International Journal of Current Engineering and Technology
E-ISSN 2277 – 4106, P-ISSN 2347 – 5161
Available at http://inpressco.com/category/ijcet

Research Article

Abstraction of Cu and Pb Ions from Aqueous Solution using *Santalum Album* (Sandal Fruit Shell) Activated Carbon

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Accepted 29 Aug 2015, Available online 31 Aug 2015, **Vol.5, No.4 (Aug 2015)**

Abstract

The physicochemical properties and adsorption performance of activated carbon prepared from sandal fruits for the removal of lead and copper from aqueous solution was investigated using batch adsorption process. The influence of important parameters like initial metal concentration, temperature, pH, adsorbent dosage and contact time were studied. The result indicated that adsorption capacity increased with increase in the initial metal concentration, pH, adsorbent dosage and contact time up to an equilibrium point when adsorption stabilizes or decrease with further change in the parameters. The sorption process either decreases with increased temperature or does not change with changed in temperature. FTIR analysis results of the adsorbent includes; 3250-3400 cm^{-1}; 1640-1670 cm^{-1}; 1000-1260 cm^{-1} which revealed the presence of functional groups such as the carboxylic acid or alcoholic O-H bond stretching, amine (N-H) bond stretching, C=O bond of carbonyl or amide groups, C-O and O-H bond stretching of alcohol and ethers. The surface area, iodine number, bulk density, particle density, ash content and porosity of the adsorbent determined were; 649.5m^2/g, 614.7 mg/g, 0.921g/cm3, 0.72g/cm3 and 26.4% respectively The equilibrium sorption data proved that the process fit well into Freundlich better than Langmuir isotherm model as indicated with high correlation coefficients high > 0.95 . The results obtained in this study indicated the high adsorption ability of sandal fruit for Pb and Cu, proving it to be excellent biosorbent.

Keywords: *batch adsorption, sandal fruit, lead, copper, removal, adsorption, isotherms, surface area, pollutants, concentration.*

Introduction

In recent years, increasing awareness of water pollution and its far reaching effects has prompted concerted efforts towards pollution abatement (M. Ajmal *et al*, 2003). Contamination of aqueous environments by heavy metals is a worldwide environmental problem due to their toxic effects and accumulation through the food chain (Akbal, F. and Nuronar, 2003; Demirbas, 2008). Heavy metals are major pollutants in marine, ground, industrial and even treated wastewater (B. Dhir, 2009). The presence of heavy metals in drinking water can be hazardous to consumers; these metals can damage nerves, liver and bones and block functional groups of vital enzymes (Argun, M *et al*, 2007).

Metal ions in water can occur naturally from leaching of ore deposits and from anthropogenic sources, which mainly include industrial effluents and solid waste disposal (Bunluesin, S *et al*, 2007). Due to rapid development of industrial activities in recent years, the levels of heavy metals in water system have substantially increased over time (Elangovan, R *et al*., 2008; Hashem *et al*, 2007). Among these metal ions, the ions of Cd, Zn, Hg, Pb, Cr, Cu, Ni, etc. gain importance due to their high toxic nature even at very low concentrations.

Various methods such as precipitation, ion exchange, electrodialysis and filtration are available to isolate and remove these heavy metals from the environment. However, these methods have limitations on selective separation and high cost of investment and operation of equipment (Igwe, J. C. and Abia, A. A , 2007; Jalali, R *et al*, 2002). Adsorption is one of the easiest, safest and most cost-effective methods because it is widely used in effluent treatment processes (Juang, R *et al*, 1996). In the last few years, adsorption has been shown to be an economically feasible alternative method and an effective purification and separation technique for removing trace metals from wastewater and water supplies (Keskinkan *et al*, 2007; Langmuir I., 1918) Activated carbon is the mostly-used adsorbent; nevertheless, it is relatively expensive among other sorbents and its use depends on the degree of the

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required treatment process and the local availability of activated carbon (Aksu, Z. and Yener, J., 2001). Agricultural wastes are produced in excess of 100 million tons as a by-product of the milling industry of which 96% is generated in developing countries.

The utilization of this source of biomass would solve some disposal problem as well as access to cheaper materials for adsorption in water pollutants control (Al-Asheh, 2000). It has been reported that wood wastes such as sawdust, barks and tree leaves effectively adsorbed lead and copper species from aqueous systems (Alnaizy, R. and Akgerman, A., 2000). By using natural agricultural waste fibers, the adsorption of pollutants from aqueous solutions can be much more economical with regard to other similar physico-chemical processes (Elifantz, H. and Tel-Or, E., 2002). Biosorption is the uptake of heavy metal ions and radionuclides from aqueous environments by biological materials, such as algae, bacteria, yeast, fungi, plant leaves and root tissues, which can be used as biosorbents for detoxification and recovery of toxic or valuable metals from industrial discharges(Freundlich, H. M. F, 1906; Banat, F. A *et al*, 2000; Baylor, S. E *et al*, 1999). It has many advantages including low capital and operating costs, selective removal of metals, biosorbent regeneration and metal recovery potentiality, rapid kinetics of adsorption and desorption and no sludge generation. Biosorption technology has been shown to be a feasible alternative for removing heavy metals from wastewater (Bazrafshan, E *et al*, 2006; Beltran, F. J *et al*, 2005). The binding mechanisms of heavy metals by biosorption could be explained by the physical and chemical interactions between cell wall ligands and adsorbents by ion exchange, complexation, coordination, chelation, physical adsorption and micro-precipitation (Benguella B and Benaissa, H, 2002). The diffusion of the metal from the bulk solution to active sites of biosorbents predominantly occurs by passive transport mechanisms and various functional groups such as carboxyl, hydroxyl, amino and phosphate existing on the cell wall of biosorbents which can bind the heavy metals (Cheung, C. W, 2001) Cost is an important parameter for comparing the sorbent materials (Cossich, E. S, 2002). The aim of this study is to undertake adsorption studies of Cu and Pb removal by modified sandal fruit waste biomass.

2. Materials and Methods

2.1 Biosorbents Collection and Preparation

The low cost adsorbents used in this study were derived from fruits of sandal tree (santalum *album*). This waste was selected because of its availability and desirable physical characteristics. The sample was obtained from home environment in Ankpa local Government area, Kogi State, Nigeria, where it is generated as primary agricultural waste. These were extensively washed to remove dirt and other particulate matter that might interact with sorbed metal. They were washed with distilled water, sun dried and ground. The sample was sieved to particle size of 200µm. The material after sieving was soaked for twenty four hours in a solution prepared from sulphuric acid, then placed in a crucible and positioned at the center of a muffle furnace preheated to 500^0C for 1 hr to produce the activated carbon (AC) which was cooled in desiccators.

2.2 Synthetic Wastewater Preparation

Stock solutions (1000 mg/L) of, Pb and Cu were prepared by dissolving the required gramme of $Pb(NO_3)_2$ and $CuSO_4.5H_2O$ in 1 L of distilled water. The stock solutions were diluted with distilled water to obtain the desired initial concentrations.

2.3 Batch adsorption studies

The experiments were carried out in the batch mode for the measurements of adsorption capacities, and to generate adsorption kinetics (Dadhich, A. S. *et al*, 2004). The effect of pH (1, 2, 3, 4, 5and 6), contact time (30-180 minutes), adsorbent dose (0.2-1g/l) and initial metal ion concentration (10-50mg/l) on biosorption at room temperature were studied using stopper bottles. The initial pH of solution was adjusted by using 0.05 M HCl or 0.05M NaOH without changing the volume of the sample. After agitating the sample for the required contact time, the contents were centrifuged and filtered through Whatman No.41 filter paper and unadsorbed Cu and Pb in the filtrate were analyzed by atomic absorption spectrophotometer (Dae, W. C., 2005).

The adsorption capacity, q_e, was calculated as:

$$q = \frac{V\,(Ci - Cf)}{S} \qquad (1)$$

q = Metal ion uptake capacity (mgg^{-1}), C_i = initial concentration of metal in solution, before the sorption analysis (mgI^{-1}), C_f = final concentration of metal in solution, after the sorption analysis (mgI^{-1}), S = dry weight of biosorbent (g), V = solution volume (L). The difference between the initial metal ion concentration and final metal ion concentration was assumed to be bound to the biosorbent.

2.4 Characterization of Sandal fruit

The chemical characterization of sandal fruits was performed after grinding and sieving. The following parameters were measured: ash content was evaluated in a muffle furnace at 550ºC for 8 h (Dakikiy, M. *et al*, 2002); organic matter was calculated by subtracting ash from dry matter; the iodine number was determined based on method used by Danati-Tilaki, R. *et al*, (2004) by using the sodium thiosulphate volumetric method; the specific surface area of the activated carbon was estimated using Sear's method (Kahraman, S. *et al*,2008); Bulk density and particle density were determined using method used by Karthikeyan, T. *et al*, (2005); porosity was determined from the values obtained for bulk density and particle density; functional groups were determined by FTIR; Surface morphology was determined by scanning electron microscope.

2.5 Adsorption Isotherms

Adsorption from aqueous solution is usually correlated by Freundlich and Langmuir isotherms. The Langmuir model makes assumptions such as monolayer adsorption and constant adsorption energy while the Freundlich model deals with heterogeneous adsorption. Langmuir equation of adsorption isotherm according to Keskinkan, O. *et al*, (2004) is:

$$Ce\ /\ qe\ =\ 1/qmax\ b\ +\ Ce\ /\ qmax \qquad (2)$$

Where q_{max} and b are the Langmuir constants. The plot of Ce / qe vs Ce / qmax is linear and the constant q_{max} and b is evaluated from slope and intercept.

The Freundlich equation of adsorption isotherm according to Davis, T. A. *et al*, (2003) is:

$$log\ q\ =\ log\ K\ +\ (1\ /\ n)\ log\ Cf \qquad (3)$$

Where q is the amount adsorbed per unit mass of adsorbent and C_f is equilibrium concentration. The plot of log q vs log Cf is linear and constants K and n is evaluated from slopes and intercepts.

2.6 Adsorption Kinetics of Pb and Cu

The pseudo first order and second order kinetic model have been widely used to predict the metal adsorption kinetics.

The metal adsorption kinetics following the pseudo first order model is given by Entezari, M. H. *et al*,(2003) as;

$$dq/dt\ = K_i\,(qe - q) \qquad (4)$$

where

q : Amount of metal adsorbed at any time (mg/g), (mol/g)

qe : Amount of metal adsorbed at equilibrium time (mg/g), (mol/g)

ki : Pseudo first order rate constant (min-1)

A pseudo-second order rate model reported as developed by American Society for Testing and Materials, (1986) was applied in the following form;

$$t/q_t = 1/h_o + 1/(q_e)t \qquad (5)$$

Where

h_o = the initial adsorption rate (mg/g min)

q_e = the amount of metal ion adsorbed at equilibrium (mg/g)

q_t = the adsorbed at time t (mg/g)

The initial adsorption rate, h_o, as t'→ 0 is defined as:

$h = K_2 q_e^2$

Where,K_2 is the pseudo second order rate constant for the adsorption process (g/mg min).The initial adsorption rate h_o, the equilibrium adsorption capacity, and the rate constant K_2 were determined from the slope and intercept of the plot of t/q_t against t.

3. Result and Discussion

3.1 Physicochemical Properties of Sandal fruit adsorbent

The physicochemical characteristics of the adsorbent were analyzed as outlined under materials and methods and are summarized in table 1 below.

Table 1: Physicochemical properties of Sandal fruit adsorbent

Parameter	Adsorbent Values
Bulk density (g/cm^3)	0.92
Ash (%)	4.45
Iodine number(mg/g)	649.5
Surface area(m^2/g)	615
Particle density (g/cm^3)	1.25
Porosity (%)	26.4

The results were reported as the average values of the analyzed samples obtained from the duplicate experiments. The specific surface area of velvet tamarind further confirmed their porous nature (Al-Qodah, Z., and Shawabkah, 2009).

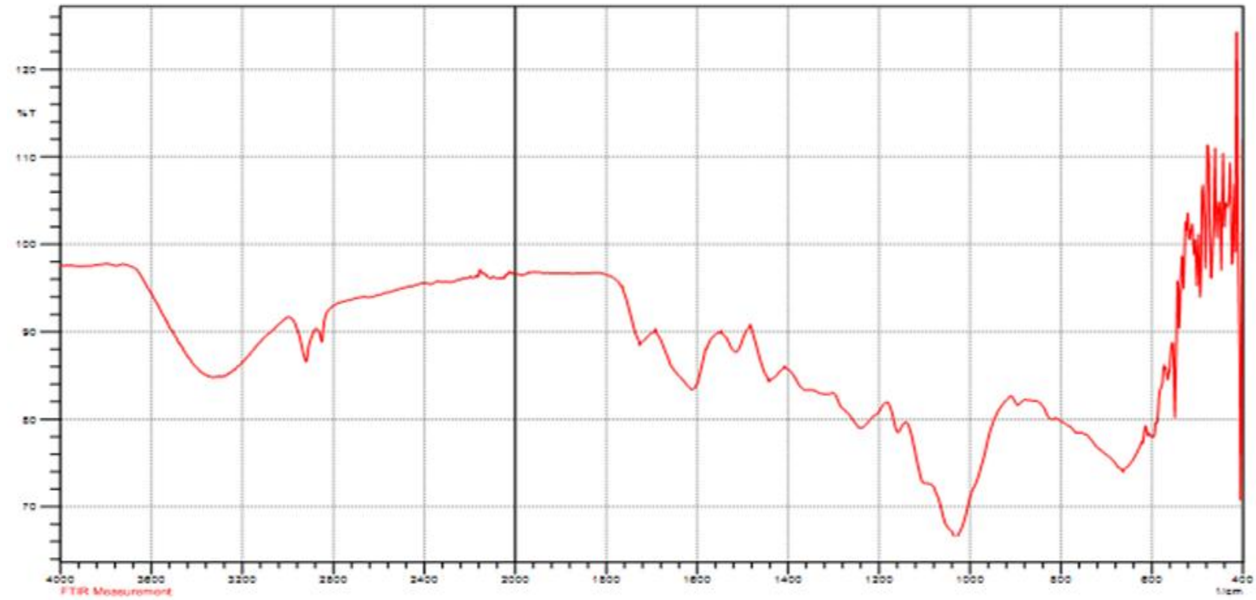

Figure 1 Fourier Transforms Infrared (FTIR) spectra of Sandal fruit before treatment

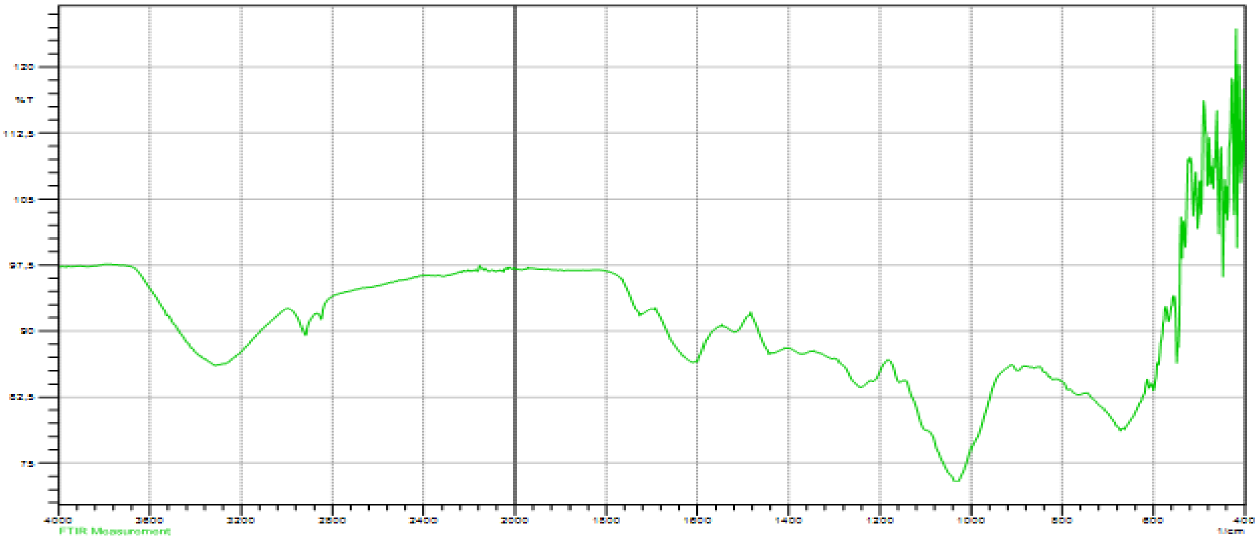

Figure 2 Fourier Transforms Infrared (FTIR) spectra of Sandal fruit before treatment

3.2 Fourier Transform Infrared Analysis of Adsorbent

Figure 1and 2 below showed the FTIR spectral of adsorbents sandal fruit before and after treatment. The FTIR spectral of adsorbent (sandal fruit) before the adsorption of metals were used to determine the vibration frequency changes in the functional groups. The spectra of adsorbents were measured within the range of 400 – 4000cm^{-1} wave number. The pre-adsorption FTIR analysis results (figure 1) suggested the presence of such functional groups as the carboxylic acid or alcoholic O-H bond stretching which may overlap with amine (N-H) bond stretching at peaks between 3250-3400 cm^{-1}; possible C=O bond of carbonyl or amide groups within 1640-1670 cm^{-1}; C-O and O-H bond stretching of alcohol and ethers at 1000-1260 cm^{-1} of the finger-print region. These identified regions may be indicative of functional groups responsible for the individual metal-binding activity of the adsorbent (Alzaydian, A. S, 2009)

3.3 SEM Images

The morphology of sandal fruit biomass was studied by using Scanning Electron microscope (SEM). SEM images obtained at different magnifications were shown in Figures 3 below.

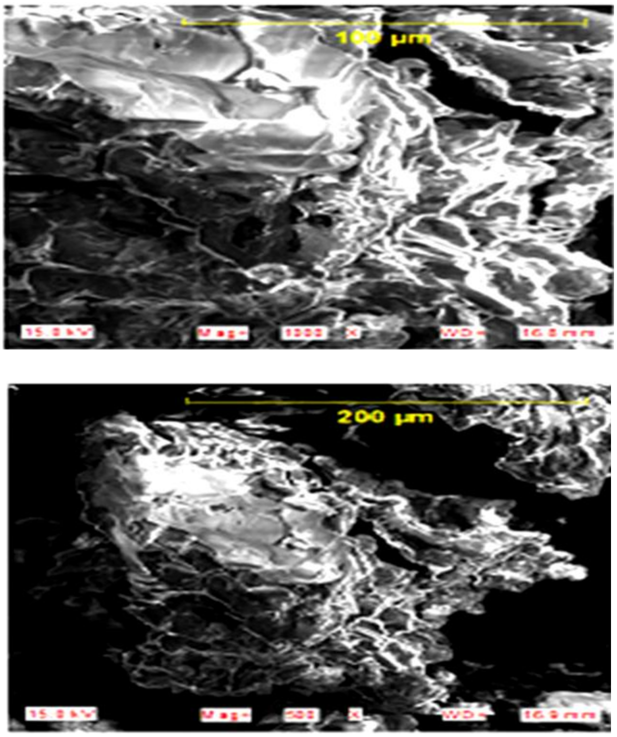

Figure 3: SEM images of sandal fruit

According to Nameni, M., (2008), adsorbent with a surface area of $144m^2/g$ and above can be classified as micro porous. Porous nature and fibril structures are an indication of availability of more active sites on the adsorbent (Association of Official Analytical Chemists, 1990)

3.4 Effect of Initial metal ion concentration

The amount of metal ions adsorbed is a function of the initial concentration of the adsorbate (metal ion), making it an important factor in effective adsorption. The effect of initial metal ion concentration (10 to 50 mg/l) on the adsorption of Pb and Cu ions onto modified sandal fruit is shown in Fig. 4 below.

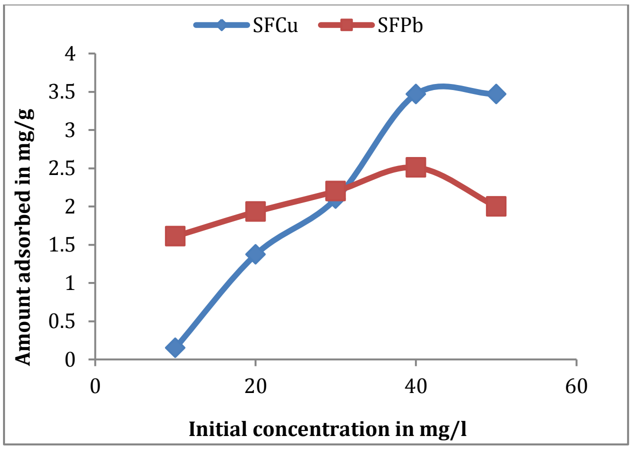

Figure 4 Plot of amount of Pb and Cu ions adsorbed by Sandal fruit in mg/g versus Initial concentration of the metals in aqueous solution (Temp.28 ± 2^0C; pH.5.5, Agitation 200 rpm)

Initial concentrations of the metals were varied from 10 to 50 mg l^{-1} and quantity of adsorbent was kept constant at 1 gm l^{-1}. It was found that, as the concentration of Pb and Cu ions in solution increases, the amount adsorbed by the adsorbent increases. The adsorption capacity of the adsorbent for metal ions increased with the metal concentration, as the increasing concentration gradient overcomes the resistance to mass transfer of metal ions between the aqueous phase and the adsorbent (Esplugas, S. *et al*, 2002). A higher concentration in a solution means higher concentration of metal ions to be fixed on the surface of the adsorbent (Figueira, M. W. *et al*, 2000). At maximum concentration of 42 mg/L, 3.7 mg/g of Cu(II) ions were adsorbed while 2.5mg/g of Pb was adsorbed at maximum concentration of 40mg/g. The results showed that the amount of the metal ions bound by the cellulosic substrate depended on the metal ions type and the concentration of the metal ions. The level of metal ions uptake followed this order Cu>Pb. The difference in the uptake levels of the metal ions can be explained in terms of the difference in the ionic size and atomic mass of the metal ions, the mode of interaction between the metal ions and the substrate (Gholami, F.*et al*, 2006),. The initial faster rate of removal of each metal ion could be due to the availability of more adsorbent active sites at the beginning due to large surface area of the adsorbent; adsorption kinetics depends on the surface area of the adsorbent (Han, W. *et al*, 2004). Sandal fruit has surface area of $615m^2/g$. The initial faster rate of adsorptions might also be due to the progressive increase in the electrostatic interaction between the metal ions and the absorbent active sites. In addition, higher initial concentrations led to an increase in the affinity of the metal ions towards the active sites (Khalid, N. et al, 2000).

3.5 Effect of temperature

The results regarding the effect of temperature on the biosorption of Cu and Pb ions by sandal fruit are shown in Figures 5 below.

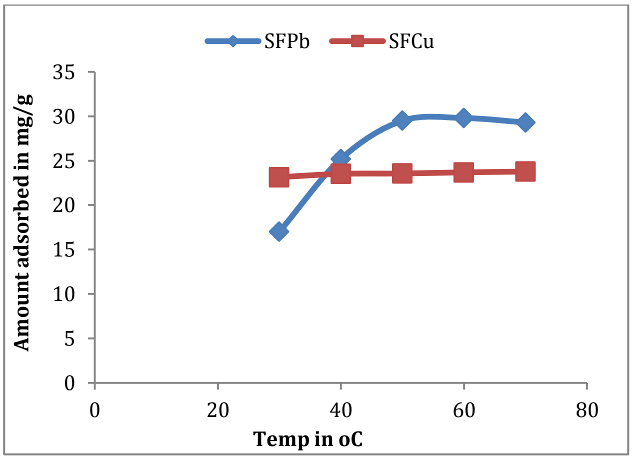

Figure 5 Plot of amount of Cu and Pb ions adsorbed by Sandal fruit versus Temperature (pH.5.5, Agitation 200 rpm for 90 minutes, Initial conc. (Ci) 100 mg/l^{-1}).

The figure showed the adsorption of heavy metals ions namely, Cu^{2+} and Pb^{2+} onto sandal fruit at five different temperatures of 30⁰C, 40⁰C, 50°C, 60⁰C and 70⁰C. The uptake of Cu did not show any significant changes with increase in temperature which shows that changes in temperature has no effect on the adsorption of Cu by sandal fruits. According to Lathasreea, S. *et al*, (2004) increasing the temperature will only increase the rate of adsorbate diffusion across the external boundary layer and in the internal pores of adsorbent particle because liquid viscosity decreases as temperature increases. The uptake of Pb ions increased considerably from 16 to 27mg/g with increase in temperature from 40ºC to about 45ºC and become stable. The temperature higher than 40ºC can cause a change in the texture of the biomass and thus reduced its sorption capacity (Lesko, T. M., 2004). Temperature affects the equilibrium capacity of the adsorbate depending on whether the reaction is exothermic or endothermic (Low, K. S., 2000). Biomass contains more than one type of sites for metal binding and the effect of temperature on each site is different and contributes to overall metal uptake (Ma, W. and Tobin, J. M., 2003)

3.6 Effect of contact time

Contact time play a very important role in efficient removal of heavy metals using sandal fruit. The influence of contact time on the adsorption capacity for Cu and Pb is shown in figure 6 below.

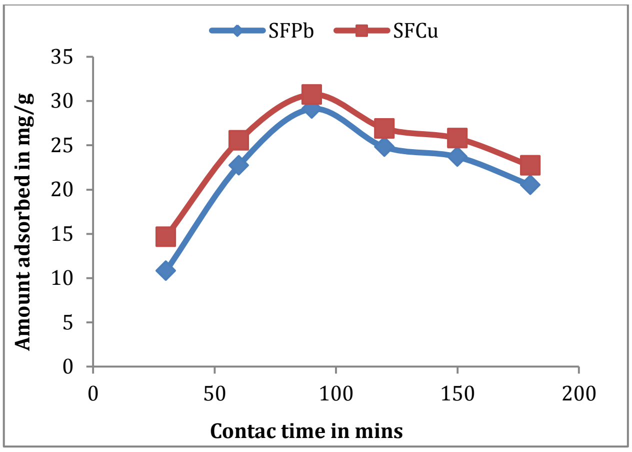

Figure 6; Plot of amount of Pb and Cu ions adsorbed by Sandal fruit versus contact time (Temp.28±2⁰C; pH.5.5, Agitation 200 rpm , Initial conc. (Ci) 100 mg/l⁻¹)

The result clearly revealed that the rate of adsorption of both metal ions increases with time up to an equilibrium time of 90 minutes and decreases thereafter. At the maximum contact time, 27 and 31 mg/g of Pb and Cu were adsorbed respectively. This differential sorption of metal ions may be ascribed to the difference in their ionic radii as it follows in the study by Mahamuni, N. N. and Pandit, A. B.,(2005).It may also be due the reductant behavior of the biomass (Mahvi, A. H. *et al*, 2004). Cu ions have more reductable behaviour as compared to Pb so it is higher uptake by *santalum album* biomass. The result clearly revealed that the rate of adsorption is higher at the beginning which could be due to availability of a large number of active sites. As these sites are exhausted, the uptake rate is control by the rate at which the adsorbate is transported from the exterior to interior sites of the adsorbent particles (Mahvi, A. H. and Bazrafshan, E., 2005).

3.7 Effect of Adsorbent dosage

The effect of varying the adsorbent mass on the adsorption of Pb and Cu is shown in Figure 7 below. Amount of metal ions adsorbed increases as the adsorbent mass increases which are due to increment in the number of binding sites for the ions . To achieve the maximum biosorption capacity of the biosorbent for Cu and Pb, the biomass concentration was varied from 0.2 to 1 g/l and it was found that a concentration of 0.8g/l was sufficient for maximum biosorption of 6.9 and 7.4mg/I for Cu and Pb ions respectively. It is seen from this Figure that a further increase in biomass does not affect the sorption percentage greatly which is in agreement with literature reports indicating lower biosorbed metal concentrations (q) at high adsorbent concentrations (Mahvi, A. H. *et al*, 2007a). The primary factor explaining this characteristic is that adsorption sites remain unsaturated during the adsorption reaction, whereas the number of sites available for adsorption site increases by increasing the adsorbent dose.

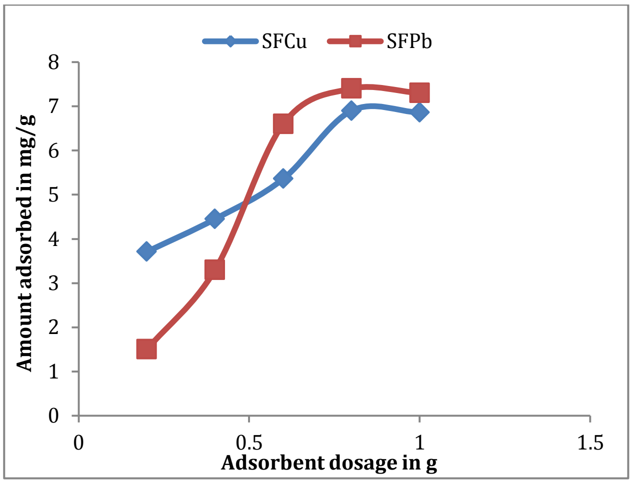

Figure7; Plot of amount Cu and Pb ions adsorbed by sandal fruit versus adsorbent dosage (Temp.28±2⁰C; pH.5.5, Agitation 200 rpm , Initial metal conc ; 100 mg/l)

3.8 Effect of pH

pH controls the metal ion dissolution and the magnitude of the electrostatic charge in the medium (Mahvi, A. H *et al*, 2005). The percent of metal sorption varies with pH of the medium. The experimental results of Cu and Pb sorption using sandal fruits at varying pH ranges was shown in the Figure 8. Effect of pH on biosorption was studied over a range of 1 to 6.

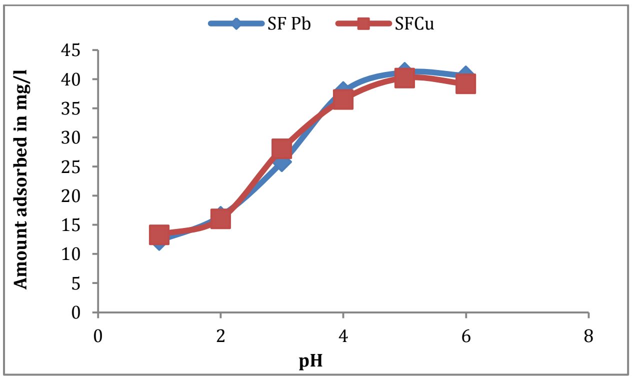

Figure 8 Plot of amount of Cu and Pb ions adsorbed bysandal fruits versus pH (Temp.28±2^{0}C; Agitation 200 rpm , Initial metal conc ; 100 mg/l)

The biomass showed high sorption of 41.2 and 40.23mg/l for Pb and Cu at pH 5.6. The sorption of Pb and Cu decreases with further increase in pH. The optimal pH for the biosorption of the metals by sandal fruit is therefore 5.6. At low pH value, the H^+ ions compete with metal cation for the exchange sites in the system thereby partially releasing the metal cations (Mahvi, A. H. *et al*, 2007b). pH affects both cell surface metal binding sites and metal chemistry in water. At low pH values, the functional groups of the biosorbent are closely associated with the hydronium ions and repulsive forces limit the approach of the metal ions. With increasing pH, more functional groups such as amino and carbonyl groups, would be exposed leading to attraction between these negative charges and the metals and hence increases in biosorption on to the surface of adsorbent (Schwarzenbach, R. P *et al*, 2003) The lower uptake at higher pH value is probably due to the formation of anionic hydroxide complexes (Sekhar, K.C. *et al*, 2003).

3.9 Equilibrium Model

The Langmuir and Freundlich parameters are determined from a linear regression presented in Table 2 below, to examine the relationship between uptake capacity (q) and aqueous concentrations (Ci) at equilibrium. Sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are the most widely used (Singh, K. K. *et al,* 2006), The Langmuir and Freundlich adsorption constants evaluated from the isotherms with correlation coefficients are presented in Table 2, which illustrates the relationship between adsorbed and aqueous concentration at equilibrium.

Table 2; The values of Freundlich and Langmuir Isotherms parameters obtained from the plot

Heavy metal	Adsorbent	Freundlich			Langmuir		
		R^2	K_f	n	R^2	Qm	b
Cu	Sf	0.898	0.002	0.479	0.49	0.814	0.022
Pb	Sf	0.932	0.814	3.115	0.983	2.941	0.134

Table 3; The values of First- order and second order parameters obtained from the plot

Heavy metal	Adsorbent	First Order			Second Order		
		R^2	K_1	q_e	R^2	q_e	K^2
Cu	Sf	0.717	0.001	0.02	1	52.632	0.0004
Pb	Sf	0.132	0.001	0.045	0.949	47.619	0.0004

Both models represent better absorption process for Pb due to high value of correlation coefficients (R^2). Constant b in Langmuir is related to the energy of absorption through the Arrhenius equation. The higher value of b represents the higher affinity of the biosorbent for the metal ions (Sud D. *et al*, 2008). According to the data in Table 2, the affinity order of sandal fruits biosorbent is: Pb > Cu. The q_{max} value is the maximum value of q, is important to identify the biosorbent highest metal uptake capacity and as such useful in scale-up considerations (Sud D. *et al*, 2008). The magnitude of the experimental q_{max} for *sandal fruits* biomass found to be 0.814 and 2.941 mgg-1 for copper and lead metal ions are comparable with theoretically calculated q_{max} values from Langmuir and Freundlich isotherm models. The maximum absorption capacity of 2.941 observed of Pb on sandal fruit is suggesting that it is a potential biosorbent for removal of lead. q_{max} can also be interpreted as the total number of binding sites that are available for biosorption and q as the number of binding sites that are in fact occupied by the metals. Qmax for Pb > Cu. Small value of K indicate the minimal adsorption and large value indicates more adsorption (Verma, V. K. *et al,* 2008) while 1/n is used as an indication of whether adsorption remains constant (at 1/n = 1) or decreases with increasing metal ions concentrations (with $1/n \neq 1$).

3.10 Adsorption Kinetics of Pb and Cu:

The adsorption kinetic of Cu^{2+} and Pb^{2+} ions were modeled using the pseudo first order and pseudo second order equations and the result were presented in table 3. The pseudo second order model seem to provide better correlation with the adsorption data of Cu^{2+} and Pb^{2+} with correlation values of more than 0.9.

4. Conclusion

The present work evaluated the potential of sandal fruit for the removal of Cu and Pb from aqueous solutions. The results obtained in this study indicated high adsorption ability of sandal fruit for Pb and Cu. The equilibrium sorption data proved that the process conformed to Freundlich better than Langmuir isotherm model as depicted with high correlation coefficients. The data fit into the second-order kinetic model. The concentration of the heavy metals analyzed during the study decreased significantly during the experimental period, proving the subtrates to be excellent biosorbent. Therefore, it can be well utilized as an inexpensive biosorbent for the removal of heavy metals from an aqueous solution.

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