Removal of lead (II) and copper (II) ions from aqueous solution by baobab (Adononsia digitata) fruit shells biomass

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Abstract: *High concentration of heavy metals in the environment can be detrimental to a variety of living species. The purpose of this research was to explore the use of baobab (Adsononsia digitata) fruit shells in the removal of lead(II) and copper(II) ions from aqueous solutions. Batch experiments were conducted to determine the effect of varying adsorption parameters on the removal of aqueous lead and copper ions. The adsorption of Pb(II) was found to be maximum at pH 5.5 using adsorbent dose of 0.7 g. The adsorption of Cu(II) was found to be optimum at pH 6 using adsorbent dosage of 0.9 g. The adsorption data conformed to Langmuir, Freundlich and Temkin isotherms. However the Temkin isotherm showed the best fitting model with highest R^2 values for both lead and copper (0.9977 and 0.9967) respectively. Baobab fruit shells can be used as a cost effective adsorbent for the removal of lead(II) and copper(II) ions from aqueous solutions in the treatment of industrial effluent.*

Keywords: *Adsorption, baobab, biosorbent, copper, isotherm, lead*

I. Introduction

Rapid industrialization has led to increased disposal of heavy metals and radio nuclides into the environment. The industries mainly responsible for the discharge of waste water containing metals are mining and mineral processing, pigment manufacture, painting and photographic industry, metal working and finishing processes [1]. Since metals are non-biodegradable and may bioaccumulate in living tissues [2], their removal from the waste waters is nowadays legally imposed. Removal of heavy metals and radio nuclides from metal-bearing wastewater is usually achieved by physico-chemical processes before discharging the effluents into natural water-body systems. Physico-chemical processes include precipitation, coagulation, reduction [3], ion exchange [4], membrane processes (ultrafiltration, electrodialysis and reverse osmosis) and adsorption [5].

These techniques have inherent limitations such as sensitive operating conditions, low metal removal efficiency and production of secondary sludge which is costly to dispose [6]. Adsorption has been shown to be the most promising option for the removal of metal ions from aqueous streams. Activated carbon is the most commonly used adsorbent for adsorption due to its effectiveness and versatility [7, 8]. However the high cost of activated carbon limits its use in adsorption.

The need for more economical and effective methods for the recovery of metal ions from wastewater have resulted in the development of alternative separation technologies. One such alternative process is biosorption, which utilizes various natural materials of biological origin such as bacteria, fungi, yeast and algae.

These biosorbents possess metal sequestering properties and can be used to reduce the concentration of heavy metal ions from ppm to ppb level [9]. Biosorbents which have been previously used include palm-nut shell [10] groundnut hull [11], Bambara groundnuts hulls [12] and sunflower husk [13].

This research focuses on the use of baobab shells as a biosorbent for the removal of lead and copper ions from waste water. Baobab fruit shells have no economic benefit. To the best of our knowledge there is no evidence in literature showing the use of baobab shells as a biosorbent for removal of lead and copper ions.

II. Method

2.1 Preparation and preservation of the baobab fruit shells

The baobab fruit shells (BFS) were rinsed with distilled water to remove dust and impurities deposited on the surface. The BFS were air-dried and then oven dried at 80°C to constant mass. The dried shells were pulverized and sieved to obtain particle sizes less than 300 μm. The baobab shell powder was soaked in 0.1 M HNO_3 for 24 h. Acid treatment was done to remove or mask functional groups and to expose more ion binding sites. The mixture was filtered and the powder residue washed with distilled water several times to remove any acid contents. The filtered biomass was dried in an oven at 105°C. The dried biomass was preserved in air-tight glass bottles to protect it from moisture [11].

2.2 Characterisation of biosorbent

Functional group elucidation was done using Fourier Transmitter Infrared (FTIR) spectrometer (Digilab Merlin 2000 series). Characterisation of the treated biomass was done before and after metal adsorption.

2.3 Equilibrium adsorption studies
2.3.1 Effect of pH

The effect of pH on metal adsorption was monitored over a pH range of 2 to 6.5. In this study, 100 ml of separate solutions (25 ppm Pb^{2+} and 8 ppm Cu^{2+} ions) were transferred into 250 ml conical flasks agitated at 200 rpm for 150 min with 0.5 g biosorbent. The mixtures were filtered and the filtrate analysed for residual metal ions using FAAS (Shimadzu 50 B).

2.3.2 Effect of contact time

The investigation was done to determine the optimum time for adsorption of both lead and copper ions using the baobab fruit shells. The biosorbent (0.5 g) was contacted with 100 ml separate solutions of 25 ppm Pb^{2+} and 8 ppm Cu^{2+} ions adjusted to pH 5.5 and 6 respectively. The solutions were agitated at 200 rpm for different contact times (10-150 min). The mixtures were filtered and residual metal ions in filtrate analysed using FAAS.

2.3.3 Effect of biosorbent dosage

The effect of quantity of the baobab fruit shells used was investigated by equilibrating separate 100 ml solutions of lead (25 ppm) and copper (8 ppm) ions with different masses of the adsorbent (0.1-0.9 g) agitated at 200 rpm for 120 min. The mixture was filtered and the residual metal ions in filtrate analysed using FAAS.

2.3.4 Effect of initial metal concentration on monosorption

Separate 100 ml solutions of copper and lead ions with different initial concentrations (10-100 ppm) were contacted with optimised adsorbent dosage (0.7 g for Cu at pH 5.5 and 0.9 g for Pb at pH 6). The mixtures were agitated at 200 rpm for 200 min. The mixtures were filtered and filtrate analysed for residual metal ions.

2.3.5 Effect of initial metal concentration on binary sorption

The effects of initial concentrations of Pb^{2+} and Cu^{2+} ions in binary sorption were carried out at optimised adsorbent dose, contact time and pH by varying the initial metal ion concentration in the ratio 1:2.

The conical flasks were agitated at 200 rpm for 120 min. The mixtures were filtered and filtrate analysed for residual lead and copper ions using FAAS.

III.   Results and Discussion

3.1 FTIR characterisation

The FTIR spectra of BFS before and after biosorption are shown in Figs. 1 and 2 respectively. The -OH, -NH, carbonyl and carboxylic groups are important sorption sites. The peak at 3420 cm^{-1} is attributed to –OH and –NH groups. The absorption peaks between 1760 and 1600 cm^{-1} are characteristics of carbonyl groups stretching. The presence of –OH group, coupled to carbonyl group confirms the presence of carboxylic acid groups in the biosorbent [11]. The peaks around 1440 cm^{-1} indicate the presence CH_2 and CH_3 groups while peaks around 1420 cm^{-1} can be attributed to the aromatic CH and carboxyl-carbonate structures.

After biosorption, the broadening of –OH peak at 3420 cm^{-1} and carbonyl groups at 1640 cm^{-1} was observed (Fig. 2). This indicates the participation of hydroxyl and carbonyl groups in the biosorption of lead(II) and copper(II) ions. Similar spectra were obtained for biosorption studies of metal ions using groundnut hull [11], cashew nut shells [14] and palm nut shells [10].

3.2 Equilibrium studies on biosorption of Pb^{2+} and Cu^{2+}
3.2.1 Effect of pH

The effect of pH on the adsorption of lead(II) and copper(II) ions is shown in Fig. 3. The uptake and equilibrium sorption capacity of metal removal from aqueous solution are strongly affected by the pH [15]. At the same time, the state of chemically active sites is changed by the solution pH [11]. The maximum adsorption of lead(II) and copper(II) ions was achieved at pH 5.5 and 6 respectively. At pH values higher than 6.5, both metals ions were precipitated. Therefore the removal of metal ions at higher pH values is due to the formation of precipitates rather than adsorption [16]. The biosorption capacity (Q_e) increased with increase in pH up to pH 5.5 for lead(II) ions and pH 6 for copper(II) ions. The increase in metal adsorption with increase in pH is due to a decrease in competition between hydrogen ions and metal ions for the surface sites and also due to decrease in positive surface charge.
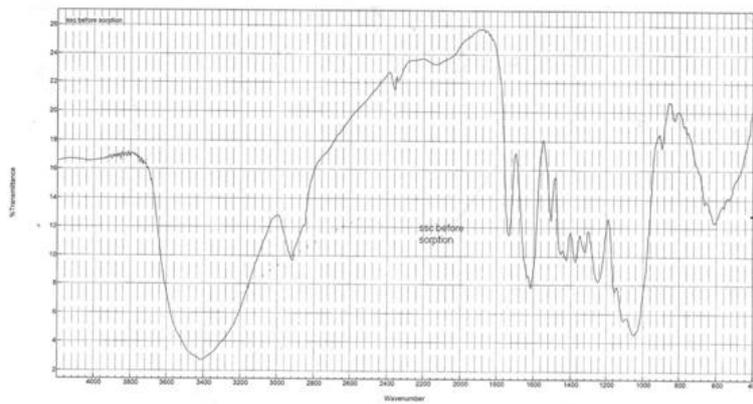
Figure 1: FTIR spectra of baobab fruit shells before biosorption
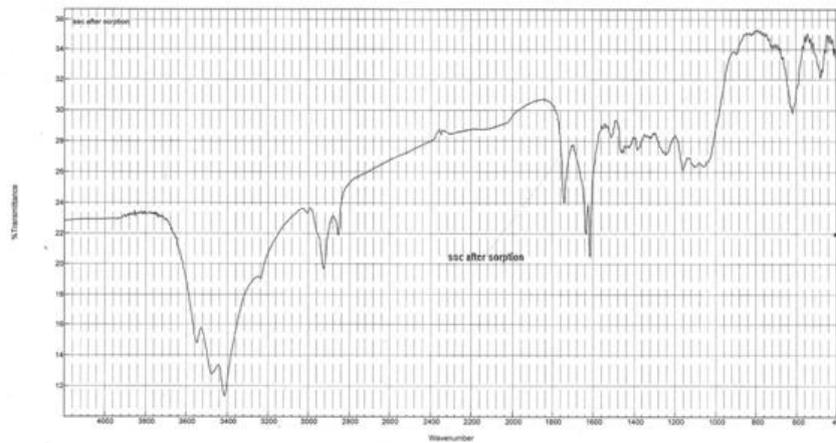

Figure 2: FTIR spectra of baobab fruit shells after biosorption

As the pH increases, more negatively charged surface becomes available thus facilitating greater metal adsorption. At low pH, higher concentration and mobility of H^+ ions favour H^+ adsorption compared to metal ions. According to Onundi et al. [17] metal ions are more soluble in solution at lower pH values and this reduces their adsorption. At lower pH, the surface of the adsorbent is surrounded by hydronium ions (H^+) thereby blocking metal ions from binding sites on adsorbents.
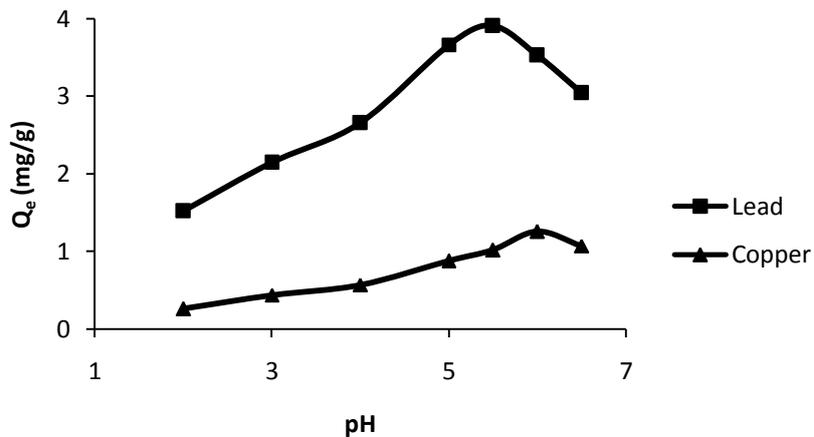

Figure 3: Effect of pH on the sorption of Cu^{2+} and Pb^{2+} ions

3.2.2 Effect of contact time

The effect of contact time on the biosorption of lead(II) and copper(II) is shown in Fig. 4. The amount of the adsorbed metal ions increases with increasing time until it levels off after some (90 min for Cu^{2+} and 120 min for Pb^{2+}). A constant adsorption is indicative of equilibration due to saturation of adsorption sites. Rapid adsorption of metal ions during the initial stages was due to the large initial concentration gradient between the adsorbate in solution and the number of available vacant sites on the adsorbent surface. The adsorption capacity for Cu^{2+} was lower than for Pb^{2+} ions.
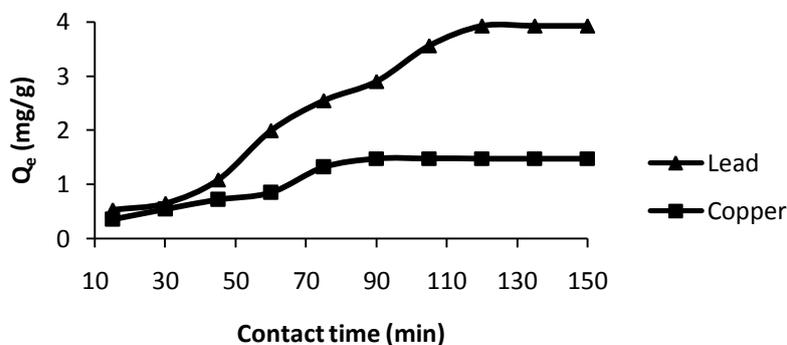

Figure 4: Effect of contact time on the sorption of Cu^{2+} and Pb^{2+} ions

3.2.3 Effect of biosorbent dosage

The effect of adsorbent dosage on the adsorption of lead(II) and copper(II) is shown in Fig. 5. There is an increase in adsorption capacity with increasing adsorbent dosage up to a maximum of 0.9 g for Cu and 0.7 g for Pb giving corresponding maximum percentage metal removal of 78 and 68% respectively. Further increment in adsorbent dosages resulted in decline in adsorption capacity. The initial increase in adsorption capacity with increasing adsorbent dosage is explained by the increase in the number of exchangeable sites for metal ion adsorption [17]. The decline in adsorption beyond certain adsorbent dosages could be due to the aggregation/agglomeration of sorbent particles at higher dosages which would lead to a decrease in the total surface area of the adsorbent particles available to the metal ions. As a result the adsorption capacity of the adsorbent is not fully utilised [18].
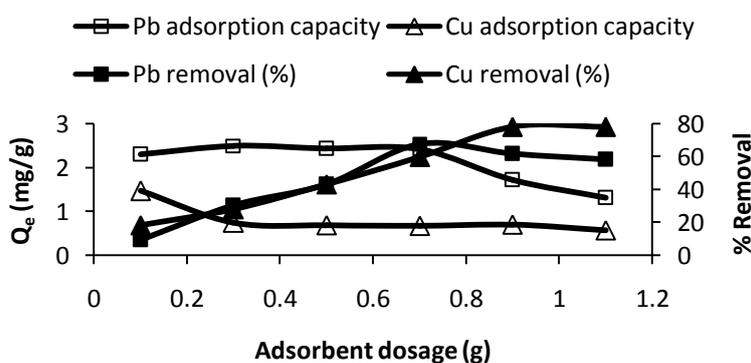

Figure 5: Effect of adsorbent dosage on adsorption of Cu^{2+} and Pb^{2+} ions

3.2.4 Effect of initial metal concentration on monosorption

The effect of initial concentration on the monosorption of copper and lead ions is shown in Fig. 6. For both metal ions, an increase in initial concentration resulted in increase in the adsorption capacity. This can also be explained in terms of increase in adsorption sites coverage as the metal ion concentration is increased [19].

High metal concentration saturates the adsorbent sites more quickly thereby decreasing the overall percentage metal removal. A similar trend was observed by Andal and Sakthi [20].
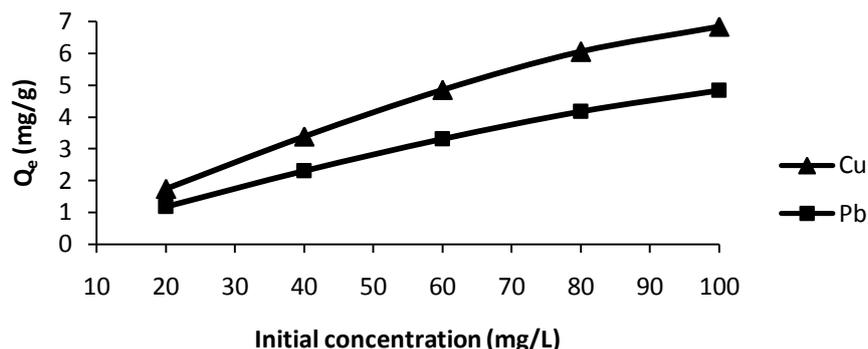
Figure 6: Effect of initial metal ion concentration on adsorption capacity

3.3 Adsorption isotherms

The Langmuir (eqn 1), Freundlich (eqn 2) and Temkin (Eqn 3) isotherms were applied to the equilibrium studies to test for data conformity. The linear forms of the isotherms are represented by equations 1-3.

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ} * \frac{1}{C_e} \qquad (1)$$

Where, Q (mgg^{-1}) and b (Lmg^{-1}) are the Langmuir constants related to the maximum adsorption and energy of adsorption respectively and C_e is the equilibrium concentration of the adsorbate (mgL^{-1}).

$$\log q_e = \log K + \frac{1}{n} \log C_e \qquad (2)$$

Where, k and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity respectively of the adsorbent.

$$X = a + b \ln C \qquad (3)$$

Where, C is the concentration of the adsorbate in solution at equilibrium (mgL^{-1}), X is the amount of metal adsorbed per unit weight of adsorbent (mgg^{-1}), a and b are constants related to adsorption capacity and intensity of adsorption.

It was observed that the Langmuir adsorption isotherm satisfactorily describes the sorption of copper and lead ions from aqueous solutions using baobab shells as indicated by the high correlation coefficients(R^2) of 0.9949 and 0.9961 respectively (Fig. 7). The applicability of the Langmuir isotherm indicates good monolayer coverage of lead(II) and copper(II) ions on the surface of baobab shells which consequently suggests the formation of a mono layer on the adsorbent surface in the given concentration range [21]. The fact that the Langmuir isotherm fits the experimental data very well may be due to the homogenous distribution of active sites on the adsorbent since the Langmuir equation assumes that the surface is homogenous. Thus the applicability of the Langmuir isotherm in the present system indicates the monolayer coverage of lead(II) and copper(II) ions on the outer surfaces of the adsorbent [19]. The calculated model parameters with correlation coefficients are shown in Table 1. The adsorption capacity, Q_{max}, (mgg^{-1}) of copper is higher than that of lead.

The affinity of the two metals for the adsorbent surface in terms of b is higher for lead. The values of b were fairly low which implies low surface energy in the process and consequently low bonding between metal ions and the baobab fruit shells. Qaiser et al. [11] reported the maximum adsorption capacities for lead on groundnut hull (31.54 mgg^{-1}) and baggase fly ash (2.5 mgg^{-1}).
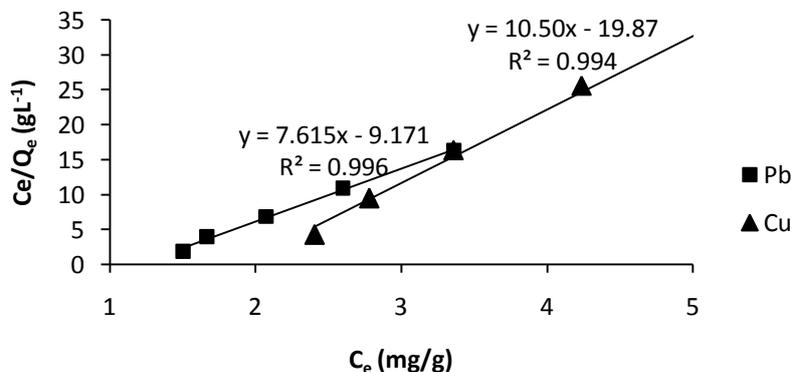

Figure 7: Langmuir isotherm for the adsorption of Pb^{2+} and Cu^{2+} on shells of baobab

The Freundlich isotherms for lead and copper adsorption are shown in Fig. 8. It was observed that the Freundlich adsorption isotherm also conforms to the sorption of lead and copper ions from aqueous solutions using baobab fruit shells. However, the level of conformity is to a less extent compared to the Langmuir adsorption isotherms as indicated by lower correlation coefficients values of 0.9755 and 0.973 for Pb^{2+} and Cu^{2+} respectively. The values of n (1.57 and 1.61) for lead and copper respectively, confirm that the baobab shells have a heterogeneous surface since the values satisfy the heterogeneity condition where n must be in the range 1 < n < 10 [22]. The values of 1/n ranging from 0 to 1 are a measure of adsorption intensity or surface homogeneity as the values approach zero. Values for 1/n less than 1 indicate normal Langmuir adsorption isotherm while those values above 1 are indicative of cooperative adsorption [23]. The values of K_F for lead (0.95) and copper (0.90) imply that there was low uptake of the metal ions onto the adsorbent surface.
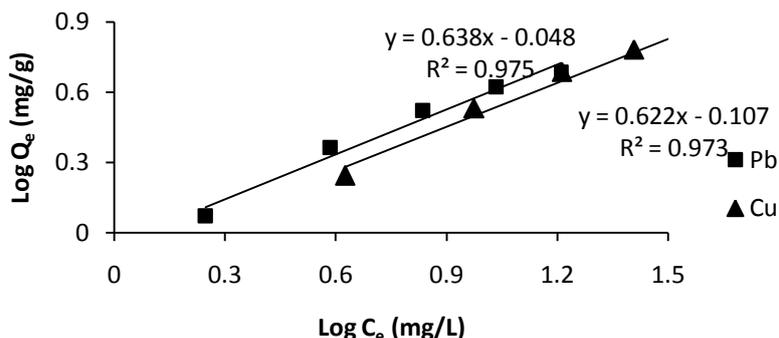

Figure 8: Freundlich isotherms for the adsorption of Pb^{2+} and Cu^{2+} on shells of baobab

Table 1: Isotherm model parameters

Model	Parameter	Pb	Cu
Langmuir	Q_{max}	7.65	10.56
	b	0.11	0.05
	R_L	0.48	0.50
	R^2	0.9961	0.9949
Freundlich	K_f	0.95	0.90
	n	1.57	1.61
	R^2	0.9755	0.9730
Temkin	K_T	1.04	1.37
	b_T	645.59	457.34
	R^2	0.9977	0.9967

Fig. 9 shows the Temkin isotherms for the adsorption of copper and lead. The Temkin isotherm takes into account the occupation of the more energetic adsorption sites [24]. Of the three isotherms under consideration, the Temkin adsorption isotherm best describes the sorption of lead and copper ions from aqueous solutions using baobab shells as indicated by the highest correlation coefficients of 0.9977 and 0.9967 for lead and copper respectively and b_T values of 645.59 KJmol^{-1} and 457.34 KJmol^{-1} respectively. The intensity of sorption (K_T) and the heat of sorption (b_T) for lead and copper confirm further that the data best fit the Temkin isotherm.
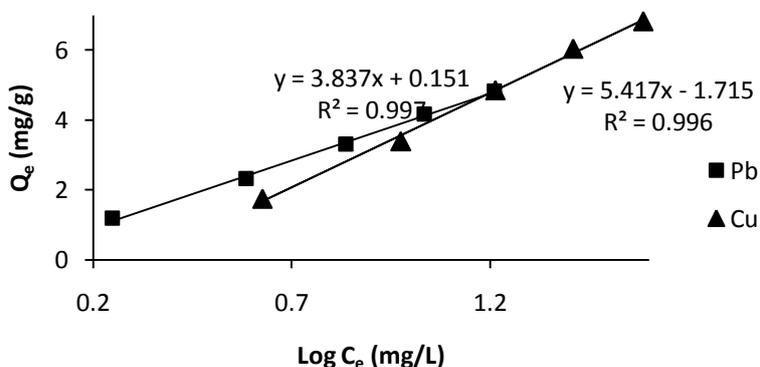

Figure 9: Temkin isotherms for the adsorption of Pb^{2+} and Cu^{2+} on shells of baobab

3.3.3 Effect of initial metal concentration on binary sorption

The Cu-Pb binary competitive sorption was tested by the Langmuir model as shown in Figs. 10 and 11. The binary combination in which copper was the primary ion (Cu-Pb) fitted the competitive Langmuir model better than that for lead as indicated by a higher correlation coefficient value. The results indicate that there is competitive interaction in sorption of Cu^{2+} and Pb^{2+} in the binary system.
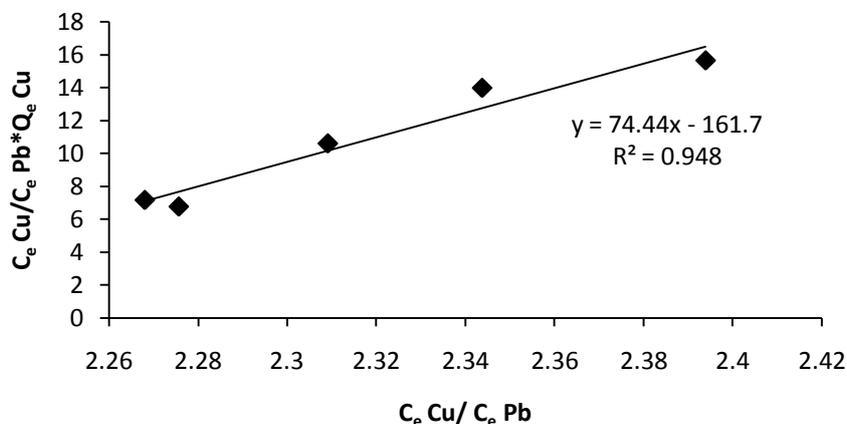

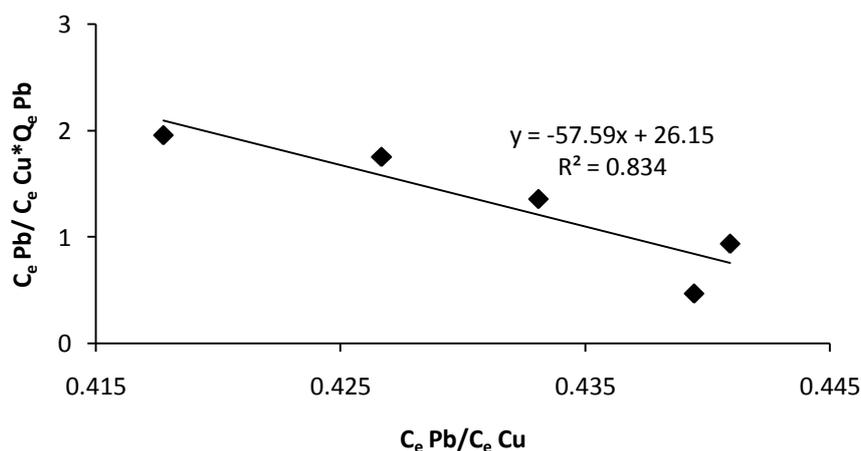**Figure 10: Cu-Pb binary sorption on baobab fruit shells**

Figure 11: Pb-Cu binary sorption on baobab fruit shells

The effectiveness of baobab shells was compared to other biosorbents reported in literature (Table 2). It appears that BFS adsorb lead and copper quite well.

Table 2: Comparison of Q_{max} of baobab fruit shells with other biosorbents

Biosorbent	Q_{max} (mg/g)		Reference
	Pb	Cu	
Crab fish	19.83	-	[25]
Groundnut hull	31.54	-	[11]
Palm shell	1.34	1.58	[17]
Bombax ceiba saw dust	40.49		[20]
Baobab shells	7.65	10.56	Current study

IV.   Conclusion

This study has demonstrated that baobab fruit shells has favourable properties for the biosorption of lead and copper ions from aqueous solutions and the adsorbent properties are enhanced by acid treatment. The biosorption of lead and copper ions was highly dependent on experimental parameters such as contact time, initial metal concentration, pH and adsorbent dosage. The adsorption of Pb(II) was found to be optimum at pH 5.5, adsorbent dose of 0.7 g, metal ion concentration of 10 ppm and contact time of 120 min. The adsorption of Cu(II) was found to be optimum at pH 6, adsorbent dose of 0.9 g, metal ion concentration of 20 ppm and contact time of 120 min. The Temkin fitted best to the adsorption data. There is need for further studies to investigate

the use of baobab fruit shells in treating industrial effluent. This could be a cost effective method of utilising waste baobab fruit shells in removing lead and copper from industrial wastewater.

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