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BIO-ADSORBENT ACTIVITY OF CERTAIN FRUIT CORTEXES FOR REMOVAL OF HEAVY METALS IN POLLUTED WATER SAMPLE FROM SILTARA INDUSTRIAL AREA

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ABSTRACT

The biotic and abiotic components of environment interact with each other to maintain a balance but the alteration of these components creates imbalance in the nature and results in pollution. Various factors are directly and indirectly affecting the environment and have become a serious threat in human health systems causing life threatening diseases. One of the major concerns that cause environmental pollution is water pollution. The presence of heavy metals and toxic substances in the water may harm the human health due to the bioaccumulation of metals into the body by various uses and purposes. The removal of heavy metals from the water by various physical and chemical methods is quite expensive and sometimes need additional steps which may take long time. In the present study it is aimed to remove heavy metals from water by using natural bio-adsorbent which are easily available in our surroundings and are economically low in cost. The wastewater is collected from Siltara industrial area and the traces of heavy metals are detected by analytical technique and wastewater is being treated with bio-adsorbent. The sample is further studied for pH and test for heavy metal detection after treatment with bio-adsorbent. The results shows that the cortex of the fruits with the high potential to be used as support for heavy metal removal in future.

KEY WORDS : Pollution, Bio-adsorbent, Heavy metals

INTRODUCTION

Heavy metal pollution in aquatic systems has become a serious global environmental concern due to their adverse effect; accumulation in soil, water and plants; and their non-degradable nature. Metal ions are also mobilized into food chain as a result of leaching from waste dumps, polluted soil through water bodies. The contaminated water causes toxic effects on human health (Pandey *et al*., 2008). Water pollution is now considered as a global problem and its control is becoming an important concern in recent years (Robinson *et al*., 2001). The renowned industrial area near Raipur, Chhattisgarh is Siltara. The area is fully covered by small to large companies. The hazardous metal ion enters into water stream from industrial dumping and antropogenic activities which leads to increase in the concentration of metal ions at next higher level (Monsor and Adhoum, 2002). The hazardous pollutants such as lead, cadmium, zinc, cyanide and copper mainly responsible for producing toxicity in water. Cyanide is one of the most hazardous chemical and also toxic to human beings and animals since it binds to key iron containing iron enzymes, i.e. cytochrome oxidase which is required for cells to respire aerobically. It also results in either acute or chronic poisoning to humans and animals (Chena and Liu, 1999). Lead is also a toxic heavy metal and it targets the brain, blood, kidney and thyroid gland. Even a very low concentration of heavy metals in water can be very toxic. The main source of metal in water is the effluents of processing industries such as electroplating and metal finishing, mining, steel tempering, automobile parts manufacturing, pharmaceuticals and coal processing units (Ansari *et al*., 2011). To control pollution nearby area of Siltara and protect the water as well as environment contaminated wastewater must be treated before use and discharge into environment. A conventional wastewater treatment method includes ion exchange filtration, electrochemical treatment, reverse osmosis, membrane technologies and evaporation. The disadvantages of the convectional technology is that they requirean expensive chemicals which leads to the production of toxic chemical sludge and their disposal is neither economic nor ecofriendly (Ahluwalia and Goyal, 2007; Hanif *et al*., 2007). In recent years many studies are devoted to remove the heavy metals by adsorption using agricultural material. Adsorption is an important process for removal as it is simple to operate and no hazardous chemicals are required in this process. To make the adsorption attractive and achievable, novel low cost adsorbents with high adsorption capacities are required. Varieties of agro based materials have been widely reported for their ability to remove contaminants from wastewater (Moussavi and Khosravi, 2010; Sahranavad *et al*., 2011; Gonen and Serin, 2012). To remove metals adsorbents such as carbon-based and magnetic materials (Yang, 2013), polymer (Abo-Fara, 2009) and composite (Zhang, 2013) have been continuously developed. At the same time, many ordinary and raw adsorbents such as waste biomass have gradually aroused the attention of researchers because of their salient advantages such as easy availability, low cost and environment-friendliness. Consequently, employing waste biomass such as tree leaves (Chakravarty*e t al*., 2010), sawdust (Bozic *et al*., 2009), corn stalk (Chen *et al*., 2012) and tea waste (Wan, 2014) as adsorbents for heavy metal removal based on the concept of treating the waste with waste materials has developed the considerable attention in recent years. However, the subsequent treatment of the waste biomass after heavy metal adsorption was reported in previous researches. In the accumulation of metal ion at the sorbate-biosorbent interface reduce the sorbent concentration in the solution (Horsfall and Spiff, 2004).

The objective of the present study is to provide an alternate strategy for elimination of heavy metals such as Pb, Cd and zinc from the waste water body using bio-adsorbents prepared by modification of waste materials from banana, orange and kiwi cortex. They are excellent source of biomass. The activity of prepared bio-adsorbent was investigated for its adsorbent dose, pH, contact time and initial metal ion concentration on the adsorption capacity.

MATERIALS AND METHODS

Material collection and preparation

The different fruits were purchased from the local market of Siltara, Raipur.The cortexes (banana, orange and kiwi) were cut into small pieces cleaned thoroughly with tap water and make sure there is no dirt or pulp membrane remains. Materials were dried at 40 ^{o}C in convection oven for 6 days and milled using mortar and screened to obtain two different particle sizes (1 mm and 2 mm). Further, the powders were treated for alkalization with 0.5 N NaOH for 20 min.(Navarro, 2006). The powders were passed through gauze and rinse with distilled water several times to eliminate excess of NaOH. Finally, all the bio sorbent powders were dried again at 40 ^{o}C and kept on dryer until use.

Reagents

The chemicals used in the preparation of reagents were of analytical grade. The stock solutions of heavy metal (cadmium, lead and zinc) were prepared 1000 mg/L. The working standard solution of metal ion were prepared by diluting 100 mL of stock standard solution to 1 liter of distilled water. A 5 mL of solution was diluted with 50 mL of distilled water to achieve a solution containing 10 mg/L of selected ion. These different concentrations were used throughout the experiment. The pH of the solution was maintained using 0.1 M HCl and 0.1 M NaOH. The whole experiment was conducted at 25^{o}C.

Biosorption Procedure

The adsorption process were conducted by measuring 50 mL of wastewater sample and poured in 250 mL conical flask and 0.5 g of adsorbent was added. The conical flask was placed on rotary shaker for 160 rpm at 28^{o}C to ensure equilibrium. The sample was filtered by a membrane and used to analyze the concentration of the metal ion present on filtrate. The adsorption capacity of the cortex was calculated using the following equation:

$$qe = \frac{(P0 - Pe)}{W} \times V$$

Where $P0$ is the initial concentration of the heavy metal present in wastewater before the adsorption and Pe is the final concentration of heavy metal present after the adsorption for a period of time (mg/L) respectively. V is the volume of wastewater used and W is the mass of adsorbent used.

RESULTS AND DISCUSSION

Enormous modern technologies already exist to eliminate the contaminants from air soil and water. The use agriculture waste were determined as raw material with a high potential to be used as support for metal removal as they are cost efficient and easily available and easy to operate. A different particle size (1 mm and 2 mm) of kiwi cortex powder is used to check the capability of metal retention. According to result, metal ion with a 1mm particle size show better retention capacity as compared with 2 mm particle size (Fig. 1) and considering this result, only 1mm particle size powder were used in further experiment with all other cortexes. The % removal was calculated using Eq. 2. Considering the particle size, it was found that smaller particle size expose more contact surface area and results highest biosorption value. The experimental data, agreed with expected result, and fruit cortex with 1 mm particle size resulted better for metal removal.

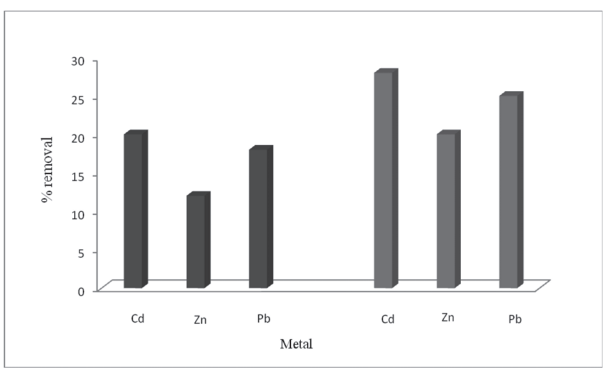

Fig. 1. Removal of heavy metal with two dfferent particle size (the blue bar 2 mm and red bars 1 mm) of kiwi cortex powder.

Effect of particle size on removal efficiency

In this assessment, two different particle sizes (1 mm and 2 mm) of the cortexes were used to determine the influence of particle size on metal removal efficiency. The % removal of heavy metal from the solution was calculated using the following equation:

$$\% \text{ Metal removal} = \frac{P0 - Pe}{P0} \times 100$$

Where, % metal removal is ratio of the difference in metal concentration before and after adsorption.

Metal removal using banana, orange and kiwi cortex showed in Fig. 2. In this case, overall removal of Pb, Cd and Zn with orange cortex (65%, 72% and 45%) compared with the results for banana cortex (where the overall removal of Pb, Cd and Zn was 31%, 34% and 20%). For kiwi cortex the result for Pb, Cd and Zn was (60%, 78% and 49%) respectively. The cell walls of plants are rich in polysaccharides and pectin compound as galacturonic acid polymer (Fry, 2004) which can be ionized with an alkaline treatment and generate negative charges ion at interface that may bind metallic cations. The banana cortex has higher amount of cellulose, pectin and starch than orange or kiwi cortex (Khalil *et al*., 2006; Yapo *et al*., 2007). For the removal of cadmium, similar using orange and kiwi cortex and gives high value of biosorption 70 % respectively, whereas banana cortex achieved only 30% removal of cadmium. In case of zinc. the removal percentage using orange, banana and kiwi cortex 45%, 20% and 49% respectively. This result can be explained by composition of banana that this material can remove cadmium and Pb better than other metal as it is rich in starch and cellulose which is reported previously.

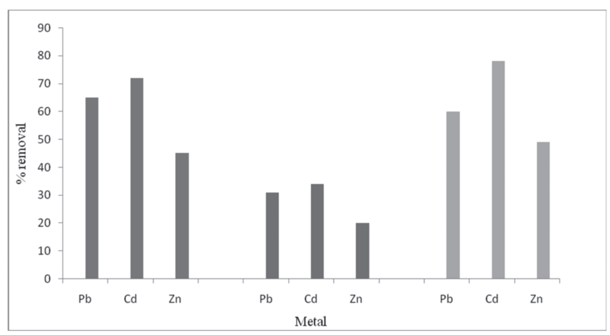

Fig. 2. Removal of heavy metals using 1 mm particle size of fruit cortex (the Blue bar orange, the Red bars Banana and the Green bars kiwi).

The capacity of biosorption is calculated using Eq.1. The result (Table 1) shows that the kiwi cortex is capable of absorbing approximately 490 mg of cadmium per gram and 280 mg of Zn per gram and 340 mg of Pb per gram. For orange and banana cortex retention rate was for Cd (470 mg/g and 198 mg/g), followed by Pb (328 mg/g and 120 mg/g) and finally Zn (250 mg/g and 130 mg/g). Volesky and Holand, who worked with microbial biomass and Cd, Cu and Pb, report (q) values in the range of 11–215 mg/g of biomass for Cd, 1.2–152 mg/g for Cu and 53–600 mg/g for Pb (Volesky and Holand, 1995). In our case, the best q values were obtained for kiwi cortex 490 mg/g for Cd and 470 mg/g of Cd using orange cortex. The order for maximum adsorption capacity of these heavy metals for kiwi and orange was Cd> Pb > Zn and for banana Cd > Zn > Pb.

Effect of adsorbent dose

Bioadsorbent dosage is an essential parameter strongly affects the sorption capacity. Different amount of adsorbents (0.1- 2.0 g) were added to different conical flask containing 25 mL of waste water solution. It is observed, as shown in Table 2 that the percent removal initially increases with increase in adsorbent dose (up to 2 g/L) for selected metal. From above observation, it is evident that higher concentration of adsorbent gives more exchangeable sites or surface and increase the percent removal as the adsorption is surface phenomenon (Asubiojo and Ajelabi, 2009). Similar results were reported by researchers for a variety of adsorbent systems.

Table 1. Biosorption capacity of different cortex powders

Biosorbent/ Metal	Pb (mg/g)	Cd (mg/g)	Zn (mg/g)
Orange	328	470	250
Kiwi	340	490	280
Banana	120	198	130

Effect of wastewater pH on metal removal

The effect of solution pH on metal removal was studied and pH varied from acid to alkaline (pH 2-10) as shown in Fig.3. With increase in solution pH 2 to 6, % removal of heavy metal increase stability, reaches maximum value 85% and decreases from pH 6 to 10. During the experiment, the higher metal removal occurred at pH 6.0 for Cd, Pb and Zn in all fruit cortexes. The above observation can be explained on the basis of surface chemistry of adsorbent and effect of pH on the adsorption revealed that mechanism of metal removal was possibly mainly due to metal immobilization in the rhizosphere and absorption through roots and partially by precipitation (Barakat, 2011). The pH of solution alters the surface charge of the adsorbent as well as the degree of ionization and speciation of contaminants.

Effect of contact time

The effects of contact time on the adsorption capacity of three metal ions on fruit cortex were

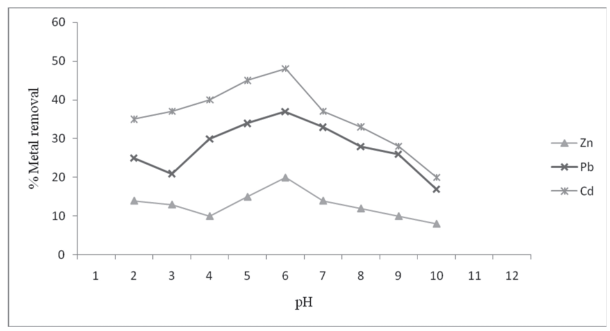

Fig. 3. Effect of pH on removal percetage of Cd, Pb and Zn ions onto banana cortex.

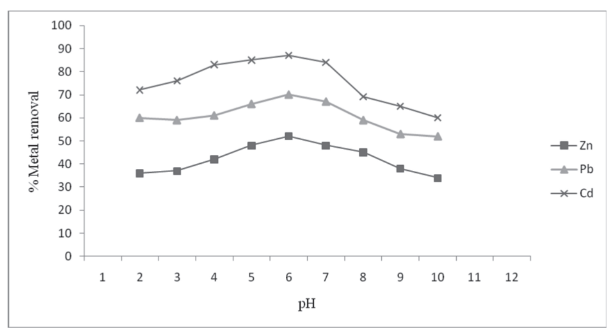

Fig. 4. Effect of pH on removal percetage of Cd, Pb and Zn ions onto kiwi cortex.

Table 2. Effect of adsorbent dose on removal of metal (Pb, Cd and Zn) using fruit cortex

Adsorbent Dose (g)	% removal								
	Banana			Kiwi			Orange		
	Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb	Zn
0.2	30	28	15	65	57	46	61	55	36
0.4	34	33	19	68	62	48	65	60	40
0.8	38	37	23	71	65	51	68	63	44
1.0	43	40	26	75	70	55	70	68	48
2.0	48	44	30	78	74	58	73	71	52

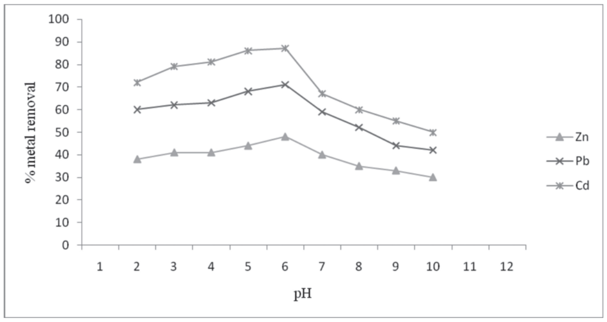

Fig. 5. Effect of pH on removal percetage of Cd, Pb and Zn ions onto orange cortex.

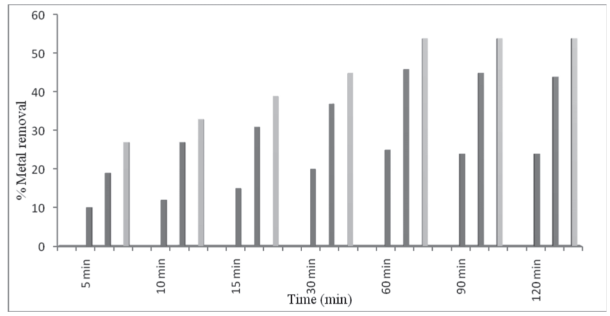

Fig. 7. Effect of contact time on removal percentage of Zn ion onto cortex powder (the red bars represent Banana, the blue bars orange and the green bars kiwi).

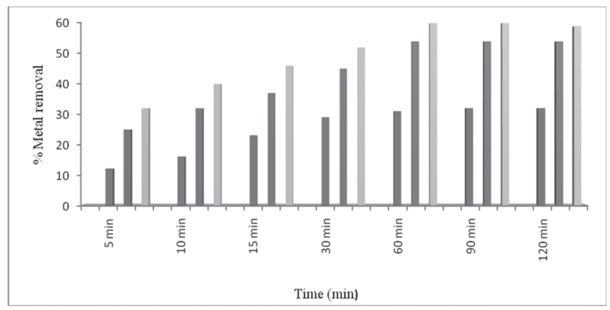

Fig. 8. Effect of contact time on removal percentage of Pb ion onto cortex powder (the red bars represent Banana, the blue bars orange and the green bars kiwi).

studied. It is observed that the adsorption process proceeds rapidly and equilibrium concentration of metal removal is achieved within 60 min for all the fruit cortex respectively and thereafter remains fixed which indicates the saturation of active sites. Figs.6, 7 and 8 indicates that relation of contact time, between % metal removal and time (min) is 15%, 35% and 40% of cadmium and 10%, 19% and 37% of zinc removal is achieved by banana orange and kiwi cortex at a very short time of 5 minutes and highest value 35%, 65% and 72% of cadmium and 25%, 46% and 54 % of zinc removal were obtained after 60 min. In case of Pb 12%, 25% and 32% removal of metal obtained after 5 min and highest 31%, 54% and 60% removal obtained after 60 min using banana, orange and kiwi cortex respectively. Hence, after certain time the rate of % removal of heavy metal become constant and reaches equilibrium. The period of contact time of 60 min for further studies was fixed for all cortex powder respectively.

Effect of heavy metal concentration in waste water

The effect of metal concentration was investigated by adding a 0.5 g of adsorbent powder in a conical flask containing 25 mL of waste water (heavy metal) at different concentrations of 5 ppm, 10 ppm, 15 ppm ppm, 25 ppm, 50 ppm and 100 ppm respectively at pH 6.0. The flask was shaken for 60 min at 158 rpm. It is observed that the effect of metal ion concentration on removal of Cd, Pb and Zn ions by banana orange and kiwi decreases respectively with an increase in initial concentration of metal ions. This results indicates that is adsorption process highly depends on initial concentration of metal ions because all of the adsorbents had a limited number of active sites and get saturated above a certain concentration (Gode and Pehlivan, 2005).

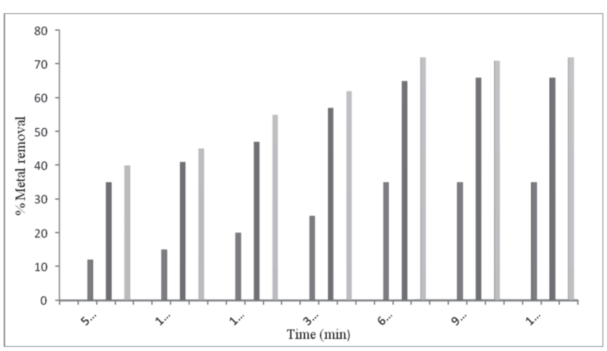

Fig. 6. Effect of contact time on removal percentage of Cd ion onto cortex powder (the red bars represent Banana, the blue bars orange and the green bars kiwi).

CONCLUSION

Different technologies have been used to eliminate contaminants from water bodies. One of those is use agricultural wastes to eliminate the heavy metals from fruit waste peel or cortex. The waste cortexes of the different fruits were determined to be raw materials with a high potential to be used as support for heavy metal biosorption. Among the main advantages of the use of these materials are their availability, low cost and the fact that they do not require culture or synthesis for their production. The use of citric cortex from orange and other organic waste such as banana cortex to remove heavy metals using their chemical composition as polysaccharides can be applied for metal sorption in surface and underground water. The cell walls of the plant are rich in polysaccharides mainly cellulose and pectin compound. This pectin like compound can be ionized with an alkaline treatment and can generate negative charges that may bind metallic cations. This last part of this study opens a new door to find what kind of compound alone or mixed helps to bound heavy metal in a specific or non-specific way. Small particle size show highest metal removal with related to an increase in the contact surface allowing better adsorption. More research on this field is required to determine same result using small particle size. Three fruit cortexes (Banana, orange, kiwi) were tested and according to results the adsorption was found to be depending on pH, adsorbent dose and contact time. The optimum pH was found to be 6.0 for Cd, Pb and Zn for all the fruit cortexes. The cadmium, lead and zinc ions attained equilibrium within 60 min. Finally, it is concluded that the results included in this work is the beginning study of this kind of materials and improve their property to remove toxic heavy metals from water.

REFERENCES

Abo-Fara, S.A., Abdel-Aal, A.Y., Ashour, I.A. and Garamon, S.E. 2009. Removal of some heavy metal cationsby synthetic resin purolite C 100. *J. Hazard Mater*. 169 : 190-194.

Ahluwalia, S.S. and Goyal, D. 2007. Microbial and plant derived biomass for removal of heavy metals from wastewater. *Bioresour. Technol*. 98 : 2243-2257.

Aksu, Z., Calik, A., Dursun, A.Y. and Demircan, Z. 1999. Bisorptin of iron (III) Cyanide complex ion on *Rhizopus arrhizus* : application of adsorption isotherms. *Process Biochem*. 34 : 483-491.

Ansari, T.M., Hanif, M.A., Mahmood, A., Ijaz, U., Khan, M.A., Nadeem and Ali R. M. 2011. Immobilization of rose water biomass for uptake of Pb (II) from aqueous solution. *Biotechnol. Res. Int*. 11 : 1-9.

Asubiojo, O.L. and Ajelabi, O.B. 2009. Removal of heavy metals from aque-ous solution by sawdust adsorption. *J. Environ. Chem. Toxicol*. 91 : 883-890.

Barakat, M.A. 2011. New trends in removing heavy metals from industrial waste-water. *Arab. J. Chem*. 4 : 361-377.

Bozic, D., Stanlovic, Gorgievski, V., Bogdanovic, M. and Kovacevic, G. 2009. Adsorption of heavy metal ions by sawdust of deciduoud trees. *J. Hazard. Mater*. 171 : 684-692.

Chakravarty, S., Mohanty, A., Sudha, T.N., Upadhyay, A.K., Kona, J., Sircar, J.K., Madhurkar, A. and Gupta, K.K. 2010. Removal of Pb (II) ions from aqueous solution by adsorption using bael leaves (*Aegle marmelos*). *J. Hazard Mater*. 173 : 502-509.

Chen, S., Yue, Q., Gao, B., Li, Q., Xu, X. and Fu, K. 2012. Adsorption of hexavalent chromium from aqueous solution by modified corn stalk: a fixed-bed column study. *Bioresour. Technol*. 113 : 114-120.

Chena, S.C. and Liu, J.K. 1999. The response to cyanide of cyanide resistant *Kelbsiella oxytoca* bacterial strain. *FEMS Microbiol. Ecol*. 175 : 37-43.

Fry, S.C. 2004. Primary cell wall metabolism: tracking the careersof wall polymers in living plant cells. *New Phytol*. 61 : 641-675.

Gode, F. and Pehlivan, E. 2005. Removal of Cr(VI) from aqueous solution bytow Lewatit-anion exchange resins. *J. Hazard. Mater*. 119 : 175-182.

Gonen, F. and Serin, D.S. 2012. Adsorption study on orange peel: removal of Ni (II) ions from aqueous solution. *Afri. J. Biotechnol*. 11(5) : 1250-1258.

Hanif, M.A., Nadeem, R., Zafar, M.N., Akhtar, K. and Bhatti, H.N. 2007. Kinetic studies for Ni^{2+} biosorption from industrial waste water by *Cassia fistula* (Golden shower) biomass. *J. Hazard Mater*. 139 : 345-355.

Horsfall, Jr. M. and Spiff A.I. 2004. Effect of metal ion concentration onthe biosorption of Pb^{2+} and Cd^{2+} by *Caladium bicolor* (wildcocoyam). *Afr. J. Biotechnol*. 4: 191-196.

Khalil, H.P.S., Alwani, M. and Mohd, A.K. 2006. Chemical composition,anatomy, lignin distribution, and cell wall structure of Malaysianplant waste fibers. *Bio Research*. 1 : 220-232.

Monsor, L. and Adhoum, N. 2002.Modified activated carbon for removal of copper, zinc, chromium and cyanide from wastewater. *Sep. Purif. Technol*. 26: 137-146.

Moussavi, G. and Khosravi, R. 2010. Removal of cyanide from waste water by adsorption onto pistachio hull wastes: parametric experiment kinetic and equilibrium analysis. *J. Hazard Mater*. 183 : 724-730.

Navarro, A.E., Ramos, K.P. and Maldonado, H.J. 2006. Elucidacon del efectodel pH en la adsorcion de metales pesados mediante biopolímerosnaturales: cationes divalentes y superficies activas. *Rev. Iberoam. Polim*. 7 : 113-126.

Pandey, P.K., Verma, Y., Choubey, S., Pandey, M. and Chadrasekhar, K. 2008. Biosorptive removal of cadmium from contaminated ground water and industrial effulents. *Bioresour. Technol*. 99 : 4430-4427.

Robinson, T., Chandran, B. and Nigam, P. 2001. Studies on the decolourisation of an artificial textile effluents by white root fungi in N-rich and N- limited media. *Appl. Microbiol. Biotechnol*. 57 : 810-814.

Sahranavad, M., Ahmadpour, A. and Doosti, M.R. 2011. Biosorption of hexavalent chromium ions from aqueous solution using almond green hull as a low cost biosorbent. *Euro. J. Sci. Res*. 58 (3) : 392-400.

Volesky, B. and Holand, Z.R. 1995. Biosoprtion of heavy metals, *Biotechnol. Prog*. 11 : 235-250.

Wan, S., Ma, Z., Xue, Y., Ma, M., Xu, S., Qian, L. and Zhang Q. 2014. Sorption of lead (II), cadmium (II), and copper (II) ions from aqueous solutions using tea waste. *Ind. Eng. Chem. Res*. 53 : 3629-3635.

Yang Pu, Y., Zheng, X., Wang, H., Su, D. and He, Y. J. 2013. Adsorption and desorption of thallium (I) on multiwalled carbon nanotubes. *Chem. Eng. J.* 219: 403-410.

Yapo, B.M., Lerouge, P., Thibault, J.F. and Ralet, M.C. 2007. Pectins fromcitrus peel cell walls contain homogalacturonans homogenous with respect to molar mass, rhamnogalacturonan I and rhamnogalacturonan II. *Carbohydr. Polym*. 69 : 426-435.

Zhang, Q., Du, Q., Hua, Jiao M., Goa, T. and Pan, F. 2013. Sorption enhancement of lead ions from water by surface charge polystyrene-supported nano-zirconium oxide composites. *Environ. Sci. Technol*. 47 : 6536-6544.