# Removal of Zinc and Lead Ions from Liquefied Natural Gas Flow Station Wastewater using Modified and Unmodified Water Hyacinths Biomass

**Augustine Avwerosuo Chokor, Ph.D.**

Department of Chemistry, Federal University, Otuoke, Nigeria.

E-mail: aachokor@gmail.com

## ABSTRACT

In this study, an investigation into the adsorption capacity of water hyacinth biomass (WHB) and oxalic acid modified WHB in removing metals (Zn and Pb) ions from wastewater (industrial effluent) was assessed. The impact of the matrix (presence of other ions) on the adsorption of Zn and Pb were also studied by comparing the adsorption of single-metal ions solutions containing equal molar ions to that of the wastewater. The adsorption process was carried out, under two varying conditions of contact time and adsorbent dosage. The concentrations of heavy metals before and after the adsorption process were analyzed using atomic adsorption spectrophotometer (AAS).

The initial concentrations of zinc and lead ions were 113.00 and 2.16mg/L, respectively, in the effluent. These exceeded the limits recommended in effluent discharges to surface water by the Federal Ministry of Environment (FMENV) in Nigeria. The effect of biosorbent dosage on heavy metal removal was studied using 2, 4, 6, 8 and 10g/100mL doses. The result shows the maximum percentage adsorption for zinc was achieve at 6g/100mL dosage, with the unmodified and modified adsorbent removing 87.087 and 93.677% Zn respectively. While the maximum adsorption for lead was obtained at 10g/100mL biosorbent dosage, with the unmodified and modified forms of adsorbent removing 42.315 and 43.840% Pb respectively. The adsorptions of the metals particularly Pb in their single metal ions solutions were more compared to that of the wastewater solution. The adsorption tended to reach a reasonable equilibrium at 50minutes of contact time for Zn with both modified and unmodified WHB, as well as for Pb with the modified WHB. These correspond to 93.677%, 87.087%, and 43.840% adsorption, respectively.

Lead adsorption by the unmodified WHB however, did not attained equilibrium until 75minutes of contact time was exceeded. The modified WHB tended to show higher adsorption capacity for Zn and Pb ions than the unmodified form. This difference was however, significant only for Pb ions at 0.05 probability. The mark reduction in initial concentrations of zinc and lead ions in the wastewater resulting from water hyacinth biomass adsorption, particularly the modified form is an indication of its ability to removed heavy metal from wastewater.

(Keywords: water hyacinth, zinc, lead, biosorbent, adsorption, single metal ions solution.)

## INTRODUCTION

Activities such as mining, agricultural, industrial, oil and gas exploration, and exploitation have often resulted in the generation of large amount of wastewater containing a number of pollutants. One of such important class of pollutants is heavy metals. They are widely distributed in nature and so, soils, sediments, water, and living organisms naturally contain ranges of normal background concentrations. Some metals such as Zn, Cu, Cr, and Mg are essential components of living organisms including Man where they serve to maintain growth and body functions. At higher concentrations however, many become harmful as they tend to accumulate in human tissues thereby constituting great health and environmental risks (Igwe and Abia, 2006).

Other elements such as Pb, Cd, and Hg have no known functions in metabolic processes and such elicit toxic effects even at very low concentrations (White *et al*., 2007). Excessive presence of metals in aquatic environment may depress growth of living organisms. Fishes and other aquatics may accumulate toxic metals in their body tissues. Biomagnifications through the food chain to animals and humans present severe detrimental effects (Saidi, 2010). Although individual metals elicit specific toxicity, the signs normally associated with most heavy metals toxicity include: gastrointestinal disorders, diarrhea, stomatitis, tremor, hemoglobinuria, ataxia, paralysis, vomiting, convulsion and depression (Duruibe, *et al*., 2007).

Toxicity due to lead accumulation may result decrease in hemoglobin production. Lead being a systemic toxicant, several body organs and systems such as: kidneys, liver, central nervous system, hematopoietic system, endocrine system and reproductive system malfunctions or disorders are associated with lead poison (Ibrahim, *et al*., 2006; Sharma and Mogra, 2014; Singh, *et al*., 2018; ATSDR, 2019). Zinc though an essential element, can results in system dysfunctions with consequent impairment in growth and development when presence in excess amount (Nolan, 2003; Duruibe, *et al*., 2007).

Several techniques have been developed for the removal of metals from contaminated waters. These include precipitation, ion exchange, liquid extraction, membrane filtration, electrochemical process, and adsorption with synthetic materials like alumina and activated carbon (Igwe and Abia, 2006; Rafique and Nazir, 2013). The facts that the applications of these techniques are not only expensive, but most time ineffective in removing metals present in aqueous solutions at low concentrations, necessitated the shift to biosorbents.

Biosorbents are easily prepared, cost-effective and eco-friendly. Many biomaterials (e.g. maize cob and husk, cassava waste, sawdust, chistosan, coconut fiber, sugarcane bagasse, sunflower stalk, etc.) have been assessed for their biosorptive character with some showing positive indications as feasible biosorbents for metals removal from solutions (Adie, *et al*., 2012; Rafique, *et al*., 2013; Michalak, *et al*., 2013; Fomina and Gadd, 2014).

Water hyacinth is a free-floating perennial aquatic plant which has in recent time constitute public nuisance. The plant grows prolifically in water particularly nutrient enriched water. Wind and water currents help to distributes them widely in rivers, lakes, streams, ponds, ditches and water course. The weed block boat access and impact transportation, fishing activities and free flow of drainage. It deoxygenates water bodies and results smothering of aquatic lives. Also, it may cause increase in incidence of several diseases because it offers breeding spots for mosquitoes and other disease vectors (Mailu, 2001). It therefore thought that, finding suitable use for water hyacinth biomass (WHB) will provide a two-fold advantage to environmental problem. First, it will reduce the nuisance value of WHB as there will be large increase of their harvest. Secondly, it will provide a cheap and renewable source of raw materials.

Most of studies on batch adsorption by biosorbents have been carried out on laboratory induced concentrations using distilled water. Also when multi-elements ions are involved, it is normally done with equal molar or equal masses of the metals. However, such induced concentrations ratios (equal molar / equal mass ratio) with no other contaminants hardly occur in real wastewater systems making the results difficult to extrapolate to real life situations. This work seeks to study the feasibility of using water hyacinth biomass (WHB) and its oxalic acid modified form in adsorbing metals (Zn and Pb) from effluent wastewater from a Nigeria Liquefied Natural Gas (NLNG) flow station.

## MATERIALS AND METHODS

### Effluent Description

Wastewater samples were obtained from NLNG flow station effluent located at Gbaran Ubie, Balyesa State (Figure 1).

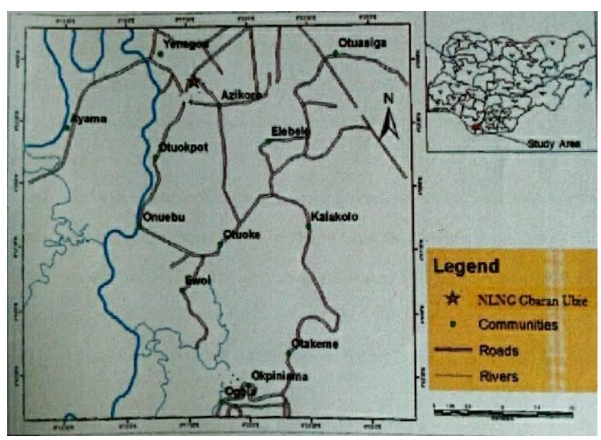


**Figure 1:** Location Map of the Sampled Effluent.

**Table 1:** Some Physico-Chemical Characteristics of the Wastewater.

| Parameters | Properties |
|---|---|
| pH | 5.74 |
| Turbidity (NTU) | 10.85 |
| Conductivity (µs/cm) | 259.24 |
| Total dissolved solid(mg/L) | 147.20 |
| BOD (mg/L) | 49.41 |
| COD (mg/L) | 72.97 |
| Zn (mg/L) | 113.00 |
| Pb (mg/L) | 2.16 |

The wastewater had a foul smell and a pale yellowish color. Some other physico-chemical characteristics of the wastewater are shown in Table 1. Water hyacinth (*E. Crassipes*) used for this study were harvested from the Otuoke river, Bayelsa State.

The water hyacinths were first washed several times with distilled water to remove any adhering impurities. The biomass was then sun dried and kept in a plastic bag. The dried biomass was grinded to small particle size using mortar and pestle and dried in an oven for 48 hrs. at 60$^o$C. The ground material was sieved (through 60mm) and stored in desiccators for use in adsorption studies. A portion of the dried water hyacinth biomass (WHB) was modified by placing the WHB in a beaker and gradually adding 0.01M of oxalic acid while stirring, until a paste is formed. The paste was allowed to dried and grinded again.

## Effect of Biosorbent Dosage on Metals Removal Efficiency

Different amount of biosorbent dosages (modified and unmodified) viz; 2, 4, 6, 8 and 10g were each transferred into beakers containing 100mL of the wastewater. The solutions were agitated for 30 minutes and then filtered. 50mL of each filtrate were digested and the concentrations of Zinc and Lead ions in the solutions were determined by Atomic Adsorption Spectroscopy (AAS).

## Effect of Contact Time on Metals Removal Efficiency

The effect of contact time was studied using a constant weight of modified and unmodified biosorbent (6g). This was added to five different beakers containing 100mL of the wastewaters. The solutions were agitated for the different periods of time (25, 50, 75, 100, and 125minutes). The solutions were then filtered, and the filtrates analyzed for Zinc and Lead ions with AAS after digestions with nitric acid.

## Effect of the Presence of other Ions

The effect of the presence of other ions on the adsorption process was assess by preparing single-ions solutions of the metals (Zn and Pb) with equal molar concentrations as those in the wastewater solution using distilled water and the metal cations in their nitrates forms. The adsorption was then carried out with 2g/100mL biosorbent dose at a contact time of 30 minutes.

## Evaluation of Experimental Data

**Amount Adsorbed**: the difference between the original concentrations of metals in solutions and that after agitation with the adsorbent (WHB) for a period of time, is regarded as the amount adsorbed.

**Percent Adsorption**: the percentage of zinc and lead ions adsorbed by WHB was calculated from the differences between the initial ($C_o$) and equilibrium ($C_e$) concentrations, that is:

$$percent\ adsorption = \frac{(C_o - C_e)100}{C_o}$$

Where, $C_o$ and $C_e$ are the concentrations before and after adsorption, respectively.

## RESULTS AND DISCUSSION

The concentrations of Zn and Pb before and after adsorption with various doses of water biomass hyacinth – unmodified and modified – are respectively shown in Figure 2 and Figure 3, while Figure 4 shows the percent adsorption for both metals using the unmodified and modified adsorbents.

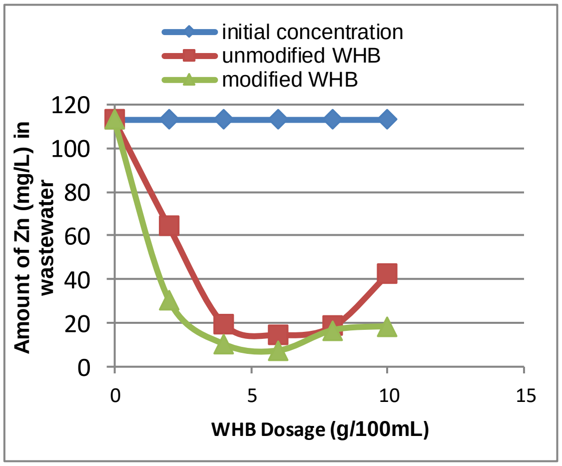


**Figure 2:** Concentrations of Zn in Wastewater before and after Adsorption with Different Doses of Modified and Unmodified WHB.

Figure 2 shows the concentrations of Zn before and after adsorptions with different doses of water hyacinth biomass (WHB) for both unmodified and modified forms. The reduction in concentrations of Zn in the wastewater solutions with increase dose of adsorbent meant that biosorption of Zn increases as the initial dosage of biosorbent increases. This attributed to increasing binding sites for ions as the number of adsorbent particles increases (Rao, *et al*., 2010; Witek-Krowiak, *et al*., 2011).

It can be seen that the maximum reduction of Zn concentration (Figure 2), corresponding to maximum adsorption (Figure 4) by both the unmodified and modified WHB was recorded at 6g/100mL dosage. At this maximum adsorption, there was reduction in concentration from 113.00mg/L Zn to 14.592 and 7.145mg/L for the unmodified and modified WHB, respectively. This represents 87.087 and 93.677% adsorption respectively for the unmodified and modified WHB (Figure 4).

There was no advantage in further increasing the dosage above this as it only leads to less adsorption of Zn. This probably is due to adsorption of more of water in preference to the metal by the adsorbent at high loadings. However, the sharp peak in adsorption of Pb (Figure 4) after 6g dosage shows that competitive adsorption is more at play than preferential adsorption of water. At high dosage, with much of Zn already adsorbed, Pb can now favorably compete for adsorption sites with Zn, hence the sharp increase in Pb adsorption correspond to that of Zn decline.

The modified WHB tended to show higher capacity to reduce the concentration of Zn ions in the wastewater than the unmodified. The difference, however, was not significant at 0.05 probability.

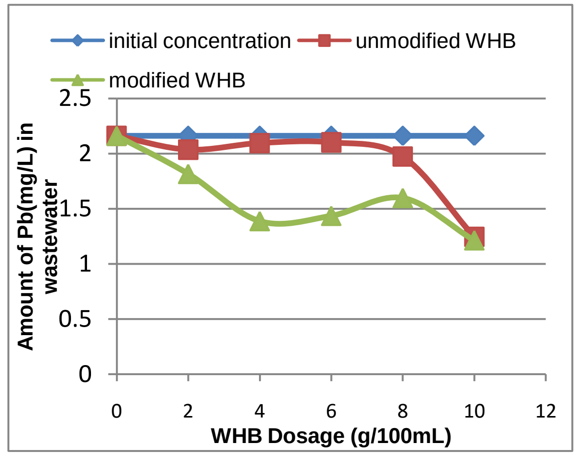


**Figure 3:** Concentrations of Pb in Wastewater before and after Adsorption with Different Doses of Modified and Unmodified WHB.

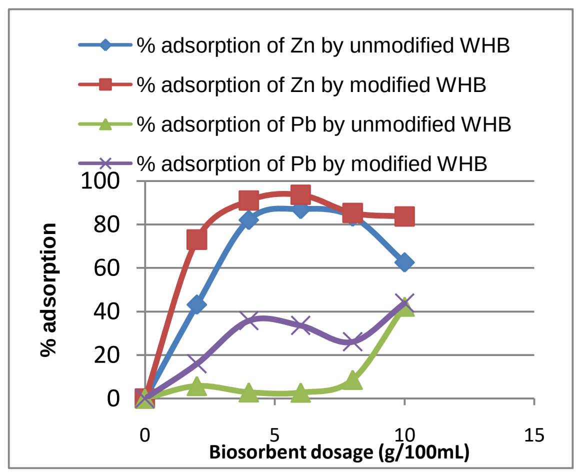


**Figure 4**: Percent Adsorption of Zn and Pb at varying Doses of Modified and Unmodified WHB.

Figure 3 also shows that the modified WHB was more effective in reducing the concentration of lead (Pb) ions in the wastewater. For instance, after adsorption with the unmodified WHB, the concentrations at 2 and 4g/100mL dosages were respectively reduced from 2.16mg/L to 2.035 and 2.095mg/L whereas, for the modified WHB, the concentrations were reduced to 1.815 and 1.385mg/L, respectively. These represent 5.787 and 2.870% adsorption for the unmodified and 15.972 and 35.787% adsorption for the modified

WHB (Figure 4). Comparison of the modified and unmodified WHB using t-sampling statistic shows significant difference in lead adsorption ($P < 0.05$). The oxalic acid modified WHB adsorbed more Pb from solution than the unmodified substrate probably because, oxalic acid donates proton causing the adsorbent surface to become protonated. These protonated surfaces have more attraction for metal ions thereby promoting speedy adsorption (Tijani *et a*l., 2011).

Figure 4 shows clearly that the percent adsorption for Zn increases with increase in biosorbent dosage to maximum at 6g dosage after which further addition of dosage resulted in decrease in percent adsorption. The adsorption of lead was marked by an initial increase, it then slopes (decreases slightly) following further increase in biosorbent dosage, only to peak (increases sharply) again at still further increase biosorbent dosage. This behavior of Zn and Pb in the wastewater can only be explained in terms of competitive adsorption. Zn been present in large excess compared to Pb, had an initial competitive advantage in occupying the adsorption sites than lead.

The effects of contact time on the adsorption of Zn and Pb ions as reflected in the change in concentrations Zn and Pb ions in wastewater solution over varying time of contact with the adsorbents are shown in Figures 5 and 6. Figure 7 shows the comparative percent adsorption for both metals ions with both unmodified and modified WHB.

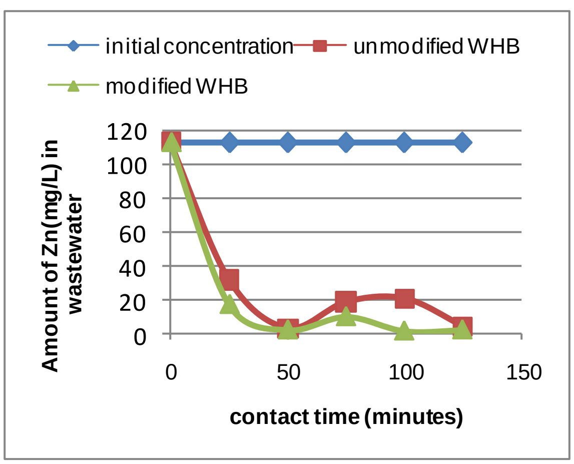


**Figure 5:** Change in Concentrations of Zn in Wastewater at Different Contact Time (minutes) with Modified and Unmodified WHB.

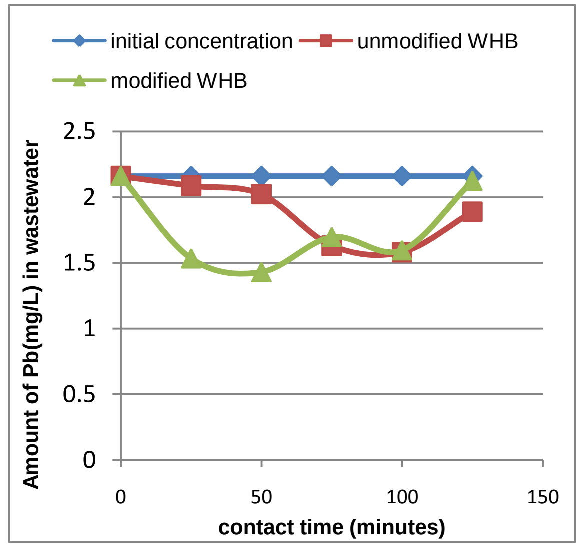


**Figure 6:** Change in Concentrations of Pb in Wastewater at Different Contact Time (minutes) with Modified and Unmodified WHB.

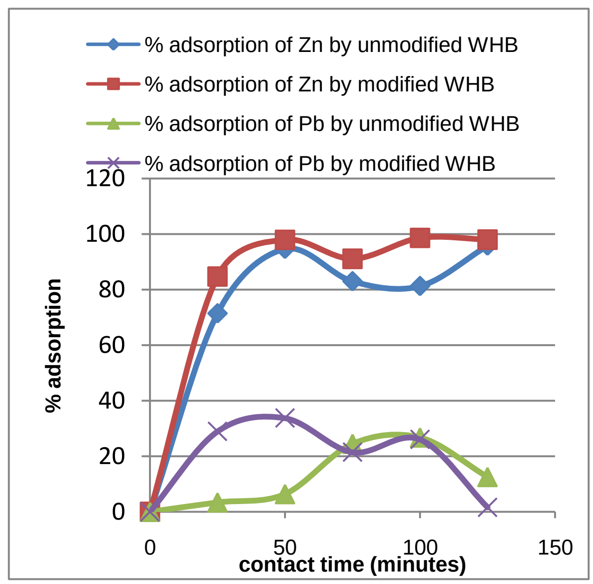


**Figure 7**: Percent Adsorption of Zn and Pb at Different Contact Time by Unmodified and Modified WHB.

The results show progressive increase in percentage adsorption from the first minute to 50 minutes. At 25 minutes of contact time, the percent adsorption for the unmodified water hyacinth biomass (WHB) was 71.43% for Zn and 3.38% for Pb. while at 50minutes it was 94.64% Zn and 6.39% Pb. The modified WHB however show 84.70% and 28.94% adsorption at 25 minutes for Zn and Pb, respectively, and at 50 minutes of contact time, the percent adsorption was 97.99% and 33.75%, respectively, for Zn and Pb. The adsorption tends to reach a reasonable equilibrium at 50 minutes of contact time for Zn with both modified and unmodified WHB, as well as for Pb with the modified WHB. The unmodified WHB however, did not witness Pb attained equilibrium until 75 minutes of contact time is exceeded.

The contact time between the adsorbate and adsorbent plays an important role in adsorption process with adsorbent which adsorb the highest amount of adsorbate within the shortest time being the most desirable for practical applications. Adsorption being a dynamic process, involving both adsorption and desorption, there are instances were more than one equilibrium time are established. This is noticeable for Zn adsorption by both the modified and unmodified WHB at contact time of 50minutes, and at 100 and 125 minutes for the modified and unmodified, respectively (Figures 5 and 7).

At the main equilibrium time (50 minutes of contact time), the modified WHB tended to show much capacity to reduce the concentrations of the metals (Zn and Pb) ions that is, it shows higher adsorption capacity than the unmodified form in the wastewater. The consequence of grafting a carboxyl group on the adsorbent surface by treatment with the oxalic acid enhances the binding potential of the sorbent and thus increases the number of binding sites (Tijani, et al., 2011; Michalak, *et al*., 2013). Some researchers have shown that Pb ions co-presence with other ions of smaller sizes (such as Cu, Zn) in solution exhibit greater adsorption at equilibrium time than the smaller ions (Mahmood, et al., 2010; Tijani, *et al*., 2011). This is predicated on the fact that ions with smaller sizes are heavily hydrated making their size larger and bulkier than the less hydrated ones like Pb ion.

The heavily hydrated ions have their migration largely hindered in aqueous solution hence the tendency of being adsorbed to the reactive surface of the adsorbents is significantly reduced. The reverse obtained in this study (i.e. higher percent Zn adsorption rather than Pb) may be due to the much higher concentration of Zn ions as compared to Pb in the wastewater. Zn been present in large amount compared to Pb had competitive advantage in occupying the adsorption sites than lead.

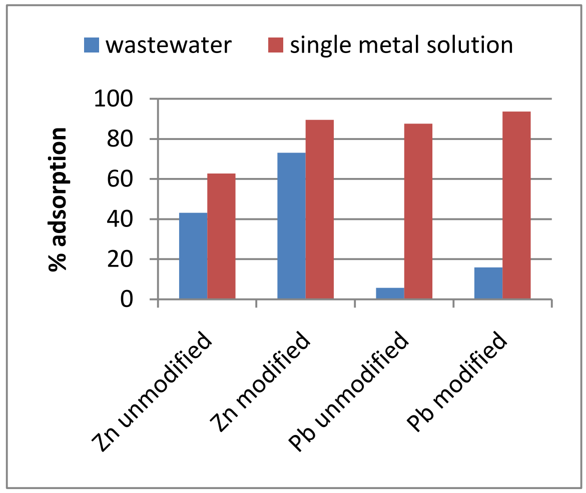


**Figure 8**: Percent Adsorption of Zn and Pb from Wastewater and Single-Metal Ion Solutions at 2g/100mL Dosage.

The effects of other ions on the adsorption process were obvious (Fig. 8), Zn in the single metal ions solution, was reduced from 113mg/L to 42.14mg/L(representing 62.73%adsorption) and 11.94mg/L (89.43% adsorption) in the unmodified and modified WHB respectively. This compared to the 64.24 mg/L (43.15% adsorption) and 30.46mg/L (73.05% adsorption) respective reduction for the unmodified and modified WHB in the wastewater shows the impact of the presence of other ions in reducing the adsorption of Zn.

A more marked increase in percent adsorption was observed for lead (Pb) ions in the single-metal solution: the percent adsorption for the wastewater and single Pb ions solution were 5.79% and 87.51% Pb, respectively using the unmodified WHB. These correspond to a decrease in concentrations from 2.16mg/L to 2.035 and 0.27mg/L, respectively. For the modified WHB, the percent adsorption was 93.67% in the single Pb ion solution as against 15.97% in the wastewater solution. The impact of other ions on Pb adsorption was more evident compare to that of Zn probably because of the low concentration of Pb in the wastewater. This implies that, the impact of the presence of other ions and overall matrix on the adsorption needs to be considered in modelling the adsorption processes.

## CONCLUSION

The degree of adsorption of metals (Zn, Pb) from the wastewater by water hyacinth (*Eichhornia crassipes*) biomass (WHB) which is reflective of the capacity to remove the metals from solution was a function of the biosorbent dosage and contact time. A contact time of 50 minutes was particularly effective for Zn adsorption for the modified and unmodified WHB. However, for Pb adsorption only the modified reached equilibrium at 50 minutes of contact time, While the unmodified lingers on to 75 – 100 minutes before it established equilibrium. The oxalic acid modified WHB bind more Zn and Pb ions than the unmodified adsorbent.

The impact of increasing biosorbent dosage, the presence or absence of other ions and the relative concentrations of these ions on the removal efficiency were obvious. Zn particularly shows higher adsorption capacity due to its very high concentration relative to Pb in the wastewater. The marked reduction in initial concentrations of zinc and lead ions in the wastewater by water hyacinth biomass particularly the modified form project great hope in its used as an efficient metals removal in wastewater, however the desorption of the metals from the biomass and reutilization of the same is a factor that demands further considerations. These data are necessary for modeling, predictability, rational approach to design and selection of optimization of treatment processes.

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## ABOUT THE AUTHOR

**Dr. A.A. Chokor,** is a Lecturer at the Federal University, Otuoke, Nigeria. He holds a Ph.D. degree in Environmental Chemistry from the University of Benin. He is a member of the Chemical Society of Nigeria. His research interests are in pollution studies and remediation technology.

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