Application of adsorbent from dum palm for the removal of manganese (II), zinc (II), and copper (II) ions from aqueous solution

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Application of adsorbent from Dum palm for the removal of Manganese (II), Zinc (II) and Copper (II) ions from aqueous solution

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Abstract: The batch adsorption of Mn (II), Zn (II) and Cu (II) ions from aqueous solution using frond and leaves of dump palm was investigated. The influence of sorption time, initial metal ion concentration and adsorbent dosage were evaluated. The results showed that these parts of dump palm have relatively high adsorption capacity for these heavy metals ions. The percentage removed was (76%), (64%), (62%) and (64%) (57%) (56%) for Mn (II), Cu (II) and Zn (II) ions respectively for frond and leaves. Adsorption equilibrium was established in 90mins for Mn (II), Cu (II) and Zn (II) ions. The equilibrium data generated fitted well for Freundlich adsorption model. The obtained results show that the both the leaves and the frond of dump palm are favourable for the sorption of the heavy metal ions.

1. Introduction

Industrial activities such as mining electroplating, tanning, metallurgical operations and manufacturing have led to the release of heavy metals into the environment (Sekar *et al.*, 2004). Unlike the organic pollutants which are biodegradable, heavy metal ions like Mn(II), Cu(II) and Zn(II) are not biogradable (Org *et al.,* 2007) thus making them a sources of great concern. Through food chain, the heavy metals bioaccumulate in living organisms and reached level that cause toxicological effects (Ko *et al.,* (2000). Human health, agricultural development and the ecosystems are all at risk unless water and land system are effectively managed *(*Rao *et al.,* (2009). The chronic effects of high level consumption of copper are liver and kidney damage (Aydin *et al.,* 2008). Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it can result into headaches, stomaches, dizziness and vomiting (Pruss-ustu *et al.,* 2004). Although human beings can handle proportionally large-concentration of zinc, too much zinc can cause adverse health problems such as stomach cramps, skin irritation, vomiting. Very high levels can damage the pancreas and disturb protein metabolisms, and cause arteriosclerosis (Igwe *et al.,* 2005). As a result of the toxicological effects of these metals, interests in heavy metals removal from waste water have been on the rise.

Several methods have been developed to remove heavy metals ions from aqueous solution before discharge into the water bodies. These methods includes, reduction, precipitation, ions exchange reverse osmosis dialysis and adsorption by coated carbon. Most of these methods are expensive so are not affordable for a developing country like Nigeria. They also have limited applications as they cannot remove metals at low concentrations (Ahalya

et al., 2005). With increasing environmental awareness and legal constraints imposed on discharge of effluents, the needs for cost – effective alternative technologies is essential for removal of heavy metals ions from industrial waste water. Agricultural wastes are characterized by ready availability, affordability, eco-friendliness and high uptake capacity for heavy, metals due to the presence of functional groups which can bind metals to effects the removal of heavy metal from effluents (Rafah *et al.,* 2009). Recent studies have shown that heavy metals can be removed using plants materials such as Sour sop seeds (Oboh and Aluyor, 2008), Cassava fibre (Egila and Okorie 2002), Coconut shell (Gimba *et al.,* 2001), Oil palm empty fruit bunch (Rafeah *et al.,* 2009), palm kernel (Tumin *et al.,* 2008), Walnut skin (Chumbar *et al.,* 2003).

However, Palm tree are very common along the major roads in Bida, Nigeria in which the fruits serve as food, although this contains low vitamins and minerals. Apart from this fruits, it is advisable to use dump part of tree as an alternative for removal of heavy metal ions from aqueous solution since its economic value is less. Therefore, the aim of this study was to investigate the removal of Mn(II), Zn(II) and Cu(II) ions from aqueous solutions.

2. Materials and Methods
2.1 Adsorbent preparation

The waste biosorbent comprising leaves and frond dump palm were prepared accordingly. The leaves were prepared as adopted from (Ngah and Hanafia 2008). While the frond was prepared separately according to method adopted by Hamand *et al.*, (2008). Collected samples were washed with deionised water to remove dirt and clipped into smaller process. The samples were dried in oven over

70^{0}C for 48 hours. They were ground using mortar and pestle into different sizes at 400 um sieve size. The chemical modifications of the sample were made according to the similar method previously described by (Vaughan *et al.,* 2001). Both modified and unmodified samples were stored in clean polyethylene containers labeled accordingly prior to analysis.

2.2 Preparation of aqueous solution

All the reagents used were of analytical grade and were prepared with high quality distilled-deionised water. An aqueous solution containing Zn(II), Mn(II) and Cu(II) ions were prepared at 1000ppm (1000mg/L concentration following the method of Saeed *et al.,*(2004).

Stock solutions were prepared from salts of copper, manganese and zinc. Other concentration 5, 10, 20, 30, 4 and 50 mg/dm^3 salts were obtained using serial dilutions methods.

2.3 Biosorption Experiments

Batch studies carried out include biosortion dose dependence, time dependence and metal ions concentration describe by (Okieiman Okiemen, (2001). 0.5g of the powdered samples was added to 50 ml of 5mg/L aqueous solution. The mixtures were shaken in a rotary shaker at 150rpm for a predetermined sorption time followed by filtration using What Man filter paper (No. 42). The filtrate containing the residual concentration of Mn (II), Zn (II) and Cu (II) ions were determined using a Flame atomic Absorption spectrophotometer (AAS). All biosorption are performed in triplicate and mean values reported. Influence of biosorbent dosage was investigated by varying the biosorbent dosage. Biosorbent masses used for the study were 0.5, 1.0, 1.5, 2.0 and 2.5g. The study was carried out at room temperature. The agitation time for this experiment was set at 90 minutes. Initial metal ion concentration were 10, 20, 30, 40 and 50mg/L.

2.4 Adsorption isotherm

The Freundlich isotherm coefficients were determined by plotting log Qe against log Co and the results are shown in Table II. The Freundlich equation is an empirical equation based on adsorption on a heterogenous surface. Mathematically the equation is written as

Log x/m = logK + 1/nlog C

3.   Results

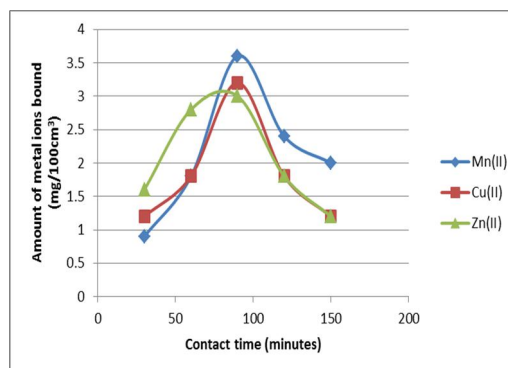Results are shown in Figures 1-12, as the following.

Figure 1: Effect of variation of contact time on the adsorption of Mn(II), Cu(II) and Zn(II) ions on Frond of Dump palm at 33^{0}C.
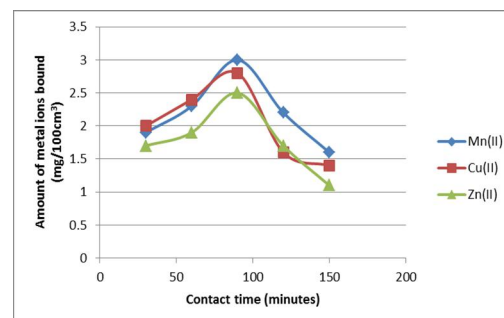

Figure 2: Effect of variation of contact time on the adsorption of Mn(II), Cu(II) and Zn(II) ions on leaves of Dump palm at 33^{0}C.
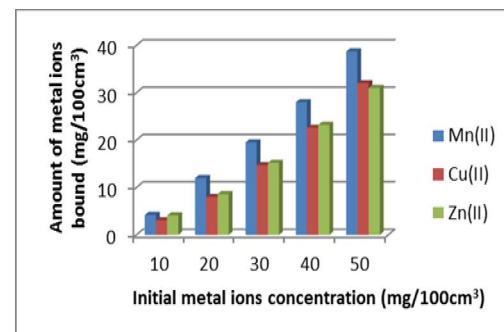

Figure 3: The effect of varying Mn(II), Cu(II) and Zn(II) ion concentrations on the adsorption by Frond at 33^{0}C for 90 minutes.
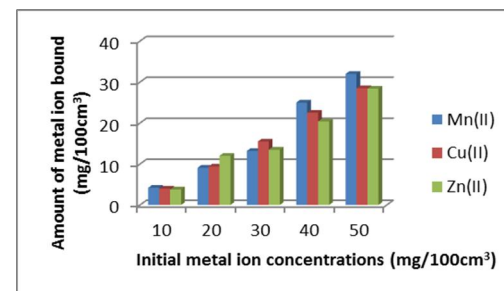

Figure 4: The effect of varying Mn(II), Cu(II) and Zn(II) ion concentrations on the adsorption by Leaves at 33^{0}C for 90 minutes.
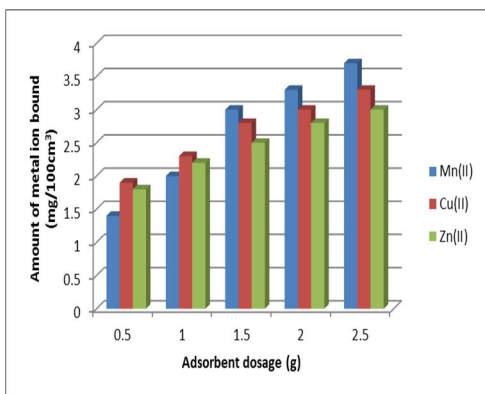
Figure 5: Effect of adsorbent dosage variation on the adsorption of Mn(II), Cu(II) and Zn(II) by Frond of Dump palm.
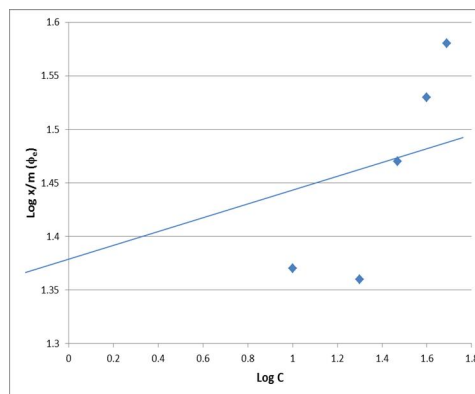

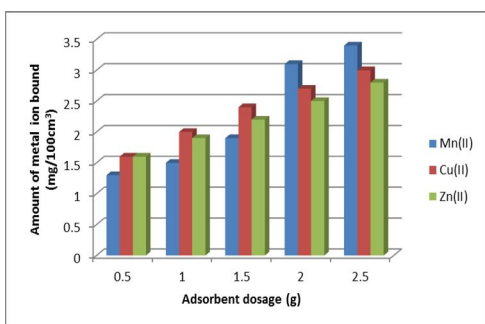Figure 9: Freudlich adsorption isotherm plot of frond substrate on adsorption of Cu (II) ion

Figure 6: Effect of adsorbent dosage variation on the adsorption of Mn(II), Cu(II) and Zn(II) by Leaves of Dump palm.

Figure 10: Freudlich adsorption isotherm plot of Leaves substrate on adsorption of Zn (II) ion

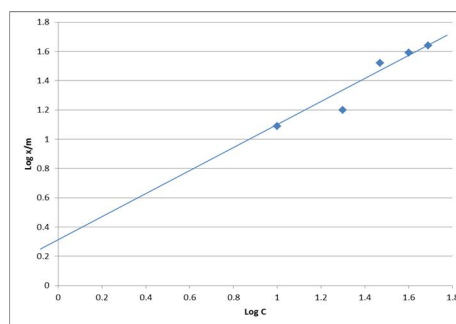Figure 7: Freudlich adsorption isotherm plot of frond substrate on adsorption of Mn (II) ion

Figure 11: Freudlich adsorption isotherm plot of Leaves substrate on adsorption of Cu (II) ion
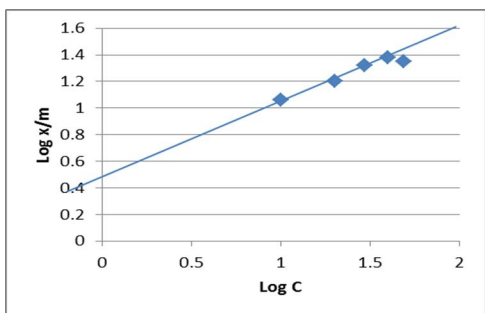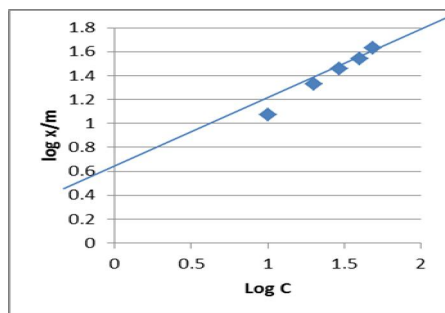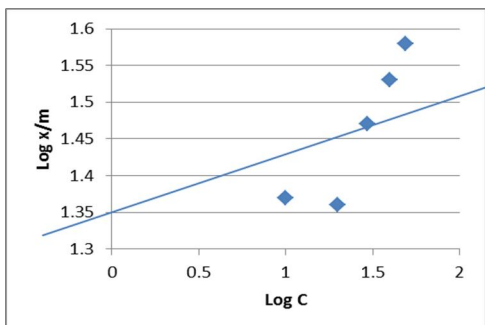

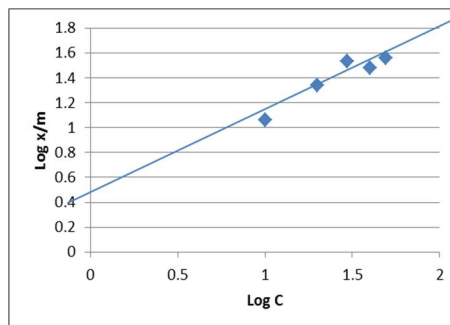Figure 8: Freudlich adsorption isotherm plot of frond substrate on adsorption of Zn (II) ion

Figure 12: Freudlich adsorption isotherm plot of Leaves substrate on adsorption of Mn (II) ion

4. Discussions

4.1 The effect of contact time on metal ion adsorption

The effect of contact time on the adsorption of Mn (II), Zn (II) and Cu (II) ions solution were shown in Figure 1 and 2. There is general increase in the % adsorption of the metal ions with time. However, the adsorption reached equilibrium in 90 minutes and that Mn (II) ions had the highest percent removal of 72.0 and 60.0 for frond and leaves respectively, followed by Cu (II) 64.0 and 56.0 frond and leaves. While Zn (II) ion had (60.0 and 50.0%) for frond and leaves respectively. There was gradual decline in adsorption after 90mins. The rapid initial rate increase followed by a slow rate at later period could be attributed to the availability of excess adsorption sites on the adsorbent. The initial high adsorption rate might possibly be due to ion exchange followed by a slow chemical reaction of the metal ions with active groups on the sample (Okuo and Oviawe, 2007). The trend observed might be due to saturation of the adsorption sites after 90mins, after which there is little or no percentage increase in adsorption despite increased agitation time. Further more Mn (II) ions had a higher removal percentage for all the adsorbent. This could be explained by considering that Mn (II) ions had a smaller ionic radius than Cu (II) and Zn (II) and as such. It tends to diffuse to the potential adsorption sites easier than other metal ions. This corrollaborated well with the finding of Abia *et al.,* (2003) who reported that ions with smaller ionic radii are more strongly attracted to the adsorbent site than the larger Hence a larger percentage of Mn (II) ions was removed more than other metal ions. The order of percentage removal is Mn **>** Cu **>** Zn in both substrates.

4.2 The effect of initial metal ions concentration on the adsorption of the metal ions.

The impact of concentration on the adsorption capacity of dump palm sample for Mn^{2+}, Cu^{2+} and Zn^{2+} are shown in Figure 3 and 4. As can be seen from the two figures, there was a general increase in adsorption of these metals up to a concentration of 50 mg/L. The result showed that the amount of metal ions bound by the cellulosic substrates depended on the metal ions types and the concentration of the metal ions. The percentage removal followed the order. Mn(II)> Cu(II) >Zn(II). The differences on the amounts of metal ion uptake can be explained in terms of difference in the ionic sizes, atomic weight of the metal ions and nature, distribution of active groups on the substrate and made of concentration and contact time. The maximum adsorption was obtained from frond samples (78%) then leave (52%). However, these metal exhibited less adsorption percentage compared to the Mn(II) ion. It has been noted the smaller the

ionic radius the higher the adsorption rate (Uzun and Guzel, (2000); Igwe and Abia, (2003).

Besides, higher initial concentration led to an increase in the affinity of the ions towards the active sites (Al-Ashel *et al.,* (2003). Further more, a comparison of the two adsorbents clearly showed that at any given metal ion concentration, Frond sample could bind more of the metal ions than leave sample. This confirmed that the nature of the cellulosic materials had a unique role on the adsorption mechanism.

4.3 The effect of variation of adsorbent mass on adsorption of metal ions

The percentage removal and uptake level of Mn (II), Cu (II) and Zn (II) ions from solutions by frond and leave samples are shown in Figure 5 to 6. It was observed that with a general increase in the adsorbent dose from 0.5g-2.5g, there is a corresponding increase in uptake level. This is due to increase in the available binding sites in the adsorbent (Oboh and Aluyor, 2008). The trend could be explained in terms of progressive increase in the electrostatic interaction between the adsorbent and metal ions. Moreover, more adsorption sites were being covered as the dose of the adsorbent increased (Igwe and Abia, 2003). An increase in percent removal of 78% and 70.0% were observed for frond and leave samples respectively as the dose increase from 0.5-2.5g. A Comparison of the two substrates clearly showed that at any given adsorbent dose of the frond could adsorb metal ion more than leave sample. This is probably due to the fact that the larger the surface area of adsorbent, the more the adsorption

4.4 Adsorption isotherm

The sorption data of the metal ions investigated on frond and trunk parts substrate were plotted logarithm mathematically as shown in Figure 7 to 12. They all fitted the Freundlich adsorption isotherm. The values of correlation coefficient as determined indicate that the adsorption process conforms to the Freundlich isotherms (Salam and Adekola, 2005). The results also show that the R^2 values for two substrates are greater than 0.9 for freundlich isotherm, so the adsorption was favourable.

Conclusion

The removal of these metal ions from aqueous solutions strongly depended on initial metal ions concentration and contact time. The maximum adsorption was obtained from frond samples than the leaves. However, the percentage removal of Cu (II) and Zn (II) ion by the two substrates were observed to be low when comparing to the amount of Mn (II) ion adsorbed.

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