



SORPTION CHARACTERISTICS OF WATER HYACINTH LEAF BIOMASS ON THE REMOVAL OF Cu (II) ION FROM AQUEOUS SOLUTION

^{1*}OBI, C

¹Department of Pure and Industrial Chemistry,
Faculty of Biological and Chemical Sciences,
University of Port Harcourt, Rivers State, Nigeria

Email: zarasexcom@yahoo.com

Mobile: +234-8036682351

ABSTRACT

Biosorption of Cu (II) ion onto a non – conventional water hyacinth biomass was investigated in column reactor system. Process parameters which include initial metal ion concentration, contact time and pH of solution were varied in order to evaluate their influence on the biosorption process. The results obtained indicate that the biosorption of Cu (II) ion on water hyacinth biomass is better at higher metal ion concentrations. The maximum biosorption capacity was found to be 14.96 mg/g, which was obtained at 300 mg/L Cu (II) ion concentration and a contact time of 30 mins was achieved. The optimum pH of 8 was established. The equilibrium data fitted well to the Langmuir biosorption model with correlation coefficient (R^2) value of 0.8363. The result equally revealed that the removal of Cu (II) ion from aqueous solution using water hyacinth biomass followed physical biosorption. Hence, water hyacinth which is regarded as nuisance in rivers is an effective biomass for the removal of Cu (II) ion contaminant from aqueous solution.

Keywords: water hyacinth biomass, biosorption capacity, Cu (II) ion removal, aqueous solution

INTRODUCTION

In moving towards the new era of science and technology, the world has observed tremendous transformations of all aspects of life. At the heart of this tremendous advancement lies the rapid industrialization occurring at various parts of the globe. Despite being the source of many distinguished benefits for mankind, this revolution has also caused significant degradation to the environment, leading to detrimental effects to human and animal and aquatic lives. One widespread phenomenon which has drawn much attention is the contamination of toxic metals such as copper, lead, zinc, nickel and chromium in the aquatic environment and these metals are sourced from chemical industries such as petrochemicals, refineries, fertilizers, pulp and paper (Kaewsarn and Yu, 2001). Heavy metal contamination may cause serious health problems such as cancer and brain damage, due to the accumulation in living tissues and organs (Mkhopadhyay, 2008). From the various types of toxic metal ions present in wastewater, copper was chosen for this biosorption studies with regard to its wide use in industry and potential pollution impact. Copper is listed as one of the pollutants found in wastewater by the United States Environmental Protection Agency (USEPA) in 1978 (Mkhopadhyay, 2008). In industrial waste, copper mainly appears to be in the form of the bivalent Cu (II), which is according to Ullmann's encyclopedia, more toxic than the metal itself. This is because it is soluble in water in its ionic form and can easily absorb into living organisms. High doses of copper in the aquatic environment generate toxicological concerns as it can deposit into the brain, liver, pancreas and myocardium (Davis *et al.*, 2000). Thus, Cu (II) concentrations of wastewater should be reduced to a value of at least 1.0 to 1.5 mg/L. The increase of metal bearing effluents into the aquatic environment has caused progressive developments in wastewater treatment.

Biosorption can be defined as the ability of biological materials to accumulate heavy metal ions from wastewater through metabolically mediated or physico – chemical pathways of uptake (Fourest and Roux, 1992). In simple word it can be described as the binding and concentration of heavy metal ions from aqueous solutions by biomass.

Biosorption is a new technology for removing metal ions from aqueous solutions and replacing conventional methods such as reduction or oxidation, ion exchange, filtration, electrochemical treatment, membrane technology, evaporation recovery, chemical precipitation, chemical lime coagulation and solvent extraction. These conventional ways has many disadvantages like extremely expensive, incomplete metal removal and generation of toxic compound.

Thus, biosorption is a good technique and have advantage over other conventional methods because of its low cost, high efficiency, minimization of chemical and or biological sludge, no additional nutrient requirement, regeneration of biosorbent and possibility of metal recovery (Kratochvil and Volesky , 1998; Dang *et al.*, 2008)

Water hyacinth (*Eichhornia crassipes*) is an obnoxious weed that has attracted worldwide attention due to its fast spread and congested growth, which lead to serious problems in navigation, irrigation, and power generation. On the other hand, when looked from a resource point of view, it appears to be a valuable resource with several unique properties. As a result, research activity concerning control (especially biological control) and utilization (especially wastewater treatment or phytoremediation) of water hyacinth has boomed up in the last few decades (Malik, 2007). Water hyacinth, among other aquatic macrophytes, has been shown to possess a great potential to remove pollutants when being used as a biological filtration system (Mahamadi, 2011). It contains much polyfunctional metal – binding sites for both cationic and anionic metal complexes. Potential metal cation – binding sites of algal cell components include carboxyl, amine, imidazole, phosphate, sulphate, sulfhydryl, hydroxyl and chemical functional groups contained in cell proteins and sugars (Mahmood *et al.*, 2010c). The weed could remove several heavy metals and other pollutants (Pinto *et al.*, 1987; Delgado *et al.*, 1993; Zaranyika *et al.*, 1994; Mahamadi and Nharingo, 2007, 2010a, 2010b). Recorded achievements triggered efforts directed towards the utilization of water hyacinth in phytoremediation.

The main objective of this study is to evaluate the biosorption characteristics of Cu (II) ion from aqueous solution using water hyacinth (*Eichhornia crassipes*). The biosorption was carried out isothermally in a column reactor system, with varying contact time, initial metal ion concentrations and initial pH of solution.

MATERIAL AND METHODS

Sample Collection and Preparation

The water hyacinth leaves used in this study was collected from Choba River, Choba community in Obio – Akpor Local Government Area of Rivers State, Nigeria. The water hyacinth biomass was sun – dried for two days. The biosorbent was prepared by washing it with 0.1N HCl (to convert alignates to alignic acid) and then rinsed with de-ionized water. The leaves were then dried further in an oven for 24 hours until the leaves became crisp. After drying, the leaves were ground by a manual grinder, to a constant size of 150µm and the resulting water hyacinth leaf powder was kept in a glass bottle ready for further experiments.

Preparation of biosorbate

The copper stock solution (1000mg/L) was prepared using analytical grades of $\text{Cu}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$. The test solutions were prepared by dilution to the desired concentrations i.e 50 – 400 mg/L of copper solution. The pH of the solution was adjusted using a 0.1M HCl and NaOH solutions.

Biosorption Process

The biosorption study was carried out by adopting a column reactor system. The column experiment was performed in a packed bed with inner diameter of 30mm and length of 500mm containing 1 g of water hyacinth leaves biomass. The various parameters are introduced into the column at 298 K and the supernatant metal ion collected was analyzed using Atomic Absorption Spectrophotometer (AAS). The amount of metal ion biosorbed per gram of the biomass q_e was calculated using the equation below:

$$q_e = \frac{C_i - C_e}{M} \times V$$

Where q_e is the amount of metal ion biosorbed per gram of the biomass in mg/g, C_i is the initial concentration of the metal ion in mg/L, C_e is the equilibrium concentration of the metal ion in mg/L, M is the mass of the biomass in grams and V is the volume of the metal ion in liters. The experiment was performed in triplicate and the mean value taken for each parameter.

Effect of contact time

The effect of contact time on the removal of copper with water hyacinth leaf biomass was investigated at different time intervals, ranging from 10 – 60 minutes at 298K. In each case, 50ml of the Cu (II) ion solution with concentration equal to 50mg/L and a corresponding mass of 1g of the adsorbent was used. The aqueous solution containing 50 mg/L Cu (II) ion was pumped through the column at a constant flow rate (15ml/min) continuously.

At the end of each time interval, the sample was collected from the outlet of the column and analyzed for Cu (II) ion using Atomic Absorption spectrophotometer.

Effect of pH

The effect of pH on the amount of Cu (II) ion biosorbed by water hyacinth leaves biomass was investigated by varying pH in the range of 2 – 12 at 298K. In each case, 50 ml of the Cu (II) ion with concentration equal to 50 mg/L and a corresponding mass of 1g of the adsorbent was used. The aqueous solution containing 50mg/L Cu (II) ion was pumped through the column at a constant flow rate (15ml/min) continuously.

At the end of 1 hour, the sample was collected from the outlet of the column and analyzed for Cu (II) ion using Atomic Absorption spectrophotometer.

The effect of initial concentration

The effect of the concentration of Cu (II) ion was investigated by adding 50 ml solution of varying concentrations of 50 – 400 mg/L with 1g of water hyacinth leaves biomass at 298K. The aqueous solution containing different Cu (II) ion concentrations was pumped through the column at a constant flow rate (15ml/min) continuously. At the end 1 hour, the sample was collected from the outlet of the column and analyzed for Cu (II) ion using Atomic Absorption spectrophotometer.

RESULTS AND DISCUSSION

Effect of metal ion concentration Cu (II) biosorption

The initial metal ion concentration plays an important role towards the performance of any biosorption process. As shown in Figure 1, the metal uptake by water hyacinth biomass increased as the initial metal ion concentration increased from 50 – 300 mg/L, where the maximum value of metal uptake was observed to be 14.90 mg/g. This observation was also in line with the research performed by two other researchers (King *et al.*, 2008; Gupta *et al.*, 1997.) According to Dang *et al.*, (2008), this result is expected as the initial metal ion concentration functions as the driving force to overcome mass transfer resistances between the aqueous and solid phases. In addition, the increase in the initial metal ion concentration also increased the number of collisions between the metal ion and the biomass hence, increasing Cu (II) ion uptake. Above this concentration, the biosorption process begins to decrease owing to the precipitation of Cu (II) hydroxide specie.

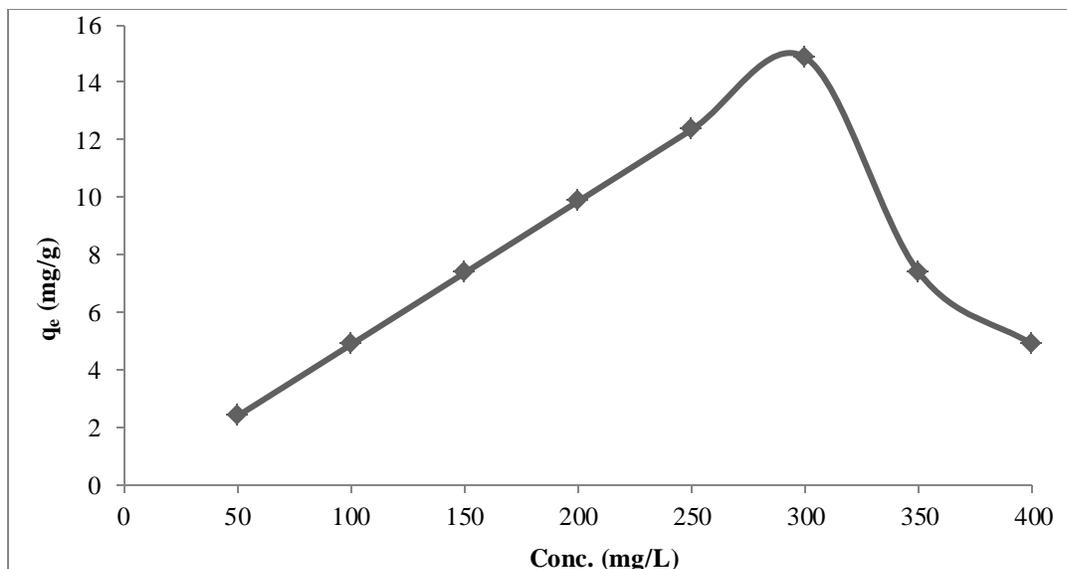


Figure 1: Effect of conc. on removal of Cu (II) ion using water hyacinth biomass

Effect of contact time on Cu (II) ion biosorption

The effect of contact time is presented in Figure 2. It was observed that a triphasic kinetic behavior revealed a rapid initial biosorption in the first 10 min, followed by a longer period of much slower sorption until about 30 mins when equilibrium was reached, after which there was no significance increase in Cu (II) ion uptake. Initially Cu (II) ion uptake was rapid because there are plenty of readily available sites for biosorption to occur. Subsequently, biosorption increased in the second phase but with a much slower rate until 30 mins when equilibrium was reached. Recent researches have shown that biosorption equilibrium is dependent on the type of biomass. Rengaraj *et al.*, (2002) and Alinnor and Nwachukwu, (2011) reported equilibrium time of 2 hours for the adsorption of phenol onto palm seed coat activated carbon and sorption analysis of nitrophenol onto fly ash.

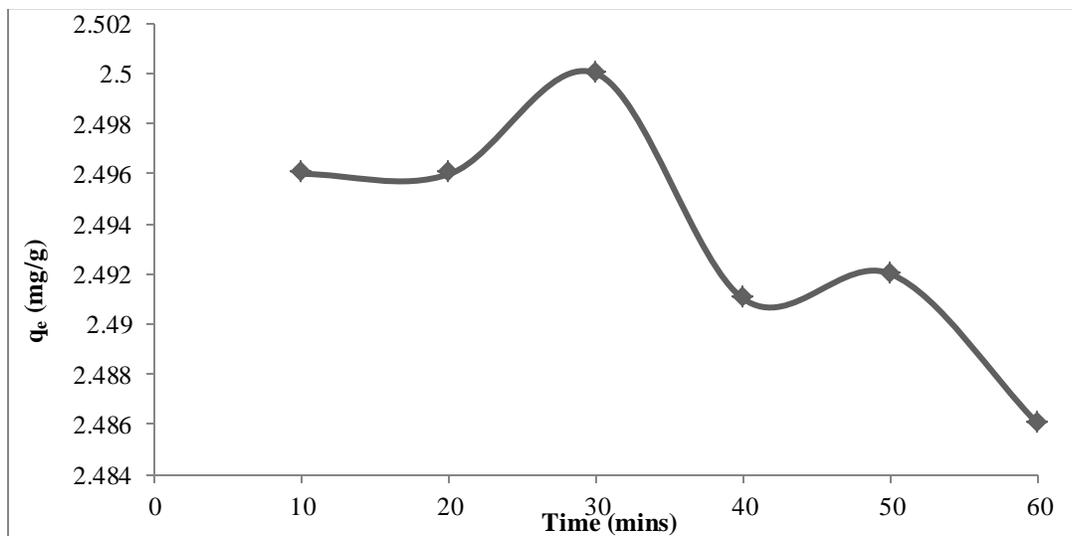


Figure 2: Effect of time on removal of Cu (II) ion using water hyacinth biomass

Effect of pH on Cu (II) biosorption

The pH of the biosorbate solution is considered one of the most important factors affecting the biosorption process. This factor is capable of influencing not only the binding site dissociation state, but also the solution chemistry of the target metal ions (Mack *et al.*, 2007). This behavior is represented in Figure 3. At lower pH, the competition of Cu (II) ion with H⁺ ions on the biomass surface lowers the uptake of Cu (II) ion (Al Subu *et al.*, 2001).

However, as the pH of the solution increases, the negatively charged biomass surface increased the electrostatic attraction with the Cu (II) ion thereby, leading to an increase in the uptake of Cu (II) ions. However, further increase in the pH resulted in the precipitation of Cu (II) ion to Cu (II) hydroxide specie (Wang, 1995).

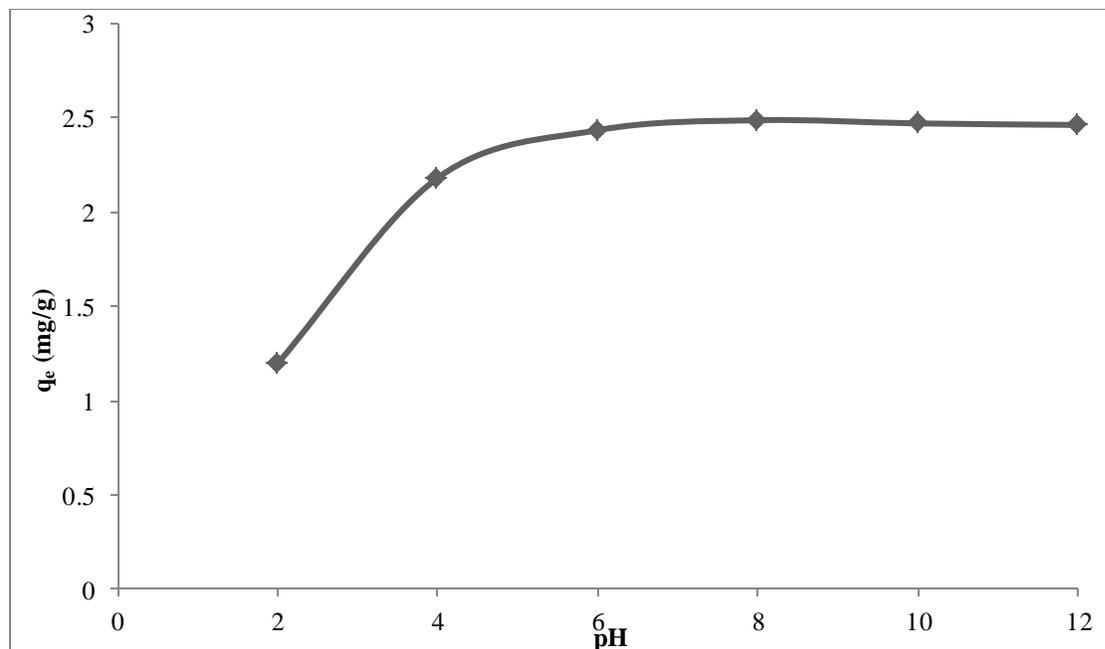


Figure 3: Effect of pH on removal of Cu (II) ion using water hyacinth biomass

Biosorption Isotherms

The Freundlich and Langmuir models were used to describe the relationship between the amount of Cu (II) ion and its equilibrium concentrations and the plots are represented in Figures 4 and 5. Langmuir isotherm constants were determined from a plot of C_e/q_e against C_e while that of Freundlich isotherm constants were determined from the plot of $\ln q_e$ against $\ln C_e$ as shown in Table 1. The isotherm correlation coefficient (R^2) of Langmuir and Freundlich model equations for the biosorption of Cu (II) ion using water hyacinth biomass was 0.8363 and 0.1994 respectively. The results obtained showed that Langmuir biosorption model was the best fit for the biosorption of Cu (II) ion using water hyacinth biomass indicating a physical biosorption.

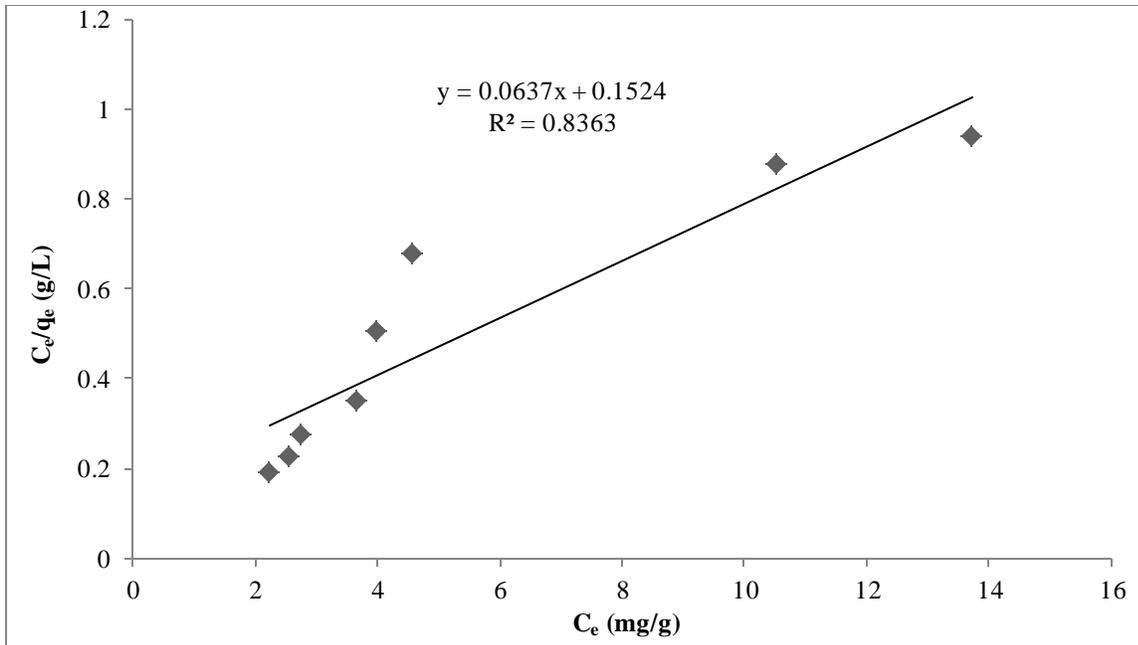


Figure 4: Langmuir plot for Cu (II) removal using water hyacinth biomass at 298K

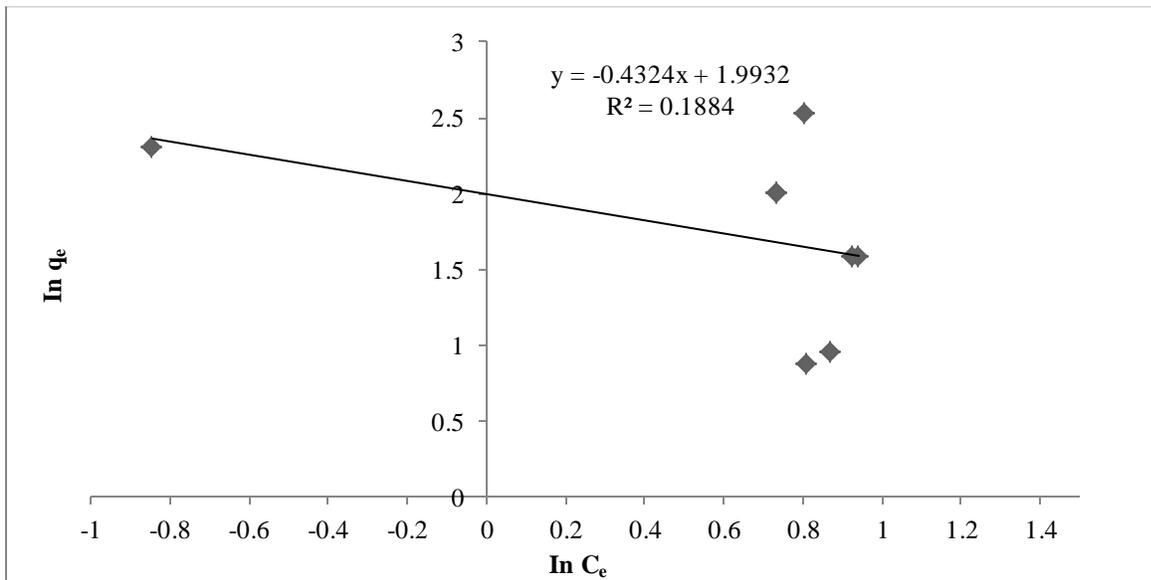


Figure 5: Freundlich plot for Cu (II) removal using water hyacinth biomass at 298K

Table 1: Langmuir and Freundlich parameters for Cu (II) ion removal at 298 K

Adsorption Models	K_L	K_F	Q_{max} (mg/g)	$\frac{1}{n}$	R^2
Langmuir	0.41		15.87		0.84
Freundlich		0.90		- 0.43	0.19

CONCLUSION

The results obtained for the removal of Cu (II) ion from aqueous solution using water hyacinth biomass revealed that the biosorption process was dependent on the pH of the aqueous solution, contact time and concentration of Cu (II) ion in the solution. The result indicated that the biosorption of Cu (II) ion decreased with increasing pH and the optimum contact time for equilibrium was 30 mins. The equilibrium data fitted well with Langmuir biosorption isotherm model with a linear correlation coefficient (R^2) of 0.8363, indicating a monolayer and physical type of adsorption. Therefore, water hyacinth biomass is a good, efficient, effective and alternative biosorbent for the removal of metal ions Cu (II) ion contaminants in water bodies.

RECOMMENDATIONS

The use of the water hyacinth plant for wastewater treatment is considered a simple technology that does not require costly machines or equipment, a large labor force or complex maintenance processes. It requires only large areas of land and a hot climate. In view of renewed interest and utilization of the unconventional water resources, including wastewater, and the desire for reduced environmental contamination at surface water sources, more studies on how water hyacinth can be used on a large scale to remediate wastewater should be conducted, because this sorption study was done in the laboratory using an aqueous solution and not practically with a wastewater that has been contaminated by copper.

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