

Intrinsic Role of pH Variables on the Sorption of Heavy Metals by Water Hyacinth (*Eichhornia crassipes*) on The Niger Delta Rivers, Nigeria

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ABSTRACT

The uptake of heavy metals (Cu, Ni, Cr, Co, Cd and Pb) at various pH levels (2.0, 3.0, 4.0, 5.0, 6.0) was studied at sample locations (Onitsha, Atani, Aboh and Bomadi) on the Niger Delta waterways. Results of analysis of digested samples analyzed using Atomic Absorption Spectrophotometry showed that chromium was detected at the highest concentration for all locations (Onitsha 4.220 mg/l, Atani 4.410 mg/l, Aboh 4.144 mg/l, Bomadi 3.198 mg/l) with sorption at pH 6.0 while cobalt was found in lowest concentration for all locations (Onitsha 0.002 mg/l, Atani 0.002 mg/l, Aboh 0.001 mg/l and Bomadi 0.001 mg/l) sorption at pH 2.0. Sorption of heavy metals was highest at pH 6.0 while at pH 2.0 the concentrations of metals absorbed was lowest. The accumulation of lead, nickel, and cadmium in water hyacinth was poor for all pH levels tested.

Keywords: accumulation, Atomic Absorption Spectrophotometry, digestion, hyperaccumulation, phytoextraction, phytoremediation

INTRODUCTION

Water hyacinth (*Eichhornia crassipes*) is a free-floating tropical aquatic plant with attractive violet flowers and shiny bright green leaves on long petioles. The plant grows rapidly at temperatures ranging from 28 to 30°C and at pH of 4.00 to 8.00. Wetlands such as lakes, streams, ponds etc. are suitable environments for the plant's growth. The rapid growth rate of the plant on such water bodies has created an environmental impact that has attracted much attention to the plant. A well developed root outlet is the source for effective uptake and hyperaccumulation of organic and inorganic substances by the plant for uptake into the plant, but these substances must be in solution, either in ground-water or in the soil solution. Water is absorbed from the soil solution into the outer tissue of the root of the plant and thus contaminants in the water can move through the epidermis to and through the Casparian strip, and then through the endodermis, where they can be absorbed, bound, or metabolized (Paterson *et al.* 1990). Chemicals or metabolites in the water absorbed in this way by the plant pass through the endodermis and reach the xylem where they are then transported in the transpiration stream or sap. These compounds then react with or partition into plant tissue, are metabolized or are released to the atmosphere through stomata pores (Shimp *et al.* 1993).

The uptake and translocation of organic and inorganic substances by the plant are also dependent on the hydrophobic (lipophilicity), solubility, polarity, and molecular weight of the substances (Briggs *et al.* 1982). Translocation of non-ionized compounds to shoots was optimal for intermediate polarity compounds that were moderately hydrophobic while more strongly bound to root surfaces or partition into root solids, resulting in less translocation within the plant (Schnoor *et al.* 1995). Very soluble organic compounds with low sorption will not be absorbed onto roots while soluble inorganic compounds, such as nutrients, can be readily taken up by the plant (Schoor *et al.* 1995). Uptake of inorganic compounds which are generally in an io-

nic or complex form is mediated by active or passive uptake mechanisms within the plant. The uptake of ions by water hyacinth could be achieved through phytoextraction, which is a phytoremediation process for contaminant removal in which the contaminant removal process is accomplished by harvesting the above-water portion of the plant along with its roots, followed by proper disposal of the contaminated plant mass. Phytoextraction using water hyacinth can be conducted to remediate contaminated surface water bodies. Monitoring and possible modification of the water pH is very necessary since pH effects alter the transport of inorganic contaminants (Bañuelos *et al.* 1990). It is suggested that the phytoextraction process is enhanced when metal availability to plant roots is facilitated through the addition of acidifying agents to the water which alters the pH. The retention of metals to water becomes weaker at a low pH resulting in more available metal for root absorption (Majeti *et al.* 2003).

The current study aimed to investigate the role pH plays in the uptake of heavy metals by water hyacinth.

MATERIALS AND METHODS

Field trips were undertaken to several locations (**Fig. 1:** Onitsha, Atani, Aboh and Bomadi) to randomly harvest water hyacinth samples. Each sample location was visited in October, 2007, which coincides with the period of rapid growth and peak dominance of the plant on the Niger Delta Rivers (Egborge *et al.* 1986). Five water hyacinth samples were harvested from each sample station and placed in clean plastic buckets that had been washed and rinsed several times with deionised water. The plant samples were also washed several times with deionised water and placed in separate plastic buckets labeled according to sample stations.

About 0.1 g of each of the salts, copper (II) sulphate, nickel(II) sulphate, chromium (III) chloride, cobalt (II) chloride, cadmium sulphate, and lead (II) chloride was weighed and dissolved in 1 L of deionised water in six separate plastic buckets previously cleaned as described earlier and the mixture was repeatedly stirred. A solution of 1 M HCl was poured intermittently

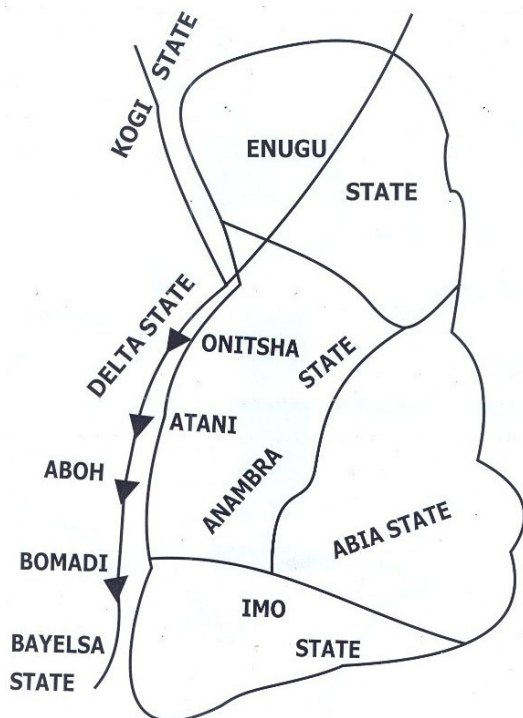


Fig. 1 Map of the Niger Delta water ways showing sample locations.

into the bucket containing copper sulphate solution until the pH of the content stabilized at 2.0. This procedure was repeated with the five other buckets for each of the salts. Onitsha sample station was chosen solely as an example to describe the procedure of sampling and analysis that was repeated in other sample stations at the stated pH levels. One water hyacinth plant from the five water hyacinth plants harvested from the Onitsha sample station was split into two halves longitudinally one half of the plant complete with root and shoot was planted in the solution containing Copper sulphate for 7 days and the containing vessel was kept under laboratory environment in the chemistry department of the Federal University of Technology, Owerri, Nigeria. After 7 days, preparation of the sample for analysis was done using the method described by Ukiwe and Ogukwe (2007). The other half of the plant samples was analyzed for its heavy metal content by acid digestion after preparing the plant sample for analysis using the method described by Ukiwe and Ogukwe (2007) using Atomic Absorption Spectrophotometry (AAS). Four other treatments were done using the remaining four harvested samples and the mean of the five analyses was determined. Other water hyacinth samples from the Onitsha sample station followed the same procedure for the five other salts in the bucket containers still at pH 2.0. The concentration (mg/l) of the metal ions in the plant was determined by preparing concentration of 0.001 to 5.000 mg/l standards of copper, nickel, chromium, cobalt, cadmium and lead ions respectively using appropriate amounts of their sulphates and chlorides with deionised water. The absorbance of these concentrations were determined by AAS at 324.7, 232.0, 357.9, 240.7, 228.8 and 217.0 nm for Cu, Ni, Cr, Co, Cd and Pb, respectively, using a 0.5-4.0, 2-8, 2-15, 2.5-9, 2-1.8 and 2.5-20 absorption optimum working range for the metals following the same order as above for wavelengths. The flame type used was Air Acetylene Oxidizing (AAO) for Cu, Co, Cd and Pb and Air Acetylene Reducing (AAR) for Ni and Cr. Plots of absorbances of standards of the metal ions against their concentrations were made. The concentration within each sample was obtained by first subtracting the absorbance of the other half of the plant that was not planted in the buckets from the absorbance of the other half of the plant that was planted for 7 days in the various salts of the metals. The final absorbance after subtraction was then interpolated to the appropriate concentrations on the graph. This procedure was repeated for the Atani, Aboh and Bomadi sample stations for pH 2.0. At pH 3.0, 4.0, 5.0 and 6.0 the same procedure was repeated for all sample stations.

RESULTS AND DISCUSSION

There are considerably good reasons why the heavy metal content of water hyacinth should be investigated, including knowledge of potential contamination of the water environment by heavy metals, which would destabilize the food chain. Studying the heavy metal concentration of this plant would allow us to perceive when these metals had accumulated to toxic levels deleterious to the water environment.

Tables 1-5 represent values for the heavy metal content at pH 6.0, 5.0, 4.0, 3.0 and 2.0, respectively for all sample stations (Onitsha, Atani, Aboh and Bomadi). From Tables 1 to 5, an increase in the amount of the metal ions at high pH values can be observed while a decrease in the concentration of metal ions is seen at low pH values. pH 6 has the highest heavy metal content while pH 2 has the lowest. There are no significant amount of Co, Pb and Cd but very high values for Cr and relatively moderate values for Ni and Cu for all sample stations. Only Cu was significantly different between pH 4 and pH 3 but showed no significance overall for all sample stations.

Acidifying agents increase the bioavailability of metals in soil leachate solution by either liberating or displacing metals from the solid phase of the soil or by making precipitated metal species more soluble (Majeti *et al.* 2003). Under acidic conditions, H^+ ions displace metal cations from the cation exchange complex of soil leachate components and cause metals to be released. Studies conducted on the amount of metals removed by non-living dry roots over absorbed masses at varying pH values showed that the highest amounts of total metals removed occurred at a pH value of approximately 6.5 (El-Gendy *et al.* 2006). The effect of pH on uptake of metals showed that a pH range between 4.0 and 6.0 was favorable for metal sorption but sorption was unfavorable at lower pH and this maybe due to competition with hydrogen ions by the metals at the root sites (El-Gendy *et al.* 2006). Very little sorption occurs at very low pH and our results are in agreement with this concept, i.e. where it has been shown that pH effect falls within other reported ranges. The high sorption of Cu and Cr by water hyacinth in this study could be attributed to the fact that these metals accumulate freely in aquatic life and are essential for the growth and development of the plant. It should be noted that no trend was observed in the rate of accumulation of the metals among sample stations.

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Table 1 Concentration (mg/l) of heavy metals of water hyacinth at pH 6.0 for various sample locations.

Sample location	Onitsha	Atani	Aboh	Bomadi
Heavy metals	Mean \pm SD X 10 ⁻² (mg/l)	Mean \pm SD X 10 ⁻² (mg/l)	Mean \pm SD X 10 ⁻² (mg/l)	Mean \pm SD X 10 ⁻² (mg/l)
Cu	3.342 \pm 7.0	3.388 \pm 3.3	3.410 \pm 14.2	3.662 \pm 1.4
Ni	1.382 \pm 55.6	1.411 \pm 1.9	1.614 \pm 18.2	1.310 \pm 2.4
Cr	4.244 \pm 16.4	4.642 \pm 15.8	4.414 \pm 2.0	3.213 \pm 3.1
Co	0.026 \pm 0.2	0.063 \pm 0.1	0.062 \pm 6.1	0.078 \pm 7.2
Cd	0.033 \pm 0.2	0.064 \pm 0.1	0.081 \pm 0.0	0.034 \pm 0.0
Pb	0.201 \pm 1.5	0.200 \pm 1.5	0.222 \pm 1.5	0.210 \pm 4.9

Table 2 Concentration (mg/l) of heavy metals of water hyacinth at pH 5.0 for various sample locations.

Sample location	Onitsha	Atani	Aboh	Bomadi
Heavy metals	Mean \pm SD X 10 ⁻² (mg/l)	Mean \pm SD X 10 ⁻² (mg/l)	Mean \pm SD X 10 ⁻² (mg/l)	Mean \pm SD X 10 ⁻² (mg/l)
Cu	3.300 \pm 1.4	3.340 \pm 2.0	3.101 \pm 1.5	3.222 \pm 5.9
Ni	1.300 \pm 15.8	1.349 \pm 0.0	1.314 \pm 2.5	1.132 \pm 0.0
Cr	4.220 \pm 2.8	4.410 \pm 1.5	4.144 \pm 9.9	3.198 \pm 0.0
Co	0.026 \pm 0.0	0.031 \pm 0.4	0.033 \pm 0.1	0.034 \pm 1.3
Cd	0.034 \pm 1.3	0.033 \pm 0.1	0.032 \pm 0.0	0.028 \pm 0.0
Pb	0.190 \pm 0.0	0.186 \pm 0.2	0.207 \pm 0.2	0.115 \pm 0.0

Table 3 Concentration (mg/l) of heavy metals of water hyacinth at pH 4.0 for various sample locations.

Sample location	Onitsha	Atani	Aboh	Bomadi
Heavy metals	Mean \pm SD X 10 ⁻² (mg/l)	Mean \pm SD X 10 ⁻² (mg/l)	Mean \pm SD X 10 ⁻² (mg/l)	Mean \pm SD X 10 ⁻² (mg/l)
Cu	3.300 \pm 14.1	3.335 \pm 10	3.001 \pm 31.6	3.064 \pm 15.8
Ni	1.280 \pm 1.5	1.320 \pm 1.0	1.288 \pm 1.5	1.264 \pm 1.1
Cr	4.100 \pm 15.8	4.240 \pm 2.0	3.781 \pm 0.9	3.610 \pm 15.8
Co	0.022 \pm 0.1	0.032 \pm 0.1	0.036 \pm 0.1	0.027 \pm 0.2
Cd	0.032 \pm 0.2	0.031 \pm 0.5	0.029 \pm 0.0	0.026 \pm 0.2
Pb	0.192 \pm 0.1	0.188 \pm 0.0	0.198 \pm 0.1	0.118 \pm 0.1

Table 4 Concentration (mg/l) of heavy metals of water hyacinth at pH 3.0 for various sample locations.

Sample location	Onitsha	Atani	Aboh	Bomadi
Heavy metals	Mean \pm SD X 10 ⁻² (mg/l)	Mean \pm SD X 10 ⁻² (mg/l)	Mean \pm SD X 10 ⁻² (mg/l)	Mean \pm SD X 10 ⁻² (mg/l)
Cu	3.310 \pm 20	2.316 \pm 15.7	2.214 \pm 9.9	2.866 \pm 1.5
Ni	1.250 \pm 1.5	1.292 \pm 1.5	1.199 \pm 34.5	1.106 \pm 10.0
Cr	3.250 \pm 15.8	3.350 \pm 15.8	2.110 \pm 15.8	2.001 \pm 15.8
Co	0.011 \pm 0.1	0.020 \pm 1.5	0.012 \pm 2.4	0.002 \pm 0.0
Cd	0.010 \pm 0.2	0.010 \pm 0.2	0.012 \pm 2.4	0.003 \pm 0.1
Pb	0.161 \pm 1.0	0.187 \pm 0.0	0.195 \pm 0.5	0.157 \pm 1.5

Table 5 Concentration (mg/l) of heavy metals of water hyacinth at pH 2.0 for various sample stations.

Sample location	Onitsha	Atani	Aboh	Bomadi
Heavy metals	Mean \pm SD X 10 ⁻² (mg/l)	Mean \pm SD X 10 ⁻² (mg/l)	Mean \pm SD X 10 ⁻² (mg/l)	Mean \pm SD X 10 ⁻² (mg/l)
Cu	2.601 \pm 15.8	2.116 \pm 15.7	2.115 \pm 19.9	2.010 \pm 2.1
Ni	0.600 \pm 1.5	1.201 \pm 1.4	1.129 \pm 1.0	1.106 \pm 10.4
Cr	2.120 \pm 15.8	3.310 \pm 0.0	1.187 \pm 1.3	1.616 \pm 2.4
Co	0.002 \pm 0.0	0.002 \pm 0.0	0.001 \pm 0.0	0.001 \pm 0.0
Cd	0.002 \pm 0.0	0.003 \pm 0.1	0.004 \pm 0.0	0.002 \pm 0.0
Pb	0.019 \pm 0.0	0.200 \pm 1.5	0.196 \pm 0.2	0.116 \pm 0.0