

Full Length Research Paper

Biosorptive removal of cobalt (II) ions from aqueous solution by *Amaranthus hybridus* L. stalk wastes

¹Egila, J. N., ²Dauda, B. E. N. and Jimoh, T.^{2*}

¹Department of Chemistry, University of Jos, Plateau State, Nigeria.

²Department of Chemistry, Federal University of Technology, Minna, Nigeria.

Accepted 1 November, 2010

The objective of this study was to investigate the possibility of using *Amaranthus hybridus* L. stalk as an alternative to high cost commercial adsorbent materials for the removal of Co (II) from aqueous solution. The experiment was carried out by batch method at 33 °C. The influence of pH, contact time and initial metal ion concentration were evaluated. It was observed that pH had marked effect on the Co (II) uptake. The optimum contact time between the adsorbent and the adsorbate was found to be 90 min. Maximum adsorption was obtained at pH 5. Freundlich models were used to correlate equilibrium data on sorption of Co (II) ion at 33 °C and pH 5, and different coefficients were calculated. The data generated, fitted well with Freundlich adsorption model. The biomass was successfully used for removal of cobalt (II) ion from synthetic aqueous solution and the technique appears industrially applicable and viable.

Key words: Biosorption, cobalt, aqueous solution, *Amaranthus hybridus*.

INTRODUCTION

Heavy metal pollution has become a serious threat today and of great environmental concern as they are non-biodegradable and thus persistent (Upendra, 2006). Treatment of polluted industrial wastewater remains a topic of global concern since wastewater collected from municipalities, communities and industries must ultimately be returned to receiving waters or to the land. Moreover, contamination of ground water is another major concern in the management of water resources. Contaminants such as pesticides (El-Geundi et al., 2005), heavy metals (Adesola et al., 2006) and organic substances (Khouider et al., 2004) arise from wide variety of processes occurring in the soil including diffusion, mechanical dispersion, chemical reaction, decay, adsorption and biodegradation. The presence of heavy metal has a potentially damaging effect on human physiology and other biological systems when the tolerance levels are exceeded. They remain a serious public health problem to human health (Ko et al., 2000; Koller et al., 2004). With increasing environmental awareness and legal constraints imposed on discharge of

effluents, the need for cost-effective alternative technologies is essential for removal of heavy metals from industrial wastewater. At present, several methods have been developed to treat industrial wastewater. These processes were found to be ineffective especially when the heavy metal ions in the contaminated media are high, that is, in order of 1 to 100 mg/l (Ahlwalia and Goyal, 2005). Operational problems and the high cost of treatment necessitate the search for new methods. Biological methods such as biosorption/bioaccumulation may provide an attractive alternative to physico-chemical methods for the removal of heavy metal ions. The adsorption process considered in this work is one of the most efficient methods used to remove heavy metals from effluent by using agricultural waste and agricultural by-products (Hashem et al., 2007). This process has an edge over the other methods due to its sludge free clean operation and complete removal of toxic metals even from dilute solution (Ahalya et al., 2003). Recent studies have shown that heavy metals can be removed using plant materials such as empty palm oil fruit bunch (Rafeah et al., 2009), sour sop seeds (Obloh and Aluyor, 2008), modified cassava fiber (Okuo and Oviawe, 2007), *Bombax malabaricum* fruit shell (Somasekhara et al., 2007), cassava fibre (Egila and Okorie, 2002), coconut shell

*Corresponding author. E-mail: teejayola01@yahoo.com. Tel: +2348057344464.

(Gimba et al., 2001), coconut husks, peatmoss, exhausted coffee (Dakiky et al., 2002), waste tea (Ahluwalia and Goyal, 2005), walnut skin, coconut fibre, cork biomass (Chubar et al., 2003), seeds of *Ocimum basilicum* (Melo and D'Souza, 2004), defatted rice bran, rice hulls, soybean hulls and cotton seed hulls (Teixeria et al., 2004). Wheat bran, hardwood (*Dalbergia sissoo*) sawdust, pea pod, cotton and mustard seed cakes are also proven as good biomass sources (Saeed et al., 2002). A range of other agricultural by-products have been used for metal removal including banana pith, tree fern and hop (*Humulus lupulus*) (Gardea-Torresdey et al., 2002).

In this study, cobalt has been chosen because of its environmental importance as related to its toxicity. Exposure to cobalt may cause weight loss, dermatitis, bleeding, vomiting, sterility, hair loss, coma, respiratory hypersensitivity and even death (Park et al., 2000; Rafeah et al., 2009). Therefore, it is of great relevance to develop a new method for its removal from water, and this is the aim of the present work.

It is worthy of mentioning that the annual production of *A. hybridus* L. (African spinach), in Minna, is on the increase as it constitute one of the major vegetables consumed in Nigeria. Consequently, large quantities of its wastes are produced and may constitute environmental nuisance as a result of lack of proper disposal. Until the present work, these wastes have not been put into any important use and no information is available on metal removal by this agricultural by-product. In this study, the capabilities of *A. hybridus* L. wastes for cobalt ion adsorption were tested at several experimental conditions such as the pH, contact time and initial cobalt concentration. The equilibrium data is described by Freundlich adsorption isotherm.

MATERIALS AND METHODS

Sample collection

The African spinach (*A. hybridus*) stalk waste was obtained from different locations within Central market, Minna. Sampling was done at random from different retailers within this market area. A composite sample was made from where the representative samples were collected for these studies.

Preparation of aqueous solution

The aqueous solution containing cobalt was prepared from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$. A 1000 mg/dm^3 stock solution of the salts was prepared. Other concentrations (5, 10, 20, 30, 40 and 50 mg/dm^3) were obtained from this stock solution by serial dilution.

Sample pretreatment

The representative samples were deoiled by soaking in hot deionized water with detergent for 24 h. They were then rinsed in hot deionized water to remove all debris, after which they were air dried

for a period of one week. The dried samples were ground using blender and sieved through a 400 μ mesh screen. The fine powder retained on the 400 μm sieve was then used for the sorption studies. This was to allow for shorter diffusion path, thus allowing the adsorbate (*A. hybridus* L. stalk) to penetrate deeper into the effluent more quickly, resulting in a higher rate of adsorption.

Adsorbent preparation for sorption studies

The 5.00 g screened fine adsorbent was soaked in excess 0.3 mol/dm^3 HNO_3 for 24 h to remove any debris or soluble biomolecules that might interact with the metal ions during the sorption process. This constitutes the chemical activation of the samples. The adsorbent was then filtered through Whatman No.41 filter paper and rinsed with de-ionised water. The rinsed adsorbent was later air -dried for 12 h.

Sorption experiment

The experimental procedure described by Okieimen and Okieimen (2001) and Egila and Okorie (2002) were modified as follows: 0.5 g of the pretreated powdered sample was shaken with 100 cm^3 of cobalt (II) solution whose concentration was 5 mg/dm^3 . The pH of the aqueous solution was adjusted to a pH of 5 to prevent hydrolysis. The bottles were shaken at various time intervals of 30 to 180 min at room temperature in a reciprocating shaker at 300 rpm. At the end of each contact period, the mixture was filtered using Whatman filter paper No. 42 and the filtrate was stored in sample bottles in a refrigerator prior to analysis. The final concentration of the metal ion in the filtrate was determined by AAS. The experiments were carried out in triplicate and the results presented as mean values.

Batch mode adsorption study

The experiments were carried out in the batch mode for the measurement of adsorption capabilities at 33°C using different concentrations of 10, 20, 30, 40 and 50 mg/dm^3 of cobalt (II) solution. 100 cm^3 of various concentrations (10.0 to 50.0 mg/dm^3) of the metal ions were placed in 250 cm^3 conical flasks, and 0.5 g of the substrate was added to each. The corked conical flask was shaken in a reciprocating shaker at 300 rpm for constant metal ion-substrate contact period of 90 min at 33°C. The separation of the adsorbents and solutions was carried out by filtration with Whatman filter paper No. 42 and the filtrate stored in sample cans in a refrigerator prior to analysis. The residual metallic ion concentrations were also determined using an atomic absorption spectrophotometer (AAS). Blank solutions were also prepared for comparison.

Data analysis

Percentage removal of cobalt (II) ions from initial solution concentration was calculated from the following equation:

$$R_{em} = \frac{C_o - C_t}{C_o} \times 100\%$$

where C_o is the initial metal ion concentration (mg/l^{-1}) and C_t is the metal ion concentration at time t (mg/l^{-1}).

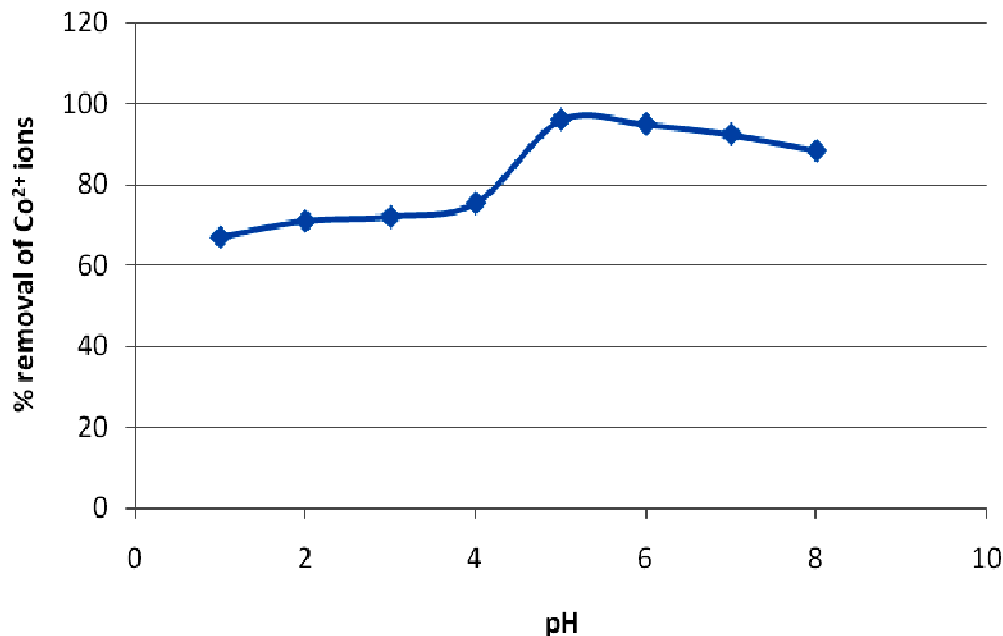


Figure 1. Effect of pH on the adsorption of cobalt (II).

Adsorption isotherm

The equilibrium adsorption isotherms data are important to develop an equation which accurately represents the results and will be useful for designing the biosorption reactors. The metal ion sorption kinetics on the adsorbent was analyzed using the Freundlich adsorption isotherm (Demirbas et al., 2004).

Freundlich adsorption isotherm

Adsorption data for wide range of adsorbate concentrations are most conveniently described by adsorption isotherms, such as the Freundlich isotherms or Langmuir isotherms (Hashem et al., 2007). The Freundlich equation was used as the model for adsorption in this study which is represented by the general formulae given below as equation:

$$\frac{x}{m} = K_f (C_e)^{1/n}$$

which can be linearized as:

$$\ln\left(\frac{x}{m}\right) = \ln K_f + \frac{1}{n} \ln C_e$$

where $\frac{x}{m}$ is the amount adsorbed per unit mass of adsorbent, C_e is the solution concentration at equilibrium, K and n are constants relating to adsorption capacity and intensity. This equation is only applicable to batch adsorber systems where sufficient time is provided to allow equilibrium between the pollutant in solution and the pollutant adsorbed on the media to occur. During the flow through the adsorbent, many of the pollutants are expected to come into contact with active surface sites and thus be retained on the surface of the adsorbing media.

RESULTS AND DISCUSSION

Influence of initial pH

Of all the experimental parameters affecting the rate of adsorption, the influence of initial pH were studied first. The percentage removal of cobalt from the aqueous solution is strongly affected by the pH of the solution as illustrated in Figure 1. The initial pH of aqueous solution was investigated over a range of 1 to 8. It was observed that with the increase in the pH of the solution, the percentage removal of cobalt (II) ions increased up to the pH 5 as shown in Figure 1. The minimum adsorption observed at low pH (pH 1 and 2) may be due to the fact that the higher mobility of H^+ ions present favoured the preferential adsorption of hydrogen ions compared to the metal ion (Ajmal et al., 2000). It would be plausible to suggest that at lower pH value, the surface of the adsorbent is surrounded by hydroxonium ions (H_3O^+), thereby preventing the metal ions from approaching the binding sites of the sorbent (Wong et al., 2003). This means that at higher H^+ concentration, the biosorbent surface becomes more positively charged such that the attraction between biomass and metal cation is reduced (Saeed et al., 2004). In contrast, as the pH increases, more negatively charged surface becomes available, thus facilitating greater metal ions removal. It is commonly agreed that the adsorption of metal cation increases with increasing pH as the metal ionic species become less stable in the solution (Unob et al., 2005). At pH 5, maximum percentage recoveries were obtained for the element in question. For the above reasons, the pH 5 was selected for the other experiment. However, the

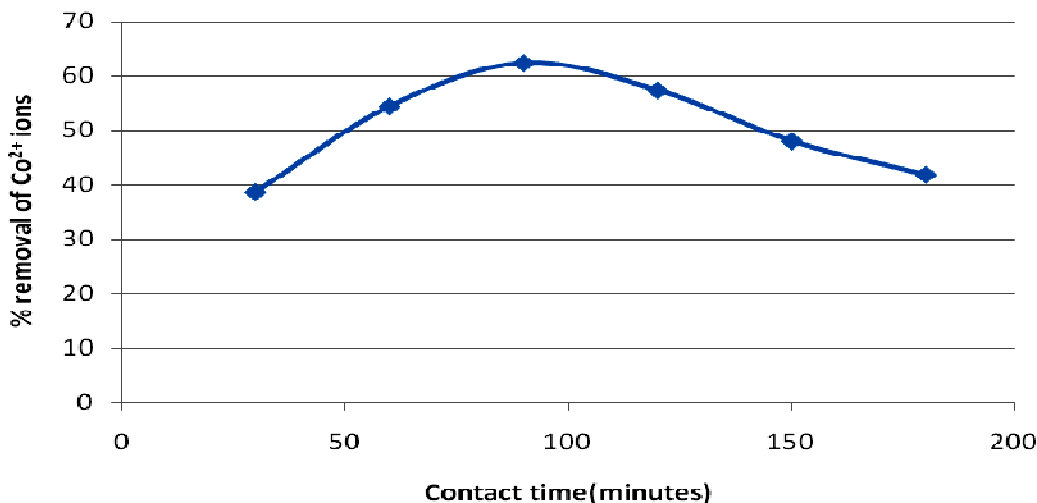


Figure 2. Effect of variation of contact time on the adsorption of Co²⁺ on *A. hybridus* L stalk at 33°C.

increase in the percentage recovery was not directly proportional to the substrates suggesting that other factors play a role in the adsorption and desorption mechanism. It is quite plausible that an initial high adsorption rate (possibly by ion exchange) followed by a chelation of the metal ions with the carboxyl group may have been the case. This pH 5 is in agreement with what was reported with *Elais guineensis* kernel waste by Tumin et al. (2008). The increase in percentage removal of metal ion due to increase in pH may be explained on the basis of a decrease in competition between proton (H⁺) and positively charged metal ion at the surface sites and also by decrease in positive charge near the surface resulting in a lower repulsion of the adsorbing metal ion.

At pH value above the range of 5 to 6, the percentage removal of Co²⁺ ion increased but at slower rate because of the competitive adsorption between hydrogen ion and the heavy metal cation. The continuation increases in the percentage uptake level of Co²⁺ ion with increasing the pH value is due to the decreases in the hydrogen ion concentration as the pH value decrease. The adsorption at near neutral pH value (pH = 7) could be attributed to the cellulose component of the substrates where site-binding adsorption might be occurring. This could also be due to the surface complexation phenomenon of functional groups present in the *A. hybridus* stalk. The removal of cobalt sometimes is probably due to the mixed effect of ion exchange and surface complexation on the surface of the wastes and the decrease in adsorption at pH greater than 7 is due to the formation of hydroxide (Mohsen, 2007).

When alkalinity increased from pH value of 7 to 8, there was a further decrease in the rate of adsorption by the substrate for Co²⁺ ions in the aqueous solution. This can be explained on the basis of weak interactive competition between the adsorbent and Co²⁺ ions which replace H⁺ bound to the adsorbent for forming part of the

surface functional groups such as -OH, -COOH, etc. A close relationship between the surface basis of the adsorbents and the anions is also evident. This is similar to other findings where the interaction between oxygen-free Lewis basic sites and the free electrons of the anions, as well as the electrostatic interactions between the anions and the protonated sites of the adsorbent are the main adsorption mechanism (Faria et al., 2004). The above results suggest that the *A. hybridus* stalk wastes can be used as a potential decontaminant for the removal of cobalt ions from aqueous solution.

Effect of contact time on removal of the cobalt (II) ion

Influence of contact time on Co²⁺ removal by the substrate is illustrated in Figure 2. The rate of metal uptake level was rapid within the first 90 min for Co(II) ion with a corresponding concentration of 63.5 mg/100cm³ after equilibrium had reached at 90 minutes, a decrease in the amount adsorbed was observed. This implied that the binding sites on the substrate were exhausted and further shaking resulted in desorption. This is not surprising because adsorption is not only diffusion controlled but this could be affected by the following processes: (i) diffusion of the solute from the solution to the film surrounding the particle; (ii) diffusion from the film to the particle surface (external diffusion); (iii) diffusion from the surface to the internal sites (surface diffusion or pore diffusion) and (iv) uptake which can involve several mechanisms: physicochemical sorption, ion exchange, precipitation or complexation (Igwe and Abia, 2005; Igwe et al., 2005). Therefore, in a mixture of the substrates and metal ion, the metal ion competes for the adsorption sites on the adsorbent. This competition could affect the diffusion properties of the metal ions, hence the adsorption capacity of the metal ions. Hence, equilibrium time is one

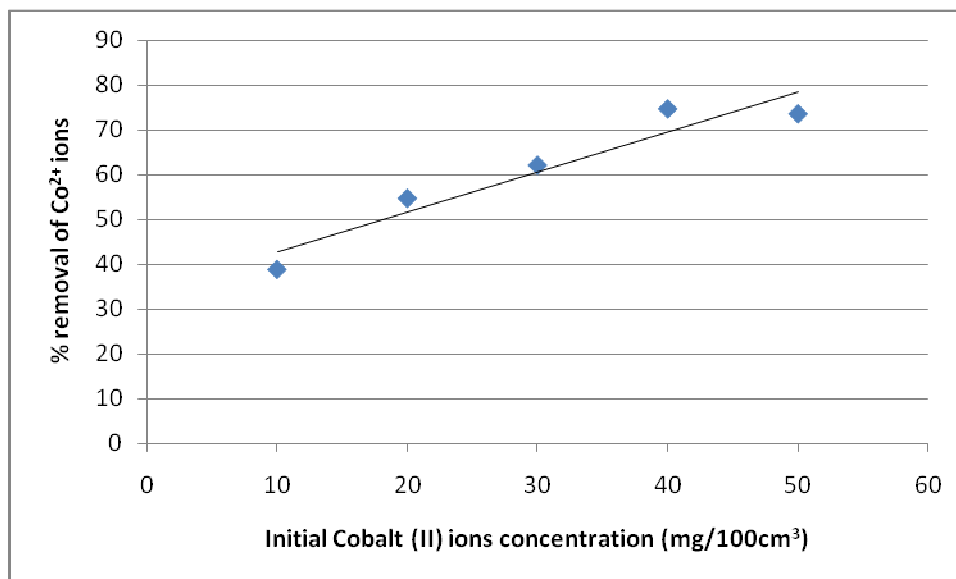


Figure 3. The effect of varying Co(II) ions concentration on the adsorption of *A. hybridus* L. stalk at 33°C for 90 min.

of the important parameter for an economical wastewater treatment system.

Effect of initial metal ion concentration

The variation in the amount of metal ion bound to the *A. hybridus* L stalk with increasing initial metal ion concentration is illustrated in Figure 3. The results showed that the amount of the metal ion bound by the cellulosic substrates depended on the metal ions type and the concentration of the metal ions. The percentage metal ions removal increased from 39.5 to 72.3% as the initial metal ions concentration increase from 10 to 40 mg/ml, for the substrate and later declined. The initial faster rate of removal of the metal ion could be due to the availability of the uncovered surface area of the adsorbents, since adsorption kinetics depends on the surface area of the adsorbent (Qadeer and Akhtar, 2005). These could also be explained in terms of the progressive increase in the electrostatic interaction between the metal ion and the adsorbent active sites, moreover, more adsorption sites were being covered as the metal ions concentration increased (Laraous et al., 2005; Gong et al., 2006). Besides, higher initial concentrations led to an increase in the affinity of the metal ion towards the active sites (Al-Asheh and Banat, 2001; Al-Asheh et al., 2003). The plausible reason for the decline in the percentage removal to 69.5% despite increase in the initial metal ions concentration to 50 mg/ml is due to the availability of smaller number of surface sites on the adsorbent for a relatively larger number of adsorbing species at higher concentrations (Khalid et al., 2000). Similar results were observed by Han et al., (2005) for the adsorption of

copper (II) and lead (II) on chaff. This finding is also in agreement with the study of Sharma (2006) who carried out an independent research on the Cd (II) removal from aqueous solution using shelled moringa (*Moringa oleifera* Lam.) seed powder.

Adsorption mechanism

The sorption data of the metal ion investigated on *A. hybridus* stalk substrate were plotted logarithmically as stated in Equation 3, where x is the mass of the adsorbate, m is the mass of the adsorbent, C is the residual concentration and Q_e is the amount of metal ions adsorbed per unit mass of adsorbent corresponding to complete monolayer coverage (Figure 4). The values of correlation coefficient R^2 indicate that the adsorption process conforms to the Freundlich isotherms (Salam and Adekola, 2005). The results also show that the R^2 value for the substrate is greater than 0.9 for Freundlich isotherm, so the adsorption was multi layered and physio-sorption type. The value of $1/n$ which is 0.71 is less than 1 and so indicates that Co (II) ion is favourably adsorbed by the *A. hybridus* L. stalk waste. A smaller value of $1/n$ indicates better adsorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent (Patil et al., 2006).

Conclusion

This study indicates a potential for the use of agricultural waste such as *A. hybridus* L. stalk in removing cobalt (II) ion from aqueous solution. The results obtained are

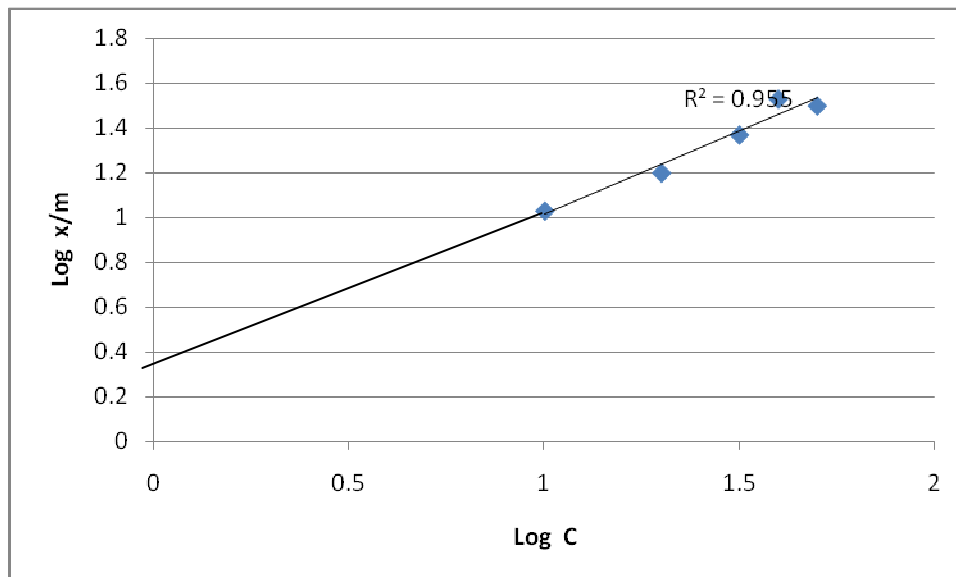


Figure 4. Freundlich adsorption isotherm. Plot of Log (x/m) against Log C for Co^{2+} ions, where x is the mass of the adsorbate, m is the mass of adsorbent and C is the residual concentration (for *A. hybridus* L. stalk).

therefore very encouraging for the industrial application of the technique. There is need to investigate other plants for use as adsorption agents with a view to improve our water quality and consequently address the issue of environmental pollution caused by heavy metals.

REFERENCES

- Adesola I, Babarinde NAO, Babalola J, Adebawale R (2006). Biosorption of lead ions from aqueous solution by maize leaf. 1(1): 023-026.
- Ahalya N, Ramachandra TV, Kanamadi RD (2003). Biosorption of heavy metals. Res. J. Chem. Environ. 7: 71-78.
- Ahluwalia SS, Goyal D (2005). Removal of Heavy Metals by Waste Tea Leaves from Aqueous Solution. Eng. Life Sci. 5: 158-162.
- Ajmal M, Rao RA, Ahmad K, Ahmad R (2000). Adsorption studies on Citrus reticulata (fruit peel of orange): removal and recovery of Ni (II) from electroplating wastewater. Hazardous Materials, 79: 117-131.
- Al-Asheh R, Banat Al-Omari Z, Duvnjak R (2003). Beneficial reuse of chicken feathers in removal of heavy metals from wastewater. Cleaner Prod. 11: 321-326.
- Al-Asheh S, Banat F (2001). Adsorption of Zn (II) and Cu (II) ions by the solid waste of the olive oil industry, Adsorp. Sci. Technol. 19: 117-129.
- Chubar N, Carvalho JR, Neiva CMJ (2003). Cork Biomass as biosorbent for Cu (II), Zn (II) and Ni (II). Colloids Surf. A: Physicochem. Eng. Asp. 230: 57-65.
- Demirbas E, Kobya M, Senturk E, Ozkan T (2004). Adsorption kinetics for the removal of Chromium (VI) from aqueous solutions on the activated carbons prepared from agricultural wastes. Water Res. 30(4): 533-539.
- Egila JN, Okorie EO (2002). Influence of pH on the Adsorption of trace metals on ecological and agricultural adsorbents. J. Chem. Soc. Nig. 27(II): 95-98.
- EI-Geundi MS, Farrag TE, EI-Ghany HM (2005). Adsorption equilibrium of a herbicide (Pendimethalin) onto natural clay, Adsorp. Sci. Technol. 23(6): 437-453.
- Faria PCC, Orfao JJM, Pereira MFR (2004). Adsorption of anionic and cationic dyes on activated carbons with different surface chemistries. Water Res. 38: 2043-2052.
- Gardea-Torresdey J, Hejazi M, Tiemann K, Parsons JG, Duarte-Gardea M, Henning J (2002). Use of hop (*Humulus lupulus*) agricultural by-products for the reduction of aqueous lead (II) environmental health hazards. J. Hazard Mater. 91: 95-112.
- Gimba CE, Olayemi JY, Ifijeh DOH, Kagbu JA (2001). Adsorption of dyes by powdered and granulated activated carbon from coconut shell. J. Chem. Soc. Nig. 26(1): 23-27.
- Gong R, Jin Y, Chen F, Chen J, Liu Z (2006). Enhanced malachite green removal from aqueous solution by citric acid modified rice straw. J. Hazard. Mater. 137: 865-870.
- Han R, Zhang J, Zou W, Xiao H, Shi J, Liu H (2005). Biosorption of copper (II) and lead (II) from aqueous solution by chaff in a fixed-bed column. J. Hazardous Mater. 133: 262-268.
- Hashem A, Akasha RA, Hussein DM (2007). Chemically modified Algae residues as a new adsorbent for Pb(II) ions from aqueous solution. Energy Edu. Sci. Technol. 19: 17-36.
- Igwe JC, Abia AA (2005). Sorption kinetics and intraparticulate diffusivities of Cd, Pb and Zn ions on maize cob. Afr. J. Biotechnol. 4(6): 509-512.
- Igwe JC, Ogunewe DN, Abia AA (2005). Competitive adsorption of Zn (II), Cd (II) and Pb (II) ions from aqueous and non- aqueous solution by maize cob and husk. Afr. J. Biotechnol. 4(10):1113-1116.
- Khalid N, Ahmad S, Toheed A, Ahmed J (2000). Potential of rice husks for antimony removal. Appl. Radiation Isotopes, 52: 31-38.
- Khouider A, Boufatit M, Hocine O (2004). Use of montmorillonite clays as adsorbent of hazardous pollutants, Desalination, 167: 141-145.
- Ko DCK, Porter JF, McKay G (2000). Optimized Correlation for the Fixed Bed Adsorption of Metal Ions on Bone Char. J. Chem. Eng. Sci. 55: 5819-5829.
- Koller K, Brown T, Spurgeon A, Levy L (2004). Recent development in low level exposure and intellectual impairment in children. Environ. Health Perspect. 112(9): 987-994.
- Laraous S, Meniai AH, Bencheikh Lehocine M (2005). Experimental study of the removal of copper from aqueous solutions by adsorption using sawdust. Desalination, 185: 483-490.
- Melo M, D'Souza SF (2004). Removal of chromium by mucilaginous seeds of *Ocimum Basilicu*. Bioresour. Technol. 92: 151-155.
- Mohsen AH (2007). Adsorption of lead ions from aqueous solution by okra wastes. Int. J. Phys. Sci. 2(7): 178-184.
- Oboh OI, Aluyor EO (2008). The Removal of Heavy metal ions from

- aqueous solution using sour sop seeds as biosorbent. Afr. J. Biotechnol. 7(24): 4508-4511.
- Okieimen CO, Okieimen FE (2001). Enhanced metal sorption by ground nut (*Arachis hypogea*) husks modified with thioglycolic acid. Bull. Piere Appl. Sci. 20c: 13-20.
- Okuo MJ, Oviawe AP (2007). Selective sorption of mixed Heavy Metal ions using Cassava fiber modified with Citric acid. J. Chem. Soc. Nig. 32(2): 247-253.
- Park JK, Han SS, Min SH (2000). Removal of toxic heavy metal ions in run offs by modified Alfalfa and juniper fibers. Proceedings of 1st world congress of the international water Association, Paris. pp. 6-12.
- Patil S, Bhole A, Natrajan G (2006). Scavenging of Ni(II) Metal Ions by Adsorption on PAC and Babhul Bark. J. Environ. Sci. Eng. 48(3): 203-208.
- Qadeer R, Akhtar S (2005). Kinetics study of lead ion adsorption on active carbon. Turk. J. Chem. 29: 95-99.
- Rafeah W, Ngaini Z, Usun Jok V (2009). Removal of Mercury, Lead and Copper from aqueous solution by activated carbon of palm oil empty fruit bunch. World Appl. Sci. J. 5(Special Issue for Environment): 84-91.
- Salam A, Adekola FA (2005). The influence of pH and adsorbent concentration on adsorption of lead and zinc on a natural goethite. Afr. J. Sci. Technol. 5(6): 55-66.
- Saeed A, Iqbal M, Akhtar MW (2002). Application of biowaste materials for the sorption of heavy metals in contaminated aqueous medium. Pak. J. Sci. Ind. Res. 45: 206-211.
- Saeed A, Muhammed I, Waheed Akhtar M (2004). Removal and recovery of lead (II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk). J. Hazardous Mater. 117: 65-73.
- Sharma P, Kumari P, Srivastava MM, Srivastava S (2006). Removal of Cd (II) from aqueous system by shelled *Moringa oleifera* Lam. seed powder. Bioresour. Technol. 97: 299-305.
- Somasekhara RK, Emmanuel KA, Ramaraju KA (2007). Removal of Mn(II) from aqueous solution using *Bombax malabaricum* fruit shell substrate. E-J. Chem. 4(3): 419-427.
- Teixeria T, Cesar R, Zezzi A, Marco A (2004). Biosorption of heavy metals using rice milling by-products. Characterization and application for removal of metals from aqueous solutions, Chemosphere, 54: 905-915.
- Tumin ND, Luqman AC, Zawani Z, Abdul Rashid S (2008). Adsorption of copper from aqueous solution by *Elais guineensis* kernel activated carbon. J. Eng. Sci. Technol. 3(2): 180-189.
- Unob F, Ketkangplu P, Chanyput P (2005). Preconcentration of Heavy metals from aqueous solution using Chitosan flake. J. Sci. Res. Chula. University, 30(1): 87-95.
- Upendra K (2006). Agricultural products and by-products as a low cost adsorbent for heavy metal removal from water and wastewater: A review: Scientific Res. Essay, 1(2): 033-037.
- Wong KK, Lee CK, Low KS, Haron MJ (2003). Removal of Cu and Pb by tartaric acid modified rice husk from aqueous Solutions. Chemosphere, 50: 23-28.