions are simultaneously present in a aqueous solution, the

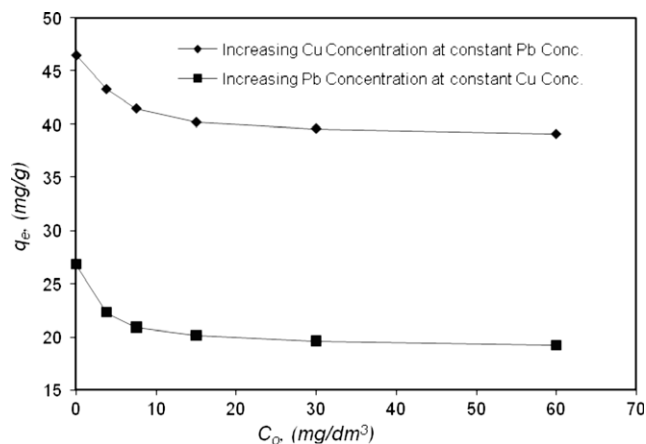


Fig. 4. Effect of the sorption of one metal ion in the increasing presence of the other metal ion.

Table 6

A comparison of chi-square, χ^2 , and coefficient of determination, r^2 , for three isotherm models.

Metal	Langmuir		Freundlich		BET		Competitive Langmuir	
	χ^2	r^2	χ^2	r^2	χ^2	r^2	χ^2	r^2
Pb–Cu	0.0059	0.9998	0.0258	0.9690	0.3075	0.9750	0.2042	0.9980
Cu–Pb	0.0006	0.9986	0.00293	0.9950	0.0016	0.9860	0.0032	0.9980

efficiency of using *Mansonia* sawdust for the removal of both metal ions from aqueous solution is reduced.

3.6. Effect of temperature

The temperature dependence of copper and lead ion biosorption onto *Mansonia* wood sawdust was studied at a concentration range of 60–140 mg/dm³ at 200 rpm with *Mansonia* sawdust dose of 2.0 g/dm³ at temperatures ranging from 299 to 329 K. Results obtained suggested that the biosorption capacity of *Mansonia* sawdust for the biosorption of copper and lead ions increased with temperature which is typical for the biosorption of most metal ions from their solution (Ho, 2003; Ho and Ofomaja, 2005; Ho and Ofomaja, 2006). When the system is in a state of equilibrium, the distribution of metal ion between the *Mansonia* sawdust and the metal in solution is of fundamental importance in determining the maximum biosorption capacity of the *Mansonia* sawdust for the metal ion from the isotherm. The Langmuir isotherm is applicable to homogeneous biosorption where each metal ion/sawdust biosorption process has equal biosorption activation energy. The excellent fit of the Langmuir isotherm to the experimental data at all temperatures studied for the biosorption of copper and lead ions onto *Mansonia* sawdust confirms that the biosorption is monolayer, where biosorption of each molecule has equal activation energy and that biosorbate–biosorbate interaction is negligible.

The Langmuir constants K_a and q_m were estimated from Langmuir isotherm plots for lead and copper ion biosorption. The magnitude of Langmuir constant, K_a , is largely determined by the heat of biosorption. The K_a values increased from 0.0196 to 0.034 dm³/mg for lead ion biosorption and 0.1852 to 0.2470 dm³/mg for copper ion biosorption as temperature increased from 299 to 329 K, indicating a higher heat of biosorption with increasing temperature. The heat of biosorption was highest at 329 K, suggesting strong biosorption of the metal ions. However, the lower biosorption at lower temperatures suggests the formation of weaker bonds at lower temperatures. The equilibrium biosorption capacities, q_m , of copper and lead ions increased from 42.4 to 57.1 mg/g for copper ion biosorption and from 51.2 to 61.7 mg/g for lead ion biosorption with increase in solution temperature from 299 to 329 K. It is evident that the biosorption of copper and lead ions onto *Mansonia* sawdust is an endothermic process, due to the direct relationship between amounts of copper and lead ions biosorbed per unit mass of sawdust at solution temperature.

3.7. Thermodynamics

The thermodynamic parameters Gibbs free energy change, ΔG^0 , for the biosorption processes using the biosorption equilibrium constant, K_a , from Langmuir isotherm. The negative values of ΔG^0 for both copper and lead ion biosorption confirms the feasibility of the process and the spontaneous nature of the biosorption. The values of ΔG^0 were found to increase from –26.24 to –29.66 kJ/mol for lead ion biosorption and from –18.66 to –21.2 kJ/mol for copper ion biosorption as adsorbate solution temperature increased from 299 to 329 K. These values are more negative than those obtained for the biosorption of copper and lead on *Acacia Arabica* sawdust: $\Delta G^0 = 0.071$ to -0.786 kJ/mol for copper ions and 0.782 to -0.786 kJ/mol at 290 to 330 K for lead ions (Mee-na et al., 2008); for the biosorption of copper on modified oak sawdust: $\Delta G^0 = -2.84$ to -3.33 at 290 to 330 K (Argun et al., 2007) and for the biosorption of lead ion onto Walnut sawdust: $\Delta G^0 = -1.68$ to -2.071 at 290 to 330 K (Bulut and Tez, 2007). The values of ΔH^0 and ΔS^0 calculated from the plot of Gibbs free energy change, ΔG^0 , versus absolute temperature, K , were given as 8.1311 kJ/mol and -0.1149 J/mol K for lead ion biosorption and 15.019 kJ/mol and -0.1096 J/mol K for copper ion biosorption.

In this study, the values of ΔH^0 were observed to be positive for the biosorption of both copper and lead ions, indicating that both biosorption reactions were endothermic. The positive value of ΔH^0 obtained reflects the affinity of the *Mansonia* sawdust for copper and lead ions and suggests some structural changes in the adsorption of copper and lead ions by *Mansonia* sawdust (Gupta, 1998). In addition, negative values of ΔS^0 obtained indicates the decreasing randomness at the solid/liquid interface during the biosorption of lead and copper ions on to *Mansonia* sawdust. It further suggests the increasing stability of both metal ions on the surface of *Mansonia* sawdust.

4. Conclusion

Biosorption of lead and copper onto *Mansonia* wood sawdust was studied. Biosorption of both metal ions were found to depend on the presence and concentrations of electrolytes in the solution. Electrolyte with divalent metal ion was found to affect the biosorption of both metal ions to a greater extent than that with monovalent metal ion. Competition between copper and lead ions for biosorption sites was stronger in the copper–lead binary metal ion system than the lead–copper binary metal ion system.

Lead ion sorption in presence of copper ions was better described by the Langmuir isotherm while copper ion sorption in presence of lead ions was better described by the Langmuir and BET isotherm indicating that sorption is likely multilayer.

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