SORPTION STUDIES ON THE REMOVAL OF ZN(II) AND CU(II) IONS FROM AQUEOUS SOLUTION USING CARICA PAPAYA SEED AND AMARANTHUS HYBRIDUS L STALK

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Abstract

Carica papaya (Pawpaw) seed and Amaranthus hybridus L (African spinach) stalk powder were used as adsorbents to study their adsorptive capacity on Zn(II) and Cu(II) ions removal from aqueous solution. Parameters such as contact time and the initial metal ion concentrations were studied to optimize conditions to be utilized on a commercial scale for the decontamination of effluents using a batch adsorption technique. The results obtained after contact period of 90 minutes showed Cu²⁺ ions had the highest percentage removal of 70.0% (Carica papaya seeds) and 69.5 %(Amaranthus hybridus stalk) followed by Zn²⁺ ions 69.0 % (Carica papaya) seeds and 66.5% (Amaranthus hybridus) stalk. The data generated for sorption isotherms ?tted the Freundlich models. From the results, both substrates have the ability to bind metal ions which could be used for the development of an efficient, clean and cheap technology for industrial wastewater treatment.

Keywords: Removal, Zn²⁺, Cu²⁺, Carica papaya seed, Amaranthus hybridus L, aqueous solution

INTRODUCTION

Today, increasing discharge of toxic heavy metal into the environment poses serious threat to human existence and thus has become a matter of concern over the last few decades (Arpa et al., 2000; Ho et al., 2002; Adeyinka et al., 2008; Agiri and Akaranta, 2009, Egila et al., 2010). It has been reported by several authors that increasing concentrations of these metals in water constitute a severe health hazard not only to human beings but other living organisms mainly due to their non degradability and toxicity (Demirbas et al., 2004). Numerous metals such as Cr, Cu, Pb, Mn, Hg, Cd, Zn etc are known to be significantly toxic. Zinc for instance finds its way into water bodies through effluents from smelters, mining, processing plants, paints and pigments, pesticides and galvanizing units. When present in the wastewater beyond the permissible limits of concentration, it becomes harmful to the living organisms (Santhy and Selvapathy, 2004). The threshold value of zinc in drinking water is 5 mg/ L and for inland surface water and marine water, it is 15 mg/L (NIS, 2003). Ingestion of > 2 g/L causes toxic symptoms like fever, diarrhea, gastrointestinal tract irritation etc in humans. Hence, it is of prime importance to prevent the accumulation of zinc from exceeding its threshold concentration.

Copper is a widely used material and its contamination exists in aqueous waste streams from many industries such as electronic and electrical, metal plating, mining, manufacture of computer heat sinks, Cu plumbing, as well as biostatic surface, as a component in ceramic glazing and glass colouring. Unfortunately, Cu is a persistent, bioaccumulative and toxic chemical that does not readily break down in the environment and is not easily metabolized (Aydin et al., 2008). It may accumulate in the human or ecological food chain through consumption or uptake and may be hazardous to human health or the environment. Drinking water that contains high levels of Cu may cause vomiting, diarrhea, stomach cramp and nausea. The chronic effects of consumption of high levels of copper are liver and kidney damage. The suggested safe level of Cu in drinking water for humans varies depending on the sources, but tends to be pegged at 1.5 to 2.0 mg/L. Hence, removal of copper from water and wastewater assumes important.. Because of their toxicity level, it is

Int. J. Chem. Sci. Vol 3 No 2, pp175-184, 2010

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necessary to remove these metals from industrial effluents before discharging aqueous waste into environment.

Several other conventional methods had been considered for the removal of metal ions from industrial effluents such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange, and membrane technologies (Demirbas et al., 2004). These methods were found not to be effective especially when the heavy metal ions in the contaminated media are high i.e. in order of 1-100 mg/L. Secondly, the operational problems and the high cost of treatment also militate against these techniques, as such this necessitates the search for alternative methods. Biological methods such as biosorption/ bioaccumulation may provide an attractive alternative to physico-chemical methods for the removal of heavy metal ions. In recent years, considerable attention has been devoted to develop unconventional materials like agricultural by-products for the removal of heavy metals from wastewater. Since these plant-based by-products represent unused resources, they are renewable, widely available and environmentally friendly. Thus, in the quest to explore the effectiveness of agricultural by-products as adsorbents, several plant based materials have been used to treat heavy metals in aqueous solutions. The removal of lead and copper ions from aqueous solutions by sago waste was reported by Ho, (2002). Singh, (2006a) reported that wheat bran removed about 87.15% of Cd(II) at pH 8.6 when initial Cd(II) concentration was 125 mg/L. Singh, (2006b) observed that 98.4% of Pb(II) was recovered from aqueous solution containing 100mg/L initial concentration of Pb(II) at pH 6.5. Other agricultural biosorbent that have been investigated were, Amaranthus hybridus L stalk (Egila et al., 2010), cassava fibre (Egila and Okonie, 2002), sugarcane waste (Gardea-Torresdey et al., 2002), coir-pith carbon (Santanarina et al., (Abia et al., 2003), cotton seed hulls (Teixeria et al., 2004), just to mention a few.

However, There is little or no studies focused on the use of Amaranthus hybridus stalk and Carica papaya seed for the removal of Cu(II) and Zn(II) ions from aqueous solutions. The efficiency of adsorbent prepared from Amaranthus hybridus stalk and Carica papaya seed in removing Cu(II) and Zn(II) ions from aqueous solution was examined in this study.

MATERIALS AND METHODS

Sample Collection

The African spinach (Amaranthus hybridus) waste and pawpaw (Carica papaya) seeds obtained from different locations were obtained from different locations within market, Minna in Niger State. Sampling was done at random from different sellers of the plant produce within this market area. A composite sample was made from where the representative samples were collected for these studies

Sample Pretreatment

The representative samples were deoiled by soaking in hot deionized water with detergent for 24 hours then rinsed in hot deionized water to remove all debris, and air dried for one week. The dried samples were ground using blender and sieved through a 400 micron mesh screen. The fine powder retained on the 400 μm sieve was then used for the sorption studies

Simulated Wastewater Preparation

All the reagents used are of analytical reagent grade and distilled deionized water was used in sample preparation. 1000 mg/l stock solutions of copper (II) from $CuSO_4.5H_2O$ and zinc (II) from Zn $(NO_3)_2.6H_2O$ were prepared. From the stock solutions, working solutions of initial concentration (5–50 mg/l) of each metal were prepared by serial dilution.

Adsorbent Preparation for Sorption Studies

The 5.00g screened fine adsorbent was soaked in excess 0.3 M HNO_3 for 24 hours to remove any debris or soluble biomolecules that might interfere with the metal ions during the sorption. This process is 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 hours.

Sorption Experiment

Effect of Contact Time

The experimental procedure described by Okiemen and Okieimen (2001) was modified as follows:

0.5g of the pretreated powdered samples were taken and shaken with 100 cm³ of a metal ion solution whose concentration was 5mg/L. The bottles were shaken at various time intervals of 30 to 180 minutes 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 using Atomic Absorption spectrophotometer, model Pye Unicam SP-9 Cambridge, UK.

Batch Mode Adsorption Study

The experiments were carried out in the batch mode for the measurement of adsorption capabilities at 33°C using different concentrations of 10,20,30,40 and 50 mg/ L for the various heavy metals studied. 100 cm³ of various concentrations (10.0 mg/ L to 50.0 mg/ L) of the metal ions were placed in 250 cm³ conical flasks, and 0.5 g of the substrate was added to each. The corked conical flask was shaken in a reciprocating shaker at 300 rpm for constant metal ion-substrate contact period of 90 minutes at 33°C. The separation of the adsorbents and solutions was carried out by filtration with Whatman filter paper No. 42 and the filtrate stored in sample cans in a refrigerator prior to analysis. The residual metallic ion concentrations were also determined using an Atomic Absorption Spectrophotometer.

Data Analysis

The amount of Zn^{2+} and Cu^{2+} adsorbed (a_t) in mg/L from the aqueous solution by the two substrates at time t was determined by using the following equations:

$$a_t = C_o - C_t \text{------(1)}$$

Percentage removal of heavy metal ions from initial solution concentration calculated from the following Equation.

$$R_m = \frac{C_o - C_t}{C_o} \times 100\% \quad \text{................(2)}$$

where C_o is the initial metal ion concentration (mg/L), and C_t is the metal ion concentration at time t

Adsorption Model

Isotherm adsorption models have been used in waste stream treatment to predict the ability of a certain adsorbent to remove a pollutant down to a specific discharge value (Ronda et al., 2007). When a mass of adsorbent and a waste stream are in contact for a sufficiently long time, equilibrium between the amount of pollutant adsorbed and the amount remaining in solution will develop. For any system under equilibrium conditions, the amount of material adsorbed onto the media can be calculated using the mass balance of .(3):

$$\frac{x}{m} = \frac{(C_0 - C_e)V}{M} \quad \text{................(3)}$$

Where x/m (typically expressed as mg pollutant/g media) is the mass of pollutant per mass of media, Co is the initial pollutant concentration in solution, Ce is the concentration of the pollutant in solution after equilibrium has been reached, V is the volume of the solution to which the media mass is exposed, and m is the mass of the media.

Adsorption data for wide range of adsorbate concentrations are most conveniently described by adsorption isotherms, such as the Freundlich isotherms or Langmuir isotherms (Hashem et al., 2007). The Freundlich equation was used as the model for adsorption in this study which is represented by the general formulae given below as (4)

$$\frac{x}{m} = K_f (C_e)^{1/n} \quad \text{.............................(4)}$$

which can be linearized as:

$$\ln\left(\frac{x}{m}\right) = \ln K_f + \frac{1}{n} \ln C_e$$

Where x/m is the amount adsorbed per unit mass of adsorbent, Ce is the solution concentration at equilibrium, K and n are constants relating to adsorption capacity and intensity. This equation is only applicable to batch adsorber systems where sufficient time is provided to allow equilibrium between the pollutant in solution and the pollutant adsorbed on the media to occur. During the flow through the adsorbent, many of the pollutants are expected to come into contact with active surface sites and thus be retained on the surface of the adsorbing media.
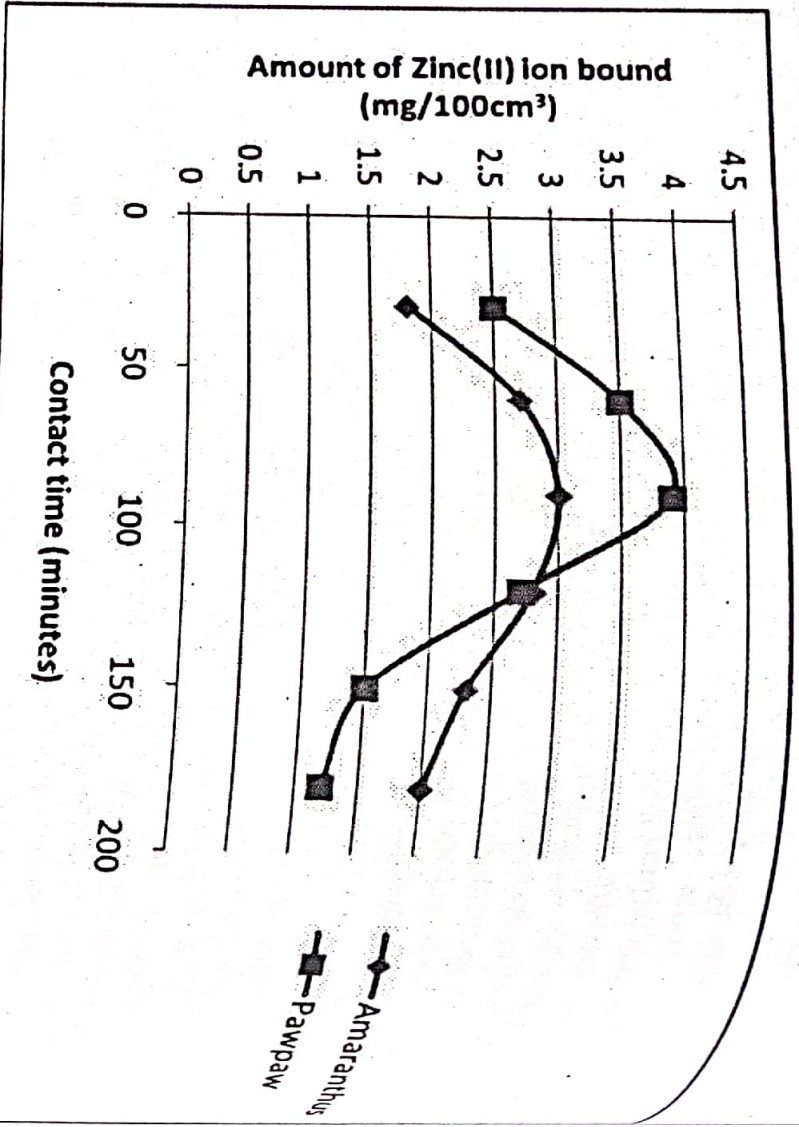
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RESULTS AND DISCUSSION

Amount of Zinc(II) Ion bound (mg/100cm³)

Figure 1: Effect of variation of contact time on the adsorption of Zn^{2+} on *Amaranthus hybridus* L and *Carica papaya* seeds at $33^{0}C$.
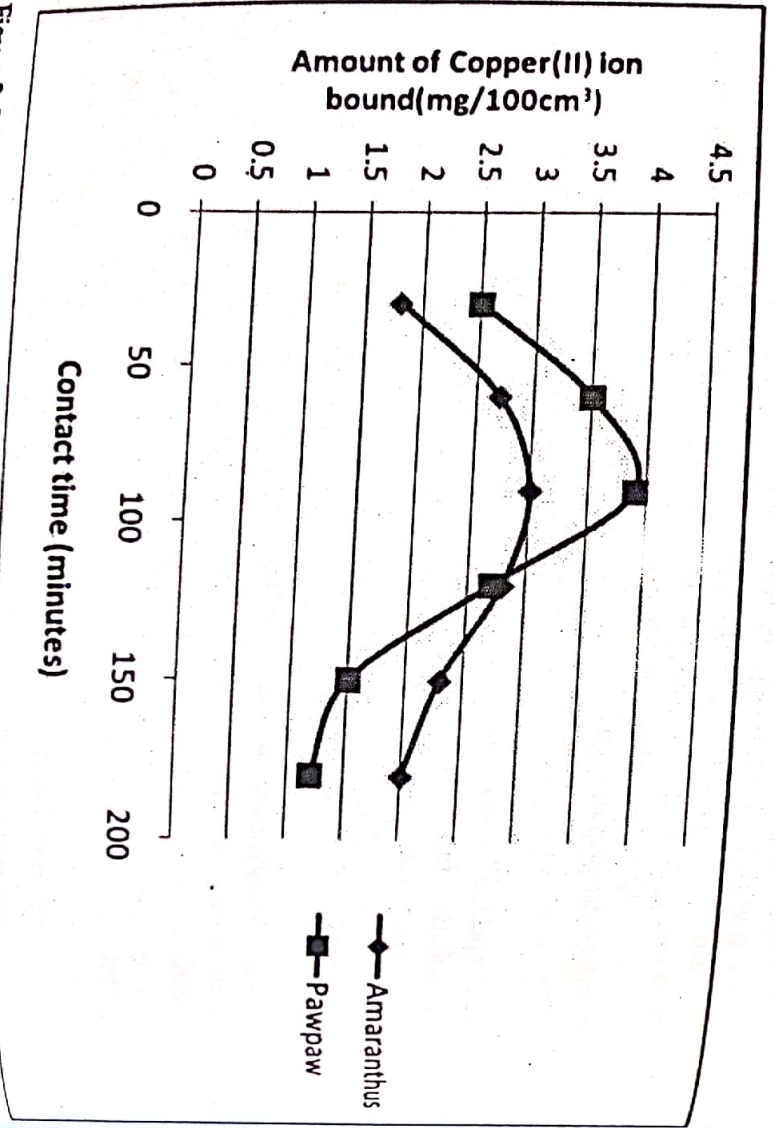
Amount of Copper(II) ion bound(mg/100cm³)

Figure 2: Effect of variation of contact time on the adsorption of Cu^{2+} on *Amaranthus hybridus* L and *Carica papaya* seeds at $33^{0}C$.

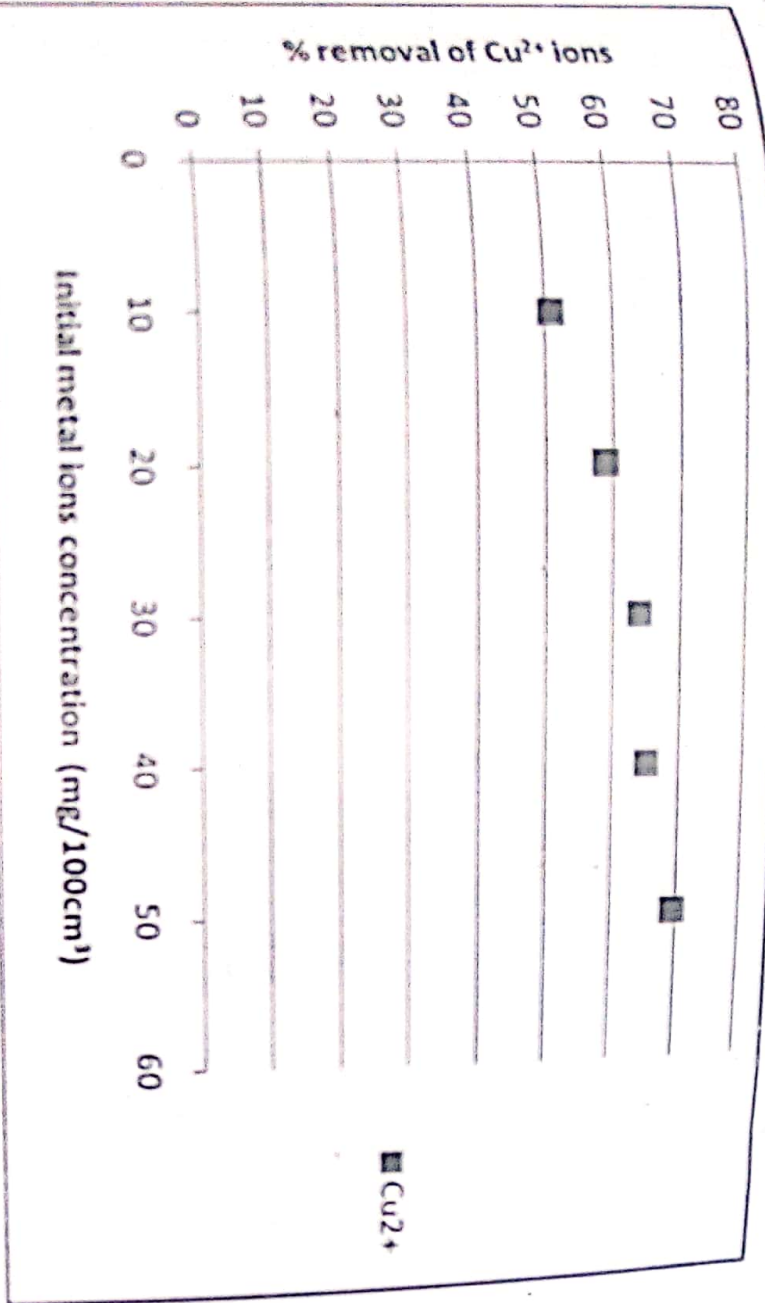Figure 3. Variation of % removal of Cu²⁺ ions with concentration on Amaranthus hybridus stalk
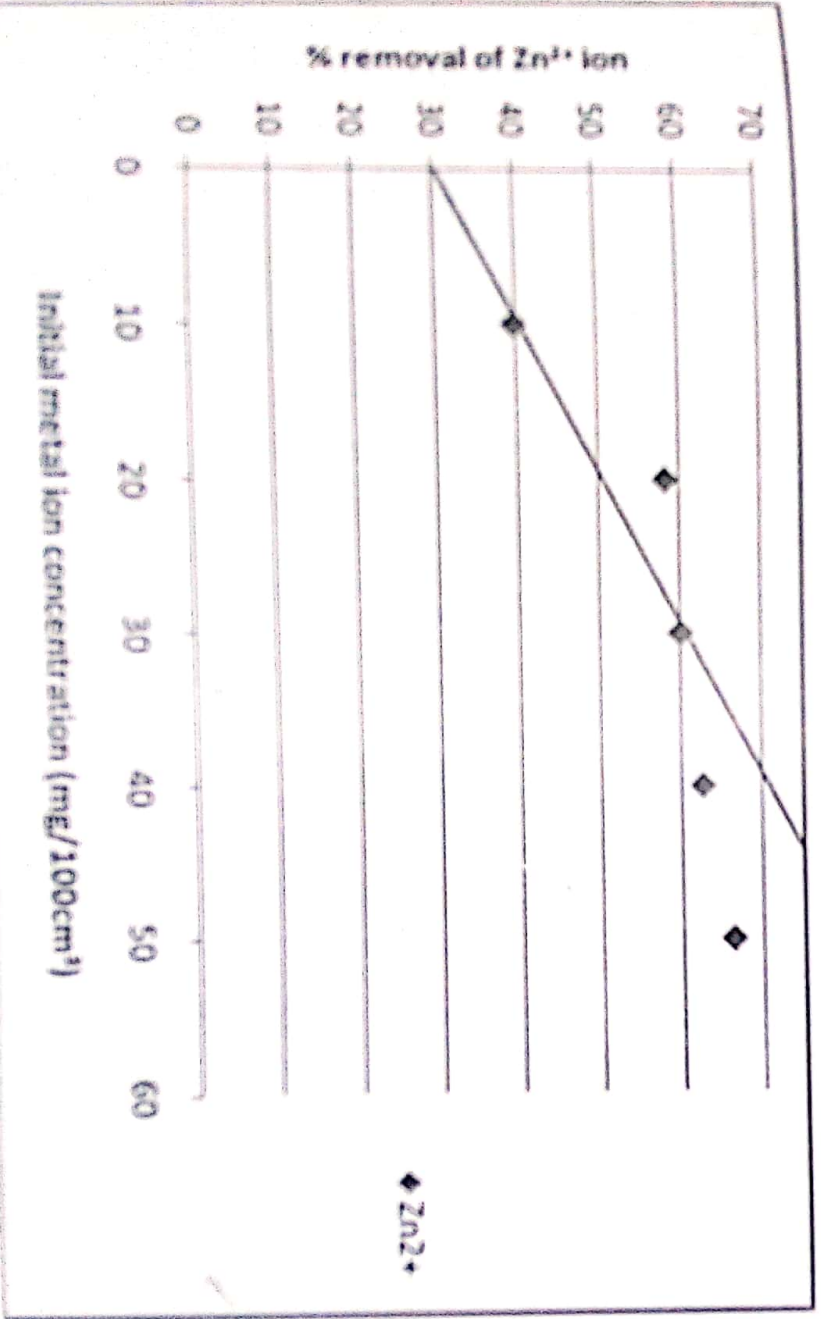

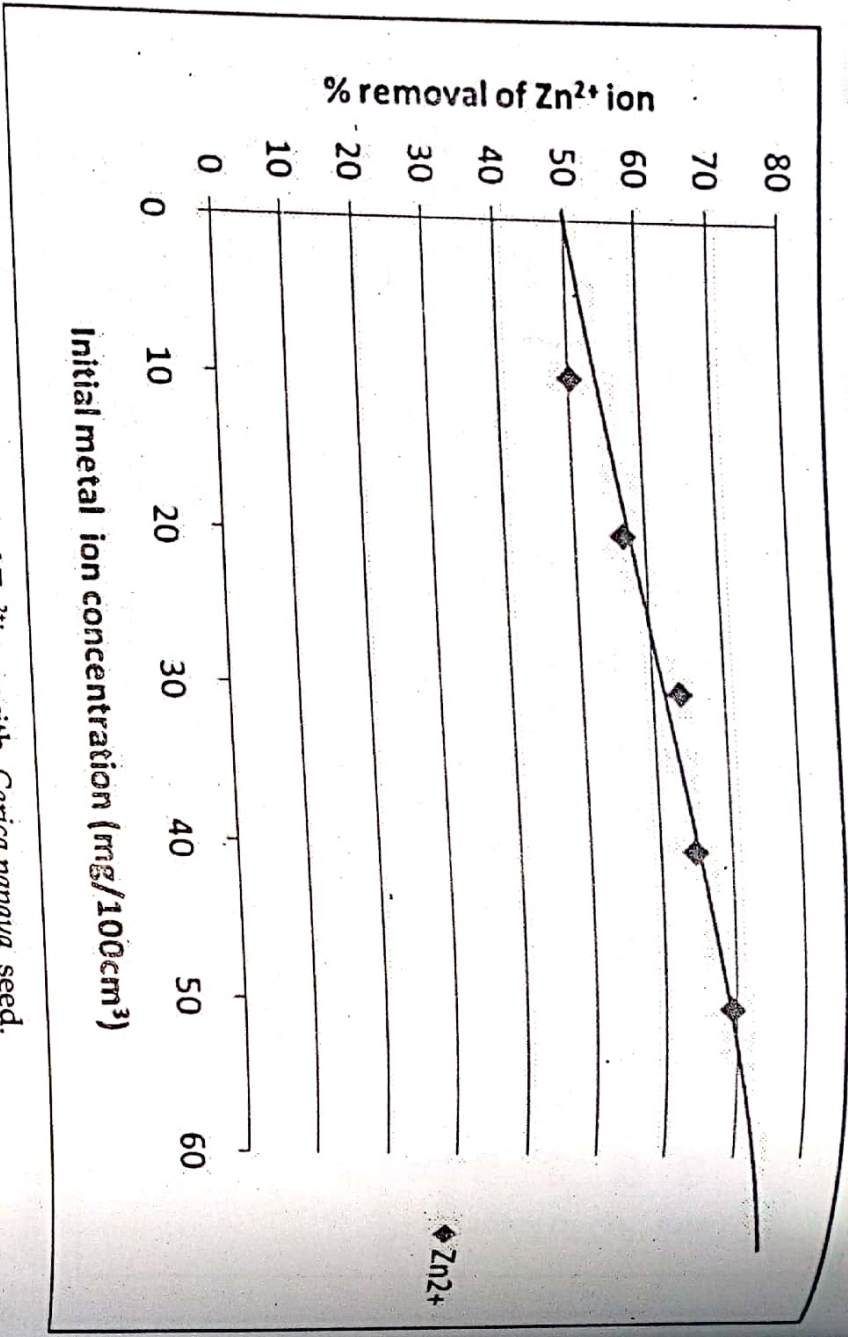Figure 4. Variation of % removal of Zn²⁺ ions with Amaranthus hybridus stalk

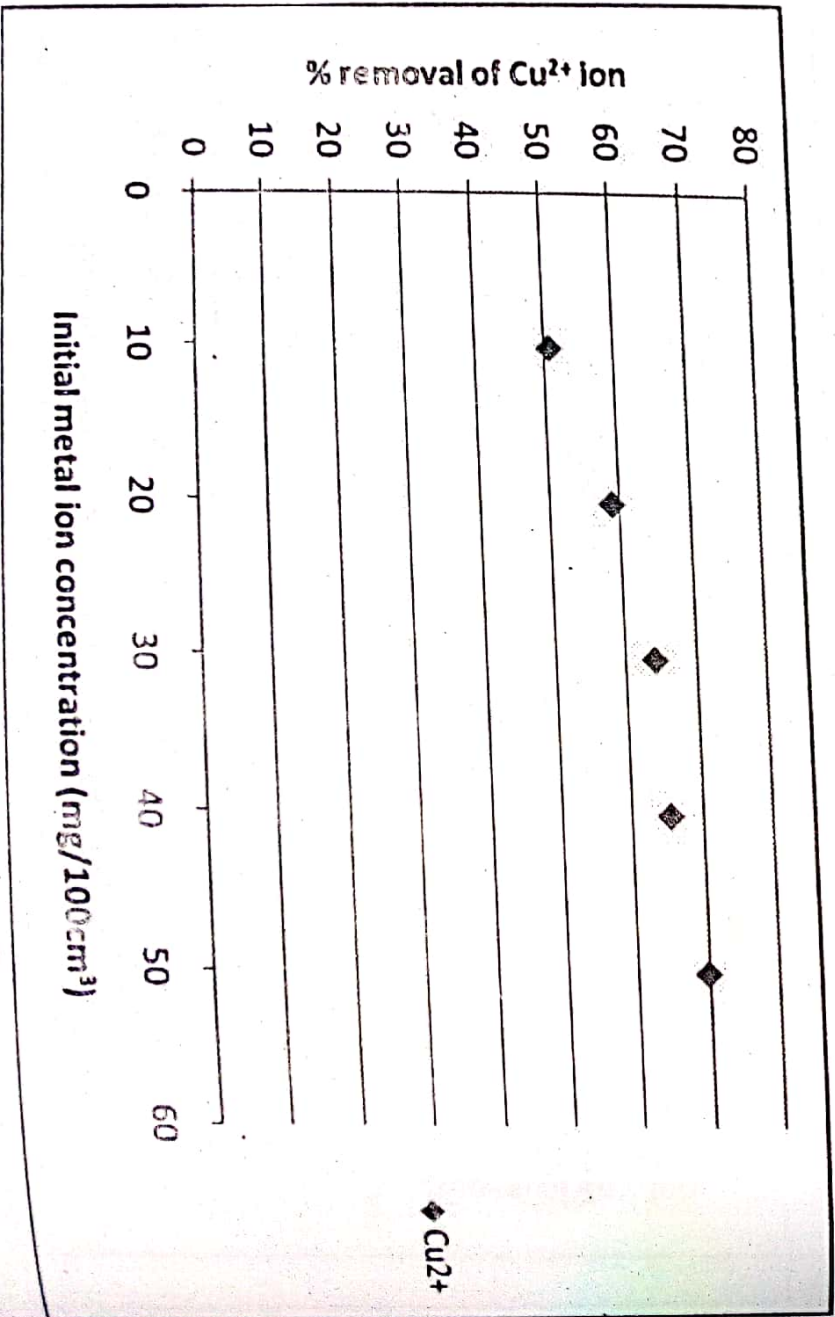Figure 5. Variation of % removal of Zn^{2+} ions with *Carica papaya* seed.

Figure 6. Variation of % removal of Cu^{2+} ions with *Carica papaya* seed

Figure 7: Freundlich adsorption isotherm plot of Log (x/m) against Log C for Zn (II) and Cu(II) ions , where x is the mass of the adsorbate; m is the mass of adsorbent and C is the residual concentration(for *Amaranthus hybridus* stalk).
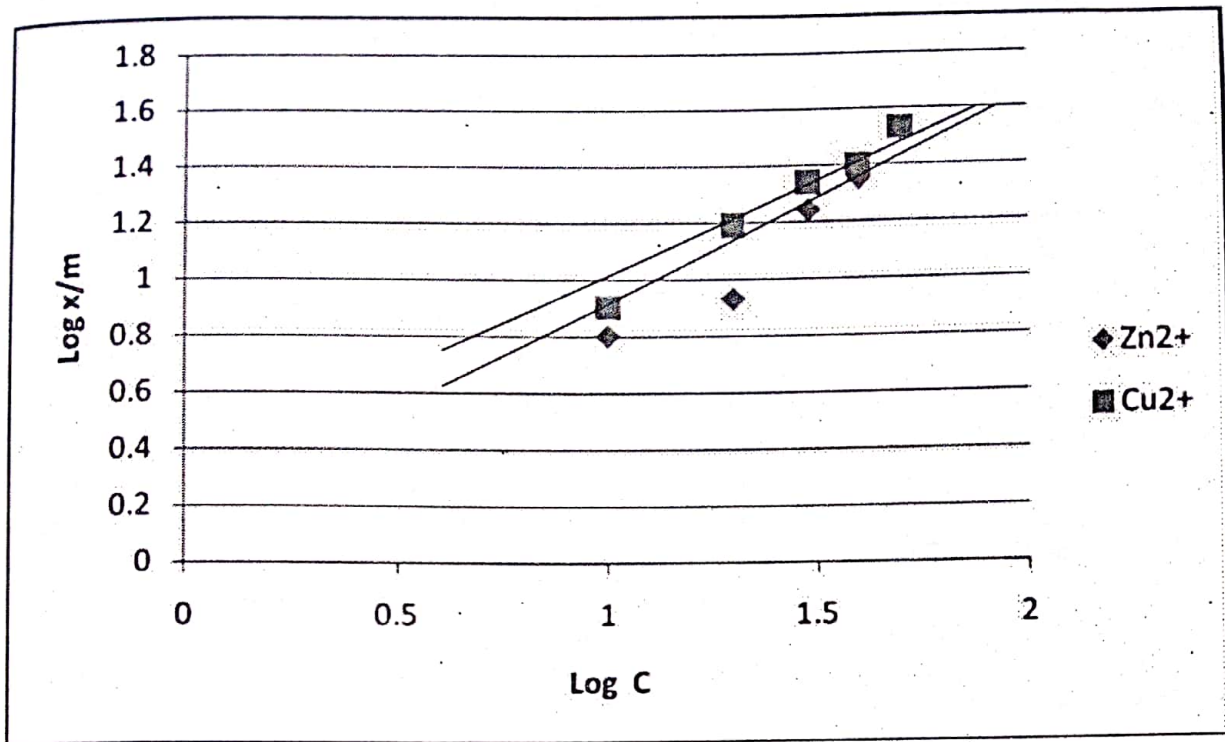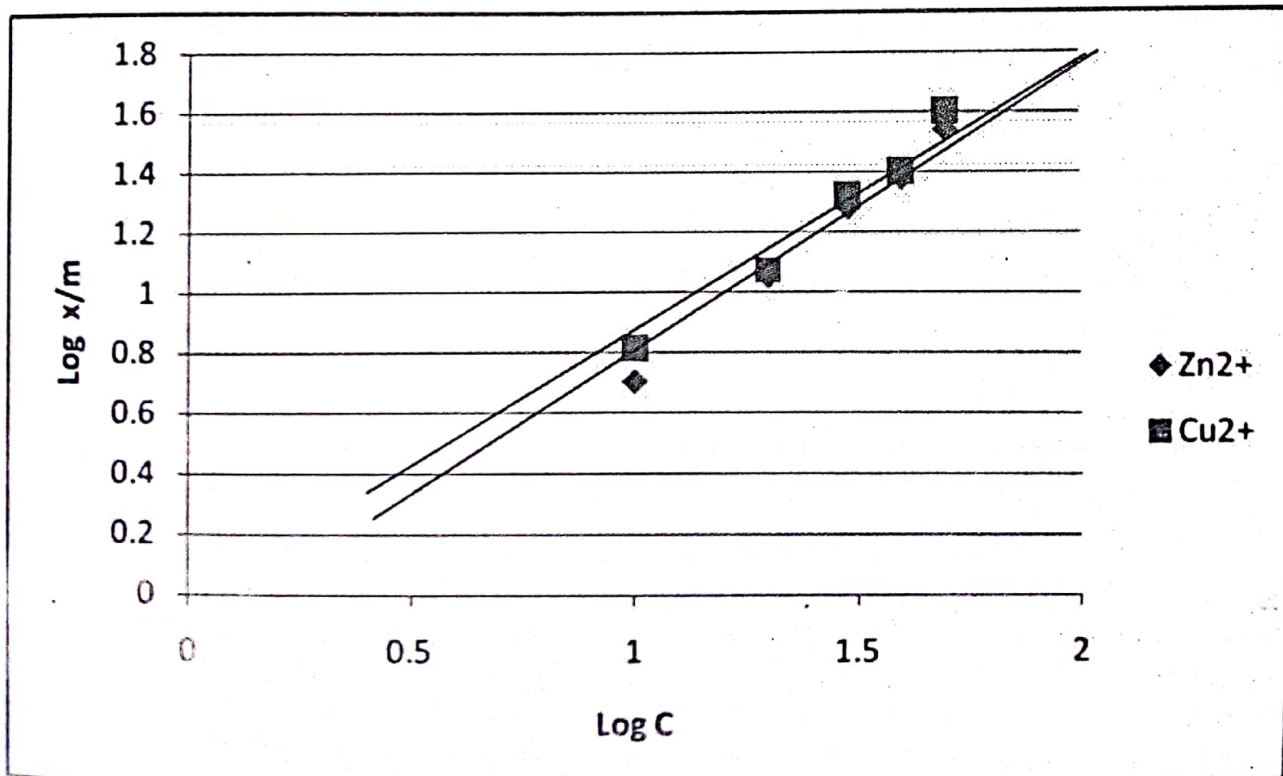

Figure 8: Freundlich adsorption isotherm plot of Log (x/m) against Log C for Zn(II) and Cu (II) ions , where x is the mass of the adsorbate; m is the mass of adsorbent and C is the residual concentration(for *Carica papaya* seeds)

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Effect of Contact Time

In the adsorption system, contact time plays a vital role, irrespective of the other experimental parameters that affect the adsorption kinetics. The effect of variation of contact time on the adsorption of Zn (II) ion and Cu (II) ion on *Amaranthus hybridus* L and *Carica papaya* seeds was investigated at the optimum initial concentration of these metal ions and the data are represented in Figures 3 and 4. It was found that the removal of metal ion increases with increase in contact time to some extent. The removal of metal ion increment reaches maximum value and then decreases with the increase in contact time. This may be due to desorption process. The relative increase in the extent of removal of metal ion after 90 minutes of contact time is negligible and hence it is the optimum contact time. The trend observed for the various 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). This difference could also be explained in terms of difference in the ionic size of metals, the nature and distribution of active groups on the biosorbent, and the mode of interaction between the metal ions and the biosorbent (Iqbal and Edvean, 2004).

Effect of Initial Metal Ion Concentration

The percentage removal and uptake level of Cu(II) and Zn(II) ions from solutions containing various amounts of the metal ions by *Amaranthus hybridus* stalk waste and *Carica papaya* seeds are shown in Figures 3 and 4 respectively as the metal ion concentrations increased from 10 to 50 mg/100cm^3. 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 removal was higher in Cu than Zn. The percentage metal ions removal increased as the initial metal ions concentration increase from 10 to 30 mg/100cm^3 for both substrates and later declined. 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 metal ions and the absorbent active sites. decline in the adsorption capacity and percent recovery despite increase in the initial metal concentration is due to the availability of sma number of surface sites on the adsorbent f relatively larger number of adsorbing specie higher concentrations (Khalid et al., 2000). Sin results were observed by Han et al., (2005) for adsorption of copper (II) and lead (II) on chaff. A the results obtained from this research w conformed to the findings by Oboh and Alu (2008) that worked on sour sop seeds as biosorb to remove heavy metals ions from aque solution. The trend of adsorption was Cu>Zn. difference among the metal ions on the rate adsorption was ascribed to the slight differenc the ionic radii. Metals with smaller ionic size h the greater affinity to active groups of the cellul materials. Competition among the metal ions adsorption sites obviously affected the adsorp capacity (Igwe et al., 2005).

Further more, a comparison of the two substra clearly showed that at any given metal i concentration, *Carica papaya* seeds could bind m of the metal ions than *Amaranthus hybridus* stalk a confirmed that the nature of the cellulosic mate had a unique role in the adsorption mechanism.

Sorption Kinetics

Krishnan and Anirudhan (2003) reported t kinetics of metal sorption is controlled by the r which determines the residence time, which is c of the important characteristics defining efficiency of an adsorbent. Sorption kinetics can controlled by several independent processes t could act in series or in parallel such as b diffusion, external mass transfer (film diffusio chemical reaction (chemisorption) and intraparti diffusion (Ho et al., 2000).

Based on the above, the sorption data of the me ions investigated on *Carica papaya* seeds a *Amaranthus hybridus* stalk substrate were plott logarithmically as shown in Figures 7 and 8, t fitted the Freundlich adsorption isotherm. The value of Cu^{2+} was (0.70) which is greater than t value obtained for Zn^{2+} in pawpaw seeds. The value of Cu^{2+} in the second sample was 0.39 wi Zn^{2+} still having the least value of 0.19. Again, t

smaller ionic radius of Cu^{2+} ions (0.73Å) might be responsible for its greater adsorptivity. This means that Cu^{2+} ions with smaller ionic radius diffused faster through the adsorbent pores faster than the bulkier Zn^{2+} ions (0.74Å). This is in agreement with what was reported by Oboh and Aluyor (2008), that during sorption of metal ions, the ions with smaller ionic radii tend to move faster to potential adsorption. The value of 1/n which is less than 1in both substrates is an indication 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 investigation revealed that *Carica papaya* seeds and *Amaranthus hybridus* are adsorbents of great potential and have proved capable of copper(II) and zinc(II) removal from aqueous solution. The Freundlich sorption process indicated favourable adsorption of copper(II) and zinc(II) by these two wastes. This showed a new trend for using *Carica papaya* seeds and *Amaranthus hybridus* in removing toxic heavy metals. Thus, the use of *Carica papaya* seeds and *Amaranthus hybridus* may contribute to the sustainability of the surrounding environment as well as a means of wastes disposal for environmental pollution control.

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