ADSORPTION OF PB(II) BY MODIFIED AND ACTIVATED CARBON PREPARED FROM Deniella oliveri STEM BARK

G. B. Adebayo*, H. I. Adegoke and F. Sidiq Department of Chemistry, University of Ilorin, Ilorin, Nigeria Accepted:30/03/2016 *Corresponding Author: adebayochem@gmail.com

Abstract

Deniella oliveri stem bark was modified using citric acid and activated chemically in the Laboratory. The samples were characterized by physico-chemical and spectroscopic methods. The physico-chemical methods used include ash content, point of zero charge, pH, moisturecontent, bulk density, volatile component and iodine value while the spectroscopic methods used are X-ray fluorescence (XRF) and Scanning Electron microscopy. The prepared adsorbents were employed in adsorption of Pb(II) ion from aqueous solution and influence of some physicochemical parameters on the adsorption process were also investigated. The adsorption data fitted the Langmuir adsorption data better than the Freundlich isotherm with correlation coefficients of 0.988 and the result of kinetics studies revealed that the data followed the pseudo-second order best which implies that the adsorption process is a chemical process. The result of this study revealed that citric acid modified bark stem has a higher adsorption capacity when compared with the activated one.

Key words: Deniella oliveri; Adsorption; Adsorption isotherm; Pollution, Heavy metals; Lead(II) ions

Introduction

In recent years, heavy metal ions discharged from industrial effluent have caused major environmental pollution problem to man especially in the developing countries like Nigeria [1]. These metal ions are known to accumulate in body system once they are introduced from a very low level to a level that are unbearable because they can cause oxidative stress by formation of free radical and cannot be detoxified by metabolic activities of the body. They are also known as common groundwater contaminants at industrial and military installation. During the last few years, increasing attention has been focused on the expiration, pre-concentration and determination of trace metal ions in the environment. This field of interest is becoming a real challenge due to the specificity, accuracy and sensitivity required by more and more stringent regulation [2]. Numerous techniques are available in this concern and have been reported [3]. These techniques include chemical precipitation, ion-exchange [4], reverse osmosis, electro-deposition, solvent extraction, use of adsorbent [5], and phyto-extraction. Adsorption process has been proven to be an effective technique among these methods.

In developing countries, the pollution control needs to be based on lower-cost technologies. Adsorbent prepared from agricultural waste are unique and versatile adsorbents because of their extended surface area, micro-porous structure, high adsorption capacity and high degree of surface reactivity [6,7]. They find their wide applications in the removal of color, odour, taste and other undesirable organic and inorganic impurities from different aqueous media [8]. Moreover, they are usually considered to be the adsorbents against which others are assessed [8]. Gueu *et al* [9] investigated the kinetics and thermodynamic of the batch adsorption of lead onto activated carbon from coconut and seed hull (CA) and (GA) of a palm tree. Maximum adsorption capacity of lead ion obtain were 4.38 and 3.77mL/g. for CA and GA at 60°C at pH 4.0. Gilbert et al [10] used defatted *Carica papaya* seeds, an agricultural waste in Nigeria as a biosorbent for the removal of Pb (II) and Cd (II) ions from aqueous solution, from their investigation, the adsorption data of metal ion fitted Freundlich Isotherm better than Langmuir with adsorption capacity of 1666.67mg/g for Pb^{2+.}

Despite the prolific use of activated carbon in water and waste water industries, it remains an expensive material. In view of the high cost and tedious procedures for the preparation and regeneration of activated carbons, there is continuing search for lowcost potential adsorbents.

Accordingly, this investigation is aimed at establishing a selective, rapid and simple procedure for the removal of lead ions from aqueous solution using citric acid stem bark of Deniella oliveri and its activated carbon. Deniella oliveri is commonly called African Copaiba balsam tree, it is a slow growing deciduous tree with a flat-topped, spreading dense crown usually growing 9-25 metres tall but with occasional specimens as tall as 45 metres. It is readily available, inexpensive and can serve as an alternative adsorbent to the existing, commercial absorbent. The metal of interest, Pb (II) is chosen based on its industrial applications and pollution impact on the environment.

Material and Methods

The stem bark of *Deniella oliveri* tree (Fig a) was collected from University of Ilorin campus, Kwara State, Nigeria. It was washed with deionized water and air dried for six days.All reagents used were of

analytical grade and were used as supplied without further purification.



Fig a: Daniella Oliveri Tree

Preparation of Modified Sample

The dried tree bark was pulverized and sieved using sieves of mesh sizes 0.42 - 0.3 mm.

A 100 g of sample was soaked in 400 ml of excess 0.3 M citric acid for 24hrs at room temperature. The air dried biomass of modified tree bark was severally washed with deionized water to remove excess citric acid until the pH of the filtrate was 7.0 (neutral) [11]. The residue was air-dried, labeled as MA and kept in a tight container.

Preparation of Activated carbon

The preparation of sample was carried out in two stages. The sample was carbonized in a muffle furnace (Carbolite R336RB) at 400°C

The raw material was weighed into a crucible and then placed in the muffle furnace. The sample was carbonized at the temperature of 400°C for 3hrs; the pyrolysed sample was activated using orthophosphoric acid [12]. The char sample was mixed with 75% concentrated orthophosphoric acid in a beaker with the weight ratio of H_3PO_4 /char to be 1.0. The slurry was evaporated at 60°C for 24hrs and a dried mixture consisting of activated char and H₃PO₄ was obtained and washed to a neutral pH [12, 13].

The sample was then poured into a beaker containing 250ml of 0.1M HCl, stirred for 1hr and finally rinsed to pH 6-7 for purification [12, 14]. The residue was air-dried, labeled as AC and kept in a tight container for characterization and application.

Characterization of Adsorbents

The samples were characterized by physico-chemical and spectroscopic methods.

pH Determination

In this research a one gram of the sample each was boiled gently in a beaker containing 100 mL of deionized H₂O for 5 min, it was then diluted to 250 mL and cooled. The pH was taken with a pH meter (pHS-25 model).

Iodine Number

Half gram of the sample was added to 20 mL of 5% by weight of HCl and boiled. After cooling to room temperature 100 mL of 0.1N Iodine solution was added. The content was shaken vigorously and filtered. 25mL of the filtrate was titrated with 0.1N Sodium thiosulphate in the presence of starch as indicator [15]. The iodine number was calculated using the formula:

(1)

(2)

Iodine No=
$$\frac{12.69 (B-A)}{W}$$

B- Volume of blank

A – Volume adsorbed

w - Weight of sample used

Ash Content

An empty dry crucible was weighed and 0.5g of sample was weighed into it. The crucible was placed in a furnace at 500°C for 2 hours. It was cooled in a desiccator and weighed [15].

$$\% \Delta sh - \frac{W_3 - W_1}{V_1} \times 100$$

 $\% \text{Ash} = \frac{W_3 - W_1}{W_2 - W_1} \times 100\%$

w₁ – Weight of empty crucible

- w₂ Weight of crucible and sample before ashing
- w₃ Weight of crucible and sample after ashing

Moisture content

The weight of dry empty crucible was taken and 0.5 g of sample was added to it. The crucible was placed in the oven at a temperature of 105°C until a constant weight was obtained. The content was cooled in desiccator and reweighed.

% moisture Content =
$$\frac{W_2 - W_3}{W_2 - W_1} \times 100\%$$
 (3)
w₁ - weight of dry crucible

 w_2 - weight of crucible + sample before drying

w₃ - weight of crucible + remaining sample after drying

Volatile Component

A dry crucible is weighed, 1g of sample is added and the total weight was noted. The crucible was placed in the furnace at 100°C for 20 minutes; it was then cooled and reweighed. At every 20 min interval, the furnace temperature was increased with 100°C and weighed. The procedure was repeated until a temperature of 500°C was reached [16].

Bulk Density

Bulk density of the modified sample and the activated sample was determined gravimetrically; an empty 10 ml measuring cylinder was weighed (w1) and then filled with water to determine its exact volume (v). The bottle was empty, dried and then filled with the sample followed by tapping to ensure compactness and reweighed (w_2) . The bulk density is given by the ratio of difference in masses to the volume of the bottle [15].

Bulk Density = $\frac{W_2 - W_1}{T}$ (4)

Point of Zero Charge (Potentiometric-Mass **Titration Method**)

Two solutions were prepared by mixing 30mL of 0.1M KNO₃ and 10mL of 0.01M HNO₃ in each of two beakers and the pH of the two solutions was measured. The first solution was tagged blank and the

other solution containing 0.5g of sample was called sample solution. The two solutions were titrated against 0.01M NaOH and the resulting pH was recorded at every 0.5mL addition of the titrant till the equivalence point was reached. The results of both titrations were plotted on the same graph and the point of intersection is the point of zero charge [15].

Spectroscopic Methods of Characterization

Scanning Electron microscopy (SEM) was carried out on both adsorbents to reveal their surface morphology. X-ray Fluorescence (XRF) analysis was also carried out on the sample to reveal their elemental composition.

Adsorption Experiment

Preparation of the stock solution of the Lead (II) ion

 $Pb(NO_3)_2$ salt (1.598 g) was weighed, dissolved in de-ionized water and made up to 1000ml mark of the standard flask to make 1000ppm of Pb(II) stock solution. The standard solutions were prepared by serial dilution. 1.25, 2.5, 3.75, 5.0, 6.25 and 7.5 mL of Pb(II) stock solution was measured into 250 mL standard flask and making it up to the mark with de-ionized water to give 5,10,15,20,25 and 30ppm respectively.

Batch Adsorption Studies

Batch experiments were conducted to investigate the adsorption capacity of the samples (modified and activated *Deniella oliveri* tree bark) on the adsorption of Pb(II) ions from aqueous solution. The initial concentration of metal ion and corresponding concentrations after adsorption were measured by atomic adsorption spectrophotometer (2380 UNICAM AAS). The metal concentration retained in the adsorbent phase (Q_e , ppm) was calculated by using the following equation [17].

$$Q_e = \frac{v(c\bar{l} - c\bar{f})}{s} \times 10^{-3}$$
 (5)

Where v = volume of solution (ml), s = amount of dry adsorbent/substrate (g), c_i = initial metal concentration (ppm), c_f = final metal concentration (ppm) and Q_e -amount absorbed.

% Adsorption =
$$\frac{cf-ci}{ci} \times 100$$
 (6)

The influence of some physico-chemical parameters on adsorption were also investigated.

Effect of Adsorbate concentration

Prepared solutions of 25 mL capacity with concentrations 5, 10, 15, 20, 25 and 30 ppm were measured into 100 mL capacity conical flask, 0.2 g of the adsorbent was added into each and agitated using anorbital shaker for 2hrs. At the end of the time the mixtures in the flask were filtered and analyzed using Atomic Adsorption Spectrophotometer (2380 UNICAM AAS)

Effect of Contact Time

Solution of 25mL capacity with the equilibrium concentration (20 ppm) was transferred into 6 different conical flasks, covered and labeled. 0.2 g each of the adsorbent was weighed into the 6 different

labeled flasks, agitated at 25° C on an orbital shaker for different contact times (30, 60, 90,120, 150 and 180mins). After each agitated time, the mixture in each flask was filtered and the filtrate was analyzed by Atomic Adsorption Spectrophotometer (2380 UNICAM AAS).

Effect of pH

Solution of 25 mL capacity with the equilibrium concentration (20 ppm) Pb (II) solution was pipetted into 8 different 100ml capacity conical flask and the initial pH measured. The initial pH in each flask was varied between 2 and 9 by the addition of 0.1M HNO₃ and 0.1M NaOH solution. 0.2g adsorbent was added and the mixture was equilibrated for 2hrs. After equilibration the mixture was filtered and the filtrate was analyzed by Atomic Adsorption Spectrophotometer (2380 UNICAM AAS).

Effect of Ionic Strength

Adsorbent sample of 0.2 g was weighed into 5mL of six different concentrations of KNO_3 solution (0.001, 0.005, 0.01, 0.05, 0.1, 0.2M) in a conical flask, 20ml of 20 mg/L Pb (II) solution was added to each and equilibrated for 2 hours. After equilibration the mixture was filtered and the filtrate was analyzed using Atomic Adsorption Spectrophotometer (2380 UNICAM AAS).

Adsorption Isotherm

The adsorption capacity data was fitted by Langmuir and Freundlich isotherms

Langmuir:
$$Qe = \frac{1}{bQ_{max}C_f} + \frac{1}{Q_{max}}$$
 (7)

Freundlich:

$$log Q_e = \log K_f + n log C_f \tag{8}$$

Where Q_e is quantity adsorbed at equilibrium (ppm), b is constant related to the energy of adsorption. Q_{max} is the mass of adsorbed solute completely required to saturate a unit mass of adsorbent (ppm) and C_f is the concentration of adsorbate after adsorption [17].

Adsorption Kinetics

Kinetic models were used to examine the rate of the adsorption process and potential rate controlling step. In this study the kinetic data obtained from batch studies was analyzed by pseudo-second order. The pseudo-second order kinetics rate equation is expressed as follows [6]:

$$\frac{dq}{dt} = K_2 (q_e - q)^2 \tag{9}$$

 k_2 is the rate constant of pseudo-second-order adsorption (g mg⁻¹). The integration of the equation above gives

$$\frac{t}{q} = \frac{1}{k_2 q_{e^2}} + \frac{1}{qe} t$$
(10)

The second order kinetic equation is applicable when the plot of t/q against t from equation (6) gives a linear relationship. The q_e and k_2 can be determined from the slope and intercept of the plot.

Results and Discussion

The physical properties of the prepared samples are shown in Table 1 below:

	Modified	Activated	
	adsorbent	carbon	
Particlesize(mm)	0.43	0.6	
pН	6.7	6.9	
Moisture	17.03	20.4	
Content (%)			
Ash content (%)	28.6	31.7	
Bulk	0.468	0.429	
Density(g/cm ³)			
Iodine value	275.88	104.06	
Point of zero	8.4	7.6	
charge(PZC)			
Volatile	78.0	69.3	
Component (%)			

$1 a D C 1^{-1} I I \gamma S C a D D C I C S O I a U S O D C I C S$	Table 1- Physical	properties	of adsorbents
---	-------------------	------------	---------------

Table 1 above shows the range of particle size of the adsorbent to be 0.43mm – 0.60mm. The range of particle sizes of adsorbent is important. The finer the particles size of absorbent, the better the access to the surface area and the faster the rate of adsorption processes. The rate of adsorption has been shown to depend inversely upon the particle size (small particle having the fastest rates) [18]. From the table the modified sample (0.43mm) will have a higher rate of adsorption than the activated carbon sample (0.6mm) due to it lower particle size as found in literature [18] and will have a higher surface area for adsorption.

Ash reduces the overall activity of adsorbent; it reduces the efficiency of reactivation. The ash content of the adsorbent from Table1 shows the presence of high ash content in activated carbon (31.7%) produced from *Deniella oliveri* than that of the modified sample (28.6%), and consequently will have lesser activity than that of the modified sample. This is inconsistent with literature value for some agricultural waste where ash content is found to be lower than that of this study [3, 12, 19].

Iodine number is the most fundamental parameter used to characterize activated carbon performance. It is a measure of activity level (higher number indicates higher degree of activation), often reported in mg/g. It is a measure of the micropore volume of the activated carbon (0 to 20 Å, or up to 2 nm) by adsorption of iodine from solution. It is equivalent to surface area of carbon between 900m²/g and 1100 m²/g. From the table above, it can be shown that the modified sample with the higher iodine number of (275.88) may have higher activity level and higher degree of micropore than that of activated carbon (104.06) because it has the higher iodine number. These values are lower than those found in literature for some adsorbents [19,20].

From Figure 1, the pHpzc is between 7 and 8.5 for both adsorbents. The chemical modification of the adsorbent surface with citric acid shows a higher point of zero charge than that of the activated carbon; therefore the activated carbon will readily undergo cationic adsorption than the modified sample. It has been reported that cations adsorption on any adsorbent will be favourable at pH value higher than the pH_{pzc}, while anions adsorption will be favoured at pH values lower than their adsorbent pH_{pzc}[21].



Figure 1: Point of Zero charge curve for Modified sample and Activated carbon.

The X-Ray Fluorescence (XRF) result as presented in Table 2 show the presence of 6 elements for MA and 10 elements for AC. There is the absence of Pb (II) on both adsorbent which makes them acceptable for the adsorption of Pb (II).

showed the surface The SEM micrographs morphology of both adsorbent at magnification of 100X, 500X and 2.00X. The results are shown below (A1, A2, A3) and (B1, B2, B3) for MA and AC respectively (Figure 2), it was observed that the modified adsorbent produced a greater pore structure and networking in all the magnified sizes (that is, open pore structure which is ideal for the adsorption of large quantity of molecules) than the activated carbon. This implies that the modified adsorbent will adsorb more adsorbate than the activated carbon. This is inconsistent with other literature reports where the activated carbon has higher pore structure and networking [12].

 Table 2: XRF Result for Modified adsorbent (MA)

 and Activated Carbon (AC)

Element	MA(ppm)	AC(ppm)
Р	1300±0	-
Cl	414±0	-
K	4854±223	1110±59
Ca	5.2103±0.0708	2407±68
Fe	500±26	78±4
Zn	1246±34	41±1
V	-	7±2
Cr	-	26±4
Mn	-	74±4
Se	-	2±0
Sr	-	18±3
Br	-	1.0±0



Figure 2: SEM micrographs showing the surface morphology of adsorbents MA and AC at magnification of 100X, 500X and 2.00X respectively.

Adsorption capacity of the adsorbents

The adsorption capacity of both adsorbents for Pb (II) is as shown in Fig.2. The amount of adsorbents used for all samples was constant (0.2g). The initial concentrations of Pb (II) were varied and volume kept



Figure. 3: Adsorption Capacity Curve for Modified adsorbent and Activated carbon

constant. It could be observed from the Fig. 3 that the adsorption of Pb (II) on the adsorbents increases steadily up to a maximum of 0.723 Pb/g activated carbon and 0.724 Pb/g modified sample at the same equilibrium concentration of 20mg/L.

Adsorption Isotherm for AC and MA

Adsorption isotherms of Pb on both adsorbent were investigated at an initial Pb (II) concentration of 20mg/L and adsorbent mass of 0.2g. The experimental data obtained (Table 3) were fitted to linearized form of Langmuir (as in equation 3) and Freundlich Isotherm (as in equation 4) for both modified adsorbent and the activated carbon respectively.

-									
	C_{f}	$1/C_{\rm f}$	Log C _f	$Q_1(MA)$	$Q_2(AC)$	1/Q1	1/Q ₂	LogQ ₁	LogQ
1.	4.926	0.203	0.692	0.125	0.130	8.000	7.692	-0.903	-0.886
2.	9.748	0.103	0.989	0.278	0.265	3.597	3.774	-0.642	-0.577
3.	14.895	0.067	1.173	0.375	0.315	2.667	2.692	-0.426	-0.429
4.	19.997	0.050	1.301	0.724	0.723	1.380	1.383	-0.140	-0.141
5.	25.001	0.040	1.398	0.637	0.510	1.569	1.960	-0.195	-0.292

Table 3: Experimental data for the adsorption isotherms of both adsorbents

The plot of the data in Table 3 for Langmuir and Freundlich isotherms give the correlation coefficient $R^2 = (MA-0.988 \text{ and } AC-0.980)$ and $R^2 = (MA-0.953 \text{ and } AC-0.956)$ respectively indicating the level of fitness of the isotherms to the experimental data, with the Langmuir of the two adsorbents revealed higher

level fitness than Freundlich(Table 4). The result shows that both adsorbent can be model by both Langmuir and Freundlich isotherm which indicate that the coverage of the sorption site was in the form of monolayer coverage.

Parameter	b(L/mg)	Qmax	\mathbb{R}^2	
Langmuir Isotherm(MA)	0.00769	3.205	0.988	
Langmuir Isotherm(AC)	0.00072	3.704	0.980	
	K _f	n	1/n	\mathbb{R}^2
Freundlich Isotherm(MA)	0.225	1.108	0.902	0.953
Freundlich Isotherm(AC)	0.210	1.050	0.952	0.956

Table 4: Linearized Langmuir and Freundlich Model parameters

From the results in Table 4, the parameter b estimated from Langmuir isotherm can be used to indicate the isotherm shape. According to McKay and Ho [6], if b >1, isotherm is unfavourable, b=1, isotherm is linear, 0 < b < 1, isotherm is favourable and b=0, then isotherm is irreversible. In this study, both b were found between 0 and 1 indicating both adsorbents produced from *Deniella oliveri* as a good adsorbent for lead (II) ion [22].

The parameter K_f estimated from the Freundlich isotherm can be used to indicate the relative adsorption capacity of the system, high value of K suggest that adsorption capacity of the adsorbent is high. n indicate whether the nature of adsorption is either favourable or unfavourable. Since all n constants are > 1 in this study, it is indicative of gradual decrease in sites available for adsorption as concentration of the lead ion in solution is increased, that is adsorption of new molecules would occur with greater difficulty. This signifies that the surface of both adsorbent prepared from Deniella oliveri stem bark is heterogeneous. Low 1/n values (<1) suggested that any large change in the equilibrium concentration of lead ion would result in a marked change in the amount of lead adsorbed [23].

In this study, the 1/n value is high indicating that change in equilibrium concentration of Pb (II) will have effect on amount adsorbed on both adsorbents. This result is consistent with previously published data [23], where adsorption of Pb (II) on different substrate (e.g. hematite, gibbsite, natural adsorbent, activated carbon, modified agricultural waste) also followed Langmuir isotherm [9, 22].

Influence of time on the adsorption of Pb (II) on both adsorbent

The data obtained for the effect of time on adsorption of Pb (II) on both adsorbent at an initial concentration of 20 mg/L are illustrated in Fig.5 below. The results show that Pb (II) adsorption on both adsorbent increased with increase in contact time and the sorption equilibrium is reached at 120 mins for both modified and activated carbon sample.



Fig.4: Effect of contact time of Pb(II) adsorption on Modified adsorbent and Activated carbon

The experimental data were analyzed according to the Pseudo-second-order rate equation [24]. Fig. 6a and Fig. 6b shows the pseudo second order plot for both modified adsorbent and activated carbon respectively.



adsorption on Modified sample

for Pb(II)



Fig.6: Pseudo-second-order plot for Pb(II) adsorption on Activated carbon.

A linear relationship was obtained for both adsorbents with good correlation in theoretical and experimental values. The correlation coefficient R^2 values of both adsorbents were higher than 0.9 (Figures 5 and 6) and the theoretical values (MA q_{cal} 0.724 and AC q_{cal} 0.723) were closer to the experimental values MA q_{exp} 0.732 and AC q_{exp} 0.729) as estimated from the plots. In view of this result, it can be said that the pseudo-second order kinetic model provided a good correlation for the adsorption of Pb (II) onto both modified adsorbent and activated carbon [24].

Influence of pH on sorption of Pb(II) on both adsorbent

The effect of pH on Pb (II) adsorption on the modified adsorbent and the activated carbon prepared from the stem bark of *Deniella oliveri* were studied at an initial pH range of 2-9 for 2 hrs contact time and Pb (II) initial concentration of 20mg/L.

For the modified sample, sorption increased with pH up to a maximum of 0.724mg/L which correspond to pH of 7.0, after which sorption decrease with increase

in pH. Similarly, for the activated carbon sample sorption increased with pH up to a maximum of 0.723mg/L which correspond to pH of 7.0 after which adsorption also decrease with pH. The results showed that pH had significant effect on sorption of Pb (II) on both adsorbent. The pH effect on Pb (II) sorption are generally related to the point of zero charge (pzc) of both MA and AC. Point of zero charge of a surface influence the adsorption of Pb (II) on the adsorbents, as well as electrostatic repulsive forces between them. Above the pzc values, both adsorbent have a net negative surface charge (anionic) and will have high affinity for Lead (II) ions and below the pzc value activated carbon has a net positive surface charge (cationic) and will exchange anions [21].

Influence of ionic strength on the adsorption of Pb (II) on both adsorbent

Adsorption of Pb (II) on absorbents was investigated at different concentration of background electrolyte and Pb (II) initial concentration of 20mg/g. The results obtained for both modified and activated adsorbent indicated that Pb (II) adsorption on both adsorbents is dependent on ionic strength of the background electrolyte. The adsorption capacity increased linearly to the optimum at 0.05M KNO₃ in both modified adsorbent and activated carbon, after which there was no significant changes with increase in the ionic strength.

Conclusion

This study showed that a good adsorbent for the removal of Pb (II) from aqueous solution can be obtained from modified adsorbent and activated carbon produced from Deniella oliveri stem bark. The modified sample is more efficient in the adsorption or removal of Pb(II) ion than the activated carbon produced from it. It also showed that Pb (II) adsorption increases with time and equilibrium is reached within 120 mins. The pH had a great impact on adsorption of Pb (II) ion by activated and modified adsorbents with maximum quantity adsorbed at pH 7-8. The experimental data fitted Langmuir isotherm which indicate monolayer coverage. It can be concluded that the adsorption of Pb (II) on adsorbent is dependent on pH, contact time and initial concentration of Pb (II) solution. Deniella oliveri is inexpensive and readily available, thus this study provides cost effective means of removing metal ions from aqueous solution. The pseudo-second order kinetic model was found to provide a better correlation for the adsorption data which shows that the reaction process is chemisorption.

References

- J. M.Okuo (2006). Removal of heavy metal ions by blending periwinkle shells. J. Applied Sci., 6:567-571.
- P. Van Den Brandt, L. Voorrips, I. Hertz-Picciotto, L. Shuker, H. Boeing, G. Speijers, C. Guittard, M. Knowles, A. Wolk and A.

Goldbohm (2002). The contribution of epidemiology. Food Chem. Toxicol. 40 (2-3): 387-424.

- 3. S.E. Ghazy and S.M. El-morsy (2009). Sorption of Lead from aqueous solution by modified activated carbo prepared from olive stone. African Journal of Biotechnology. 8(17), 4140.
- 4. S.H. Tabatabaei and A. Liaghat (2004). Use of zeolite to control heavy metals in municipal wastewater applied for irrigation. Japanese journal Ion Exchange, 15(2), 62.
- 5. J. W.Paterson (1975). Waste water treatment technology. Mich: Ann Arbor Science Publishers, p.265.
- 6. V.S.Ho and G. Mckay (1998). The kinetic of sorption of basic dyes from aqueous solution by 76(4): 822-827.
- S. E. Samra (2000). Removal of Ni²⁺ and Cu²⁺ ions from aqueous solution onto lignite based carbons. Adsorp. Sci. Technol. 18(9): 761-765.
- D. C.Sharma and C. F. Forster (1996). Removal of hexavalent chromium from aqueous solutions by granular activated carbon. Water SA 22(2): 153-160
- 9. S.Gueu, B. Yeo, K. Adouby and G. Ado (2007). Kinetics and thermodynamic study of lead adsorption onto activated carbon from coconut and seed hull of the palm tree. Int. J. Environ Science. 4(1), 11.
- U.A.Gilbert, I.A. Emmanuel, A.A. Adebanjo and G.A. Olalere (2011). Biosorptive removal of Pb²⁺ and Cd²⁺ onto novel biosorbent: Defatted Carica Papaya seeds. Biomass and Bioenergy. 37(7), 2517-2525.
- G.James, D. A. Sabatini , C.T. Chiou, , D. Rutherford, , A.C. Scott , H.K. Karapanagoiti (2005). Evaluating Pheranthrene Sorption on various wood chars. Water research, 39(4): 549-558.
- 12. S.Viboon and A. Duangduen (2007). Thermal degradation and kinetics characterizations of jatropha waste under isothermal ad dynamic experiments. Materials Science Forum 561-565.
- M.A. Lilo-Rodenas, A.D. Cazorta, and S.A. Linares (2003). Understanding chemical reactions between Carbons and NaOH. An insight into the chemical activation mechanism. Carbon, 41, 267.
- 14. R. M. Strinivasa, S. Basha, H. Y.Joshi and B. Jha (2005). Evaluation of the emission characteristics of trace metals from coal and oil fined power plants and their during combustion. J. Hazard, matter. 123 (1-3), 242.
- American standard of Testing Materials. Standard test method for bulk density of activated carbon. Annual book of ASTM standards, D 2866, pp.94, pp.498-499D 4607, pp.542, D 1762, pp. 84.
- 16. International standards organisation. Determination of volatile matter content. Iso 56 2-1981.
- 17. S. Al-deqsy, M.I. El-barhouthi, A.A. Issa, M.A.

Khaisheh and G.M.Walker (2006). Sorption of Zn(II), Pb(II) and Co(II) using natural sorbents: Equilibrium And Kinetic Studies Water Research 40, 2645.

- 18. M. D. Sasanka, A. Akhtarul, S. Rajat , J. Sankar, and G. Nikhil (2009). An efficient size-selective anion binding cleft shaped receptor; A novel $[F_2(H_2O)_3]^2$ - cluster with pseudo-encapsulated Fion. Cryst. Eng. Comm. 14, 1527-1530.
- S.Mopoung and W. Nogklai (2008) Chemical and Surface Properties of longan seed activated . International Journal of Physical Sciences, 3 (10), 234-239.
- 20. K.Hwa-Young, P. Sang-Sook and R. Yu-Sup (2006). Preparation of activated carbon from paper mill sludge by KOH-activation. Korean J. Chem. Eng., 23(6), 948.

- 21. S. M.Nomanbhay and K. Palanisamy (2005). Removal of heavy metal from industrial waste water using chitosan coated oil palm shell charcoal. Electronic Journal of Biotechnology, 8(1), 43-53.
- 22. K. Jian, H. C. Joshi, S.C. Dutta, K. Saojeev and H. Pathak (2008). Biosorption of copper from waste water using Jatropha Seed Coat. Journal of Science and Industrial Research. 67, 154.
- 23. F. H. Frimmel and L. Huber (1996). Influence of Humid Substances on the aquatic sorption of heavy metal on defined minerals phases. *Environmental International*, 22 (5), 507- 517.
- 24. M.T.Uddin, M.S. Islam and M.Z. Abedin (2007). Adsorption of phenol from aqueous solution by water hyacinth ash. Journal of Engineering and Applied Science. 2(2), 11-14.