Investigation of Heavy Metals Binding to *Jatropha Curcas* Husk

Adelaja O. A*, Okoronkwo A.E., Abass L.T

Department of Chemistry, Federal University of Technology, P.M.B 704 Akure, Nigeria.
seunmt@gmail.com

Abstract: Seed coat of *Jatropha curcas* was investigated for the removal of some selected metals from aqueous solutions. The selected metal ions are Cu, Ni and Cr. In this work, impact of pH of solution and sorption time on sorption capacity was investigated. At a pH of 5.0, 6.0 and 5.0 relatively to sorption time of 120mins, 60mins and 120mins respectively, 88.88%, 99.78% and 97.81% of Ni, Cu, and Cr were removed accordingly. Adsorption data analyzed using Langmuir and Freundlich models shows that Cu and Cr however followed Langmuir isotherms and not Freundlich while Ni adsorption conforms to both Langmuir and Freundlich models. This study shows that prepared biomass of *Jatropha curcas* husk can be used as an adsorbent for removal of Cu, Ni and Cr from wastewater or any industrial effluent.

1. Introduction

The primary source of heavy metal contamination has resulted from industrial activities such as energy and fuel production, mining and smelting of metaliferous ores and post production use that contains wastes (Sarwoko and Surahmaida, 2008).Due to increased industrial activities, an alarming amount of toxic heavy metal has been released into the environment endangering natural ecosystem and public human health (Gardea –Torresday *et al*, 1996). Usually, the most common heavy metal contaminants according to the World Health Organization (WHO) are Cadmium, Chromium, Cobalt, Copper, Lead, Mercury, Nickel and Zinc. Because of their adverse effects on natural ecosystem, their removal has become of major concern (Okoronkwo and Olasehnde, 2007). Hexavalent chromium is widely used in many industrial processes such as electroplating, wood preservation, etc. Commercially available forms of hexavalent chromium (Cr(VI)) are potassium chromate and potassium dichromate. The chromium manufacturing industry produces a large quantity of solid and liquid waste containing hexavalent chromium. The treatment of these wastes is essential before discharging them to the environment. Cr(VI) compounds are highly water soluble, toxic and carcinogenic in mammals. In contrast, trivalent chromium is considered to be non-toxic as it precipitates at pH higher than 5.5 with the formation of insoluble oxides and hydroxides in soil and water systems (Chen and Hao, 1998; Jeyasingh and Philip, 2005). Copper is a very common substance in the environment and it long term exposure can cause irritation of the nose, mouth and eyes. High intake of copper can cause liver and kidney problems which could eventually lead to death. Copper does not breakdown in the environment and because of this it can accumulate in plants and animals. On copper-rich soil only limited numbers of plants has a chance of survivals because copper interrupt the activities of the soil as it negatively influence the activities of microorganism, earthworms and the decomposition of organic matter (Lenntech, 2011). Nickel is used majorly in the preparation of alloys. In human, Nickel uptake will boost when people eat large quantities of vegetable from polluted soil. High uptake of Nickel is associated with high chance of development of cancer associated with respiration system. It is essential to remove heavy metals from waste water, so that their disposal into water bodies does not cause toxicity to inhabiting body. The conventional methods of metal removals from waste water, such as precipitation, adsorption and ion exchange are expensive and may not work well at low concentration of metal ions (Ahluwalia and Goyal, 2005; Alpana *et al*, 2007). Many researchers have generated considerable interest to pursue better methods or techniques which could be cost effective to remove heavy metals from the environment of which great attention has been given to the use of both living and non- living biological materials for the remediation of toxic metals ions from industrial waste water, (Okoronkwo and Olasehinde, 2007; Volesky and May-Philips, 1995; Carvalho *et al.*, 1994). One of these technologies is bioremediation, which is the use of biological system (such as plants, bacteria, fungi, etc) in various applications of waste treatment and remediation of pollutants. Bioremediation can be engaged for specific contaminants or general approach, such as reduction of BOD and odour from organic rich sediment (Chang *et*

al., 2002). The problem existing with bioremediation and bioaccumulation of toxic metals is that the metals valence or oxidation state may be biologically converted, how it be, the metal is still present and poses an environmental threat. The processes of bioremediation rely on microorganism which precipitates or solubilizes the metal ions (Gardea Torresday *et al*.1996).

An innovative technology that is gaining momentum in the environment field is phytoremediation. P hytoremediation is the use of plant to remove toxic contamination from the environment (Okoronkwo and Olasehinde, 2007) has shown that potential of *Tithonia diversifolia* for the removal of lead from contaminated water. Mueller *et al* (1995) also have shown the potential use of *Datura innoxia* and *Lycopersicon peruvianum* to biotransform TNT waste. Also heavy metals accumulates on plants been realized in the process termed **phytoextraction** which help to remove the heavy metals from the soil Sarwoko and Surahmaida, 2008 reported the use of *Jatropha curcas* L. for phytoremediation of lead and cadmium from polluted soil.

Jatropha curcas which is also known as physic plant is found growing on uncultivated land in most part of Africa and could be used as *hedge* plant .The plant is cherished for its medicinal value and the cake can be used as livestock feed if properly processed. Jatropha is resistant to drought and pest and produces seeds containing 27-40% of oil (Achten *et al*., 2007) the plant oil is widely use for Biofuel (biodiesel) production.

Hence this study aimed at assessment of the prepared husk of *Jatropha curcas* plant in the removal of Copper, Chromium and Nickel from aqueous solution.

2. Materials and method
2.1 Sampling and biomass preparation
Jatropha Curcas fruits were collected from roadside along Akure-owo expressway in April 2007. The fruits were harvested from the plants stems .The seed were removed from the fruits and the nuts were remove and handpicked to remove impurities. The residue (nuts) is then oven dried at 90-95% and then blended using grain mill blender to acquire uniform sample size. Ten grams of *Jatropha Curcas* biomass was washed twice with 0.1m HCL by vortexing and with deionized water to remove any debris or biomolecules that might possibly interact with the metal ions. After each washing, samples were centrifuged at 760rpm for 15mins to obtain pellets (Gradea-Torrsday *et al*., 1998 Okoronkwo and Olasehinde, 2007). The washed biomass was dried and weighed to account for loss.

2.2 pH profile study

Two fifty milligrams of the washed biomass were carefully weighed separately into nine (9) beakers. Each portion of the biomass was suspended in deionized water to obtain a concentration of 5mg of biomass per ml of solute (i.e. 50mg in 1000ml of deionized water) and stirred to form a homogenous mixture. Suspension of the first beaker is designed for pH values 1 – 4 separated by 1 unit. Suspension of the second beaker is for pH 1 – 9 and the solutions are equilibrated for 10 mins as described by Okoronkwo and Olasehinde (2007). Two aliquots of 2ml were transferred from the suspensions to clean tubes each time the pH value was adjusted. Nitric acid (HNO_3) and Sodium hydroxide (NaOH) solutions (both of 0.1N) were used for the pH adjustment.

The suspension in each test tube was centrifuged for 10 minutes at 150rpm and the supernatant was discarded. Already prepared 0.1M of the metal solutions with pH values ranging from 1 – 9 were separated into different containers corresponding to each pH level. The pH for each solution was adjusted. 2ml aliquot was transferred from each solution to a test tube containing the biomass and corresponding to its pH level. After an hour, the test tubes were centrifuged for 15 minutes at 760rpm (Okoronkwo and Olasehinde, 2007), and the supernatant was transferred to clean sample tubes for metal analysis.

2.3 Time dependency
Fifty ml of solution containing a concentration of 5mg of biomass per ml of suspension was prepared and its pH was adjusted to 6.0 for Cu and 5.0 for both Cr and Ni adsorption with NaOH. The solutions were centrifuged at760rpm for 15mins and the supernatant was discarded. Re-suspension of the biomass pellet under continuous stirring by rocking took place with 50ml of 0.1mM metal solution. Two 2ml aliquot were taken from the stirred suspension and transferred to clean test tubes at time intervals of 5, 10, 15, 30, 60, 90 and 120 mins for the three metal sample solutions. The maximum time frame used in this experiment is 120 mins for the three metals of interest. The test tube samples were centrifuged and the supernatant were transferred to clean sample tubes for metal content analysis.

2.4 Metal analysis
Perkin Elmer model 3110 Atomic absorption spectrometer with deuterium background subtracted was used for the metal ions analysis. Modified methods used for analysis were adopted from the Perkin Elmer model 3110 manual. Analytical data resulting from the AAS analysis was computed statistically prior to interpretation of the data.

3. RESULT AND DISCUSSION

The sorption of solution from aqueous solution plays a significant role in water control .it is therefore important to know and be able to predict the adsorption capacity of various biomass in other to know how much to give in term of various parameter to achieve the best of adsorption for various waste water treatment.

3.1 Sorption kinetics

To determine an appropriate contact time between *Jatropha curcas* biomass and the three metal ion of interest which are Cr, Cu and Ni .The adsorption capacity as a function of time and pH, shows that sorption took place very rapidly for the three metals and in the first 5mins and therefore continued at a slower rate until equilibrium was reached in a contact time of 60mins for Cu and 120mins for both Cr and Ni. Fig.1 shows various adsorptions of *Jatropha curcas* to the metals of interest. Cu, with initial concentration of 6.354ppm and a pH of 6.0 from this Fig.1, it shows that the adsorption increases until 6.34ppm of initial concentration has been removed which amounted to 99.78% of the initial concentration has been removed which was at a sorption time of 60mins and there about at about 90mins sorption time reduced to 6.22ppm. Niveta J. *et al* (2008) found that *Jatropha curcas* seed coat was able to remove 82-89% of Cu (II) from solution containing a copper concentration of (20-50%) at sorption equilibrium of 80mins, and most copper was adsorbed between pH of 4-5 and thereafter decreased drastically. In this study, the higher percentage of Cu (II) removal could be as a result of modification of biomass with 0.1 M NaOH. As reported by Low *et al* (2002), treatment of spent grain with NaOH greatly enhanced Pb and Cd sorption. Also Okoronkwo and Olasehinde (2007) reported that treatment of *Tithonia diversifolia* with NaOH also increases its sorption capacity compared to the unmodified biomass. The Fig1 shows that, for Cr, after a sorption time of 5mins 96.6% of the initial concentration has been adsorbed, and increase thereafter to 97.8% at equilibrium time of 120mins. The adsorption Ni to the biomass at a pH of 5.0, from the graph, it shows that 63% of Nickel has been adsorbed from the solution after a sorption time of 5mins and thereafter it increased to the maximum at the equilibrium at the sorption time of 120mins, where 88.76% of Ni was adsorbed. Namasivayam *et al* (2007) reported that *Jatropha curcas* biomass at a pH of 5.0 and a contact time of 180mins, adsorbed 97.0% of Ni(II). This was as a result of increased sorption time.

3.2 pH Profile study

It is well known fact that pH of the medium affects the solubility of the metal ions and the concentration of the counter ions on the functional group of the biomass (Gardea-Torresdey *et al.,* 1998). pH is one of the most important environmental factors which influence not only site dissociation, but also the solution chemistry of heavy metals. It has been reported that adsorption increases as the pH of the solution increases (Yin *et al*, 1999). Fig 2 shows the effect of pH on the uptake of Cu, Cr and Ni by the *Jatropha curcas* biomass. From Fig 2, the uptake of Cr and Ni increases as the pH of the solution increases until a pH of 5 which was the optima pH for Cr and Ni adsorption and further increase in pH after 5.0 the adsorption decreases but it was not so for Cu which it's optimum pH was 6.0 for maximum adsorption and further increase in pH decreases the sorption capacity of the biomass.

3.3 Adsorption isotherm

Analysis of the isotherm data is important in order to develop an equation that accurately represents the results and which could be used for design purposes (Niveta Jain *et al*, 2008). This also gives information for the comparison of different biomaterials under different operational conditions (Okoronkwo and Olasehinde, 2007). The adsorption data obtained for chromium, copper and nickel, using *Jatropha curcas* biomass as adsorbent were analyzed using Freundlich and Langmuir equations.

The linear form of Langmuir's equation is written as:

$$C_e/q_e = C_e/a + 1/ab$$

where **a** (mg/g) is the maximum amount of metal ion per unit mass to form a complete monolayer on the surface and **b** is the equilibrium adsorption constant Plot of C_e/q_e versus C_e fitted with a linearised straight line with slope of **1/a**, and intercept is **1/(ab)** (Dahiya *et al.*, 2008). The adsorption data from chromium, copper and nickel were represented in Fig 3, 4, and 5. From these figures, it shows that the adsorption data of chromium, copper and nickel conforms to Langmuir isotherm.

Freundlich equation is given by:

$$q_e = K_f C_e^{1/n}$$

The linearization of the above equation gives:

$$Log\ q_e = Log\ K_f + 1/n\ Log\ C_e$$

where K_F and **1/n** are the Freundlich constants characteristics of the system, indicating the adsorption capacity and the adsorption intensity, respectively. Plot
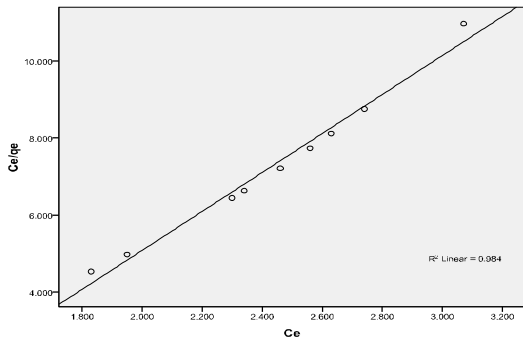
of log q_e versus log C_e, ought to be linear. The representation of the adsorptions in fig 6 and 7 show that only the adsorption data of nickel conforms to Freundlich isotherm.
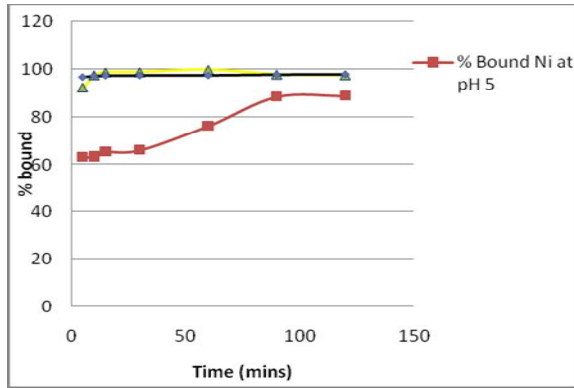
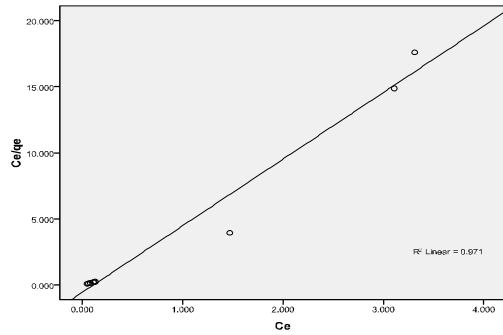**Fig.1 Percentage bound of Ni, Cu and Cr in Time dependency study**
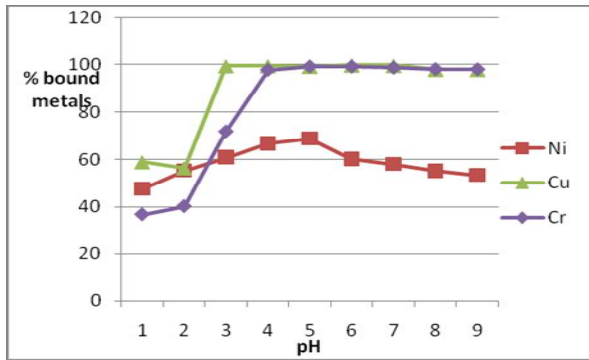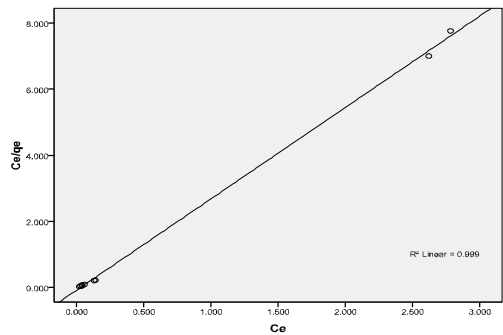

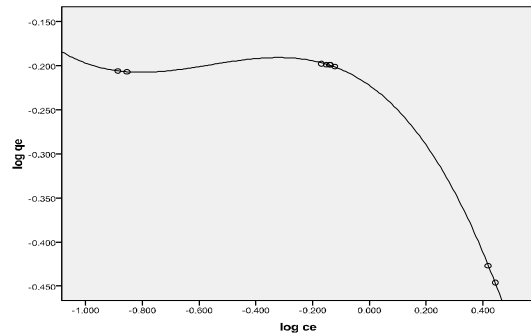**Fig.2 Effect of pH profile on metals binding on *Jatropha curcas* biomass nuts**

Fig.3 Langmuir Isotherm for the response of Cr absorbed by *Jatropha curcas* biomass

Fig.4 Langmuir Isotherm for the response of Cr absorbed by *Jatropha curcas* biomass
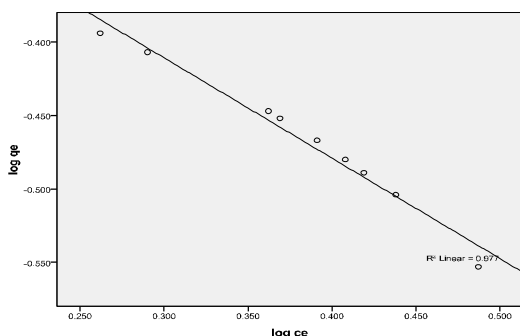

Fig.5 Langmuir Isotherm for the response of Cu absorbed by *Jatropha curcas* biomass

Fig.6 Freundlich Isotherm for the response of Cu absorbed by *Jatropha curcas* biomass

Statistical data shown in Fig. 9,10 and 11(see supplementary material) shows that the adsorption pattern of Cu vs Cr   using prepared biomass of *Jatropha curcas* at varying pH of 1-9 which gives R^2 values of 0.879 while that of Ni vs Cr and Cu vs Ni gives 0.325 and 0.365 respectively.The results from these statistical analysis indicates that there is a strong correlation associated with the sorption capacities of both Cu and Cr ($R^2 \approx$ 0.88) with increase in pH suggesting similar behavioural pattern in their sorption

4

mechanism. Similar observation was also reported by Singh *et al*(2007) where Pb and Cu exhibit relatively high sorption capacity with   increasing pH values Further studies could focus on understanding clearly the reasons for this strong relationship observed. This will enable us make further recommendation for the use of this biomass in effective treatment of wasterwater contaminated with both Cr and Cu.This suggestion   agrees   with   Dahiya   et   al   (2008) findings.This also implies that the biomass is an homogenous material for the sorption studies for chromium and copper (Dahiya *et al*.,2008).

Fig.7 Freundlich Isotherm for the response of Ni absorbed by *Jatropha curcas* biomass

4. Conclusion

The pretreated biomass of *Jatropha curcas* husk has shown effectiveness towards the adsorption of heavy metals from solution. This husk of *Jatropha curcas* is disposed as waste in biodiesel setup, and the biomass preparation can be encourage to commercial standard to replace the commercial carbon used for the removal of heavy metals from waste water. This is because it cost is lower compared to the commercial carbon, and also reduce the reliance on imported carbon and encourage the exploitation of biomass for sustainable economic development.

Correspondence to: Adelaja O. A
Department of Chemistry,
School of sciences
Federal University of Technology,P.M.B
704,Akure Ondo state,Nigeria.
Tel: +2348033942272
Email: seunmt@gmail.com

REFERENCES

Achten W.MJ, Mathijs E, Verchot L., Sjngh VP, Aerts R and Muys B. Biofuel, Bioproduct and Biorefining *The jatropha archives*. 2007;1(4):283-291.

Alihuwalia S.S and Goyal D. Microbial and plant derived biomass for removal of heavy metals from waste water. *Bioresource, technology. J.biotech.* 2005;12.006.

Carvalho R.P, K.H Chung, and B. Volesky. Effect of leached alginite and metal biosorption . *biotechnol. Let.* 1994;16:875-880.

Chang, B.V., L.C. Shiung, and S.Y. Yuan. Anaerobic biodegradation of polycyclic aromatic hydrocarbon in soil. *Chemosphere* 2002;48:717-724.

Dahiya   Sudhir,   R.M.   Tripathi,   A.G.   Hegde. Biosorption of lead and copper from aqueous solutions by pre-treated crab and arca shell biomass. *Bioresource Technology* 2008;99:179–187.

Gardea-Torresdey J.L., K.J. Tiemann, A. Hernandex, O. Rodriguez, and S. Sias. Enhanced metal binding capacity of NaOH treated Larrea-Tridentata leaf. *Proceeding of the conference on Hazardous Waste Research* 1998; 101-110

Gardea-Torresdey, J.L., Tiemann, K.J., Gonzalez, J.H.,Henning, J. A.,Townsend, M. S. Calcium and Magnesium Interference Studies for the Binding of Heavy Metal Ions in Solution by Medicago Sativa. Proceedings of the Eleventh Annual EPA Conf. on Hazardous   Waste   Research,(HSRC/WERC   Joint Conference on the Environment), Edited by L.R. Erickson,   D.L.   Tillison,   S.C.   Grant,   and   J.P. McDonald, Albuquerque, NM, 1996; 78-88.

Husar H. Adsorption of nickel (II) from aqueous solution onto activated carbon prepared from the almond husk. *J. Hazard mater*, 2003;97:49-57.

Chen   J.M.,   O.J.   Hao.   Microbial   chromium   (VI) reduction*,   Crit.   Rev.   Environ.   Sci.   Technol.* 1998;28(3):219–251.

Jeyasingh J, Ligy Philip,. Bioremediation of chromium contaminated   soil: optimization   of   operating parameters under laboratory conditions. *Journal of Hazardous Materials* 2005;**B118:**113–120.

Low K.S and C. S Lee-Lee. Sorption of cadmium and lead from aqueous solution by spent grain grain. *Process Biochem*. 2000;36:59-64.

Muller W.F., G.W. Bedell, S. Shojaee, and P.J. Jackson. Bioremediation of TNT waste by higher plants in L.E. Erickson, D.L. Tillison, S.C. Grant and J.P Macdonald (Eds.) *proceedings of 10th annual conference on Hazardous waste research,* Kansas state univ., Manhattan, KS. 1995; P.222.

Namasivayam C., D. Sangeetha and R. Gunasekaran. Removal of anions, Heavy Metals, Organics and Dyes from Water By Adsorption onto a new Activated Carbon From Jatropha Husk, an Agro-Industrial Solid

Waste. Trans IChemE, Part B, *Process Safety and Environmental Protection,* 2007;85(B2):181–184.

Nanda Kumar P. B. A., V. Dushenkov, H. Motto and I. Raskin. Phytoremediation : the use of plants to remove heavy metals from soils. *Environ. Sci. Technol.* 1995;29:1232-1238.

Niveta Jain, HC. Joshi, SC. Dutta, S. Kumar and Pathak H. Biosorption of Copper from waste using Jatropha seed coat, *J. Sci. Ind. Res,* 2008;67:154-160.

Okoronkwo A.E and Olasehinde E.F. Investigation of lead binding to Tithonia diversifolia. *Journal of applied sciences* 2007*;*7(12):1589-1595.

Sarwoke Mangkoedihardjo and Surahmaida. Jatropha curcas L. for the phytoremediation of lead and cadmium polluted soil. *World applied science journal* 2008;4(4):519-522.

Singh Alpana, Dhananjay Kumar, J.P Garr. Copper II and Lead II sorption from aqueous solution by non-living Spirogyra neglecta. *Bioresource technology* 2007;98:3622-3629.

Veglio F, F. beolchini and A. Gasbarro. Biosorption of toxic Metals: an equilibrium study using free cells of arthrobacter Sp. *Process Biochem.* 1997;32:99-105.

Volesky B. and H.A may-philips. Biosorptin of heavy metals by saccharomyces cervisae. *Applied microbiol. Biotechnology* 1995;42:797-806.

Lenntech 2011. Leuntech Solution [Online] Available at: (http://www.Lenntech.com/elements/ Ni, Cr). Accessed on August 10, 2011.

Yin P.H, Yu Q.M, and Ling Z. Biosorption removal of Cadmium from aqueous solution by using pretreated fungal biomass cultured from starch waste water. *Water Res.* 1999;33:1960-1963.

1/9/2012