KINETIC AND THERMODYNAMIC STUDY OF AQUEOUS ADSORPTION OF CD^{2+} AND PB^{2+} IONS ON ACTIVATED CARBON FROM *Nymphaea ampla* (Water Lily) ROOTS

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Abstract: Activated carbon prepared from *Nymphaea ampla* roots by chemical activation using ZnCl$_2$ was used for removal of Cd^{2+} and Pb^{2+} ions from aqueous solutions. The adsorbent samples were characterized for some physicochemical parameters. FTIR spectroscopic analysis was also carried out for functional group characterization. The percentage carbon yield and pH of the aqueous suspension of the sample was found to be 30.0±0.2% and 6.4±0.1, respectively. Its percent burn off, attrition, bulk density, iodine number surface area and normal moisture content were 6.3±0.2%, 14%, 260±1.0 kg/m^3, 335.02 mg/g, 254.4 m^2/g and 5%, respectively. The FTIR results indicated that –OH, –NH, C=N and –COO$^-$ were candidate functional groups responsible for the binding of metal ions, with high removal efficiency of 91.3% and 88.8% for Cd^{2+} and Pb^{2+} ions, respectively. The kinetic data fitted better to pseudo-second order with good correlation and low sum of error squares (SSE) compared to pseudo-first order kinetics for the adsorption of both metal ions. Thermodynamic experiments indicated that the adsorption process was feasible, spontaneous and exothermic. The results indicated that the adsorbent can be used as an effective and low-cost material for the removal of toxic metal ions from aqueous media like industrial effluents.

Keywords: *Nymphaea ampla*, cadmium, lead, adsorption isotherm, thermodynamic, AAS

Introduction

Heavy metal pollution is one of the major environmental concerns today because of their toxicity, threat to human life and the environment. They can accumulate in living tissues causing various diseases and disorders (Okafor *et al*., 2015). Many industrial processes, such as mining, refining ores, fertilizer industries, tanneries, photography, surface finishing, energy and fuel producing, steel, battery manufacturing, paper industries etc, result in the release of heavy metals to aquatic ecosystems (Achanai *et al*., 2012). Their presence in receiving lakes and streams could lead to bioaccumulation in living organisms leading to several health problems such as cancer, reduced mental and central nervous function (Karatas, 2011; Ozdes *et al*., 2009). The removal of these metals by sorption from rivers and wastewaters is important in order protect public health and the balance in ecosystems.

Conventional methods of removing toxic metals include chemical precipitation, membrane filtration, ion exchange, reverse osmosis, liquid extraction or electro-dialysis (Kumar *et al*., 2012). However, these processes have considerable disadvantages including incomplete metal removal especially at low concentrations, requirement of expensive equipment and monitoring systems, large reagent or energy requirements and generation of toxic sludge or other waste products that require disposal. Therefore, the search for new technologies for the removal of toxic metals from aqueous media has been directed towards adsorption systems as a cost-effective and eco-friendly technique used in wastewater treatment over the last few decades (Egila *et al*., 2011).

Adsorption on activated carbon has been found to be an effective process for removal of toxic metal ions, but commercial activated carbon is rather expensive. Consequently, numerous low cost biomass materials have been used to produce activated carbon (Abbas *et al*., 2013). Bernard and Jimoh (2013) investigated the removal efficiency of heavy metals (Pb, Fe, Cu and Zn) from electroplating industrial wastewater using activated carbon produced from orange peel (AOP). The results showed that the adsorption of the metal ions was dependent on contact time, adsorbent dosage and pH of the solution. The optimum contact time, adsorbent dosage and pH were found to be 60 min, 1 g and pH 6, respectively. Misihairabgwi *et al*. (2014) studied the adsorption of heavy metals (Pb, Zn, Cu, Ni, Fe, Mn, Hg, Cr, As and Cd) from aqueous solutions using activated carbons prepared from Macadamia nut shells, Baobab shells, Pigeon pea husks, Rice husks, *Moringa oleifera* husks and Marula stones. They concluded that carbons derived from Pigeon pea husks and Baobab shells showed better metal ion adsorption compared to other carbons. Budinova *et al*. (2008) investigated the removal of As(III) and Mn(II) from aqueous solutions using activated carbons from bean pods waste. They concluded that As(III) and Mn(II) adsorption capacities on the carbon obtained from agricultural waste was found to be higher than the commercial activated carbons reported in the literature. The adsorption of Pb(II) ions from aqueous solutions using activated carbon prepared from stems and leaves of dried water hyacinth was reported by El-wakil *et al*. (2014). Kinetic results revealed that the adsorption process obeyed the pseudo-second order model and intra-particle diffusion was the rate controlling step. Thermodynamic studies revealed that the adsorption was a spontaneous and endothermic process. Bernard *et al*. (2013) studied Cu(II), Fe(II), Zn(II) and Pb(II) ions removal from industrial wastewater using carbon produced from coconut shell (ACS). The results showed that, the adsorption of the metal ions was dependent on adsorbent dosage, contact time, pH and stirring rate. Kinetic studies showed that pseudo-second order reaction model best described the adsorption process. Also, the adsorption of Cr(III) onto the leaf biomass of *Calotropis procera* was reported by Overah (2011) to be a rapid process reaching equilibrium within 10 minutes at an optimum pH 5. Thermodynamic studies revealed negative value of change in free energy, ΔG^o (- 4.046 kJ/mol) as an indicator of feasibility and spontaneity of the Cr(III) bio-sorption process. A positive value of enthalpy, ΔH^o (26.099 kJ/mol) was obtained which indicated the endothermic nature of the biosorption process.

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Water lily, *Nymphaea ampla*, an aquatic hydrophyte can grow in almost any environment and is frequently found along the edges of ponds, lakes and streams (Burghardt, 2008). In this study, the potential of activated carbon prepared from *N. ampla* roots as a low-cost adsorbent for the removal of heavy metals specifically, Cd^{2+} and Pb^{2+} ions from aqueous solutions was investigated.

Materials and Methods

Reagents
All the chemicals used were of reagent grade and these include, lead (II) nitrate ($Pb(NO_3)_2$, purity: 98.5%), cadmium (II) nitrate (($Cd(NO_3)_2$. $4H_2O$, purity: 98%), zinc chloride ($ZnCl_2$, purity: 98%), sodium hydroxide (NaOH, purity: 98%), nitric acid (HNO_3, purity: 71%) BDH Chemicals Limited England, and distilled water.

Equipments
Instruments used include, pH meter (HI-96107), atomic absorption spectrophotometer (Thermo scientific 3000 series), weighing balance (HC-D), Labscience programmable muffle furnace (model Sx-4), air drying oven (memmert BE-200), water-bath (HH-4), mechanical shaker (ZD-2 Multipurpose). Other materials used were routine laboratory resources.

Sampling
The aquatic hydrophyte (*N. ampla)* was hand - harvested in August, 2015 from Laka pond at Farin Gada, Jos (9°55'N, 8°54'E), Nigeria. The *N. ampla* roots were sorted out of the whole sample (leaves and stem), kept in an improvised ice-box and transported to Chemistry Laboratory of University of Agriculture Makurdi, Benue State for sample pre-treatment and further analysis.

Sample preparation
The methods used by Gueu *et al* (2007) were adopted for sample preparation without modification. The roots collected were washed with distilled water, dried to constant weight, ground and sieved with <2 mm aperture sieve. The <2 mm material was then carbonized at 400°C for 15 min. Exactly 100 g of the carbonized material was weighed out and divided into two equal portions. A portion (50 g) was transferred into a beaker where it was impregnated with 100 mL of 1.0M $ZnCl_2$ until the mixture formed a paste. The paste was then transferred into crucible, oven-dried at 105°C, and finally introduced into the muffle furnace and heated at 500°C for 1 hour 30 min. The sample was withdrawn from the furnace and rapidly cooled in ice to assist the sample retain its hardness (attrition) prior to washing. After cooling, the sample was rinsed several times with distilled water until the flushing water presented pH range of between 6 and 7. The wet sample was then dried at 105°C for 24 h. The final product was kept in an air-tight plastic container as activated carbon prepared from *N. ampla* roots (coded NAAC). The whole process of carbonization was repeated in duplicate.

Plate 1: Dried *N. ampla* roots (a) and *N. ampla* roots activated carbon (b)

Physicochemical characterization
The activated carbon yield, pH, percentage burn off, attrition, moisture content, bulk density, pore volume and iodine number/surface area were determined using the methods described by Wuana *et al.* (2009) and Okafor *et al.* (2015) without modification. The FTIR and SEM analyses were conducted in Ahmadu Bello University, Zaria, Kaduna State using the methods described by Ketcha *et al.* (2012). The effects of initial metal ion concentration, pH and agitation time on Cd^{2+} and Pb^{2+} ions adsorption onto NAAC were determined by the methods described by Bernard *et al.* (2013). The adsorption kinetics was determined by the method described by Bernard and Jimoh (2013), by measuring adsorptive uptake of metal ions from aqueous solution at different time intervals from 10 to 90 minutes. Kinetic data were fitted using Lagergren pseudo-first order model (Lagergren, 1898), a pseudo-second order model (Blanchard *et al*., 1984) and an intra-particle diffusion model (Weber and Morris, 1963) to investigate the mechanism of adsorption and potential rate controlling steps such as mass transport and chemical reaction processes. The pseudo-first order Lagergren equation is given as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (1)$$

while the pseudo-second order equation is,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2)$$

where q_e (mg/g) is the mass of metal adsorbed at equilibrium, q_t (mg/g) the mass of metal adsorbed at time t, k_1 is the pseudo-first order rate constant of adsorption (min^{-1}) and k_2 is the pseudo-second order rate constant of adsorption (mg/g.min). The intra-particle diffusion equation can be written as follows:

$$q_t = K_d\, t^{1/2} + C \qquad (3)$$

Where C is the intercept which describes the boundary layer thickness and K_d (mg/g.min$^{1/2}$) is the rate constant of intra-particle diffusion.

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The sum of error squares (SSE) is one method used to test the validity of each model, the lower the SSE value, the better the goodness of fit to the model and is given as (Abechi *et al.*, 2011):

$$SSE = \sqrt{\sum \frac{(q_{exp} - q_{cal})^2}{N}} \qquad (4)$$

Where N is the number of data points.

The amount of metal ion adsorbed (q_e) and the adsorption efficiency (*E%*) was determined using the equation:

$$q_e \left(\frac{mg}{g}\right) = \frac{(C_i - C_e)V}{M} \qquad (5)$$

$$E(\%) = \left[\frac{C_i - C_e}{C_i}\right] x 100 \qquad (6)$$

Where C_i and C_e are initial and equilibrium metal ion concentrations in mg/L, V (L) is the volume of the metal ions solution and M (g) is the weight of adsorbent.

The thermodynamic parameters such as Gibb's free energy (ΔG^o), enthalpy (ΔH^o) and entropy (ΔS^o) changes were calculated from the following equations (Fu *et al.*, 2012; Saleem and Bhatti, 2011):

$$K_c = \frac{C_{Ae}}{C_e} \qquad (7)$$

$$\Delta G = -RTlnK_c \qquad (8)$$

$$\log K_c = \frac{\Delta S^o}{2.303R} - \frac{\Delta H^o}{2.303RT} \qquad (9)$$

Where C_e (mg/L) is the equilibrium concentration in solution and C_{Ae} (mg/L) is the equilibrium concentration on the sorbent and K_C is the thermodynamic equilibrium constant. T (^oK) is the absolute temperature and R is the universal gas constant (8.314 $JK^{-1}mol^{-1}$).

Results and Discussion
Physicochemical properties
The mean values of physicochemical properties were presented in Table 1 with their standard deviations. It shows that the adsorbent can be used on a large scale, thereby describing its suitability for a particular process.
Carbon yield
The yield is the quantity of the final product formed from the starting raw material on a scale of 100 and is dependent on temperature and time of activation (Abechi *et al.*, 2013). A high yield is required for a feasible economic production of activated carbon; a yield of 30.0±0.2% was obtained after carbonization and activation. This value is lower than 46.08% yield obtained for tamarind wood activated carbons (Sahu *et al.*, 2010) but higher than 29.4% for maize cob carbon (Okafor *et al.*, 2015).
pH
The pH of adsorbent depends on a number of factors which include preparation methodology, inorganic matter content, chemically active oxygen groups on its surface as well as the kind of treatment to which the adsorbent was subjected. Most activated carbons are specified for a pH of 6-8 (Ekpete *et al.*, 2010). In this study, the pH of the NAAC was 6.4±0.08 which is within the specified range.

Table 1: Mean values of physicochemical parameters of ZnCl₂ – activated carbon.

Parameter	Values
Yield (%)	30.0±0.2
pH$_{water}$ (solid: liquid = 1:100)	6.4±0.08
Ash content (%)	6.3±0.2
Attrition (%)	14.0±0.0
Moisture content (%)	5.0±0.0
Bulk density (kg/m³)	260±1.00
Total pore volume (cm³/g)	0.80±0.01
Iodine number (mg/g)	335.02±0.0
Surface area (m²/g)	254.40±6.0

Percentage burn off
Ash content is the residue that remains when carbonaceous portion is burnt off, and is considered an impurity. It is an indication of the quality of activated carbon and should be in the range 2 – 10% (Yang and Lua, 2003). Its low value indicates that the inherent carbon in the starting material is high (Karthikeyan and Ilango, 2008). Soleimani and Kaghazchi (2007) reported that activated carbon with high ash content is undesirable because it reduces the absorption capacity and mechanical strength of the activated carbon. Good quality activated carbon should have low ash content and the percentage ash content, 6.3±0.2%, obtained in this work for the adsorbent falls within accepted range.
Attrition
Attrition measures adsorbent's ability to withstand frictional forces by stirring and washing and is an important parameter in understanding loss of adsorbent during handling and regeneration. A high attrition loss indicates that the adsorbent may be less effective and more expensive due to frequency of maintenance and purchase of additional material (Wuana *et al.,* 2015). NAAC showed 14% attrition loss indicating its hardness/resistance to abrasion. This value is higher than 12.5% obtained for *Moringa oleifera* pod husks activated carbon (Wuana *et al.*, 2015) and less than 40.26% for bituminous coal (Qureshi *et al.*, 2007).
Moisture content
Moisture content suggests extensive porosity in the structure of adsorbents. The moisture content of the *N. ampla* roots derived activated carbon was 5.0%. It has been observed that if the moisture content of adsorbent is high, its adsorptive capacity will be reduced (Sugunadevi *et al.*, 2002). Jimoh *et al.* (2015) reported moisture content of 5.22±0.4% for activated carbon prepared from *Vitellaria pradoxa* (shea nut) shell, this is similar to the value obtained in this study.
Bulk density and pore volume
Bulk density is an important characteristic of activated carbon as it is a measure of the amount of adsorbate the carbon can hold per unit volume. It is a useful property that gives an idea of the volume activity of the adsorbent and depends on the starting raw material. Bulk density of 260±1.0 kg/m³ was recorded for the adsorbent (NAAC) which is higher than the minimum requirement of (250 kg/m³) for application in removal of pollutants from waste water (AWWA, 1991). Also, pore volume of 1.19±0.01 cm³/g shown by the adsorbent is comparable to that of other adsorbents (Boudrahem *et al.*, 2009; Bohli *et al.*, 2012).

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Iodine number/surface area

Iodine number is a fundamental parameter used to characterize activated carbon performance. It is a measure of the micro-porosity created during activation and is responsible for the large surface area of the activated carbon particles (Ekpete and Horsfall, 2011). Adsorbents with high iodine number/surface area perform better in the removal of small sized contaminants. NAAC had iodine number (mg/g) and surface area (m^2/g) values of 335.02 and 254.40, respectively. These values are higher than those reported for AC derived from *Moringa Oleifera* pods (Wuana *et al.*, 2015), but less than those for activated carbon from *Vitellaria paradoxa* shell (Jimoh *et al.*, 2015).

Table 2: FTIR Spectra for *N. ampla* Roots Activated Carbon and Spent Adsorbent

Vibrational Assignment/ Functional group(s)	Observed wave number (cm^{-1})		
	NAAC	Cd^{2+} - spent NAAC	Pb^{2+} - spent NAAC
O – H, N – H	3421.44	3404.12	3415.53
C – H	2919.91	2920.23	2919.83
P – H	2364.84	2363.92	2360.29
C – N	1684.64	1653.92	1653.90
C = C	1636.49	1636.63	1636.69
COO$^-$	1312.35	1319.49	1320.75
C – O	1033.28	1034.18	1034.35
C – Cl	669.03	668.8	668.59
C – Br	526.51	537.40	537.22
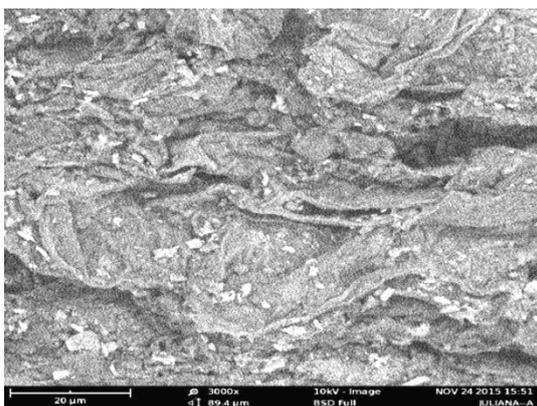
Plate 2: SEM Micrographs of unloaded adsorbent (**a**) and spent adsorbent for Pb^{2+} (**b**)

FTIR analysis

The FTIR spectrum of NAAC before and after metal adsorption was recorded in order to get information about the interaction between metal ions and binding sites as shown in Table 2. The intensity of the peaks for metal-loaded carbon was either minimized or shifted slightly. The wave number at 3421 cm^{-1} after Cd^{2+} and Pb^{2+} ions adsorption shifted to 3404 cm^{-1} and 3415 cm^{-1}, respectively. It shows that there was interaction between hydroxyl group and the metal ions. The participation of C=N group for Cd^{2+} and Pb^{2+} ions adsorption was confirmed by the shifted wave number from 1684 to 1653 cm^{-1}. The peak at 1312 cm^{-1} representing the –COO$^-$ stretching of carboxylic acid also shifted to about 1320 cm^{-1} after adsorption (Coates, 2000). Therefore it can be concluded that the functional groups which can bind the metal ions are of the type –OH, -NH, C=N and –COO$^-$.

SEM analysis

SEM analysis gives the surface morphology of an adsorbent. The SEM micrographs of adsorbent surface before (**a**) and after (**b**) lead ions adsorption are shown in Plate 2. The porous and irregular surface structure of the adsorbent can be clearly observed in the SEM image shown in Plate 2(a). Whereas in Plate 2(b), there is a clear difference in the surface morphology of adsorbent after adsorption. It showed reduced pore sizes as compared to that of the unloaded sample confirming FTIR spectra analysis.

Adsorption studies

Effect of metal ion concentration

Figure 1(a) shows the effect of initial metal ion concentration on metal ions adsorption. It can be deduced from the figure that the amount of metal ion adsorbed onto *N. ampla* roots-derived activated carbon increased with increase in the initial metal ion concentration which can be attributed to the non-saturation of sorptive sites. At low metal concentration, saturation of adsorbent by Cd^{2+} and Pb^{2+} ions could not be achieved, as the number of metal ions was smaller compared to the number of binding sites present on the adsorbent. Consequently, increasing the concentration of Cd^{2+} and Pb^{2+} ions in the solution is expected to result to increase in metal uptake until saturation of adsorbent is attained (Zubair *et al.*, 2008). The metal uptake values for Cd^{2+} and Pb^{2+} ions are in the range of 4.36 – 10.11 mg/g and 4.22 – 8.86 mg/g, respectively. However, it was discovered that Cd^{2+} ions uptake was higher than Pb^{2+} ions. Similar results were obtained for Pb(II) adsorption onto activated carbon developed from coffee residue activated with zinc chloride (Boudrahem *et al.*, 2009).

pH

The pH of the solution is an important parameter for adsorption of metal ions because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate (Awoyale *et al.*, 2013). Fig. 1(b) shows that metal ions uptake depended greatly on pH,

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where optimal metal removal occurred at pH 5.0 and then decreased at higher pH values. Cd^{2+} ion uptake increased from 3.5 to 4.4 mg/g over pH range from 2.0 to 5.0 whereas Pb^{2+} ion uptake increased from 3.5 mg/g at pH 2 to 4.0 mg/g at pH 5.0. This could be attributed to the fact that, at low pH (<5), the protonation of the active sites at carbon surface was enhanced and this hindered the formation of links between cationic metals and protonated active sites resulting in increased metal uptake (Jamal *et al*., 2015). However, with further increase in pH above 5, there was a decrease in adsorption capacity due to precipitation of insoluble cadmium and lead hydroxides (Najua *et al*., 2008).

Adsorbent dosage

Adsorbent dosage determines the sorbent-sorbate equilibrium of the system and the number of binding sites available. The effect of adsorbent dosage on the removal of Cd^{2+} and Pb^{2+} ions are shown in Fig. 1(c). The profile shows clearly that metal uptake per unit mass of the adsorbent decreased with increase in adsorbent dose. The reason for this may be attributed to the fact that at high adsorbent dosages, the available metal ions were not able to cover all the binding sites on the adsorbent resulting in low metal uptake. The decrease in adsorption capacity also may be due to the decrease in total adsorption surface area available resulting from overlapping or aggregation of adsorption sites (Boota *et al*., 2009). The maximum adsorption efficiency of 91.3% was recorded for Cd^{2+} ions while 88.8% was obtained for Pb^{2+} ions. This trend is consistent with the results obtained for Pb^{2+} and Cu^{2+} adsorption onto activated carbon from Date stones (Jamal *et al*., 2015).

Isotherm models

Adsorption isotherm profiles provide information regarding the nature and intensity of sorption for a particular adsorbate-adsorbent system. The isotherms for Cd^{2+} and Pb^{2+} ions adsorption were somewhat H – shaped (Figure 1d) indicating a high affinity rate of metals ions towards the derived activated carbon. This suggests that hydration of the metal ions was less preferred compared to sorption onto NAAC, which resulted in the preferred sorption. To describe the adsorption process of metals ions onto NAAC, four empirical isotherm models were tested as presented in Fig. 2. The Langmuir isotherm model is used to describe the relationship between the amount of adsorbed ion and its equilibrium concentration in solution and is valid for monolayer adsorption on a surface containing finite number of identical sites. The linear plots of C_e/q_e versus C_e showed that adsorption followed the Langmuir adsorption model. The values of q_{max} and K_L were calculated from the slope and intercept of the plot, respectively. These results revealed the Langmuir-type sorption isotherm to be suitable for equilibrium studies for both metals, suggesting the formation of monolayer coverage of the adsorbate on the surface of adsorbent for these metal ions (Dada *et al*., 2012). The amount of metal ions adsorbed per unit mass of the adsorbent increased with the metal concentration as expected and the sorption capacities were 12.5 mg/g and 9.80 mg/g for Cd^{2+} and Pb^{2+} ions, respectively.

a

b

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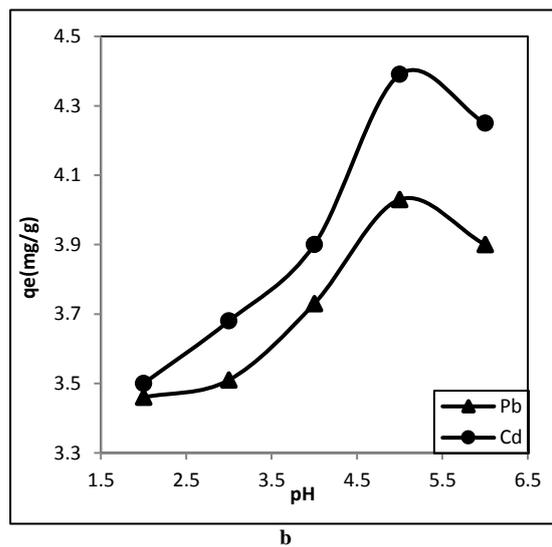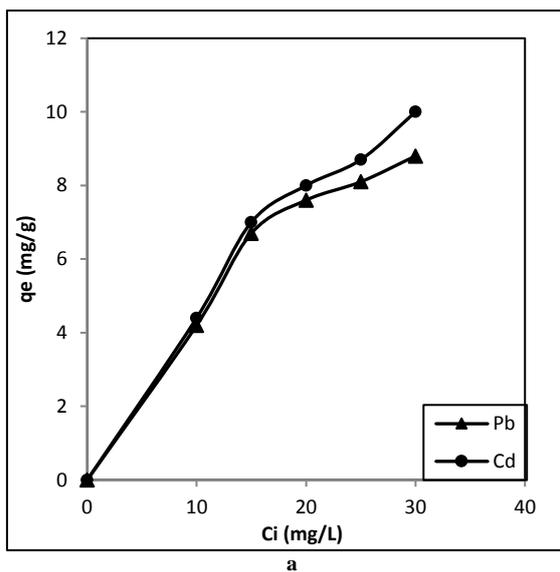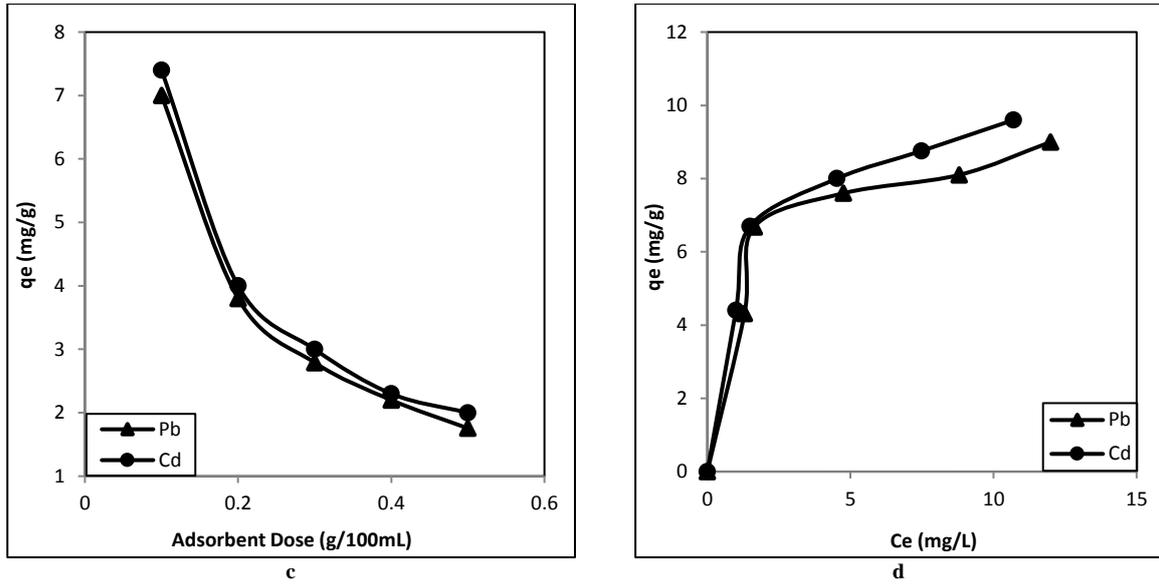
Fig. 1: Adsorption profile showing the effect of: (a) initial metal ion concentration; (b) pH; (c) adsorbent dose; (d) equilibrium phase concentration at 30°C

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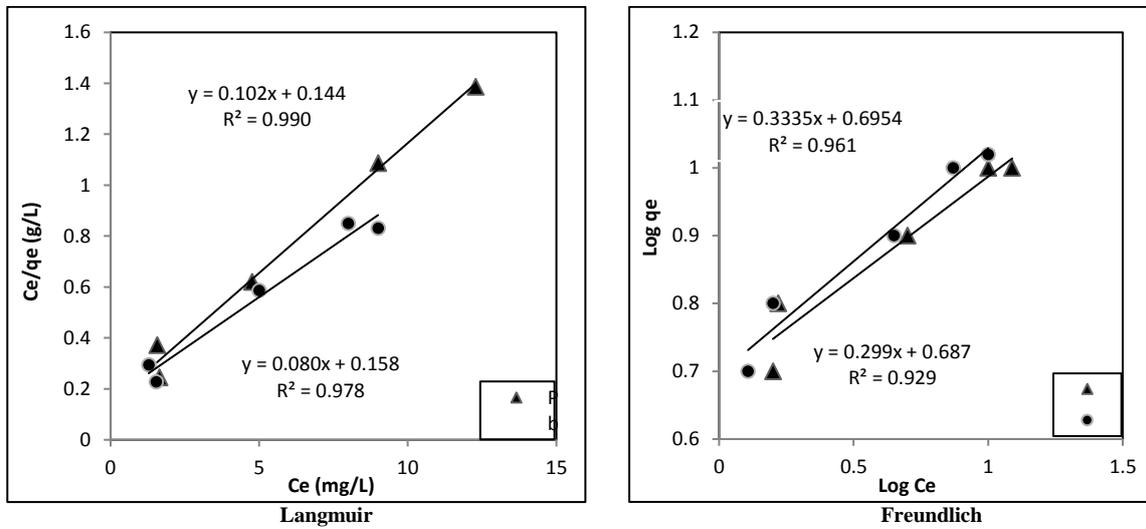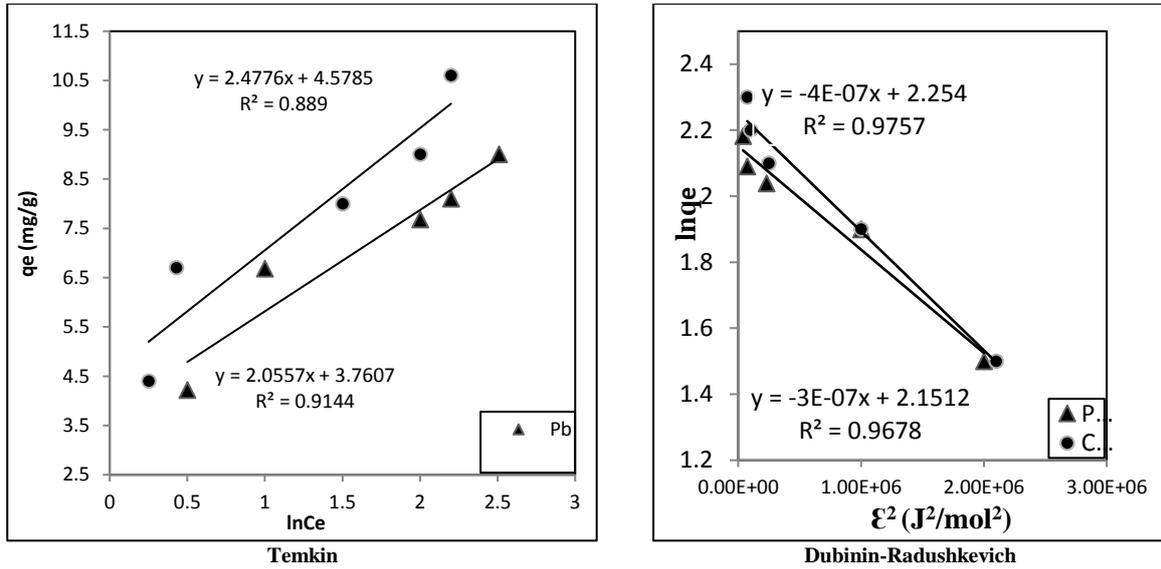
Fig. 2: Linearized isotherms for adsorption of metal ions onto *N. ampla* roots AC at 30°C
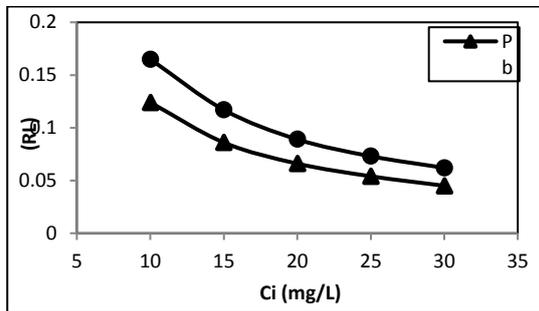
Fig. 3: Langmuir dimensionless separation factor (R_L) for adsorption of metal ions onto *N. ampla* roots AC at 30°C

The calculated R_L values for Cd^{2+} and Pb^{2+} ions at 30°C, were all less than one (Fig. 3) indicating a favourable process (Ackacha, 2013). The Freundlich isotherm assumes that adsorption process takes place on heterogeneous surfaces and that adsorption capacity is related to the concentration of the adsorbent. The two Freundlich parameters (K_F and $\frac{1}{n}$) were determined graphically by plotting $logq_e$ versus $logC_e$ (Fig. 2) for both metal ions. The K_F value of Cd^{2+} (4.95 mg/g) was greater than Pb^{2+} having the K_F value of 4.86 mg/g. The smaller ionic radius of Cd^{2+} might be responsible for its greater adsorptivity. The n values were 3.0 and 3.3 for Cd^{2+} and Pb^{2+} ions, respectively (greater than 1), indicating that the adsorption was favorable (Egila *et al*., 2011).

Temkin isotherm is based on the assumption that the heat of adsorption decreases linearly with the increase of coverage of adsorbent. From the Temkin plot of q_e versus lnC_e shown in Fig. 2, the following values were estimated: A_T = 6.35 L/g, B = 2.48 J/mol and A_T = 6.23 L/g, B = 2.06 J/mol for Cd^{2+} and Pb^{2+}, respectively. The values of B are indication of the heat of adsorption. Also, from the linear plot of Dubinin-Radushkevich (D-R) model, q_m was

determined to be 9.53 mg/g and 8.59 mg/g, the mean free energy, E= 1.12 kJ/mol and 1.29 kJ/mol for Cd^{2+} and Pb^{2+}, respectively. These energy values of D-R model confirmed that the adsorption process followed physisorption mechanism (Egila *et al*., 2011 and Jimoh *et al*., 2015).

Kinetics
The effect of contact time on the rate of metal ion uptake onto the adsorbent was investigated over time intervals from 10 to 90 min as shown in Fig. 4 (Time profile). The results showed that metal uptake increased with increase in contact time and reached maximum; 3.9 mg/g (79.7%) for Cd^{2+} adsorption at 30 min and 4.0 mg/g (80.1%) for Pb^{2+} at about 60 minutes, thereafter remaining almost constant up to 90 min. The nature of adsorbent and its available sorption sites affected the time needed to reach the equilibrium (Naiya *et al*., 2009). Similar result was reported by Jimoh *et al*. (2015) on the adsorption of Cd^{2+} from aqueous solution using *Vitellaria paradoxa* shell carbon. The kinetics of Cd^{2+} and Pb^{2+} adsorption onto the adsorbent were investigated using pseudo-first order, pseudo-second order and intra-particle kinetic models (Fig. 4). The calculated uptake (q_e,cal) values for the pseudo-second order kinetic model were all consistent with the experimental uptake (q_e,exp) values. These suggested that the adsorption processes for Cd^{2+} and Pb^{2+} ions can be well described by the pseudo-second order kinetic model. The high values of correlation coefficient (R^2) values obtained for both metals indicated that Morris-Weber model was suitable for describing the diffusion rate of Cd^{2+} and Pb^{2+} onto the adsorbent whereas low K_d values and C values greater than zero showed that the mode of transport was affected by more than one process (Itodo *et al*., 2010). Similar result was reported for the removal of heavy metals from aqueous solution using activated carbon from neem seed and husk (Alau *et al*., 2015).

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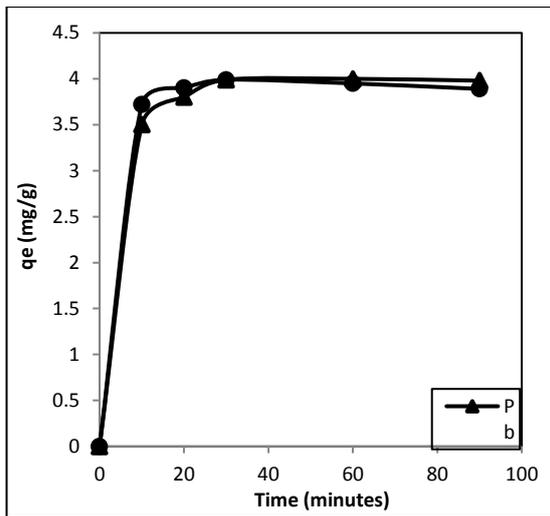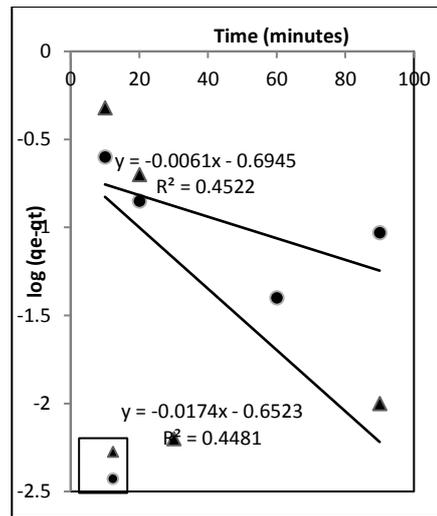
Time profile

Lagergren pseudo-first order plot
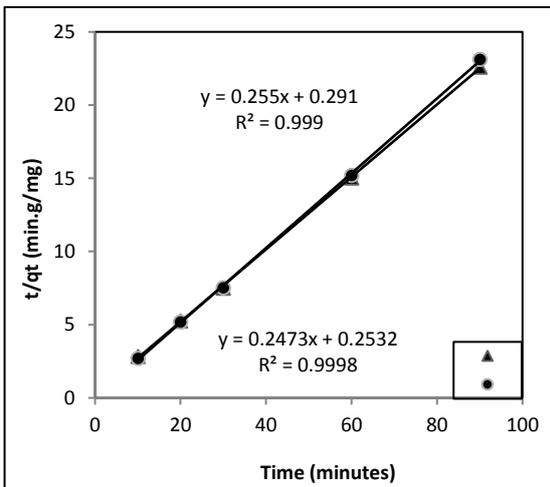
Blanchard pseudo-second order plot
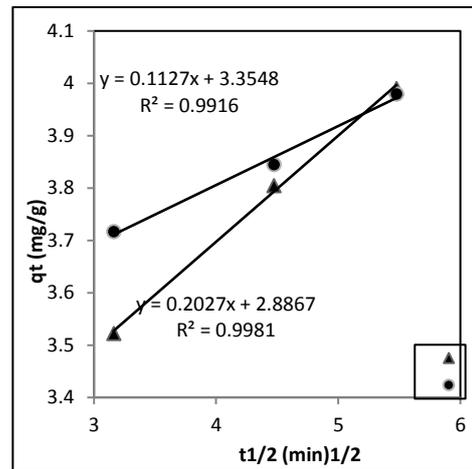
Morris-Weber intra-particle diffusion plot

Fig. 4: Kinetic data treatments for metal ions adsorption onto *N. ampla* roots AC at 30°C.
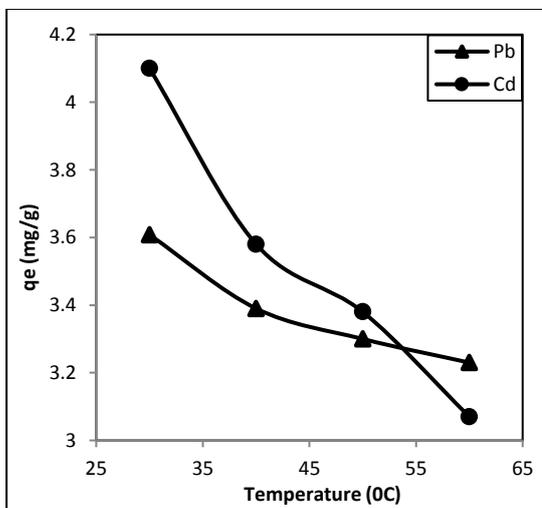
Temperature profile
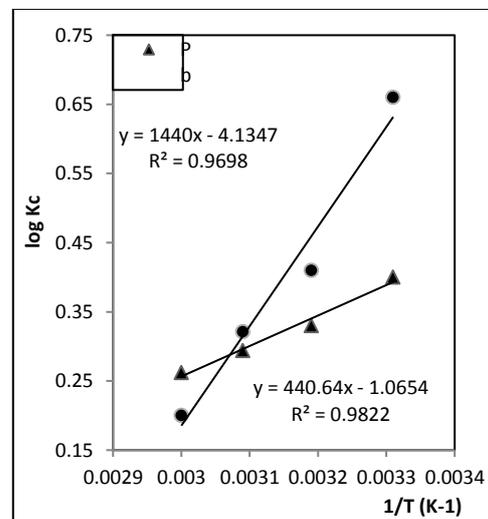
Van't Hoff plot

Fig. 5: Temperature profile and Van't Hoff plot for Cd^{2+} and Pb^{2+} adsorption onto *N. ampla* roots AC.

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Thermodynamics

Figure 5 (temperature profile) depicts the effect of temperature on the adsorption capacity of the adsorbent for Cd^{2+} and Pb^{2+} ions. The adsorption capacity decreased with increase in temperature for both metal ions, indicating that the adsorption process was exothermic. The decrease in adsorption capacity with increase in temperature might be due to decreased surface activity or weakening of the attractive forces between the adsorbates and adsorbent at higher temperatures (Ekpete *et al.,* 2010).

The values of the thermodynamic parameters for adsorption of Cd^{2+} and Pb^{2+} onto the AC derived from *N. ampla* roots are given in Table 3. The negative values of Gibbs free energy change (ΔG^o) indicated that the adsorption process was feasible and spontaneous (Saleem and Bhatti, 2011). The negative values of enthalpy change (ΔH^o) confirmed the adsorption process to be exothermic. The negative values of entropy change (ΔS^o) suggested decreased randomness at the solid/solution interface or no structural changes at adsorption sites (Deosarkar and Hangirgekar, 2012). Similar results were obtained by El-sayed *et al.* (2010) for the adsorption of Cd^{2+} (-5.821 kJ/mol) and Ni^{2+} (-5.723 kJ/mol) ions onto rice husk.

Table 3: Thermodynamic parameters of adsorption of Cd^{2+} and Pb^{2+} ions onto *N. ampla* roots AC

Adsorbate	T (^oK)	ΔG^o (kJ/mol)	ΔH^o (kJ/mol)	ΔS^o (kJ/mol.K)	R^2
Cd(II)	303	− 3.830			
	313	− 1.940			
	323	− 1.984	− 27.6	− 0.079	0.969
	333	− 1.280			
Pb(II)	303	− 2.398			
	313	− 1.939	− 8.44	− 0.020	0.982
	323	− 1.814			
	333	− 1.670			

Conclusion

The study has demonstrated that activated carbon derived from *N. ampla* roots with $ZnCl_2$ activation possesses favorable metal ion-sorptive physicochemical properties. The results indicated that the optimum pH for maximum removal of Cd^{2+} and Pb^{2+} ions was about 5.0. Increasing temperature had an unfavourable effect on the adsorptive capacity of the adsorbent. The equilibrium data were well described by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The separation factors (<1) showed that the adsorption reaction was favourable and the adsorption of metal ions onto the adsorbent followed pseudo-second order kinetics. Intra-particle diffusion proved not to be the sole rate controlling factor. The calculated thermodynamic parameters obtained showed the sorption process to be exothermic and spontaneous in nature. A close look at the data obtained showed that cadmium was adsorbed more than lead using the adsorbent. In view of these positive results obtained, it can be concluded that activated carbon derived from *N. ampla* roots can be used as an effective, eco-friendly and inexpensive adsorbent for industrial water treatment to eliminate low concentrations of heavy metal ions such as Cd^{2+} and Pb^{2+} ions.

Conflict of Interest

There is no conflict of interest in this article please.

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