Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **5(2),** 32-41, February **(2015)** *Res. J. Chem. Sci.*

Equilibrium and Thermodynamic Studies on Adsorption of Cd^{2+} and Zn^{2+} using *Brachystegia eurycoma* Seed coat as Biosorbent

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Available online at: www.isca.in, www.isca.me
Received 12th January 2015, revised 31st January 2015, accepted 14th February 2015

Abstract

The potential of B.eurycoma seed coat as biosorbent for removing Cd^{2+} and Zn^{2+} from aqueous solutions has been studied. Batch adsorption experiments were carried out as function of pH, initial metal ion concentration and temperature. Maximum metal sorption was found to occur at pH 6.0 at initial concentration of 30 mg/L and at 30°C. The maximum adsorption capacity of B.eurycoma corresponding to sites saturation was found to be 4.286 and 4.390 mg/g respectively for initial Cd^{2+} and Zn^{2+} concentration of 30 mg/L at a temperature of 40 °C. The results were analyzed by the Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherms using linearized correlation coefficient at different temperatures. Results showed that the Langmuir and Freundlich models gave the best interpretation to the equilibrium adsorption data for the Cd(II) and Zn(II) ions–B.eurycoma systems studied. The following thermodynamic parameters: ΔH, ΔS and ΔG were calculated and results obtained showed that the adsorption process was exothermic and spontaneous.

Keywords: Adsorption, *B.eurycoma,* biosorbent, isotherms, biosorption.

Introduction

Environmental pollution with heavy metals has become a colossal issue as a result of industrial and metallurgical processes which release a great number of toxic chemicals into the environment[1,2]. The heavy metals of widespread concern to human health are lead, copper, mercury, cadmium, arsenic, chromium and zinc[3-5]. Toxic heavy metals are considered as major pollutants that have direct effects on man and animals and their concentrations in our environment have reached alarming levels in terms of their effects on living organisms. Zn^{2+} which is considered an essential element for life and a micronutrient in trace amounts is a common metal ion found in effluents of a large number of industries. However, continual exposure to Zn^{2+} is detrimental to human health[6]. The toxicological effects of Zn^{2+} have been documented in the chemical literature and its presence in water and wastewaters is a potential risk for the environment and public health[5,7,8]. Cadmium is also a toxin even in relatively low dosages and is one of the major heavy metals that cause kidney damage, renal disorder, high blood pressure, bone fraction and destruction of red blood cells[9]. Cadmium(II) has also been implicated as a potential carcinogen[10-12]. Therefore, it is necessary to design feasible processes to minimize the pollution caused by Zn(II) and Cd(II) discharges and to reduce the risks associated with their presence in the environment.

The task of providing proper treatment facility for heavy metal pollutants is difficult and some of the techniques are either expensive or inefficient, hence there is pressing demand for innovative technologies which are low cost, require low maintenance and are energy efficient. The adsorption technique is economically favourable and technically easy to separate as the requirement of the control system is minimum. Instead of using commercial activated carbon, researchers have worked on inexpensive materials, such as Tea waste[13], Cassava wastes[14], modified rice husk[6], Fluted pumkin[15], waste acorn of *Quercus ithaburensis*[16], Oil palm fruit fibre[17], African Star apple shell[18] and other adsorbents, which have high adsorption capacity and are locally available. In this article, the technical feasibility of low-cost adsorbent from agricultural waste for heavy metal removal from aqueous solutions has been investigated.

B. eurycoma whose seed coat is employed as biosorbent in the present study is a plant that grows mainly along the river banks or swamps in Western and Eastern Nigeria. It is a large tree with irregular and twisted spreading branches. The seed has a roundish flat shape with brown colour and hard hull. In Nigeria, the main culinary use of the gum from *B. eurycoma* seed is in thickening soups. Thickeners are usually added as condiments in the preparation of most soups. They are known to cause increased viscosity in soups, giving it more palatability and good mouth feel. The seed coats are discarded and are considered wastes. Assessment of the Phytochemical contents of the seeds of *B. eurycoma* shows that the seeds contain Alkaloids (1.74%), Flavonoids (3.72 %), Tannins (0.70%), Saponins (0.87%) and Phenols (0.03%)[19]. Flavonoids are a group of polyphenolic compounds that are found in fruits and vegetables. These metabolites posses some functional groups and their presence in the seeds indicates that they could have potential to bind metal ions from aqueous solutions.

Material and Methods

Preparation of the adsorbents: The seeds of *Brachystegia eurycoma* were purchased from Abakaliki meat market, Ebonyi State. They were soaked in water until they became turgid. Their coats were removed, washed extensively in running tap water to remove dirts and other particulate matter and then sun-dried. They were later oven-dried for 2 h at a temperature of 50 ˚C. The dried samples were crushed using grinding mill fitted with sieves to obtain a particle size of 250 µm. The samples were stored in tight plastic containers and kept for the adsorption analysis.

100 g of the screened sample was soaked in excess of 0.3 M HNO_3 solution in a beaker, stirred for 30 min at a temperature of 30 ˚C and then left undisturbed for 24 h. They were then filtered through a whatman filter paper and rinsed severally with deionised water until a pH 7 was obtained. The adsorbents were finally air-dried. The treatment with acid opens up the pores of the adsorbent samples in preparation for the adsorption analysis and to destroy any debris or soluble biomolecules that might interfere with the metal ions during the adsorption process.

Adsorbates Preparation: Stock solutions of 1000 mg/L of each of the metal ions, cadmium and zinc were prepared from their salts, $CdSO_4.8H_2O$, and $ZnSO_4.7H_2O$ respectively. From the stock solutions, different working concentrations ranging from 5 - 30 mg L^{-1} of each of the metal ions were prepared by serial dilution. The effect of concentration on the adsorption of the metal ions was studied by transferring 25 mL of the different concentrations of the metal ions into different 250 mL conical flasks while maintaining the pH of the solutions at 6.0 and at temperature 30^0C. Thereafter, 0.2 g of the biosorbent was weighed into the flasks, corked and labeled and agitated in a rotary shaker for 1 h. At the end of the adsorption process, the content of each flask was filtered, centrifuged and the residual metal ion concentrations (C_e) analyzed. The process was also repeated at temperatures of 40 and 50 ˚C. The concentrations of the standards and the test solutions were confirmed using buck scientific Atomic Absorption Spectrophotometer (AAS) model 205. The pH of the adsorbate solutions was maintained at 6.0.

For the study on influence of pH on the adsorption process, a similar procedure was carried out just as in the case of initial metal concentration except that a fixed initial metal ion concentrations of 30 mg/L was used and the pH of the solutions adjusted from pH 2 to 8 using either 0.1 M HCl or 0.1 M NaOH solution and at a fixed temperature of 30^0C. The amount of the metal ions adsorbed was calculated by difference. The analysis was carried out in triplicates and mean residual concentrations analyzed. The amount of metal ions adsorbed at equilibrium, q_e (mg/g) was determined using the mass balance equation (1).

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (1)$$

Where C_o and C_e are the initial and equilibrium concentrations (mg/L), V is the volume of solution (L) and m the dry weight of the biosorbent (g).

Results and Discussion

Effect of pH: The amounts of zinc and cadmium ions adsorbed onto the adsorbent at the various pH values are shown in figure-1. The pH of an aqueous solution is an important parameter affecting both the amount of metal ions furnished in aqueous solution as well as the number of binding sites on the adsorbent[20]. The sorption capacity of the biosorbent increased with increase in pH of the solution and maximum pH value for adsorption of Cd^{2+} and Zn^{2+} by *B. eurocoma* was observed at pH 6.0 with adsorption capacities of 2.713 mg/g for Cd^{2+} and 2.936 mg/g for Zn^{2+} at a temperature of 30^0C and initial concentration of 30 mg/L. The decreased sorption capacity at low pH values <5, may have resulted from the protonation of the ligands at the surface of the *B. eurocoma*. The generation of hydroxonium ions [H_3O^+] in the bulk solution at low pH could result in competition between the hydroxonium ions and the metal ions for active sites and such a competition may have caused a decrease in the amount of metal ions adsorbed. But as the pH is increased, the hydroxonium ions are gradually dissociated and the positively charged Zn(II) and Cd(II) ions could bind with the free binding sites of *B. eurocoma* leading to an enhanced removal of the metal ions. Similar findings have been reported by other researchers[20,21]. The adsorbent generally showed a preferred affinity for Zn^{2+} than Cd^{2+} at the initial concentration of 30 mg L^{-1} employed.

Effect of metal ion concentration: In this study, the effect of initial Cd^{2+} and Zn^{2+} concentration on sorption onto the *B.eurycoma* was investigated in the range of 5–30 mg/L and the equilibrium uptake capacities (mg/g) at 30, 40, 50˚C are presented in figures-2 and 3. The figures show the variation of the equilibrium adsorption capacity of the *B.eurycoma* with initial Cd^{2+} and Zn^{2+} concentration and temperature. It was observed that the amount adsorbed, q_e (mg/g) increased with both increasing initial metal ion concentrations and increasing temperature under studied ranges. The maximum equilibrium adsorption capacity values were determined as 2.713, 2.885 and 2.824 mg/g for 30 mg/L initial Cd^{2+} concentration at 30, 40 and 50 ˚C, respectively and 2.936, 3.170 and 3.094 mg/g for Zn^{2+} for the same initial concentration and temperature ranges. The enhancement in the adsorption capacity may be due to the chemical interaction between adsorbates and adsorbent sites or the increased rate of intraparticle diffusion of Cd^{2+} and Zn^{2+} into the pores of the adsorbent at higher temperatures[22]. Results also showed that Zn^{2+} was better adsorbed than Cd^{2+}.

Adsorption Isotherms: A clear equilibrium distribution of the metal ions between the adsorbent (*B.eurycoma*) and liquid (bulk solution) phases is represented by adsorption isotherms. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the adsorbent for the different metal ions[23]. In order to determine the mechanism of Cd^{2+} and Zn^{2+} adsorption onto the adsorbent, the experimental data were applied to the following two-parameter isotherms: Langmuir, Freundlich, Dubinin-Radushkevich (D–R) and Temkin equations. The constant parameters of the isotherm equations for the adsorption process were calculated by regression using linear forms of the isotherm equations.

The Langmuir Isotherm model: The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no interaction among adsorbed species occurs. Based upon these assumptions, the linearized Langmuir equation is represented as[24]:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 K_L} + \frac{C_e}{Q_0} \qquad (2)$$

Where: C_e = the equilibrium concentrations of Cd^{2+} and Zn^{2+} (mg/L), q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g), Q_0 = maximum adsorption capacity corresponding to sites saturation (mg/g) and K_L = Langmuir isotherm constant (L/mg). The Langmuir parameters, Q_0 and K_L are computed from the slope and intercept of the Langmuir plots.

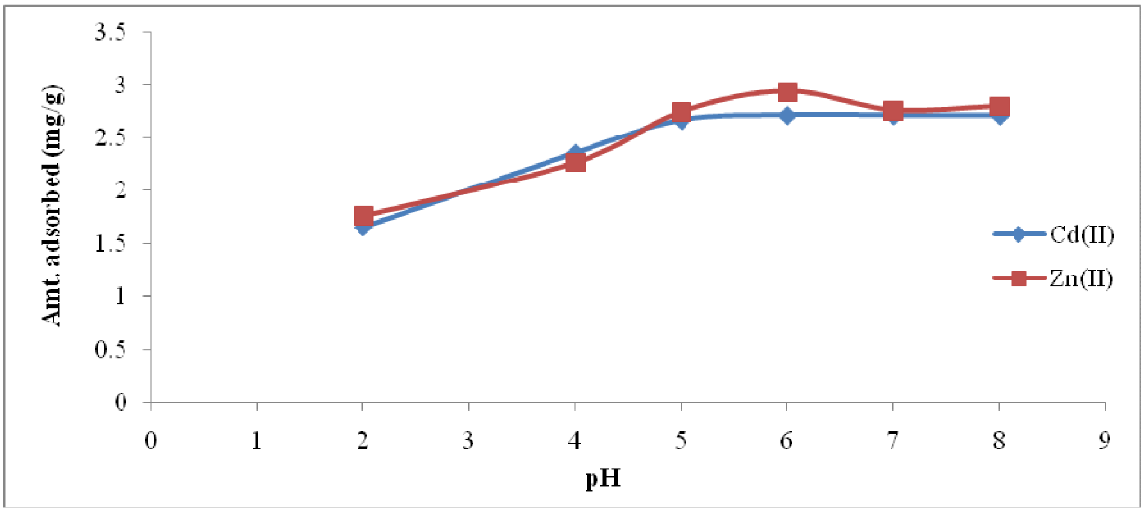

Figure-1
Effect of pH on the adsorption of Cd^{2+} and Zn^{2+} by *B.eurycoma* at 30 ^{0}C and initial conc. 30 mg/L

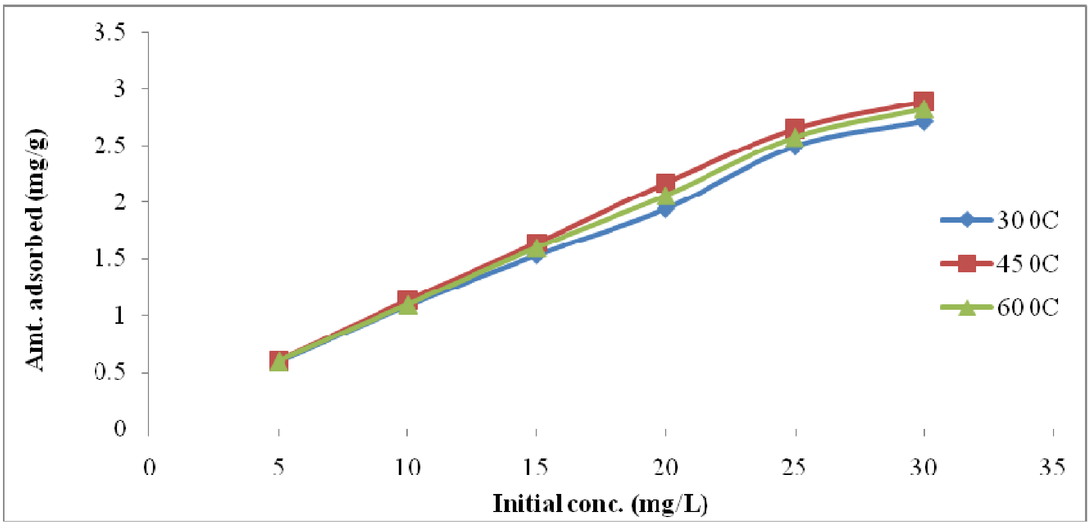

Figure-2
Effect of initial metal ion concentration on the amount of Cd^{2+} adsorbed at different temperatures

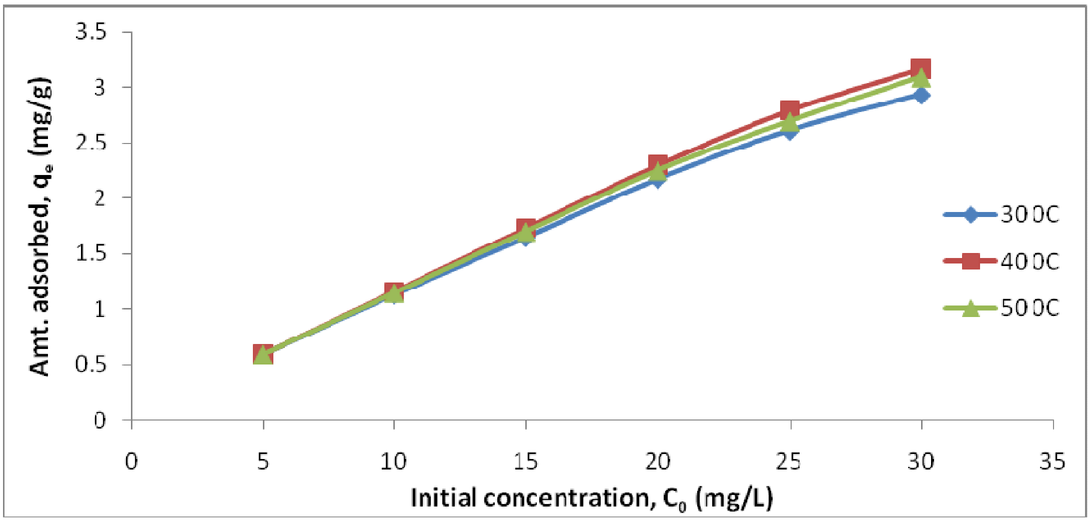

Figure-3
Effect of initial metal ion concentration on the amount of Zn^{2+} adsorbed at different temperatures

Table-1A
Langmuir Isotherm Constants for adsorption of Cd(II) and Ni(II) ions by the adsorbent at different temperatures

Parameters	**Cd^{2+}**			**Zn^{2+}**		
Temperatures	**30 ^{0}C**	**40 ^{0}C**	**50 ^{0}C**	**30 ^{0}C**	**40 ^{0}C**	**50 ^{0}C**
K_L (L/mg)	0.2513	0.3627	0.2800	0.3985	0.6022	0.4759
Q_0 (mg/g)	4.0177	4.2863	4.1445	4.1102	4.3898	4.3592
R_L at 30 mg/L	0.1171	0.0842	0.1064	0.0772	0.0525	0.0655
R^2	0.9378	0.9833	0.9735	0.9943	0.9864	0.9933

The essential features of the Langmuir isotherm are also expressed in terms of equilibrium parameter R_L, which is a dimensionless constant referred to as separation factor or equilibrium parameter[25].

$$R_L = \frac{1}{(1+K_L C_o)} \quad (3)$$

Where: C_o = initial metal ion concentration, K_L = the constant related to the energy of adsorption (Langmuir Constant). R_L value indicates the nature of adsorption to be either favourable if $0< R_L<1$, linear if $R_L =1$, unfavourable if $R_L>1$ and irreversible if $R_L=0$. From the data presented in table-1A, the R_L is greater than 0 but less than 1 indicating that Langmuir isotherm is favourable. The R^2 values > 0.9300 show that the sorption data fitted well into Langmuir Isotherm model.

The calculated Langmuir parameters, Q_0, K_L and R_L and the R^2 values are summarized in table-1A.

Equilibrium Freundlich Isotherm: The Freundlich model is derived to model the multilayer adsorption, applicable to a highly heterogeneous surface and is represented as[24]:

$$\ln q_e = \ln k_F + \frac{1}{n}\ln C_e \quad (4)$$

where K_F represents maximum adsorption capacity and n is related to the adsorption intensity and both constants are calculated from the intercept and slope of linear plots of ln q_e vs ln C_e according to equation-4.

The equilibrium Temkin isotherm: The Temkin isotherm describes the characteristic adsorption potential of the biosorbent for the metal ions. The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation[16]. The linearized form of the isotherm model is given as:

$$q_e = \frac{RT}{b_T}\ln k_T + \frac{RT}{b_T}\ln C_e \quad (5)$$

Where q_e (mg/g) and C_e (mg/L) are the amount adsorbed at equilibrium and the equilibrium concentration, respectively. T the absolute temperature in K and R is the universal gas constant, 8.314 J mol^{-1} K^{-1}.

Dubinin-Radushkevich Isotherm: The Dubinin-Radushkevich (D-R) model was applied to the equilibrium data to assess the nature of the adsorption process, *i.e.* whether it is physical or chemical adsorption. The linearized D-R adsorption isotherm is represented as[16]:

$$\ln q_e = \ln q_D - B_D \varepsilon^2 \quad (6)$$
$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

Where q_D is the theoretical saturation value (mg/g), q_e is the amount adsorbed at equilibrium (mg/g), B_D is a constant related to adsorption energy ($mol^2\ kJ^{-2}$), R is the gas constant (8.3145 J $mol^{-1}\ K^{-1}$), T is the temperature (K) and ε is the Polanyi potential which is related to the equilibrium concentration as expressed in equation (7).

The constant B_D gives an idea of the mean energy, E (kJ mol^{-1}) of adsorption per mole of the adsorbate as it is transferred to the surface of the solid from infinite distance in the solution and this energy is usually evaluated from the relation in equation-8.

$$E = \frac{1}{\sqrt{2B_D}} \quad (8)$$

It can be observed from figures 4–9 and tables-1A-C, that the adsorption of Cd^{2+} and Zn^{2+} onto *B. eurycoma* at the range of temperatures 30-50^{0}C fits quite well into the Langmuir, Freundlich and Temkin adsorption models with Langmuir and Freundlich showing best descriptions for the adsorption data. From table-1D, it was also observed that the experimental data obtained showed lower fitting into the Dubinin-Radushkevich (D-R) model. As seen from figures-4-11, the isotherms of Cd^{2+} and Zn^{2+} adsorption on *B.eurycoma* were found to be linear over the whole temperature range studied and the correlation coefficients were extremely high as shown in Tables 1A-D. The values of K_L and Q_o obtained from Langmuir plots increase with temperature increase showing optimum at 40^{0}C and decreases afterwards. The value of K_F determined from the Freundlich model changed with the rise in temperature giving maximum values at 40^{0}C. The magnitude of K_F showed high Cd^{2+} and Zn^{2+} adsorptive capacity of the *B.eurycoma* from aqueous solutions at all temperatures. Table 1B also indicated that n was greater than 1.0 at all temperatures, indicating that Cd^{2+} and Zn^{2+} were favourably adsorbed by the *B.eurycoma*. From table-1D, it can be observed that the obtained values of mean D-R energy, E_D are within the range of 1.060 -1.578 kJ mol^{-1}, indicating that physisorption may have played a dominant role in the adsorption of Cd^{2+} and Zn^{2+} onto the biosorbent. The constant obtained for Temkin isotherms are shown in table-1C. The Temkin isotherm constant in Table 1C shows that the heat of adsorption (*B*) increases with increase in temperature.

The change in enthalpy (ΔH) and entropy (ΔS) of the adsorption process was calculated from the variations of the Langmuir constant, K_L with change in temperature using the following relation:

$$\ln K = -\frac{\Delta G}{RT} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

The Gibb's free energy at 303K was evaluated using the relation:

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

Where *R* is the gas constant (8.314 J $mol^{-1}\ K^{-1}$) and *T* is the temperature (*K*). A plot of ln K versus 1/*T* yields straight line as shown in figure-12, from which ΔH and ΔS were calculated from the slope and intercept, respectively. Thermodynamic assessment of the adsorption data (table-2) showed that the ΔG values were all negative. The negative ΔG values indicate the feasibility and spontaneous nature of the adsorption process. The ΔG values obtained in this study for the metal ions were all less than –10 kJ/mol, suggesting that physical adsorption is the predominant mechanism in the sorption process and confirms the exothermic nature of the adsorption process. The positive values of ΔS may reflect the affinity of the *B.eurycoma* for the metal ions and also suggest some structural changes in the metal ions and adsorbent system, and that the freedom of the metal ions is not too restricted on the surfaces.

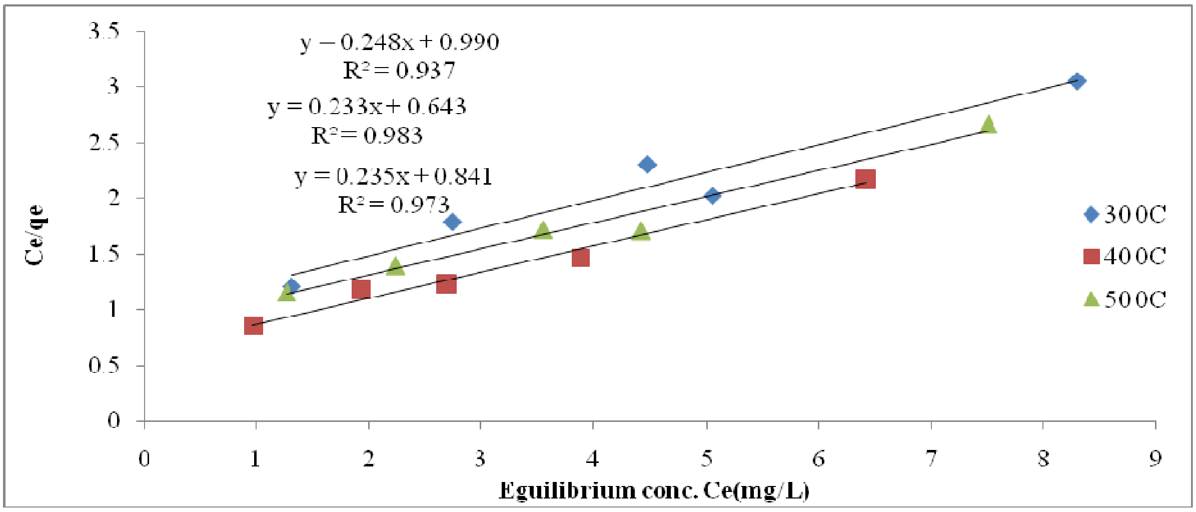

Figure- 4
Langmuir isotherm plots for adsorption of Cd^{2+} onto *B.Eurycoma* at different temperatures

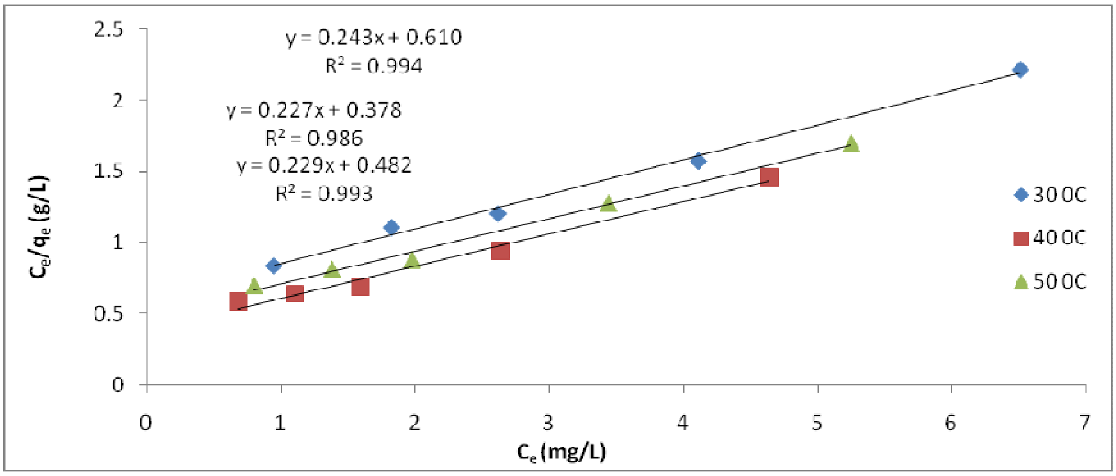

Figure-5
Langmuir isotherm plots for adsorption of Zn^{2+} onto *B.eurycoma* at different temperatures

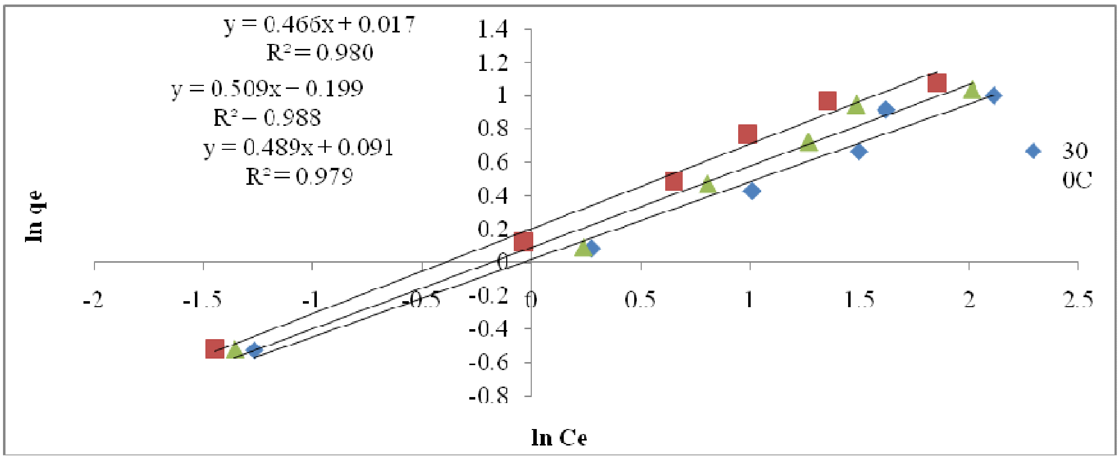

Figure-6
Freundlich isotherm plot of ln q_e vs ln C_e for adsorption of Cd^{2+} onto *B.eurycoma* at different temperatures

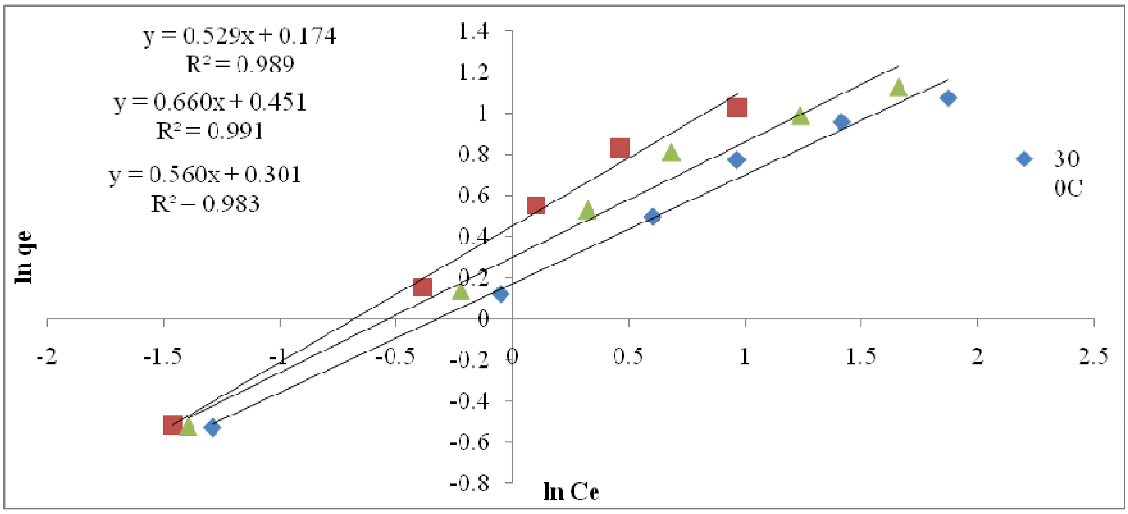

Figure-7
Freundlich isotherm plot of ln q_e vs ln C_e for adsorption of Zn^{2+} onto *B.eurycoma* at different temperatures

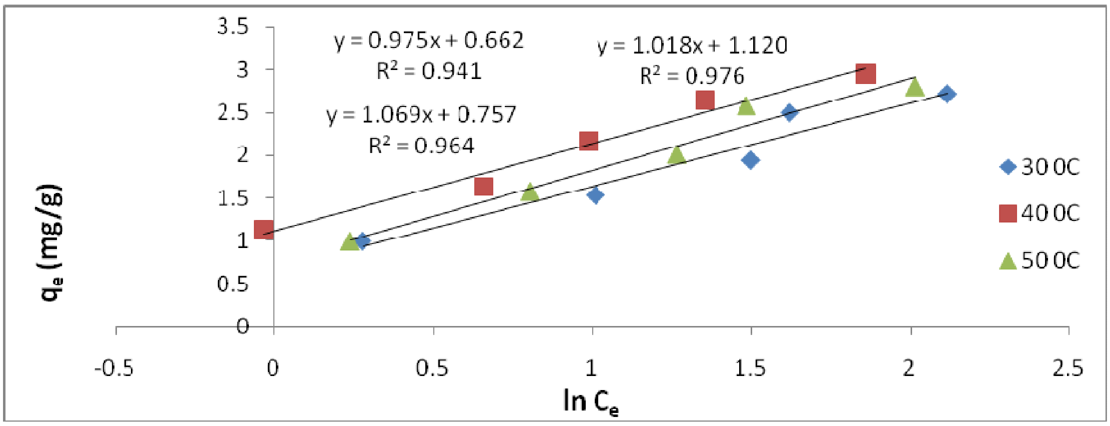

Figure-8
Temkin isotherm plot of q_e vs ln C_e for adsorption of Cd^{2+} onto *B.eurycoma* at different temperatures.

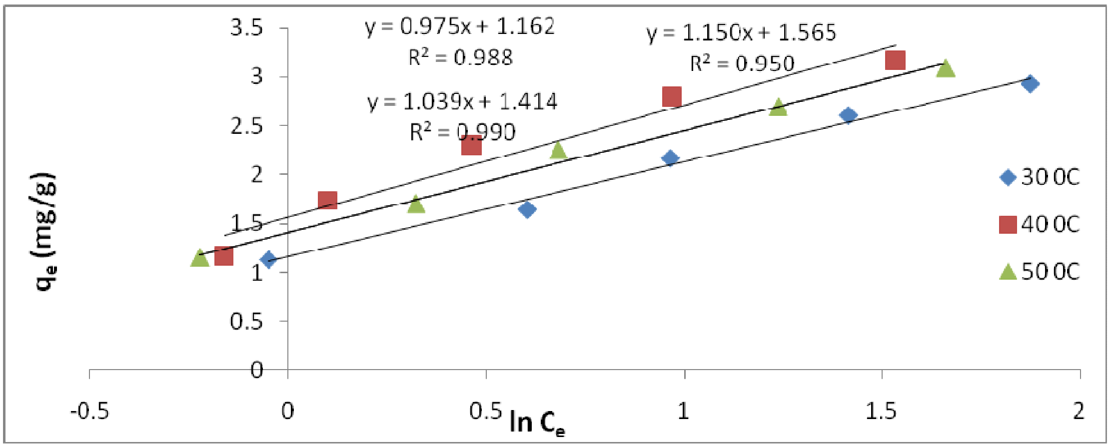

Figure-9
Temkin isotherm plot of q_e vs ln Ce for adsorption of Zn^{2+} onto *B.eurycoma* at different temperatures

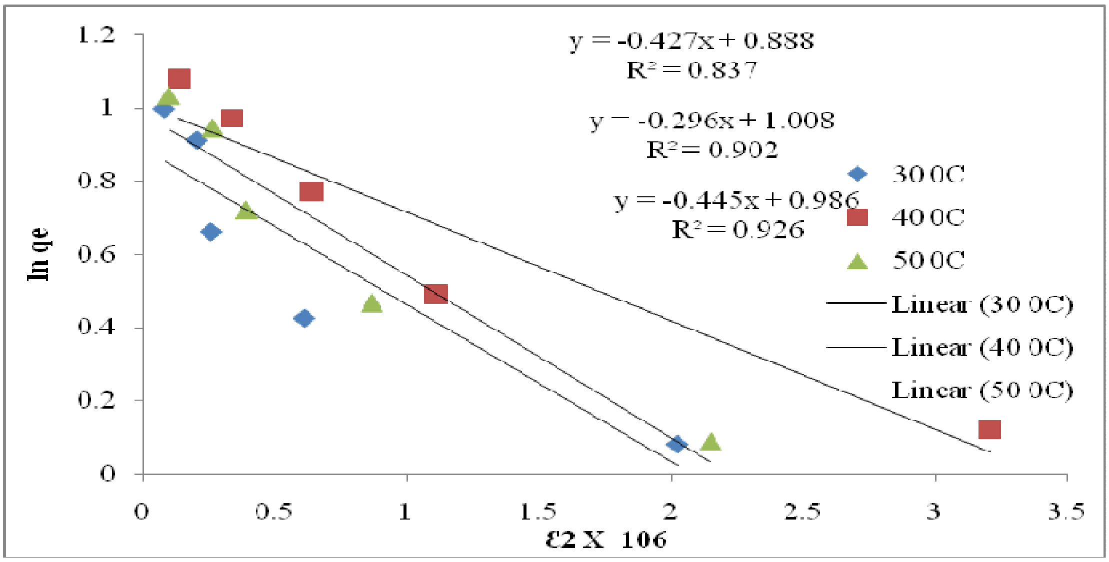

Figure-10
Dubinin-Radushkevich isotherm plot of ln qe vs ε^2 for adsorption of Cd^{2+} onto *B.eurycoma* at different temperatures

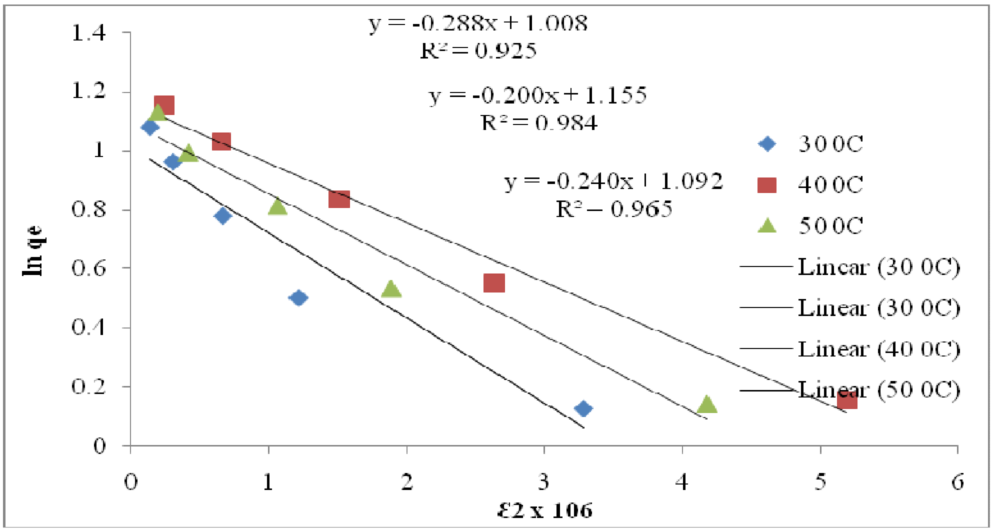

Figure-11
Dubinin-Radushkevich isotherm plot of ln qe vs ε^2 for adsorption of Zn^{2+} onto *B.eurycoma* at different temperatures

Table-1B
Freundlich Isotherm Constants for adsorption of Cd(II) and Zn(II) ions by the adsorbent at different temperatures

Parameters	**Cd^{2+}**			**Zn^{2+}**		
Temperatures	**30 ^{0}C**	**40 ^{0}C**	**50 ^{0}C**	**30 ^{0}C**	**40 ^{0}C**	**50 ^{0}C**
K_F	1.0175	1.2209	1.0961	1.1911	1.5700	1.3515
n	2.1459	1.9631	2.0433	1.8904	1.5142	1.7848
R^2	0.9802	0.9881	0.9798	0.9898	0.9914	0.9830

Table-1C
Temkin Isotherm Constants at different temperatures

Parameters	**Cd^{2+}**			**Zn^{2+}**		
Temperatures	**30 ^{0}C**	**40 ^{0}C**	**50 ^{0}C**	**30 ^{0}C**	**40 ^{0}C**	**50 ^{0}C**
K_T	1.9727	3.0053	2.0292	3.2943	3.9001	3.8991
b_T (kJ/mol)	2.583	2.474	2.355	2.583	2.190	2.423
R^2	0.9418	0.9764	0.9643	0.9888	0.9502	0.9907

Table-1D
Dubinin-Radushkevich Isotherm Constants for adsorption of Cd(II) and Zn(II) ions at different temperatures

Parameters	**Cd^{2+}**			**Zn^{2+}**		
Temperatures	**30 ^{0}C**	**40 ^{0}C**	**50 ^{0}C**	**30 ^{0}C**	**40 ^{0}C**	**50 ^{0}C**
q_D (mg g^{-1})	2.432	2.742	2.681	2.742	3.174	2.983
B_D(mol^2kJ^{-2}) X 10^{-7}	4.279	2.968	4.453	2.881	2.008	2.407
E (kJ mol^{-1})	1.081	1.298	1.060	1.317	1.578	1.441
R^2	0.8379	0.9029	0.9260	0.9250	0.9849	0.9653

Table-2
Thermodynamic parameters for the adsorption process

Metal ions	**Parameter**		
	$\Delta H\left(kJ/mol\right)$	$\Delta S\left(J/mol^{-1}K^{-1}\right)$	$\Delta G\left(kJ/mol\right)$
Cd^{2+}	**-7.394**	**2.163**	**-6.739**
Zn^{2+}	**-7.689**	**0.446**	**-7.554**

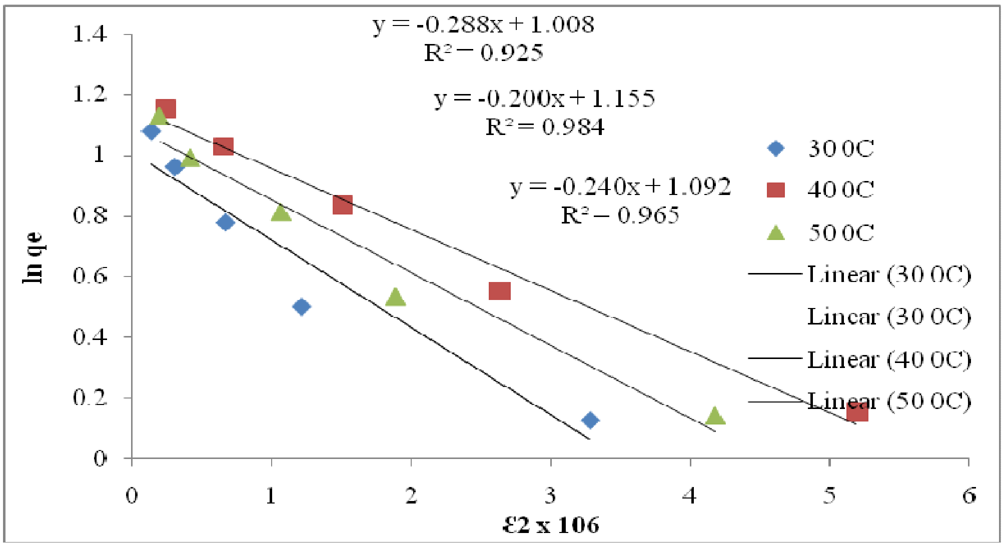

Figure-12

Plot of ln K vs 1/T for estimation of the thermodynamic parameters

Conclusion

The present study evaluates the efficiency of *B.eurycoma* seed coat in removing Cd^{2+} and Zn^{2+} from aqueous solutions. Based on the findings of the present study and information obtained from Chemical literature, the following conclusions can be drawn:

B.eurycoma is capable of removing Cd^{2+} and Zn^{2+} from aqueous solutions. The batch adsorption studies were dependent on pH, initial metal ion concentration and temperature. The optimum pH for removal of Cadmium and Zinc by *B.eurycoma* occurred at a pH 6.0.

Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin isotherm models were applied to the experimental adsorption data. Langmuir and Freundlich models provided the best description to the adsorption data at all the temperatures studied based on their high correlation coefficients.

The energy values obtained from Dubinin-Radushkevich model were all less than 8.00 kJ mol^{-1} suggesting that physisorption may have been the predominant mode of the adsorption process.

The obtained results are indication that the seed coat of *B.Eurycoma* could be applied as biosorbent for heavy metal removal from aqueous solutions and could be employed as an effective alternative method for the economic treatment of wastewater.

References

1. Nazris N., Rahmiana Z., Edison M. and Jiye J., Biosorption of Copper (II), Lead (II), Cadmium (II) and Zinc (II) ions from aqueous solution by *Nypa fruticans* Shell on batch method. *J. Chem. Pharm. Res.*, **6(12)**, 370-376 **(2014)**

2. Onwu F.K., Abii T.A. and Ogbonna A.C., Kinetic studies on the use of agricultural wastes for the removal of lead, cadmium and nickel ions from aqueous solutions, *J. Chem. Pharm. Res.*, **6(12)**, 471-480 **(2014)**

3. Cordero B., Lodeiro P., Herrero R. and Sastre de Vicente M.E., Biosorption of Cadmium by *Fucus spiralis*, *Environ. Chem.*, **1**, 180-187 **(2004)**

4. Crini G., Recent development of Polysaccharide-based materials used as adsorbent in waste water treatment, *Progress in Polym. Sci.*, **30,** 38-70 **(2005)**

5. Igwe J.C. and Abia A.A., A bioseparation process for removing heavy metals from waste water using biosorbents. *African Journal of Biotechnol.*, **5(12)**,1167-1179 **(2006)**

6. Dada A.O., Olalekan A.P., Olatunya A.M. and Dada O., Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn2+ Unto Phosphoric Acid Modified Rice Husk, *IOSR Journal of Applied Chem.*, **3(1)**, 38-45 **(2012)**

7. Volesky B., Detoxification of metal-bearing effluents: biosorption for the next century, *Hydrometallurgy,* **59,** 203–216 **(2001)**

8. Bhattacharya A.K., Mandal S.N. and Das S.K., Adsorption of Zn(II) from aqueous solution by using different adsorbents, *Journal Chem. Eng.,* **123**, 43–51 **(2006)**

9. Krishnan K.A. and Anirudhan T.S., Removal of Cadmium(II) from aqueous solutions by steam-activated sulphurised carbon prepared from sugar-cane bagasse

pith : Kinetics and Equilibrium Studies, *Water SA*, **29(2)**, 147-156 **(2003)**

10. Filipic M., Molecular mechanisms of cadmium induced mutagenicity, *Human Exp. Toxicol.*, **25,** 67-77 **(2006)**

11. Akesson A., Julin B. and Wolk A., Long-term dietary cadmium intake and postmenopausal endometrial cancer incidence: a population-based prospective cohort study, *Cancer Res.*, **68,** 6435-6441 **(2008)**

12. Kumar R., Abraham T.N and Jain S.K., The removal of cadmium ions from aqueous solutions using silica support immobilized with 2-hydroxyacetonephenone-3-thiosemicarbazone, *2nd International Conference on Environmental Science and Development*, **4,** 48-52 **(2011)**

13. Manoj K.G., Sarita S., Ashok K.S. and Sanjay V., Study on removal of arsenic from aqueous solutions by low cost adsorbent, *International Journal of Chem. Stud.*, **2(3)**, 30-35 **(2014)**

14. Horsfall M. Jnr. and Spiff A.I., Equilibrium Sorption Study of Al^{3+}, Co^{2+} and Ag^{+} in Aqueous Solutions by Fluted Pumpkin (*Telfairia Occidentalis* HOOK f) Waste Biomass, *Acta Chim. Slov.,* **52,** 174-181 **(2005)**

15. Malkoc E. and Nuhoglu Y., Determination of kinetic and equilibrium parameters of the batch adsorption of Cr(VI) onto waste acorn of *Quercus ithaburensis*, *Chem. Eng. Proces.,* **46**, 1020-1029 **(2007)**

16. Abia A.A. and Asuquo E.D., Sorption of Pb(II) and Cd(II) ions onto chemically unmodified and modified iol palm fruit fibre adsorbent: Analysis of pseudo second order kinetic models, *Indian Journal of Chem.Technol.*, **15,** 341-348 **(2008)**

17. Onwu, F.K. and Ogah S.P.I., Studies on the effect of pH on the sorption of cadmium(II), Nickel(II), lead(II) and chromium(VI) from aqueous solutions by African white star apple *(Chrysophyllum albidium)* shell. *African Journal of Biotechnol.*, **9(42)**,7086-7093 **(2010)**

18. Igwe O.U. and Okwu D.E., Phytochemical composition and anti-inflammatory activities of *Brachystegia eurycoma* seeds and stem bark, Der Pharma Chemica, **5(1)**, 224-228 **(2013)**

19. Ogbonna A.C., Abii T.A. and Onwu F.K., Equilibrium studies on biosorption of lead, cadmium and nickel ions using cassava waste biomass, *J. Chem. Pharm. Res,* **6(12)**, 418-432 **(2014)**

20. Farghali A.A, Bahgat M., Allah A.E. and Khedr M.H., Adsorption of Pb(II) ions from aqueous solutions using copper oxide nanostructures, *Journal of Basic and Applied Sci.*, **2**, 261-71 **(2013)**

21. Karthikeyan T.S., Rajgopal L.R., Miranda, Chromium(VI) adsorption from aqueous solution by *Hevea Brasilinesis* sawdust activated carbon, *J. Hazard. Mater.*, **B124**, 192–199 **(2005)**

22. Dursun G., Çiçek H. and Dursun A.Y., Adsorption of phenol from aqueous solution by using carbonised beet pulp, *J. Hazard. Mater.*, B125, 175–182

23. Anusiem A.C.I., Onwu F.K and Ogah S.P.I., Adsorption Isotherm Studies of Ni (ll), Cd (ll) and Pb (ll) ions from Aqueous Solutions by African White Star Apple (*Chrysophyllum albidium*) Shell, *International Journal of Chem.*, **20(4)**, 265-274 **(2005)**

24. Chengwen S., Shuaihua W., Murong C., Ping T., Mihua S. and Guangrui G., Adsorption Studies of Coconut Shell Carbons Prepared by KOH Activation for Removal of Lead(II) From Aqueous Solutions, *Sustainability*, **6,** 86-98 **(2014)**