

Adsorption of Lead (II) and Copper (II) Ions from Mono Synthetic Aqueous Solutions Using Bio-Char from *Ficus natalensis* Fruits

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Abstract

Many science-based institutions in most developing countries use heavy metal containing salts in practical teaching sessions. The commonly used chemicals are the salts of lead (II) and copper (II) and the wastes generated end up into the environment when untreated. Thus, a study was done to remove lead (II) and copper (II) ions from mono synthetic aqueous solution using bio-char from Ficus natalensis fruits (FNF). This was done at varied pH, contact time, temperature, bio-char dosage level, salinity and metal ion concentration using the batch approach. The residual metal concentrations were determined using the atomic absorption spectrophotometer. The optimum pH for the adsorption of copper (II) and lead (II) ions was found to be 4.0 and 5.0 respectively. The maximum percentage adsorption of copper (II) and lead (II) by the FNF bio-char was established at 60 minutes contact time, 47.5°C and 0.4 g adsorbent dose. Increase in the metal ion concentration and the presence of interfering ions in the aqueous solution lead to decrease in the percentage adsorption. The highest adsorption capacity was found to be 161.29 mg/g and 1250 mg/g for copper (II) and lead (II) ions respectively. The thermodynamic parameters indicated the feasibility of the adsorption of copper (II) and lead (II) on the bio-char of FNF. Thus, bio-char from FNF may be used as an adsorbent in waste management where copper (II) and lead (II) ions are present at a concentration range of between 5 and 100 mg/l.

Keywords

Bio-Char, Ficus natalensis Fruits, Heavy Metal, Wastewater

1. Introduction

Heavy metal pollution is a serious problem globally owing to their toxicity and

non-biodegradability [1]. Heavy metals such as mercury, cadmium, chromium, zinc, copper, and lead are toxic and poisonous at high concentrations [2]. For instance, in children below six years of age if exposed to as low as 5 μ g/dl of lead , they suffer from reduction in intelligence quotient (IQ), disabilities in learning, stunted growth, impaired hearing, behavioural problems, disorders in-attention and kidney damage [3]. High amounts of lead in children may result into mental retardation, coma, or even death [4]. In adults, lead increases blood pressure, fertility problems, nerve disorders, muscle and joint pain, irritability, memory impairments [5]. Accumulation of copper in the body at levels above 1.0 g causes gastrointestinal mucosal ulcerations and central-nervous system (CNS) manifestations including headache, dizziness and convulsions [4].

Mainly aqueous solution mixtures containing heavy metals are used during practical teaching in school laboratories with poor means of effluent disposal especially in developing countries. The effluents containing heavy metal ions like lead (II) and copper (II) are in most cases discharged into the environment, and then taken up by plants, animals, and humans. This is because, the conventional methods for removal of such heavy metals from effluents are sometimes not affordable, due to the costs involved, as well as being inefficient to remove low metal ion concentrations particularly in the range of 1 - 100 mg/l [3].

Of recent, the capacity of plant materials in adsorbing heavy metal ions has been widely used to develop new technologies which are cheap, efficient and environmental friendly for laboratory effluent treatment especially when the metal ion concentration is as low as 1 mg/l [4] [6]. Biomass materials and plant wastes have been successfully used for metal ion bio-sorption and this technology needs to be developed further for sustainable use in pollution abatement programme [7].

This study, therefore, investigated the removal of lead (II) and copper (II) ions from standard mono synthetic aqueous solutions at different conditions using bio-char from *Ficus natalensis* fruits (FNF).

2. Materials and Methods

2.1. Collection and Preparation of Adsorbent

Fresh FNF were collected by hand picking from Bwanda village, Kalungu District, Uganda. The fruits were dried under the laboratory shade at room temperature. The dried fruits were pulverised using a porcelain pestle and mortar and sieved using a plastic sieve of particle size 710 μ m [8]. *Natalensis* fruit FNF bio-char was prepared by burning the fruits powder on a Kjeldahl apparatus at 150°C for four hours [8]. The black material formed was the bio-char, which was kept in clean and transparent polyethylene sample bags for further use.

2.2. Preparation of Standard Mono-Synthetic Aqueous Stock Solutions

Aqueous stock solution of copper (II) ions was prepared by dissolving 2.79 g of

analytical grade pentahydrate copper (II) sulphate ($CuSO_4 \cdot 5H_2O$) in one litre of double distilled water. In the same way, the aqueous stock solution of lead (II) ions was prepared by dissolving 3.69 g of lead (II) nitrate ($Pb(NO_3)_2$) in one litre of double distilled water. The stock solutions were each diluted to make solutions of 5, 10, 20, 40, 50, 60, 80, 100 mg/l [9].

2.3. Batch Adsorption Experiments

The experiments were carried out at varying conditions (pH, contact time, temperature, adsorbent dose, metal ion concentration and salinity) to assess the performance of bio-char from FNF in removing lead (II) and copper (II) ions from standard mono synthetic aqueous solutions. Experiments done were in triplicates and the average amounts of metal ions adsorbed were obtained and used accordingly [10].

The effect of varying pH (1, 2, 3, 4, 5, 6, 7, and 8) values on removing copper (II) ions (50 mg/l, 100 ml) was determined using the bio-char 0.2 g in a 250 ml conical flask at 25°C. Each mixture made was shaken at 100 rpm using an end-over-end shaker for one hour, filtered through Whatman filter paper (No. 42) and the concentration of copper (II) ions remaining were determined using atomic adsorption spectrophotometer (AAS). Adsorption percentage at equilibrium, A_{eq} was calculated using Equation (1).

$$A_{eq}\left(\%\right) = \left(\frac{C_o - C_e}{C_o}\right) * 100 \tag{1}$$

where C_o and C_e is the initial and equilibrium metal concentrations (mg/l) in the standard aqueous solution respectively [10]. The pH was adjusted using 0.1 M sodium hydroxide or 0.1 M sulphuric acid. The procedure was repeated for adsorption of lead (II) ions from the standard aqueous solutions prepared.

The other factors studied were varied as follows; contact time (1, 10, 20, 30, 40, 50, 60 and 70) minutes at an optimum pH of 5 obtained from this study; temperature (25°C, 30°C, 35°C, 40°C, 45°C, 50°C, 55°C and 60°C) at pH 5 for one hour; adsorbent dose (0.1, 0.2, 0.3, 0.4, 0.5 and 0.6) g at 25°C, pH 5 for one hour; salinity (5, 10, 15, 20, 25 and 30) g/l of potassium chloride or sodium chloride at 25°C, pH 5 for one hour. The initial metal ion concentration of copper (II) and lead (II) was varied as (5, 10, 20, 40, 50, 60, 80 and 100) mg/l each in 100 ml, at 25°C, pH 5 for one hour. Then in addition to A_{eqp} adsorption capacity, Q_e was determined using Equation (2).

$$Q_e \left(\text{mg/g} \right) = \frac{V \left(C_o - C_e \right)}{W}$$
(2)

where C_o and C_e is the initial and final metal concentration (mg/l) in solution respectively, V is the volume (ml) of the solution, W is the mass (g) of the bio-char used. For the school effluents collected from secondary schools in Uganda, pH was adjusted to pH 5 and adsorbent dosage level was set at 0.4 g for 60 minutes at 45°C.

3. Results and Discussion

3.1. Effect of pH

Adsorption of lead (II) and copper (II) ions was found to be highly dependent on pH (**Figure 1**). The optimal pH was 5 and 4 for copper (II) and lead (II) ions respectively. This means that the adsorption of copper (II) and lead (II) ions mostly occurs at an acidic pH. The low adsorption at low pH was as a result of hydroxonium ions (H_3O^+) domination that competed with the metal ions for the active binding/active sites on the bio-char as described by the chemical Equation (3).

$$M^{2+} + 2H_2O \rightarrow M(OH)^+ + H_3O^+$$
 (3)

The overall bio-char surface becomes positive and so, the metal ions suffer from strong repulsive forces [11]. It should further be noted that pH affects the solubility of the metal ions due to the counter ion concentration on the functional groups of the adsorbent and the degree of ionization of the adsorbate during the reaction [12].

As pH increases, percentage adsorption also increased because of reduction in the competition from hydroxonium ions due to the formation of $M(OH)_3^-$ complex as described by chemical Equation (4), and the complex formed readily binds with the positively charged active sites of the bio-char [13]

$$M^{2+} + 3H_2O \rightarrow M(OH)_2^- + 3H^+$$
(4)

The increased negative charge density on bio-char surface increases the attraction of the positively charged ions resulting in the increasing percentage removal of the metal ions [14]. Above the optimum pH greater than 6, probably precipitation of the metal ion by hydroxides took place, which led to low removal of the metal ions by the bio-char [12] [15] as described by chemical Equation (5).

$$M^{2+} + 2OH^{-} \rightarrow M(OH)_{2}$$
(5)





Results obtained in this study are in agreement with [7] [15] [16] where they reported increase in adsorption as pH increased and decreased after the optimum pH.

3.2. Effect of Contact Time

Increased adsorption in both cases, **Figure 2** was due to the availability of many vacant sites, which provided a large surface area for more ions to get adsorbed onto the bio-char active sites [17] [18] [19].

However, the adsorption of copper (II) was lower owing to the fact that hydroxonium ion is more attracted towards the active site than the copper ion, unlike the lead ions with a high charge density [20]. Beyond 60 minutes, there was no further increase in the adsorption due to equilibrium set by the already adsorbed and metal ions still in solution [21]. The results obtained in this study are in agreement with those obtained by [22]. The higher the charge density, the slower the rate of movement of ions towards the central bio-char sites and hence less ability to get adsorbed onto the active sites [20] [23].

3.3. Effect of Temperature

At temperatures of up to 30° C and 40° C (**Figure 3**), there is a low linear increase in percentage removal of both ions. This may be due to low kinetic energy possessed by ions, hence few ions reach the bio-char active sites [21].







Figure 3. Effect of temperature on adsorption of copper (II) and lead (II) ions using FNF bio-char.

At optimal temperature, the adsorption was attributed to the increased diffusion rate of ions onto the bio-char sites since diffusion is an endothermic process [2] [24]. Beyond 47.5°C, the adsorption of both metal ions from aqueous solution reduced due to desorption of the adsorbed species [8] [25] [26].

3.4. Effect of Adsorbent Dose

The increase in adsorption of both metals with bio-sorbent amounts, **Figure 4** is due to the increasing surface area on the bio-char [27], creating a higher availability of the binding sites that complexed the individual metal ions [3] [28].

The adsorption of lead (II) and copper (II) ions remained almost constant after the adsorbent dose of 0.4 g due to the reduction in the intercellular distance of the bio-char sites caused by the complexed ion species leading to shielding of binding sites from the unbounded metal ions [3]. Chaouch *et al.*, [29] reported that the difference in adsorption of metal ions is related to their susceptibility to hydration. The hydrated ionic radius of lead (II) (4.01 Å) is less than that of copper (II) ions (4.19 Å). Since it is difficult for hydrated ions with larger volume to approach the center of the bio-sorption sites, copper (II) ions with high hydrated ionic radius was less adsorbed to the active sites of FNF bio-char than lead (II) ions with a less hydrated ionic radius.

3.5. Effect of Metal Ion Concentration

Initially, the high percentage removal of both ions from aqueous solution as given in **Figure 5** is caused by the high ratio of bio-char surface sites to metal ions in the solution [30]. The general decrease in the removal of metal ions with increasing metal ion concentration is due to the reduction in the available bio-char surface active sites to metal ions [31]. At higher metal ion concentrations, the high collisions of ions and high diffusion rate, brings about low percentage removal, which also causes the saturation at the bio-char surface sites [5] [32]. The bio-char has a higher affinity for lead (II) ion than copper (II) ion because of competition for the active sites with hydronium ion, and hence a less



Figure 4. Effect of amount of bio-char on adsorption of copper (II) and lead (II) ions using FNF bio-char.



Figure 5. Effect of ion concentration on adsorption of copper (II) and lead (II) ions using FNF bio-char.

binding ability towards the bio-sorbent. The higher the relative electronegativity value, the higher the adsorption. Adsorption also increases with increasing pKa value of the metal, thus copper with a higher pKa (8.0) is adsorbed better than lead (pKa, 6.3) [33]. A similar trend of results, that is, decreasing adsorption percentage as the concentration of metal ions increases have been reported [34].

3.6. Effect of Interfering Ions (Salinity)

As per **Figure 6**, the efficiency of the adsorption process of both ions was lowered by the presence of the sodium or potassium ions in the solution matrix. Lead (II) was more adsorbed than copper (II) ions in the presence of the sodium and potassium ions. This may be brought by the different affinities of the ions for the active sites on the FNF bio-char.

Varank *et al.* [20] have reported that charge density plays an important role in their competitive abilities by regulating ions' accessibility to the pores of the sorbents. The smaller the charge density is, the greater the ability of the ions to be adsorbed. Potassium ions showed a higher tendency of competition for the active site than sodium ions. This may be as a result of the difference between the hydrated ionic radii of potassium and sodium ions, that is, the smaller the ionic radius of the cation, the greater the influence towards competition on the binding sites, hence potassium ions (2.32 Å) being more influential than sodium (2.76 Å). The results are in agreement with the work of [20] where the adsorption decreases with increasing concentration of interfering ions.

3.7. Adsorption Isotherms

The Langmuir and Freundlich adsorption isotherms were used to describe the behavior of copper (II) and lead (II) ions onto the bio-char surface due to their commonality in use. The Langmuir takes an assumption that the sorption occurs at specific homogeneous sites within the bio-char [35]. The data was checked using the Langmuir isotherm equation: $\frac{C_e}{q_e} = \frac{1}{K_L q_o} + \frac{C_e}{q_o}$ by plotting a graph of

 $(\frac{c_e}{q_e})$ against (c_e) where K_L and q_o are Langmuir constants related to rate of



Figure 6. Effect of interfering ions on the adsorption of copper (II) and lead (II) ions using FNF bio-char.

adsorption and adsorption capacity respectively, and $\frac{1}{q_o}$ is the slope. The data fitted well in the Langmuir isotherm model for lead (II) ions as shown in **Figure** 7 with regression coefficient (r^2) of 0.9732. The results for copper (II) less fitted the model with r^2 of 0.6479 (**Table 1**). The linearity of the plot (**Figure 7**) indicates the validity of the Langmuir equation that supports monolayer formation on the surface of bio-char.

The separation factor (R_L) is the dimensionless form of the Langmuir isotherm given by $R_L = \left(\frac{1}{1+K_lC_o}\right)$, and it is observed that the separation factor R_L is 0.167 for lead (II) and 0.035 for copper (II) ions which justifies that the adsorption process was favorable ($0 < R_L < 1$) [36].

To check heterogeneity adsorption, data was fitted on the Freundlich equation; $\log q_e = \log K_f + \frac{1}{n} \log C_e$. A plot of $\log q_e$ against $\log C_e$ yielded a straight line. From the slope, *n* was 1.922 and 3.604 for lead (II) and copper (II) ions indicate a physical adsorption process. The Freundlich adsorption isotherms for copper (II) and lead (II) ions are presented in **Figure 8** and the parameters obtained are given in **Table 1**. It can therefore be concluded that the adsorption of lead (II) was better for both Langmuir and Freundlich adsorption isotherms than for copper (II) ions. A comparison was made of FNF biochar against other adsorbents that have been used to remove copper (II) and lead (II) ions from aqueous solution. It can be observed that FNF biochar compare well with the other adsorbents listed in **Table 2**.

3.8. Thermodynamics of Adsorption

The equilibrium constant (K_c), standard Gibbs free energy change (ΔG°), entropy change (ΔS°) and enthalpy change (ΔH°) of adsorption were calculated using Equations (6), (7) and (8).



Figure 7. Langmuir adsorption isotherm for the adsorption of lead (II) and copper (II) ions.



Figure 8. Freundlich adsorption isotherm for the adsorption of lead (II) and copper (II) ions.

Table 1. Langmuir and Freundlich adsorption isotherm parameters for the adsorption of copper (II) and lead (II) ions from aqueous solution using FNF bio-char.

Metal ion		Freundlich isotherm					
	r ²	$q_m ({ m mg/g})$	K_l (L/Fmg)	R_L	r ²	п	$K_f(mg/g)$
Pb ²⁺	0.9732	1250	0.16	0.167	0.9799	1.922	199.43
Cu ²⁺	0.6479	161.29	0.188	0.035	0.4668	3.604	105.58

 q_m is the maximum adsorption capacity, K_l is the binding affinity which gives the extent of adsorption, n is the adsorption intensity and K_r is the binding capacity.

$$K_c = \frac{C_o}{C_e} \tag{6}$$

where K_c is the equilibrium constant, C_o is the concentration of metal ions adsorbed (mg/g) on the biosorbent at a given temperature and c_e is the initial

Material	<i>q</i> _m (mg/g)	Source	
CuO nanostructures	125 (Pb ²⁺)	[36]	
Rice husk	133.34 (Cu ²⁺)	[27]	
Rice husk	45.5 (Pb ²⁺)	[15]	
Prosopis juliflora	201.08 (Cu ²⁺)	[20]	
Cymbopogon citrusstem	1000 (Pb ²⁺)	[37]	
Wasted black tea	166.67 (Cu ²⁺)	[38]	
E mate la mais frantés la também	1250 (Pb ²⁺)	Comment starks	
<i>r. natalensis</i> fruits blochar	161.29 (Cu ²⁺)	Current study	

Table 2. Comparison of the current work with other researchers.

metal ion concentration (mg/l). The K_c values were used to determine the standard Gibb's free energy change, ΔG° , enthalpy change, ΔH° and entropy change, ΔS° for adsorption of copper (II) and lead (II) ions on bio-char of FNF as given by Equations (7) and (8).

$$\Delta G^{\circ} = -RT \ln K_c \tag{7}$$

where ΔG° the free energy change of adsorption, *T* is the absolute temperature in Kelvin, *R* is the universal gas constant. The K_c may be expressed in terms of the ΔG° and ΔS° as a function of temperature as given by the Van't Hoff's reaction isotherm in Equation (8).

$$\ln K_c = \left(\frac{-\Delta H^\circ}{R}\right) \left(\frac{1}{T}\right) + \left(\frac{\Delta S^\circ}{R}\right)$$
(8)

From **Figure 9** the results of ΔG° , ΔH° and ΔS° are as presented in **Table 3**. The negative values of ΔG° indicate the feasibility of the adsorption process, though less feasible with temperature.

The positive values of ΔH° and ΔS° indicate that the adsorption process of copper (II) and lead (II) ions on FNF bio-char was endothermic and favorable respectively [36]. This particular adsorption is therefore a multimolecular layer and reversible with the bonds majorly weak van der Waal's.

3.9. Adsorption of Copper (II) and Lead (II) Ions from School Laboratory Effluents

In this study, laboratory effluents were collected from three secondary schools and analysed to determine the amount of lead (II) and copper (II) ions present and subsequently removed. The results obtained are as given in **Table 4**. The values obtained gave the basis for selecting concentration range that could be available for the use of FNF bio-char and provide evidence that the bio-char can be used to treat effluents. All the effluents were adjusted to the pH of 5, adsorbent dosage level set at 0.4 g for 60 minutes at 47.5°C.

The low percentage adsorption could be attributed to ion interferences in which several other salts and acids containing chlorides, nitrates, sulphates,



Figure 9. A graph of $\ln K_c$ against 1/T.

Table 5. Thermodynamic parameters for the adsorption of copper (11) and lead (11) ions	Table 3	Thermody	ynamic	parameters	for the	adsorpt	ion of o	copper	r (II) ai	nd lead	(II) ions
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Temperature	ΔG° J	∙mol ⁻¹	ΔH° J·	$\Delta S^{\circ} J^{1} \cdot K^{-1} \cdot mol^{-1}$		
(K)	Cu	Pb	Cu	Pb	Cu	Pb
298	-928.330	-369.158				
303	-887.294	-332.527				
308	-458.883	-281.678	+12,192.481	+4577.688 (1.094 kcal/mol)	+37.794	+14.042
313	-256.169	-252.421	(2.914 kcal/mol)			
318	-105.347	-42.302				
323	-85.259	-34.910				

Table 4. Adsorption of copper (II) and lead (II) ions from school laboratory wastes.

	Matal (ma/l)	School				
	Metal (mg/l)	А	В	С		
Concentration	Cu	49.88 ± 0.67	60.46 ± 3.14	32.48 ± 1.44		
present	Pb	27.72 ± 1.37	68.56 ± 0.70	52.62 ± 2.08		
0/ a decomption	Cu	45.80	15.80	68.98		
% adsorption	РЬ	62.18	59.06	85.45		

A: St. Theresa Girls' Secondary School, Bwanda, Kalungu District; **B**: St. Joseph's Secondary & Technical School Kiteredde, Kyotera District; and **C**: St. Joseph's Secondary School Butenga, Bukomansimbi District.

could have been used during laboratory sessions. Thus, wastes with copper (II) and lead (II) ions in the above range of concentrations may effectively be removed by the bio-char of FNF provided effects such as ion interference are minimized.

4. Conclusion

The bio-char from FNF at 47.5°C showed an ability to absorb copper (II) and

lead (II) ions from aqueous solutions endothermically. The process took place efficiently at pH of 5 and 4, with adsorbent dosage level of 0.4 g for 60 minutes. The maximum adsorption capacity was 161.29 mg/g for copper (II) and 1250 mg/g for lead (II) ions when fitted in the Langmuir model. Bio-char from FNF may therefore be adopted as a potential material to use during treatment of waste aqueous solutions from industries and school laboratories containing heavy metals especially those of copper (II) and lead (II) ions at a concentration range of between 5 and 100 mg/l.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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