



Original Paper

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Adsorption of Pb^{2+} and Cu^{2+} ions from aqueous solutions by mango tree (*Mangifera indica*) saw dust

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ABSTRACT

The removal of heavy metal ions Cu^{2+} and Pb^{2+} from aqueous solution using mango tree (*Mangifera indica*) saw dust as adsorbent under different experimental conditions was investigated. The effects of pH, contact time, temperature, adsorbent dosage and initial metal ion concentrations for the removal of Cu^{2+} and Pb^{2+} ions from aqueous solutions were studied using atomic absorption spectrophotometer. The results showed that increasing the amount of adsorbent led to an increase in the percent removal of lead and copper. The optimum pH obtained was pH 6 for copper and pH 8 for lead, with percentage removal of 99.9% Pb^{2+} ions and 70.1% Cu^{2+} ions. It was observed that *Mangifera indica* saw dust removed more of Pb^{2+} than Cu^{2+} ion in all the adsorption experiments.

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INTRODUCTION

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. Although sources such as agricultural and sewage disposal also contribute. Unlike organic pollutants, the majority of which are susceptible to biological degradation, heavy metal ions do not degrade into harmless products (Ko et al., 2000; Ikhuoria and Okieimen, 2000; Arowolo, 2004; Okuo et al., 2009). Their presence in the atmosphere, soil and water even in traces can cause serious problems to all living things (Guptal et al., 2001; Kadriavelu et al., 2008; Okuo et al., 2008). Man's exposure to heavy metals comes from industrial activities like mining, smelting, refining and manufacturing

processes (El-Geundi et al., 2005; Iqbal et al., 2005; Wankasi et al., 2005; Abia and Asuquo, 2006; Adesola et al., 2006). The assimilation of relatively small amounts of lead over a long period of time in the human body can lead to the malfunctioning of the organs and chronic toxicity (Tanguank et al., 2009). Copper is essential to human health but, like all heavy metals it is potentially toxic as well. For example, continued inhalation of copper containing sprays is linked with an increase in lung cancer among exposed workers (Horsfall et al., 2004; Moshen, 2007). The adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost (Babarinde, 2002; Demibras, 2003). Generally, many reports have appeared on the

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development of activated carbon from cheaper and readily available materials. The low cost agricultural wastes such as rubber seed coat, sugar cane bagasse, rice husk, maize cob, sawdust, oil palm etc are used for the elimination or sorption of heavy metals from solutions (Horsfall and Spiff, 2005; Wankasi et al., 2005; Pavasant et al., 2006). Apart from the plant based material chemical modification of various adsorbents, phenol formaldehyde cationic matrices (Singanum et al., 2006), sulphur containing modified silica gels and commercial activated charcoals are also employed (Verwilghen et al., 2004). The purpose of this work was therefore to investigate the potentials of *Mangifera indica* saw dust as an adsorbent for removing lead and copper from aqueous solutions. The objectives of this study therefore are: (1) to investigate the potential use of (*Mangifera indica*) saw dust as an adsorbent for the sorption of lead and copper ions from aqueous solutions; (2) to investigate the effect of temperature, contact time, metal ion concentration, pH, adsorbent mass dose and also the efficiency of (*Mangifera indica*) saw dust in removing these metal ions from aqueous solutions.

MATERIALS AND METHODS

Mangifera indica sawdust used for the work was obtained from a local sawmill along Iwofe road by Saint John's Bus Stop, Rumuolumeni, Port Harcourt. The sawdust was air dried for 5 days and then oven dried (Galen Kamp, Model OV -160, England) at 105 °C for 2 h and crushed using a blender. The powdered material was sieved using a 106 µm mesh Tyler sieve, to obtain a fine biomass. 500 g, of the sieved adsorbent was soaked in 250 ml 0.3 M HNO₃ solution for 24 h, and later washed thoroughly with distilled water until a pH of 7.0 was attained. The rinsed adsorbent was then air dried for 12 h, ground and sieved with 105 µm, particle size for use. (Horsfall et al., 2003).

All reagents used were of analytical grade and distilled water was used in sample preparation. A stock solution of Pb²⁺ ion from lead chloride (PbCl₂) was prepared by

dissolving 0.7474 g of PbCl₂ in 1000 cm³ distilled water and for Cu²⁺ ion, 0.3981 g, of CuSO₄ was dissolved in 1000 cm³ distilled water. From the stock solutions, working solutions of initial concentration (100 mgL⁻¹) of each metal were prepared by serial dilutions.

Adsorption experiments

Effect of initial metal ions concentration

Batch adsorption experiments were performed by contacting 1.0 g of the adsorbent with 100 mL of aqueous solutions of different initial concentrations (40-100 mgL⁻¹) at pH 6 and 8 for lead and copper respectively. The experiment was performed for 1 hour at 150 rpm using 250 ml Erlenmeyer flask containing 100 ml of different lead and copper concentrations at room temperature 30 °C. Continuous mixing was provided during the experimental period with a constant agitation speed of 150 rpm for better mass transfer with a high interfacial area of contact. It was filtered, centrifuged for 5 minutes and analysed with atomic absorption spectroscopy (AAS).

The initial pH of each of the solutions was adjusted to the optimum pH value by drop-wise addition of 0.1 M NaOH and 0.5 M HNO₃ except for the experiment of the effect of pH where the study was carried out at different pH values.

Effect of pH

The effect of pH on the amount of Pb²⁺ and Cu²⁺ metal ions was analyzed over the pH range from 2-10. In this study, 100 ml metal ions concentration of 100 mgL⁻¹ was measured into seven 250 ml conical flasks and 1.0 g of the biomass was added and the pH of the solutions in the flask was adjusted with 0.5 M HCl and 0.1 M NaOH solutions, such that the pH values of the solutions in the conical flasks were 4, 6 and 10 respectively. The various pH values of the solutions were then taken with a digital pH meter. The solution was filtered using Whatman No 40 filter paper and the residual metal ions concentration analyzed.

Effect of temperature

100 ml Pb²⁺ metal ion concentration of 100 mgL⁻¹ was measured into eight 250 ml conical flasks. 1.0 g of the biomass with particle size 106 µm was then weighed and added to these solutions. The conical flasks were then labelled temperatures of 10, 20, 30, 40, 50, 60, 70 °C and 80 °C, respectively. The flasks were agitated at 150 rpm and heated on thermostatic water bath to the appropriate temperatures. The suspensions were then filtered using Whatman No 40 filter paper, centrifuged for 5 minutes and analyzed. The same experiments were also carried out using Cu²⁺ ion.

Effect of contact time

The effect of contact time on the removal of Pb²⁺ ions was carried out for a period of 120 min at a time interval of 20 min.

Effect of adsorbent dosage

Different masses of the biomass ranging from 1-7 g were accurately weighed and transferred into several 250 ml conical flasks. 100 mgL⁻¹ of metal ion solutions of Pb²⁺ was added to each of the conical flasks. The flasks were tightly covered with cellophane and shaken for 1 hour, the suspensions were filtered through Whatman No 40 filter paper, centrifuged for 5 minutes and analysed. The same experiments were also carried out using Cu²⁺ ion. The procedures used are similar to those earlier reported (Vasudaran et al., 2003; Babarinde et al., 2006; Xu et al., 2006; Babarinde et al., 2008).

RESULTS

The percentage removal of metal ion by saw dust was calculated using the following equation:

$$\%R = \frac{[(C)_0 - C_e]}{C_0} \times 100 \quad \dots\dots(1)$$

R is removal and C₀ = initial metal concentration in solution (mgdm⁻³) and C_e = the metal concentration in solution at equilibrium (mgdm⁻³).

The concentration of lead and copper retained in the adsorbent was also calculated according to the following equation:

$$q_e = \frac{[(C)_0 - C_e]}{C_0} \frac{V}{m} \quad \dots\dots(2)$$

Where q_e (mgg⁻¹) is the amount of chromium or zinc sorbed by the adsorbent. C₀ and C_e (mgL⁻¹) are the initial and equilibrium concentrations of the metal ions respectively. V (L) is the initial volume of metal ions concentration and m (g) is the weight of the adsorbent.

The results of the five different studies are shown in Figures 1-5. It was observed that Pb²⁺ ion was generally more adsorbed in all the adsorption experiments. From the graph in Figure 1 it was observed that as the concentration increased from 40-100 mgL⁻¹ the rate of adsorption increased.

The result of the pH study showed that maximum adsorption occurred at pH 6 for copper and pH 8 for lead (Figure 2). The percentage copper adsorbed was lower than the percentage for lead. More than 99% of lead was removed compared to 70.1% of copper.

The optimum temperature for Pb²⁺ and Cu²⁺ ions removal was observed to be 20 °C as shown in Figure 3. As the temperature increases, the amount of Pb²⁺ and Cu²⁺ ions removed decreased.

The relationship between contact time and the percentage removal of pb²⁺ and Cu²⁺ ions from solution by bumper saw dust biomass is presented in Figure 4. From the plot, it is seen that the adsorptive capacity of Pb²⁺ and Cu²⁺ metal ions increased from 15.4%-87.4% and 12.3%-80.4% when contact time was increased from 20 to 60 min for both metal ions respectively.

The effect of adsorbent dosage is shown in Figure 5. The amount of adsorbent employed was found to influence the efficiency of the adsorption process. The percentage of lead and copper ions removed increased with increasing adsorbent dosage until the surface became saturated and further increase had no effect. The increase was highest with 7.0 g removing 85.4% lead and 78.8% copper.

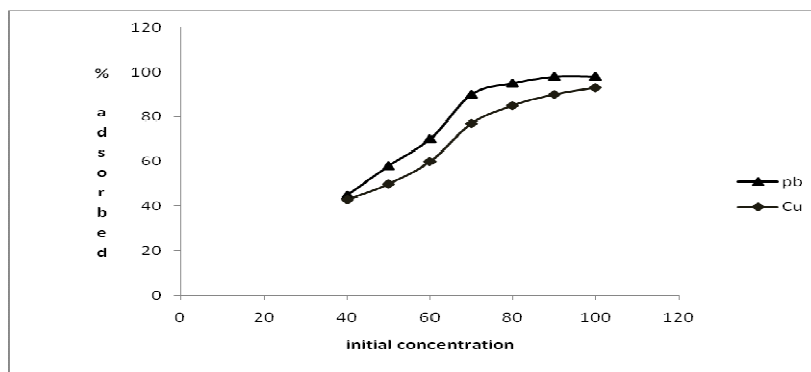


Figure 1: Effect of initial concentrations on sorption behaviour of Pb^{2+} and Cu^{2+} ions from solution. Initial concentration= 40-100 mgL^{-1} , pH=6 and 8, equilibrium time =1 hr, Temp=30 °C.

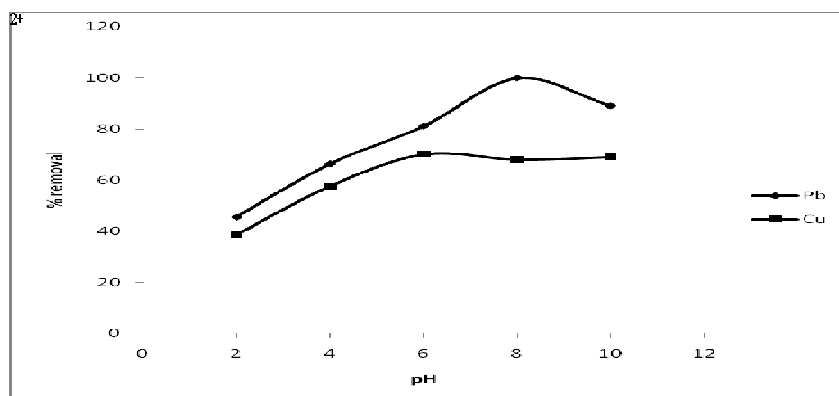


Figure 2: Effect of pH on sorption behaviour of Pb^{2+} and Cu^{2+} ions from solution. Initial concentration= 100 mgL^{-1} , pH=6 and 8, equilibrium time =1 hr.

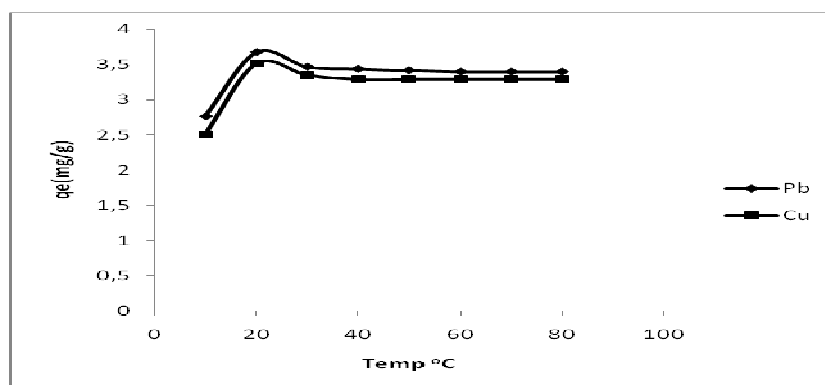


Figure 3: Effect of temperature on sorption behaviour of Pb^{2+} and Cu^{2+} ions from solution. Initial concentration= 100 mgL^{-1} , pH=6 and 8, equilibrium time =1 hr.

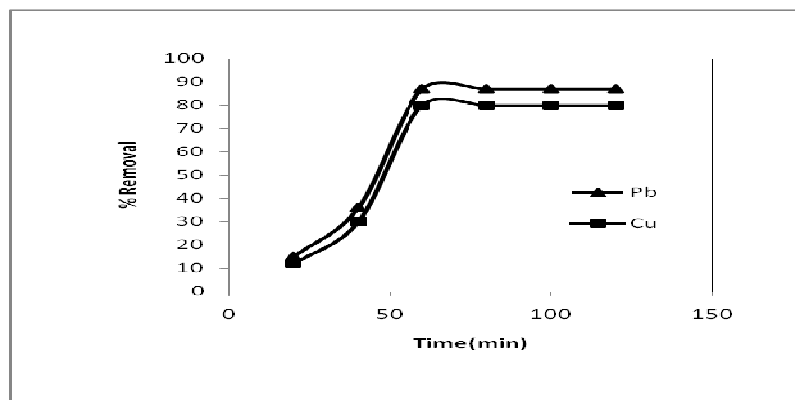


Figure 4: Effect of contact time on the percentage removal of Pb²⁺ and Cu²⁺ ions from solution. Initial concentration= 100 mgL⁻¹, pH=6 and 8, Temp=30 °C.

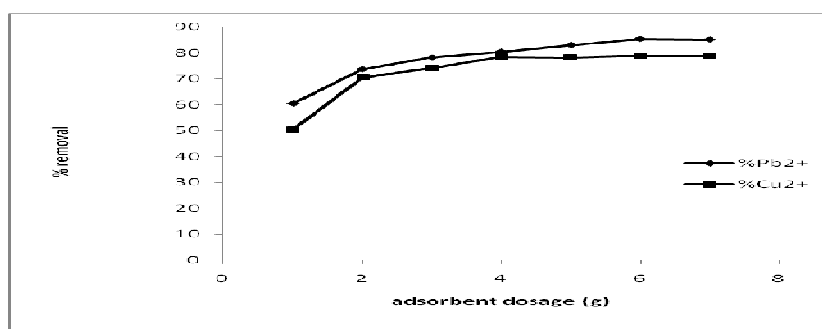


Figure 5: Effect of adsorbent dosage on sorption behaviour of Pb²⁺ and Cu²⁺ ions from solution. Initial concentration= 100 mgL⁻¹, pH=6 and 8, equilibrium time =1hr, Temp=30 °C.

DISCUSSION

It was observed that Pb²⁺ ion was generally more adsorbed in all the adsorption experiments. The variations in adsorption of these metal ions might be due to their differences in physical and chemical properties of both heavy metal ions. It might also be due to a combination of factors such as hydrogen bonding, precipitation and formation of insoluble metal complexes as reported by (Horsfall et al., 2004; Pavasant et al., 2006; Moshen 2007). It was observed that as the concentration increased from 40-100 mgL⁻¹ the rate of adsorption increased. This is due to the presence of more metal ions in solution as the concentration increases. Adsorption capacity also increases as concentration increases until the adsorbent reaches its threshold.

Maximum adsorption occurred at pH 6 for copper and pH 8 for lead. The percentage copper adsorbed was lower than the percentage for lead. More than 99% of lead was removed

compared to 70.1% of copper which showed that (*Mangifera indica*) bumper sawdust is more favourable for the removal of lead than copper in solution. The adsorptive capacities of Pb²⁺ and Cu²⁺ ions increased but at a slower rate because of the competitive adsorption between hydrogen ion and the heavy metal cations. The continuation increases in the adsorptive capacities of Pb²⁺ and Cu²⁺ ions with increasing pH value is due to the decreases in the hydrogen ion concentration as the pH value decreased. With the increase in pH for 8-10 for lead and 6-10 for copper, the degree of protonation of the adsorbed functional group decreased gradually and hence removal decreased. A close relationship between the surface basicity of the adsorbents and the anions is evident. This is similar to the findings of Oboh et al. (2009).

The differential sorption of the two ions may be ascribed to the difference in their ionic radii (Pb²⁺ is 0.120 and Cu²⁺ is 0.092). The

smaller the ionic radius, the greater its tendency to hydrolyse leading to reduced sorption. The maximum sorption efficiency of copper at pH 6 may be due to the interaction of Cu^{2+} , $\text{Cu}(\text{OH})^+$, $\text{Cu}(\text{OH})_2$ with surface functional groups present in sawdust. Decrease in adsorption at high pH may be due to the formation of soluble hydroxyl complexes.

The optimum temperature for Pb^{2+} and Cu^{2+} ions removal was observed to be 20 °C. As the temperature increases, the amount of Pb^{2+} and Cu^{2+} ions removed decreased. Adsorption processes are normally exothermic. High temperature increases entropy and this leads to reduction in the stability of metal ion, thereby increasing its randomness and consequently reducing the amount of heavy metal ions available for binding at elevated temperatures.

From the plot of the relationship between contact time and the percentage removal of Pb^{2+} and Cu^{2+} ions from solution, it is seen that the adsorptive capacity of Pb^{2+} and Cu^{2+} metal ions increased from 15.4%-87.4% and 12.3%-80.4% when contact time was increased from 20 to 60 min for both metal ions respectively. At a time interval of 20 min and an initial metal ion concentration of 100 mgL^{-1} adsorption of the amount of copper and lead removed by the biomass increased until a contact time of 60 min. The maximum adsorption for both metal ions occurred at contact of 60 min. For both copper and lead the percentage copper removal was above 80 percent. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

The amount of adsorbent employed was found to influence the efficiency of the adsorption process. The percentage of lead and copper ions removed increased with increasing adsorbent dosage until the surface became saturated and further increase had no effect. The increase was highest with 7.0 g removing 85.4% lead and 78.8% copper. The increase can be explained by a greater availability of exchangeable sites or surface area at higher amount of the adsorbent. The significant increase in uptake was observed when the dose was increased from 2-6 g/L. Any further addition of adsorbent beyond this point did not cause any significant change in the adsorption.

This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles (Senthil and Kithikar, 2009).

Conclusions

The following conclusions were drawn from the above experiment:

1. Adsorbent prepared from (*Mangifera indica*) saw dust can be used for the removal of Pb^{2+} and Cu^{2+} metal ions in aqueous solutions.
2. The maximum percentage removal occurred at pH 6 for copper and pH 8 for lead.
3. *Mangifera indica* saw dust removed more lead than copper ions in solution.
4. Low temperature favoured the adsorption of lead and copper ions.

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