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Agricultural waste as a low cost adsorbent for heavy metal removal from wastewater

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Biosorption was carried out in a batch process to test the suitability of *Amaranthus hybridus* (African spinach) stalk and *Carica papaya* (pawpaw) seed for removal of Mn (II) and Pb (II) ions from aqueous solution. The amount of metal ions removed from solution depended on the metal ion-substrate contact time, ion concentration and ion type. The contact time was 90 min for both substrates. The results indicated that the amount of absorbed metal ions varied with substrates materials, and the order of removal of heavy metals by the biosorbents was Mn (II)>Pb (II). Furthermore, Mn (II) had higher removal percentages than Pb (II) ions in both substrates. In all cases, *C. papaya* seeds showed greater adsorptive capacity than *A. hybridus* stalk. The result from both biomasses significantly fitted the Freundlich adsorption isotherm. The results obtained through the study showed both substrates are favourable for sorption and removal of heavy metal from aqueous solution.

Key words: *Amaranthus hybridus* stalk, *Carica papaya* seeds, adsorption, manganese, lead, contact time.

INTRODUCTION

The removal of toxic metals from sewage and industrial waste water is a matter of great interest in the field of water pollution, which is a serious cause of water degradation (Zheng- Guo et al., 2002; Rao et al., 2009; Egila et al., 2010). Pollution by heavy metal ions has become a major issue world over due to their possible toxic effects (Aydin et al., 2008). Exposure to Lead (Pb) for instance, is widely recognized as a major risk factor for several human diseases, and the structure of industrial ecological systems have made exposure to Pb unavoidable for most people alive today (Needleman, 1999; Pruss-Ustun et al., 2004; WHO, 2000). Mn (II) ion removal from discharge waters is serious problem in many countries. Although dissolved Mn (II) ion is not known to be toxic and even blocks the toxic effect of H^+ ion, but it has undesirable effects on water use. These include training laundry and ceramic fixtures such as toilets where concentrations are greater than 0.05 mg/L (U.S. Environmental Protection Agency, 1994). In drinking water sources, the secondary maximum contaminant level (SMCL) for Mn (II) ion must not exceed 0.05 mg/L (Aydin et al., 2008). Pb (II) ion is also known to bioaccumulate through the food chain often associated with heavy metals such as Zn (II),Cu (II), Cd (II), Mn (II) and Hg (II) that are released into the aqueous environment through variety of sources such as metal smelters, effluents from plastics, textiles, microelectronics and wood preservative producing industries and usage of fertilizer and pesticides (Bhatti et al., 2007; Qiu et al., 2008). These metals ions are stable and are known to be persistent environmental contaminants since they cannot be degraded or destroyed. They are harmful to aquatic life and water contaminated by them remains a serious public health problem to human health (Ko et al., 2000; Koller, et al., 2004). It therefore becomes imperative to determine these metal ion concentrations in bodies of water.

Environmental concerns have motivated many physic-chemical methods for heavy metal removal from aqueous solution. These methods include liquid-liquid extraction (LLE), co-precipitation, resin chelation, electrochemical deposition, ion exchange, coagulation or flocculation and solid -phase extraction (SPE) (Juang and Shiau, 2000;

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Amuda and Amoo, 2006; Amuda and Alade, 2006; Amuda et al., 2006). These techniques however, have disadvantages such as incomplete metal removal, high reagent and energy requirements and generation of toxic sludge or other waste products (Ahalya et al., 2003; Igwe et al., 2005).

Due to increasing environmental awareness and legal constraints imposed on discharge of effluents, the need for cost effective alternative technologies is essential for removal of heavy metals from industrial wastewater. An innovative technique that is both efficient and economical is biosorption. This has evolved as the frontline of defense especially for metals that could not be removed by other techniques (Mohan and Singh, 2001). This creates a need for the conversion of fiber (Okuo and Oviawe, 2007), *Bombax malabaricum* fruit shell (Somasekhara et al., 2007 agricultural products and by-products to useful and value-added products (Kumar and Bandyopadhyay, 2006). Recent studies have shown that heavy metals can be removed using plant materials such as empty palm oil fruit bunch (Rafeah et al., 2009), sour sop seeds (Oboh and Aluyor, 2008), modified cassava, cassava fibre (Egila and Okorie, 2002), coconut shell (Gimba et al., 2001) and *Wolffia globosa* (duck weed) (Upatham et al., 2002). The removal of lead and copper ions from aqueous solutions by sago waste was reported by Ho et al. (2002). Also a range of other agricultural by-products used for metal removal include banana pith, tree fern, and *Humulus lumpus* (hop) (Gardea-Torresdey et al., 2002). It is worthy of mentioning that the annual production of *Amaranthus hybridus* (African spinach) stalk and *Carica papaya* (pawpaw) is on the increase in Minna metropolis most especially along agricultural land and wastelands as they constitute one of the major vegetables and fruits consumed in Minna, Niger State, Nigeria. Despite the essential benefit derived from consuming vegetables and fruits, large quantities of their wastes constitute environmental pollution due to lack of proper waste disposal system.

Until this present work, little or no information is available on the suitability of using these wastes in removing heavy metals from aqueous solution. This research is designed to study the removal of toxic heavy metal ions by African spinach stalk (*A. hybridus* L) and pawpaw seed (*C. papaya* L) from aqueous solution and to offer these adsorbents as alternative to high cost commercial adsorbent materials.

MATERIALS AND METHODS

Sample and sampling preparation for sorption studies

African spinach (*A. hybridus*) stalk waste and pawpaw (*C. papaya*) seeds were obtained from different locations within Former Mobil market, Minna, Niger State, Nigeria. Sampling was done at random from different retailers within this market area. A composite sample was made from where the representative samples were collected for these studies.

Sample pretreatment for sorption studies

5.00 g screened fine adsorbent was soaked in excess 0.3 moldm^{-3} HNO$_3$ for 24 h to remove any debris or soluble biomolecules that might interact with the metal ions during the sorption process. This constitutes the chemical activation of the samples. The adsorbent was then filtered through Whatman No.41 filter paper and rinsed with de-ionised water. The rinsed adsorbent was later air dried for 12 h.

Simulated wastewater preparation

Simulated wastewater samples containing Mn (II) and Pb (II) ions were prepared from MnCl$_4$ and PbNO$_3$. 1000 mg/L stock solutions of each of the salts were prepared. Other concentrations (10 to 50 mg/L) were obtained from this stock solution by serial dilution. Fresh dilutions were used for each experiment. The pH of the simulated wastewater was adjusted to a pH of 5 to prevent hydrolysis. The concentration of metal ions in simulated wastewater was analyzed by Atomic Absorption Spectrophotometer.
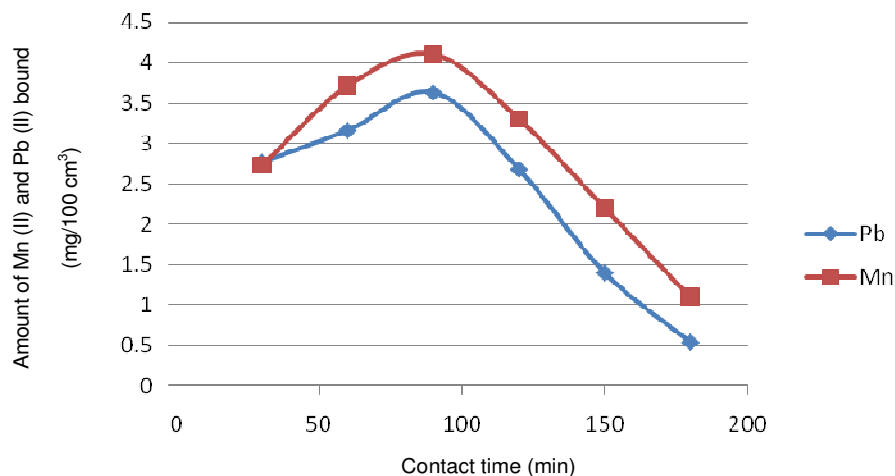
Effect of contact time

The experimental procedure described by Okieimen and Okieimen (2001) was modified as follows: 0.5 g of the pretreated powdered samples were taken and shaken with 100 cm^3 of a metal ion solution whose concentration was 5 mgdm^{-3}. The bottles were shaken at various time intervals of 30 to 180 min at room temperature in a reciprocating shaker at 300 rpm. At the end of each contact period the mixture was filtered using Whatman filter paper No. 42 and the filtrate was stored in sample bottles in a refrigerator prior to analysis. The final concentration of the metal ion in the filtrate was determined by Atomic Absorption Spectrophotometer (AAS), model Pye Unicam SP-9 Cambridge, UK.

Effect of concentration

The equilibrium sorption was carried out at 33°C using a concentration range of 10 to 50 mgdm^{-3}. 0.5 g of the substrates was weighed into a 250 cm^3 conical flask and 100 cm^3 of the metal ion solution was measured into each conical flask containing the substrates. The conical flask was shaken for 90 min at room temperature in a reciprocating shaker at 300 rpm. The substrates were removed from the mixture by filtration and the concentration of the residual ions in the solution was determined. The amount of metal ions adsorbed from solution was determined by difference.

RESULTS AND DISCUSSION

Figures 1 shows that the amount of Mn (II) and Pb (II) ions adsorbed by the substrate initially increased with contact time up to a maximum of 4.1 mg/100 cm^3 and 3.63 mg/100 cm^3 respectively and then decreased thereafter. Similarly, the amount of Mn (II) and Pb (II) ions bound in both *A. hybridus* stalk were 3.32 mg/100 cm^3 and 2.82 mg/100 cm^3 after 90 min of contact time as shown in Figure 2. For both adsorbents, there was a progression in the rate of adsorption although it was not linear at any time as shown in Figures 1 and 2. It was also observed that the rate of adsorption increased significantly for the metal ions present for 90 min of

Figure 1. Effect of variation of contact time on the adsorption of Mn^{2+} and Pb^{2+} on *C. papaya* seeds at 33°C.
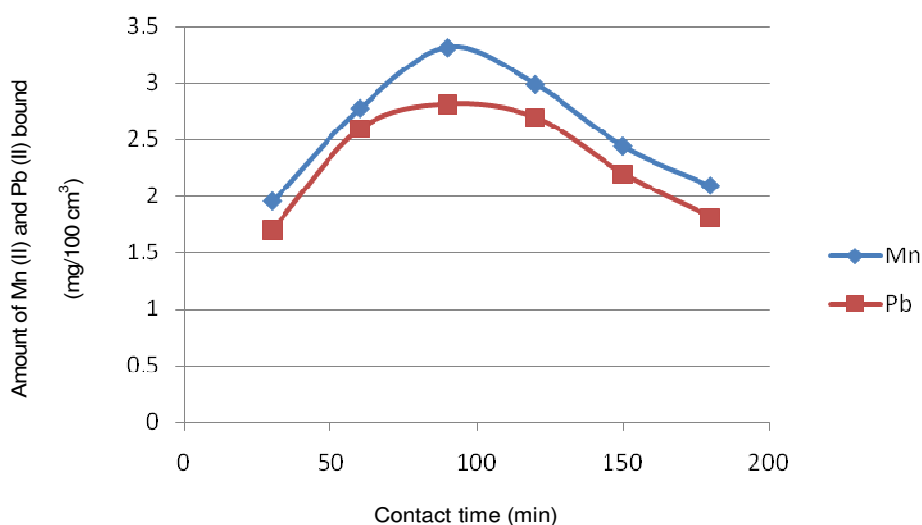

Figure 2. Effect of variation of contact time on the adsorption of Mn^{2+} and Pb^{2+} on *A. hybridus* L stalk at 33°C.

contact time. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system. The trend observed for the metal ions in the two substrates under the same experimental conditions revealed that the pattern of adsorption is a function of the substrate as well as that of the metal ions (Egila and Okorie, 2002; Egila et al., 2010).

Furthermore, manganese with small ionic size was observed to have adsorbed at a faster rate. This may be explained by considering the ionic radii which was observed for Mn^{2+} with higher rate of removal at equilibrium time than Pb^{2+}. This has been observed on other biological adsorbents as reported earlier (Abia et al., 2003; Horsfall et al., 2003). Therefore, the smaller the

ionic size, the greater its affinity to reactive sites. The results showed that the adsorption of cations with larger ionic radii would be less likely compared with smaller ionic radii. Since Mn^{2+} has smaller ionic radii, it is possible that Mn^{2+} ions would diffuse faster through the adsorbent pores faster than the bulkier ions like Pb^{2+}. According to Abia and Asuquo (2006) during sorption of metal ions, the ions of smaller ionic radii tend to move faster to potential adsorption.

The uptake level of Mn (II) and Pb (II) ions from solutions containing various amounts of the metal ions by *C. papaya* seeds are shown in Figure 3, while Figure 4 represent the amount of Mn (II) and Pb (II) ions adsorbed at varying concentration using *A. hybridus* stalk as the
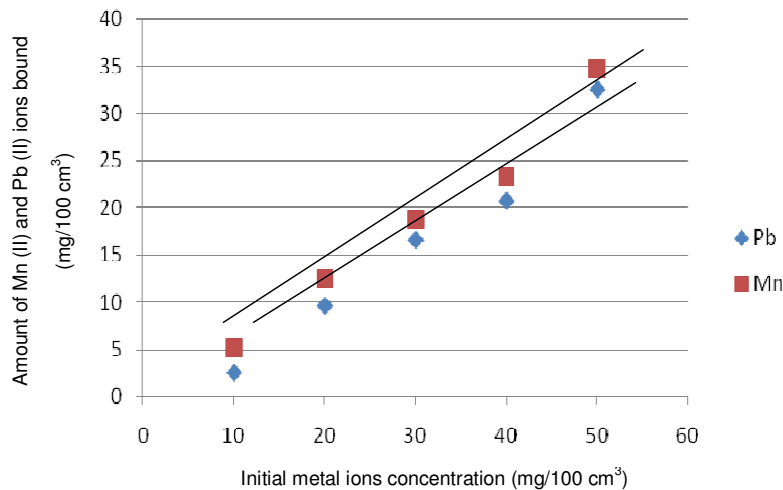
Figure 3. The effect of varying Mn(II) and Pb(II) ions concentration on the adsorption of *Carica papaya* seeds at 33°C for 90 min.
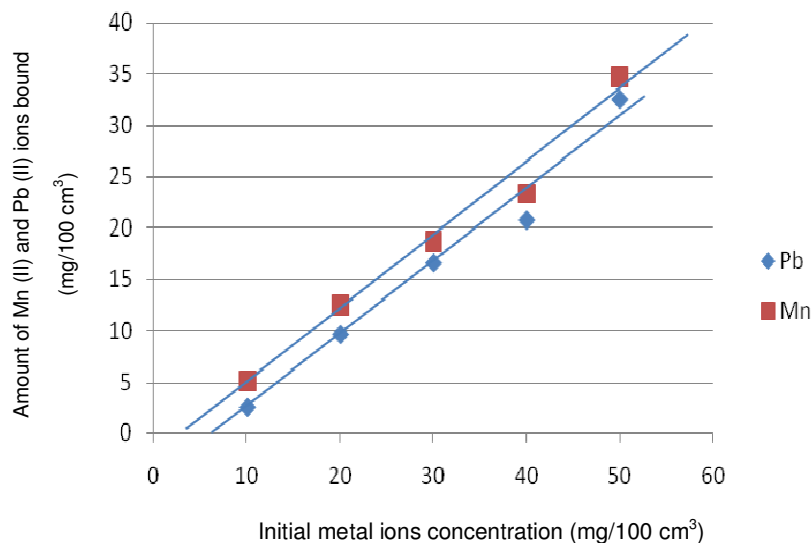

Figure 4. The effect of varying Mn(II) and Pb(II) ions concentration on the adsorption of *A. hybridus L stalk* at 33°C for 90 min.

metal ions concentration increases from 10 to 50 mg/100 cm³. The results showed that the amount of the metal ions bound by the cellulosic substrates depended on the metal ions type and the concentration of the metal ions. The level of metal ions uptake and percentage removal followed this order Mn>Pb. For the two substrates, the difference in the uptake levels of the metal ions can be explained in terms of the difference in the ionic size and atomic weight of the metal ions, the mode of interaction between the metal ions and the substrate. The initial faster rate of removal of each metal ion could be due to the availability of the uncovered surface area of the

adsorbents, since adsorption kinetics depends on the surface area of the adsorbent (Qadeer and Akhtar, 2005). The trend could also be explained in terms of the progressive increase in the electrostatic interaction between the metal ions and the absorbent active sites. Moreover, more adsorption sites were being covered as the metal ions concentration increased (Laraous et al., 2005; Gong et al., 2006). Besides, higher initial concentrations led to an increase in the affinity of the metal ions towards the active sites (Al-Asheh et al., 2003).

Furthermore, a comparison of the two substrates clearly showed that at any given metal ions concentration,
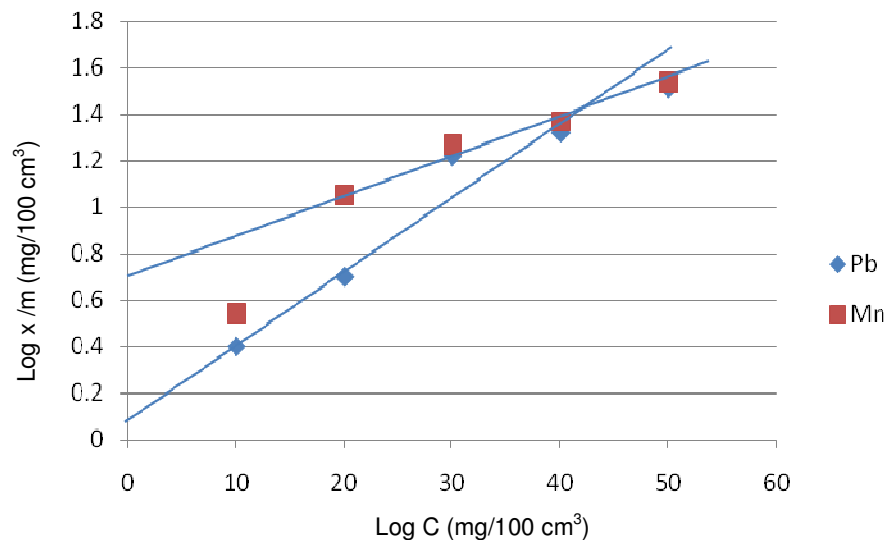
Figure 5. Freundlich adsorption isotherm. Plot of Log (x/m) against Log C .for Mn (II) and Pb(II) ions , where x is the mass of the adsorbate, m is the mass of adsorbent and C is the residual concentration(for *C. papaya* seeds).
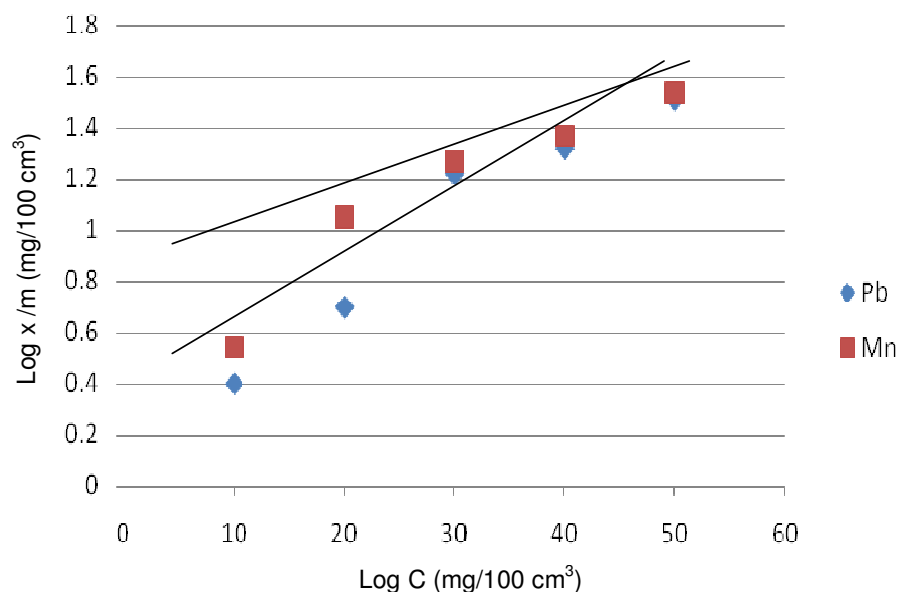
Figure 6. Freundlich adsorption isotherm. Plot of Log (x/m) against Log C. for Mn (II) and Pb (II) ions, where x is the mass of the adsorbate, m is the mass of adsorbent and C is the residual concentration(for *A. hybridus* L stalk).

C. papaya seeds could bind more of the metal ions than *A. hybridus* stalk. This confirmed further that the nature of the cellulosic material had a unique role in the adsorption mechanism. When the sorption data of the metal ions investigated on *C. papaya* seeds and *A. hybridus* stalk substrate were plotted logarithmically as shown in Figures 5 and 6 respectively, they fitted the Freundlich adsorption isotherm. The K-value of Mn^{2+} (0.70) is greater than Pb^{2+} having the lowest value of 0.10 in paw-paw seeds. The K- value of Mn^{2+} in the second sample is 0.69 with Pb^{2+} still having the least value of 0.09. Again, the smaller ionic radius of Mn^{2+} might be responsible for its greater adsorptivity. The value of 1/n. which is less than 1 is an indicative of favourable adsorption. A smaller

value of 1/n indicates better adsorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent (Patil et al., 2006).

Conclusion

This preliminary study therefore indicates a potential for the use of agricultural waste such as pawpaw seeds as well as African spinach stalk in removing heavy metal ions from wastewater. There is need to investigate other plants for use as adsorption agents with a view to improve our water quality and consequently address the issue of environmental pollution caused by heavy metals.

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