Use of *Carica papaya* as a Bio-Sorbent for Removal of Heavy Metals in Wastewater

W. E. Igwegbe, B. C. Okoro, J. C. Osuagwu

***Abstract*---**The study assessed the effectiveness of Pawpaw (*Carica papaya*) wood in reducing the concentrations of heavy metals in wastewater acting as a bio-sorbent. The following heavy metals were considered; Zinc, Cadmium, Lead, Copper, Iron, Selenium, Nickel and Manganese. The physiochemical properties of *Carica papaya* stem were studied. The experimental sample was sourced from the trunk of a felled matured pawpaw tree. Wastewater for experimental use was prepared by dissolving soil samples collected from a dump site at Owerri, Imo state of Nigeria in water. The concentration of each metal remaining in solution as residual metal after bio-sorption was determined using Atomic absorption Spectrometer. The effects of pH and initial heavy metal concentration were studied in a batch reactor. The results of Spectrometer test showed that there were different functional groups detected in the *Carica papaya* stem biomass. There was increase in metal removal as the pH increased for all the metals considered except for Nickel and Manganese. Optimum bio-sorption occurred at pH 5.9 with 5g/100ml solution of bio-sorbent. The results of the study showed that the treated wastewater is fit for irrigation purpose based on Canada wastewater quality guideline for the protection of Agricultural standard. This approach thus provides a cost effective and environmentally friendly option for treating wastewater.

***Keywords*—**Biomass, bio-sorption, *Carica papaya*, heavy metal, wastewater.

I. INTRODUCTION

HEAVY metal pollution is one of the most important environmental problems today. Heavy metal ions have lethal effects on all forms of life and these enter the food chain through the disposal of wastes in water channels. From among various metal ions, Lead, Mercury, Cadmium, and Chromium (VI) are at the top on the toxicity list [1]. Biosorption can be defined as the removal of metal or metalloid species, compounds, and particulates from solution by biological material [2]. Three kinds of heavy metals are of concern, including;

- Toxic metals {such as Mercury (Hg), Chromium (Cr), Lead (Pb), Zinc (Zn), Copper (Cu), Nickel (Ni), Cadmium (Cd), Arsenic (As), Cobalt (Co), and Tin (Sn), etc.},
- Precious metals {such as Lead (Pd), Platinum (Pt), Silver (Ag), Gold (Au), and Ruthenium (Ru) etc.} and
- Radionuclides {such as Uranium (U), Thorium (Th), Radium (Ra), and Americium (Am), etc.} [3].

Wastewater, a liquid form of waste (both industrial and otherwise), has been found to contain a considerable amount of heavy metals, especially for industries with high need for heavy metals in their production processes or those that make use of raw materials containing heavy metals. Wastes containing heavy metals from these industries are directly or indirectly being discharged into the environment causing serious environmental pollution and even threatening human life [4]. From statistical records, more than 60% of indigenous industries have trace of heavy metals in their wastewater [5].

Eliminating heavy metal usage is often extremely expensive and disposal of metals and metal containing materials inevitably cause environmental pollution [6]. On the other hand, some heavy metals such as Cobalt, Copper, Strontium, Manganese, Molybdenum, Vanadium, and Zinc are required by living organisms at trace amount (moderate or harmless concentration) as dietary supplements. They are also known to be an integral part of some products such as drugs, plastics, petroleum products, etc.

Methods for removing metal ions from aqueous solution mainly consist of physical, chemical, and biological technologies. Conventional methods for removing metal ions from aqueous solution have been suggested, such as chemical precipitation, filtration, ion exchange, electrochemical treatment, membrane technologies, adsorption on activated carbon, evaporation etc. However, chemical precipitation and electro-chemical treatment are ineffective, especially when metal ion concentration in aqueous solution is among 1 to 100 mg/l, and also produce large quantity of sludge required to treat with great difficulty. Ion exchange, membrane technologies and activated carbon adsorption process are extremely expensive when treating large amount of water and wastewater containing heavy metal in low concentration, they cannot be used at large scale. In recent years, applying biotechnology in controlling and removing metal pollution has been paid much attention, and gradually becomes hot topic in the field of metal pollution control because of its potential application. Alternative process is biosorption, which utilizes various certain natural materials of biological origin, including bacteria, fungi, yeast, algae, etc. These bio-sorbents possess metal-sequestering property and can be used to decrease the concentration of heavy metal ions in solution from ppm to ppb level. It can effectively sequester dissolved metal ions out of dilute complex solutions with high efficiency and quickly,

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therefore it is an ideal candidate for the treatment of high volume and low concentration complex wastewaters [7].

A large quantity of materials has been investigated as biosorbents for the removal of metals or organics extensively. The tested biosorbents can be basically classified into the following categories: bacteria (e.g. *Bacillus subtillis*), fungi (e.g. *Rhizopus arrhizus*), yeast (e.g., *Saccharomyces* cerevisiae), algae, industrial wastes (e.g., *S. cerevisiae* waste biomass from fermentation and food industry), agricultural wastes (e.g. corn core, *Carica papaya* stem) and other polysaccharide materials, etc. [8]. The role of some groups of microorganisms has been well reviewed, such as bacteria, fungal, yeast, algae, etc. These tested biomasses have been reported to bind a variety of heavy metals to different extents [9].

The objective of the study was to investigate the effectiveness of Pawpaw (*Carica papaya*) wood as a bio-sorbent in reducing the concentrations of heavy metals in waste water. *Carica papaya Linnaeus*, (pawpaw), belongs to the family of *Caricaceae*. Papaya is not a tree but an herbaceous succulent plant that possess self-supporting stems. [10]. This research was conducted in Owerri, the capital city of Imo State. Owerri is located within the south eastern Nigeria between longitude 7001'44''E of the Greenwich and latitude 5030'01''N of the equator. The area is low lying with good road network and it is drained by Imo, Kwa-ibo and Bonny rivers and their tributary [11].

II. Materials and Methods

The heavy metals considered include; Zinc, Cadmium, Lead, Copper, Iron, Selenium, Nickel, and Manganese. The sample used for the study was obtained from a felled trunk of matured pawpaw tree.

The materials used in the field study include; Hand Auger, 100cm meter rule, sterilized cellophane bags, cutlasses, 250ml flask.

The biosorbent sample was obtained from the felled trunk of a matured pawpaw tree. To obtain wastewater containing a considerable level of heavy metals, soil samples were collected at various depths below the soil surface from an old dumpsite at Owerri Imo state. This was done by the use of soil augar. These soil samples were collected with sterilized cellophane bags and subsequently dissolved in distilled water to obtain wastewater during the laboratory procedure.

The materials for laboratory study include; atomic absorption spectrophotometer, oven, flask(250ml), bunsen burner, mechanical shakers, hand-held pH meter, weighing machine, a bowl, masking tape, cylindrical plastic tubes. The reagents for laboratory study include; concentrated hydrochloric acid, distilled water.

The debarked papaya trunk was cut into small pieces (2cm by 2cm) after which they were soaked in boiling water for 30 minutes. The boiled papaya was washed thoroughly under tap water, and left for 2-3 hours in distilled water, changed 3-4 times. This was done in an attempt to soften the biosorbent (*Carica papaya*). The washed wood pieces were grinded into fibers (diameter: 0.05-0.2mm; length: 2.5mm) and oven dried at 80^0C and used for biosorption studies.

Batch biosorption assay was carried out in 250ml flasks by transferring 100ml of 10mg/l metal solutions and 1g (10g/l) papaya wood cubes. Three different weights of the biosorbent i.e.; 1g, 3g, and 5g were each, differently introduced into a 100ml of the wastewater prepared. These mixtures were shaken at 100rpm for a time interval of 60mins each, after which the suspension was separated by decantation and collected in 3 different small cylindrical tubes and labelled. The residual metal ion concentration was determined, from which was computed the quantity of metal biosorbed by papaya wood per gram. The process was repeated twice at 6.8 and 5.9 pH variations of the wastewater. The pH variation was acheived by introducing some droplets of concentrated hydrochloric acid into the wastewater stream, initially at pH of 7.8.

The concentration of each metal, remaining in solution as the residual metal after biosorption was determined using atomic absorption spectrophotometer (UNICAM-969).

All chemicals used in this work were analytical reagent grade and were used without further purification. Lead, Cadmium, Copper, Zinc, Iron, Nickel, Selenium and Manganese ion solutions were prepared by dissolving the corresponding analytical salts of $Pb(NO_3)_2.2H_2O$, $Cd(NO_3)_2$, $Cu(NO_3)_2.3H_2O$ Zn2(NO3)2, Fe2SO4, MnCO3, respectively in distilled water. The diluted solutions were kept in a glass container at room temperature. A solution with a concentration of 50 mg/l of each metal was used as adsorbate material. The concentration of each metal was measured using a flame Atomic Absorption Spectrophotometer (AAS, type: SHIMADZU, Model: 7200, JAPAN). Before the biosorption process was initiated, the pH of each solution was adjusted to the required value by adding 0.1 M HNO_3 or 0.1 M NaOH solutions. All the glassware used for dilution, storage and experimentation were cleaned with detergent, thoroughly rinsed with tap water, soaked overnight in a 20% HNO_3 solution and finally rinsed with distilled water before use.

The effects of pH, contact time, temperature, and initial heavy metal concentration on the removal efficiency were studied in a batch reactor. All the study experiments were carried out in 250 ml flasks containing 100 ml of metal solution and 1 g dose of *Carica Papaya* biomass. Effect of pH was measured using a 50 mg/l metal concentration at room temperature, and the pH range was from 2-6. Effect of contact time was measured using 50 mg/l heavy metal concentration at room temperature and the pH was fixed at 4 for all metal solution.

To obtain the optimum pH for heavy metal biosorption by papaya wood, the removal of Zinc (ii) and Cadium (ii) from their aqueous solutions was studied at different pH values.

The quantity of papaya wood was varied at 1g, 3g, and 5g/100ml to determine the optimum quantity of biomass needed for maximum sorption.

Equilibrium experiments were carried out at different weights of biomass (0.05, 0.1, 0.3, 0.5, 0.8, 1, 2, and 3 g). Each weight was thoroughly mixed with 100 ml of heavy metal solution at 50 mg/l concentration. Eight flasks of 250 ml capacity were placed in a rotary shaker type (Edmund Buhler, 7400 Tubingen Shaker-SM 25, Germany) at 200 rpm for 3 h to obtain equilibrium. It was found from the preliminary experiments that these conditions lead to equilibrium conditions. The mixtures were then filtered using filter paper (type: WATMAN No.42, ash less, diameter 7 cm), then the residual concentration of Lead, Cadmium, Copper and Arsenic in solution was determined using AAS. The uptake value at equilibrium was calculated using equation:

$$q_e = \frac{V(C_i - C_e)}{m} \quad (1)$$

where, q_e is the uptake of metal(mg/g); C_i and C_e are the initial and equilibrium metal concentrations in the water (mg/l), respectively; V is the volume of solution (l); and m is the mass of adsorbent (g).

The effect of biosorbent dosage on heavy metal removal was studied using varying concentration of the biosorbent (1 to 10 g). The concentration of heavy metal solution used for this study was 1mg/l, 2mg/l, 3mg/l, 4mg/l, and 5mg/l. The volume of heavy metal solution was 100 mL using an initial pH of 7.8 in 250 ml Erlenmeyer flask at 50°C under orbital shaking for 60 min.

The removal percentage (R%) was estimated based on the ratio of difference in heavy metal concentration before and after adsorption (C_i − C_e) to the initial concentration of the heavy metal in the aqueous solution (C_i), as represented in:

$$R\% = \frac{(C_i - C_e)}{C_i} * 100 \quad (2)$$

III. Results and Discussions

The physiochemical properties of the *Carica papaya* stem biomass were measured and the results are presented in Tables I and II. The results of show that there are different functional groups detected in the *Carica papaya* stem biomass.

TABLE I
PHYSIOCHEMICAL PROPERTIES OF *CARICA PAPAYA* BARK

Parameter	Quantity	Unit
pH	7.18	
Conductivity	2.54	Ms/cm
Bulk Density	0.2715	g/cm^3
Specific gravity	0.2715	%
Ash	1.75	%
Organic matter	3.49	%
Carbon content	1.08	%
Fibre	4.26	%
Moisture	6.84	%

Figs. 1-3 present the % removal at various points for pH values of 7.8, 6.8, and 5.9 respectively. The results show that percentage removal of Manganese and Nickel reduced with additional concentrations of biomass. However, the reverse was the case for the other metals in which the percentage reduction increased with increase in biomass concentration. Of significant note is the pattern of reduction of lead which made a negative slope from 1g/100l to 3g/100ml and thereafter increased in positive slope.

TABLE II
POSSIBLE FUNCTIONAL GROUPS OF *CARICA PAPAYA* (CHEMICAL PROPERTIES)

Bond position (cm-1)	Possible
1000–1100	S = O stretching of S vi oxides C = S stretching
1400 -1500	C – X stretching of Fluoride K – CH_3 bonding of alkanes C= C aromatic compounds C = C stretching of alkenes
1600 – 1700	C = C bonding of aromatic C = O Stretching of amide C = N amides and oximes N – H bonding of primary and secondary amines and amides
2000–2200	C ≡ C stretching of Alkyne
2800–3000	C – H stretching of Alkanes C – H of Aldebyde C – H stretching of Alkyl
3200–3600	OH Hydrogen bonded of alcohol and phenol. R – OH of carboxylic acid

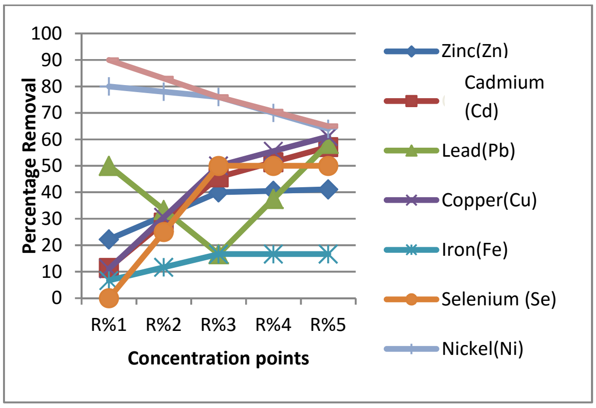

Fig. 1 Heavy Metal % Rremoval at pH 7.8

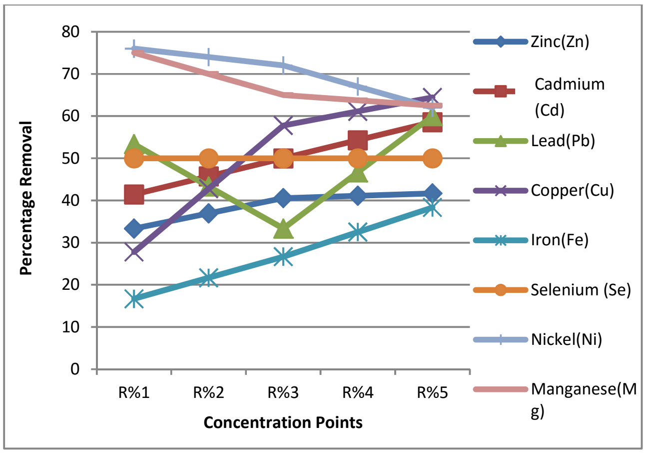

Fig. 2 Heavy metal % removal at pH 6.8

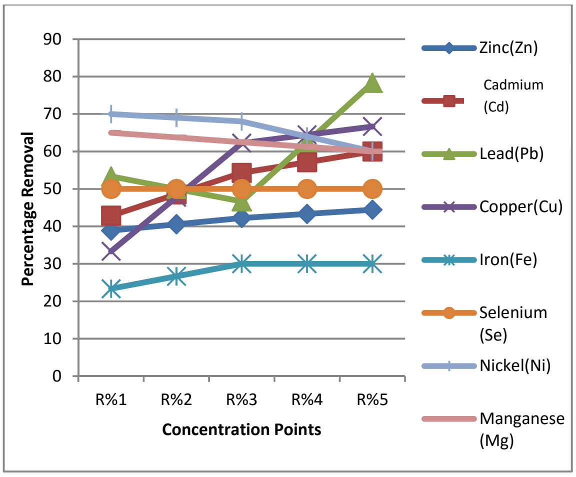

Fig. 3 Heavy metal % removal at pH 5.9

Figs. 1-3 show comparative plots of the heavy metal levels after treatment at different pH levels and waste water quality guidelines. The Canada wastewater quality guideline for the protection of Agricultural standard was adopted to evaluate the suitability of the wastewater for irrigation purpose. From the results, the levels of all the metals are within acceptable limits except for cadmium and manganese

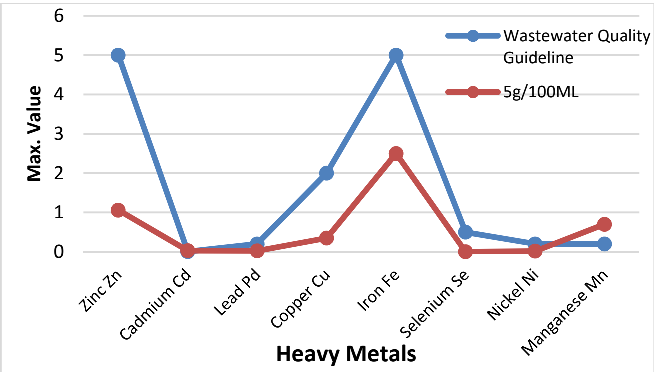

Fig. 4 Experimental Results and Quality Guidelines at pH 7.8

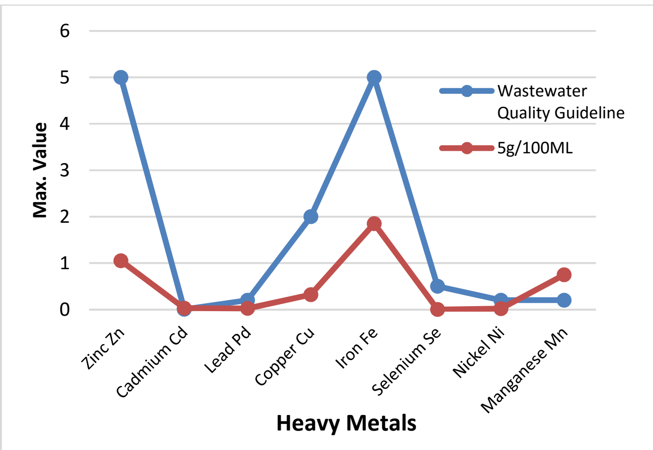

Fig. 5 Experimental Results and Quality Guidelines at pH 6.8

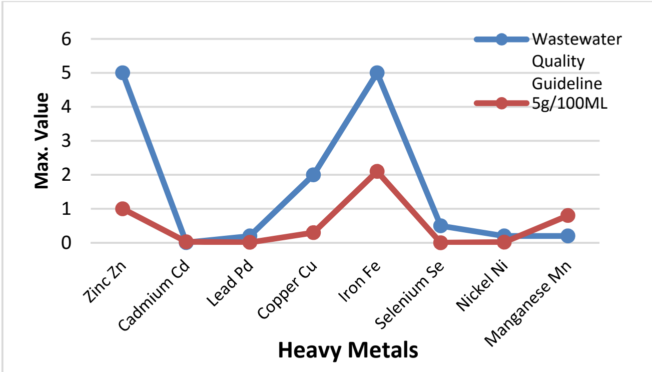

Fig. 6 Experimental results and Quality Guidelines at pH 5.9

To obtain the optimum pH for heavy metal biosorption by papaya wood, the removal of Zinc and Cadmium from their aqueous solutions was studied at different pH values. It was deduced that the biosorption was least at the initial pH 7.8 (0.4g Zinc, and 0.008g Cadmium). This could be explained based on the fact that active sites were protonated, bringing about a competition between H^+ and metal ion (M^{2+}) for occupancy of the binding sites [12]. An increase in biosorption occurred from pH 6.8 to pH 5.9 (0.6g zinc/.02g Cadmium to 0.7g Zinc/0.03g Cadmium). The increase in metal removal as the pH increases in acidity can be explained on the basis of decrease in competition between protons and metal cations for the positive surface charge resulting in a lower electrostatic repulsion between the surface and metal ions. Optimum biosorption was reached at pH 5.9, with 0.7g Zinc and 0.03g Cadmium biosorption.

At pH 5.9 (optimum biosorption pH), 1g/100ml solution of biosorbent achieved the removal of 0.7g of Zinc, 0.03g of Cadmium and 0.032g of Lead. Also 0.3g, 0.7g, 0.001g, 0.035g and 1.3g of Copper, Iron, Selenium, Nickel and Manganese respectively were removed by the same biosorbent solution.

Similarly 3g/100ml solution of biosorbent achieved the removal of 0.76g of Zinc, 0.038g of Cadmium, 0.028g of Lead, 0.56g of Copper, 0.9gm of Iron, 0.001gm of Selenium, 0.034g of nickel and 1.25g of Manganese.

For a biosorbent solution of 5g/100ml; 0.80g of Zinc, 0.042g of Cadmium, and 0.047g of Lead were removed from the waste water. The solution pH has been reported to be the most important variable governing the biosorption of metal ions by biosorbent [12].

IV. Conclusion and Recommendations

Results of the study showed that metal adsorption changes with pH variation. The increase in metal removal as the pH increases in acidity can be explained on the basis of decrease in competition between protons and metal cations for the positive surface charge resulting in a lower electrostatic repulsion between the surface and metal ions.

Cadmium and Manganese are found to be higher on treated wastewater than Canada wastewater quality guideline for the protection of Agricultural water uses while the concentration of other six heavy metals fall below the wastewater table standard which means that the treated wastewater is fit for discharge either into the river or use for irrigation. It may be recommended for any other purpose.

Papaya tree, after its time frame of fruit bearing, could be absolutely considered a waste. The usage will encourage waste re-usability. It is very easy to get and the technology involved in processing it is not difficult. It does not really have any toxic effect on the environment, hence, environmental safety is guaranteed when in use.

Finally, in order to attract more usage of biosorbent technology, some strategies have to be developed where further processing of biosorbent can be done to regenerate the biomass and then convert the recovered metal into usable form.

REFERENCES

[1] Volesky, B. (1994) Advances in biosorption of metals: selection of biomass types. FEMS Microbiology Reviews. (14): 291-302.
[2] Gadd, G.M. (1993) Interactions of fungi with toxic metals. New Phytologist. 124:25-60
[3] Weng, J. and Chen, J. P. (2006) Biosorption of heavy metals by Saccharomyces cerevisiae: a review. Biotechnol. Adv. 24: 427-451.
[4] Kapoor, A. and Viraraghavan, T. (1995). Fungal biosorption- an alternative treatment option for heavy metal bearing wastewaters: a review. Bioresourse. Technol. 53: 95-206.
[5] Nwala G. N., 1990. The removal of heavy-*metal* ions from aqueous solutions by using dried activated carbon, 7-10.
[6] Nriagu, J. O. (1989). A global Assessment of Natural Sources of Atmospheric Trace Metals, Nature, 338: 47-49.
[7] Weng, J. and Chen, J.P. (2006) Biosorption of heavy metals by Saccharomyces cerevisiae: a review. Biotechnol. Adv. 24: 427-451.
[8] Vijayaraghavan, K. and Yun, Y.S. (2008) Bacterial biosorbents and biosorption. Biotechnol. Adv. 26: 266-291.
[9] Gupta, R., Ahuja, P., Khan, S., Saxena, R. K. and Mohapatra, H. (2000) Microbial biosorbents: meeting challenges of heavy metal pollution in aqueous solutions. Curr. Sci. 78: 967-973.990).
[10] Dick, G. (2003). "Papaya": A tantalising taste of the Tropics. Maricopa County Master Gardener Volunteer information, University of Arizona Cooperative Extension. www.papaya Maricopa-hort@ag.arizo.edu.
[11] Ezeigbo C.U. (1990): "A Doppler Satellite Derived Datum for Nigeria". Acta Geodaetica Geoph. Mont. Hung., Journal of Hungarian Academy of Science, Akadémiai Kiadó, Budapest. Vol. 25 (3 – 4), pp. 399 – 413 (1990).
[12] Saeed, A., Waheed Akhter, M. and Iqbal, M. 2005. Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. Sep. Purif. Technol. 45, 25–31.