REMOVAL OF LEAD AND CADMIUM FROM AQUEOUS SOLUTION USING ACTIVATED CARBONS FROM DESERT DATE AND SHEA NUT SHELLS

Z. Abdullahi, A. I. Ajai* and Y. A. Iyaka

Department of Chemistry, Federal University of Technology, Minna, Niger State, Nigeria
Corresponding author: talk2alexajai@gmail.com, ajai.ike@futminna.edu.ng

Abstract:	Shells of *Balanitesaegyptiaca* (desert date) and *Vitellariaparadoxa* (shea nut) activated with 1.00 mol/dm^{3}H$_2$SO$_4$and their blends were investigated for the removal of Pb and Cd from aqueous solution. Effects of operational parameters, such as contact time, pH, initial metal ion concentration and temperature were investigated. The adsorption process was found to be dependent on all the factors investigated. The optimum pH for the removal of Pb was 6, while Cd was found to be 8. Optimum contact time for Pb and Cd was 90 min. Highest removal of Pb and Cd was 70 and 65%, respectively. The adsorptive capacity of all the adsorbent used was in the order AC$_2$>AC$_4$>AC$_3$>AC$_1$. Experimental data tested fitted better into the Freundlich isotherm compared to the Langmuir isotherm. Adsorption kinetic of the process was best described by pseudo-second order model. Thermodynamic investigations showed that the process was spontaneous, feasible, and endothermic and proceed with increasing randomness.
Keywords:	Adsorption, *Balanitesaegyptiaca*, heavy metals, kinetic, *Vitellariaparadoxa*,wastewater

Introduction

Environmental pollution is at present, one of the most serious global issues of great concern (Renge*et. al.,* 2012). Industrialization is necessary for nation's development however; it is also contributing to increasing level of pollutants such as heavy metal in the environment especially in water bodies. The term heavy metal is defined as a group of metals or metalloids with density greater than 5g/cm^{3}with high atomic number and is toxic even at a low concentration. Untreated industrial effluents from industries such as electroplating, petroleum refining, paint manufacturing, tanneries, mining activities, metal smelting, printing and photographic industries discharge heavy metals such as copper, cobalt, cadmium lead, mercury, zinc, and chromium into water bodies (Ngah and Hanafiah, 2008). Some of these heavy metals like zinc, iron and copper are nutritionally essential but becomes toxic at high concentration, while some like lead, mercury and cadmium are very toxic even at low concentration. These toxic metals are non-biodegradable, due to these, their concentration increases along the food chain and they bio- accumulate in the living tissues (Ahamed and Begum, 2012).

Cadmium is known to cause health effect such as itai-itai disease, hypertension, kidney, liver and lung disfuntion (Murithi*et al.,* 2014). The International Agency for Research on cancer has classified cadmium as number one human carcinogen. The maximum allowable concentration of cadmium in drinking water has been set at 0.005 mg/L by the World Health Organization (Amir and Edriss, 2007). Lead is a highly toxic metal and no safe level is known. It interferes with a number of body functions affecting the central nervous system mostly in developing fetus and young children and also the renal system (Kalia and Flora, 2005).

Due to the necessity for water of high quality, it absolutely becomes necessary to treat waste water so as to remove heavy metal before their discharge into aquatic environment. Some conventional methods which have been employed for the removal of heavy metal from waste water includes Nanofiltration, Reverse Osmosis, Chemical precipitation, Ion exchange, and Electrodialysis. Most of these methods have some draw backs such as inefficient metal removal especially when the concentration of the metal is low and in the range of 1 – 100mg/L, high energy requirement, high cost and generation of toxic sludge which is also difficult to treat (Ghasemi*et al.,* 2012). Adsorption however offers a better alternative for heavy metal removal because it is simple, easy to design and cost effective when compared to the conventional methods. Adsorption is the adhesion of atoms, ions or molecules from gas, liquid or dissolved solid on a surface creating a film of adsorbate on the surface of the adsorbent. This process continues until equilibrium is established between the adsorbent and the molecules of the surrounding fluids (Nitin and Sachin, 2012). Various adsorbents materials have been used ranging from commercial activated carbon, polymer materials, micro-organisms, zeolites, and various plant and animal waste (Thakur and Parmar, 2013).

In recent time, there is an increasing research on the investigation of various plant and animal waste in both raw and modified form for heavy metal removal. Activated carbon can be generated from this waste biomass to serve as substitute for commercial activated carbon which is still expensive (Giwa*et al.,* 2013). These includes, tea factory waste (Kailas, 2010), palm tree (Ahmed, 2010), Bael fruit shell (Anusha, 2011), Palm oil kernel shell (Wahi and Senghie, 2009), and Orange and Potato peels (Rafique and Nazir, 2013). This present study is aimed at investigating the adsorptive capacity of Desert date and Shea nut shells and their blends for the adsorption of cadmium and lead from aqueous solution of heavy metal by batch adsorption.

Materials and Methods

Sample collection
Desert date *(Balanitesaegyptiaca)* was obtained from Bida market in Niger state. Shea nut shell *(Vitellariaparadoxa)* was obtained from Sakpe village in Niger state. The samples were identified and authenticated by a Botanist in the department of Biological Sciences, Federal University of Technology, Minna, Niger State Nigeria,

Sample pretreatment
Desert date was soaked in water to remove the fleshy part and was then cracked to obtain the seed shell while Shea nut shell was obtained from Shea nut butter processors from Sakpe village of Niger State. The two samples were then washed several times with tap water to remove sand and other dirt present and air dried for a period of two weeks. It was grinded using mortar and pestle and sieved using 300 μm mesh sieve.

Preparation of activated carbon
The grinded and sieved desert date and Shea nut shells were carbonized in an electric furnace at a temperature of 450°C for a period of 20 min until a black powder was obtained. Chemical activation was done by separately mixing the carbonized sample with 1 mol/dm^{3}H$_2$SO$_4$ in the ratio of 1:10 (w/v). The mixture was sieved after 20 min using 300

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μmmesh sieve and WhatmanNo.1 filter paper. The residue was oven dried at 70ºC for 12 h. The blends were prepared by mixing equal amount of each of the carbonized samples with 1 mol/dm^{3}H$_2$SO$_4$. The mixture was sieved and oven dried as described above to give 1:1 blend ratio of the adsorbents. 2:1 blend ratio of the adsorbents was prepared by mixing two parts to 1 part of carbonized Shea nut and Desert date shells with 1 mol/dm^{3}H$_2$SO$_4$for chemical activation.

Determination of physicochemical properties of adsorbents
Ash content
The ash contentwas determined according to the method reported by Egila*et al*., 2012 with some modifications. This was carried out by carbonizing 3 g of each of the raw samples at 450°C for 20 min followed by chemical activation using 1 mol/dm^3 and sieved. The residues were oven dried. Ashing was done by burning the activated samples in an electric furnace at a temperature of 550°C for 4 h until a greyish ash was obtained. Ashing of 1:1 blend ratio was done by taking 1.5 g of each of the raw samples and were carbonized, activated, sieved and oven dried. It was then ashed as described above. Ashing of 2:1 blend ratio was also done by weighing 2 g of Shea nut and 1 g of Desert date samples and then carbonized. Chemical activation, sieving and oven drying and ashing were carried out according to the same procedure. The ash content for all samples were determined as:

$$\text{Ash (\%)} = \frac{\text{Weight of the ash}}{\text{Weight of the original precursor}} \times 100 \quad \text{……… 1}$$

Electrical conductivity and pH
Electrical conductivity and pH were determined by weighing 1 g of each of the activated carbons into 100 cm^3 beaker containing 40.0 cm^{3}distilled water. It was stirred using a glass rod and then allowed to stay for 20 min. The pH was determined using a digital pH meter and conductivity determined as μS/cm using conductivity meter.

Percentage yield
The percentage yield was determined by carbonizing 3 g of each of the raw samples at 450°C for 20 min followed by chemical activation and sieving. The residues were then oven dried at 70ºC for 12 h. 1:1 blend ratio was prepared by taking 1.5 g of each of the raw samples and were carbonized, activated together and dried. 2 g of Shea nut and 1 g of Desert date samples were also carbonized, activated together and dried to give 2:1 blend ratio of the activated carbon.

The percentage yields for the samples were determined as the ratio of the weight of the activated carbon to the weight of the original precursor.

$$\text{\% yield} = \frac{\text{Weight of activated carbon}}{\text{Original weight of the precursor}} \times 100 \quad \text{……… 2}$$

Bulk density
The bulk density of Desert date was determined by filling a 25.0 cm^3 measuring cylinder with the activated carbons and the cylinder was gently tapped for about 2 min until a compressed sample was obtained. The bulk density was determined as the weight of the sample divided by the volume occupied in the cylinder after a specified compaction process. This was carried out for all the activated carbons.

$$\text{Bulk density} = \frac{\text{Mass}}{\text{Volume}} \text{g/cm}^3 \text{……………….. 3}$$

Simulation of aqueous solution of heavy metals
Stock solution of 1000 ppm Pb and Cd were prepared from PbNO$_3$and Cd (NO$_3$)$_2$4H$_2$O using distilled water. This was prepared by dissolving accurately weighed 1.60 g of analytical grade PbNO$_3$and 2.74 g Cd (NO$_3$)$_2$4H$_2$O in a 1 dm^3 volumetric flask using distilled water, shaken thoroughly and made up to the mark with more distilled water respectively, Other concentrations of 5, 10, 20, 30, 40, and 50 ppm were prepared from the stock solutions by serial dilution. These

were kept for sorption study by batch process using the activated Desert date *(Balanitesaegyptiaca)* and Shea nut shell *(Vitellariaparadoxa)* and their different blend ratios. After the various batch adsorption study with the simulated heavy metal solutions, they were subjected to atomic absorption spectrophometeric analysis using AAS model Buck Scientific Model 210 VGP to determine the adsorption efficiency of the adsorbent and their blend ratios.

Batch adsorption study
The batch adsorption study method as reported by Amuda*et al.* (2007) with some modification was used for this study.

Effect of contact time
Into a 250 ml volumetric flask was weighed 0.50 g of each of the activated samples and shaken with 40 cm^3 of each of the metal ion solution of 5 ppm for various time intervals of 30, 60, 90, 120 and 150 min in a mechanical shaker at 300 rpm (rotation per min). The mixture was filtered at the end of each contact time using Whatman No 1 filter paper, and the filtrate was stored in a polyethylene sample bottle and stored in a refrigerator. The residual metal ion was analyzed using atomic absorption spectrophotometer, Buck Scientific Model 210 VGP.

The optimum contact time obtained for each metal for the 4 samples was used to study the effect of other parameters such as pH, initial metal ion concentration and temperature.

Effect of pH of the solution on heavy metal adsorption
Into a 250 ml volumetric flask was measured 40.0 cm^3 of 5 ppm of each of the metal ion solution and the pH adjusted using 0.1 mol/dm^{3}HCl and 0.1 mol/dm^{3}NaOH in the pH range of 2, 4, 6, 8, and 10 using a pH meter and were then shaken with 0.50 g of each of the activated carbon for 90 min and the mixture was filtered using Whatman filter paper number 1. The filtrate were then stored for AAS analysis.

Effect of initial metal ion concentration
Into a 250 cm^{3}conical flasks containing 40.0 cm^3 of each of the metal ion solution of concentration 10, 20, 30, 40 and 50 ppm was weighed 0.50 g of each of the adsorbents and the mixture was shaken using mechanical shaker while keeping other parameters constant. After filtering, the filtrate was stored for AAS analysis.

Effect of temperature
The effect of temperature on adsorption of Cd and Pb was studied using constant temperature water bath to vary the temperature in the range of 30 to 70°C. 0.50 g of the adsorbents was weighed into separates 250 cm^3 conical flasks containing 40.0 cm^3 of the metal ion solution and was suspended in the water bath with the aid of a retort stand at varying temperature. The mixture was filtered after a period of 90 min and the filtrate was stored for analysis.

Data analysis
The adsorptive capacity q$_e$, of the adsorbents expressed as milligram of the metal ion per gram of the dry mass of the biomass was evaluated from the expression,

$$q_e = (C_o - C_e)V/m \quad \text{……………………………… 4}$$

The percentage (%) removal of heavy metal was calculated from the expression,

$$\text{\% Removal} = C_o - C_e/C_o \times 100 \quad \text{……………… 5}$$

Where: C$_o$ is the initial concentration of the metal ion in mg/dm^3, Ce is the equilibrium concentration of the metal ion in the solution, V is the volume (dm^3)of the solution, m is the mass (g) of the adsorbent used.

Adsorption isotherm
In order to predict the nature of the adsorption process adsorption isotherms are used. Langmuir and Freundlich isotherms are the earliest known of such isotherms and were applied in this study.

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Langmuir isotherm

Langmuir isotherm assumes that dynamic equilibrium exists between adsorbate and adsorbent and the adsorption of metal ion occurs on a homogeneous surface by a complete monolayer coverage and constant adsorption energy (Amuda*et al.,* 2007).

The linear form of the isotherm equation is given as:

$$C_e/q_e = 1/bq_m + C_e/q_m \quad \ldots\ldots\ldots\ldots \quad 6$$

Where:C_e is the equilibrium concentration of metal ion in solution in mg/g, qe is the adsorption capacity in mg/g of the metal ion adsorbed per gram of the adsorbent, $q_m$is the maximum metal uptake and b is Langmuir constant related to the affinity between the adsorbent and the adsorbate.

Freundlich isotherm

Freundlich isotherm is based on adsorption onto heterogeneous surface and assumes that different adsorption sites with several energies are involved (Ghasemi*et al*., 2012; Ahamed and Bagum, 2012). The Freundlich isotherm equation is given as;

$$q_e = K_f(C_e)^{1/n} \quad \ldots\ldots\ldots\ldots\ldots \quad 7$$

The linear form of the equation is given as:

$$Log q_e = \log K_f + 1/n \log C_e \quad \ldots\ldots\ldots\ldots \quad 8$$

Where:K_f is a Freundlich constant which give the adsorption capacity and n is the heterogeneity factor. When n is less than 1, the adsorption process is favourable. A plot of Ce/qe against Ce and log qe against log Ce gives the Langmuir constants b and qm and Freundlich constants Kf and n respectively which were evaluated from the slopes and intercepts.

Adsorption kinetics

The kinetics of adsorption for Cd(II) and Pb(II) were analysed using pseudo-first order and pseudo-second order models.

T*he pseudo-first order model*

The pseudo-first order kinetic equation is expressed as:

$$Log_{(qe-qt)} = \log_{qe} - k_1/2.303t \quad \ldots\ldots\ldots\ldots\ldots \quad 9$$

Where:q_e is the amount of metal adsorbed at optimum time t in (mg/g)

$q_t$is the amount of metal adsorbed at any time t in mg/g

$k_1$is the pseudo - first order rate constant in min^{-1}.

A plot of Log(qe-qt) against t is linear which was used to evaluate k_1 and qe from the slope and intercept of the graph, respectively.

The pseudo-second order model

The pseudo-second order kinetic equation is expressed as:

$$t/q_t = 1/k_2q_e^2 + t/q_e \ldots\ldots\ldots\ldots\ldots 10$$

Where:q_e and q_t are the amount of metal adsorbed in (mg/g) at equilibrium and at time t; k_2 is the rate constant for pseudo-second order in (mg/g/min).

A plot of t/qt against t is linear which was used to evaluate k2 and qe from the slope and intercept.

Adsorption thermodynamic

The effect of temperature on adsorption was used to study the adsorption thermodynamic parameters such as change in Gibb's free energy (ΔG), Enthalpy change (ΔH) and Entropy change (ΔS). The Vant Hoff equation, (eqn. 9) was applied to predict whether the adsorption process was endothermic or exothermic.

$$1 nK = -\Delta H/RT + \Delta S/R \quad \ldots\ldots\ldots\ldots\ldots \quad 11$$

Where: T is the temperature in Kelvin, R is the universal gas constant in kJ/molK and K is the equilibrium constant refer to as Boltzmann distribution ratio which is evaluated as q_e/C_e.

A plot of l nK against 1/T gives a linear plot. The value of ΔH and ΔS was evaluated from the slope and intercept of the graph respectively and were substituted in (eqn. 10) to obtain the Gibb's free energy change at various temperatures.

$$\Delta G = \Delta H – T\Delta S, \quad \ldots\ldots\ldots\ldots\ldots \quad 12$$

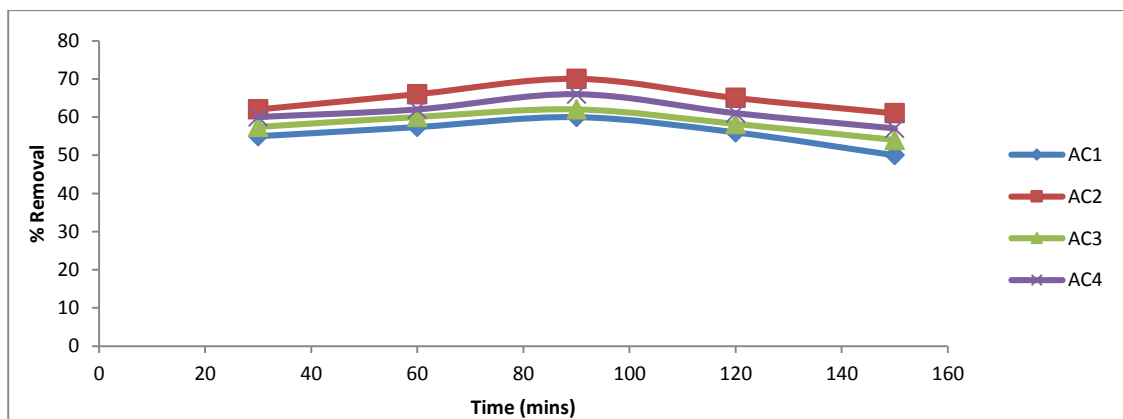### Results and Discussion

The physicochemical characteristics of the various adsorbent are shown in Table 1. From the result, the ash content for AC$_1$, AC$_2$, AC$_3$andAC$_4$ are 7.40, 6.20., 7.10 and 6.60% while the adsorbent yields for AC$_1$, AC$_2$, AC$_3$andAC$_4$ are 49.0, 53.00, 51.00 and 51.80%, respectively. The bulk densities are 0.42, 0.51, 0.44 and 0.45 g/cm3, while the pH are 5.80, 5.70, 5.90 and 5.90 respectively. The conductivity forAC$_1$, AC$_2$, AC$_3$andAC$_4$ are 115.00, 135.30, 122.00 and 120.00 μS/cm.

Table 1: Physicochemical characteristics of the adsorbents

Parameter	Adsorbents			
	AC$_1$	AC$_2$	AC$_3$	AC$_4$
Ash content (%)	7.40±0.18	6.20±0.13	7.10±0.15	6.60±0.14
Yield (%)	49.00±3.25	53.00±5.52	51.00±4.00	51.60±4.25
Bulk density (g/cm^3)	0.42±0.01	0.51±0.12	0.44±0.10	0.45±0.15
pH	5.80±0.12	5.70±0.10	5.90±0.15	5.90±0.15
Conductivity (μS/cm)	115.00±3.50	135.30±5.50	122.00±4.35	123.00±4.38

AC$_1$ - Activated Desert dateshell;AC$_2$- Activated Shea nutshell; AC$_3$ - Blends of activated Shea nutand Desert date shells in ratio of 1:1; AC$_4$ - Blends of activated Shea nut and Desert date shells in the ratio of 2:1

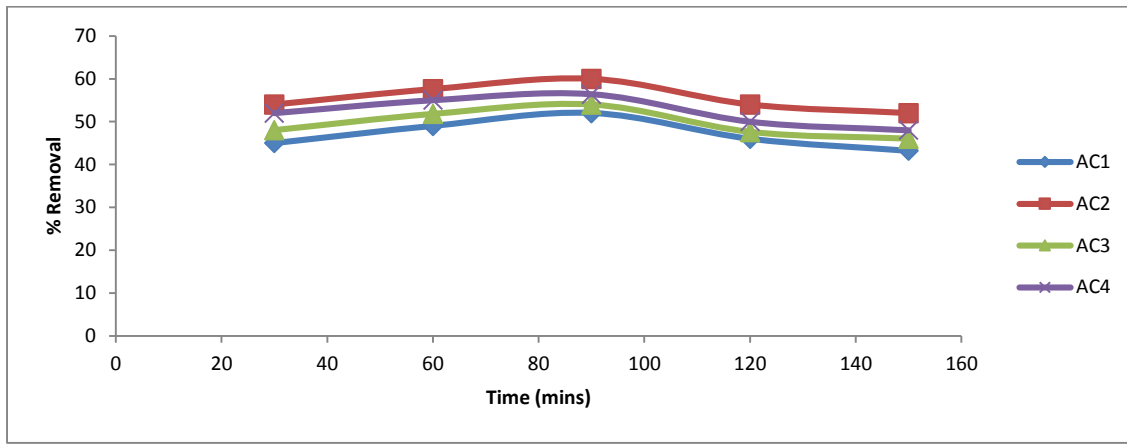**Fig. 1:** Effect of variation contact time on adsorption of Pb by the adsorbents

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Fig. 2: Effect of variation of contact time on the adsorption of Cd by the adsorbents
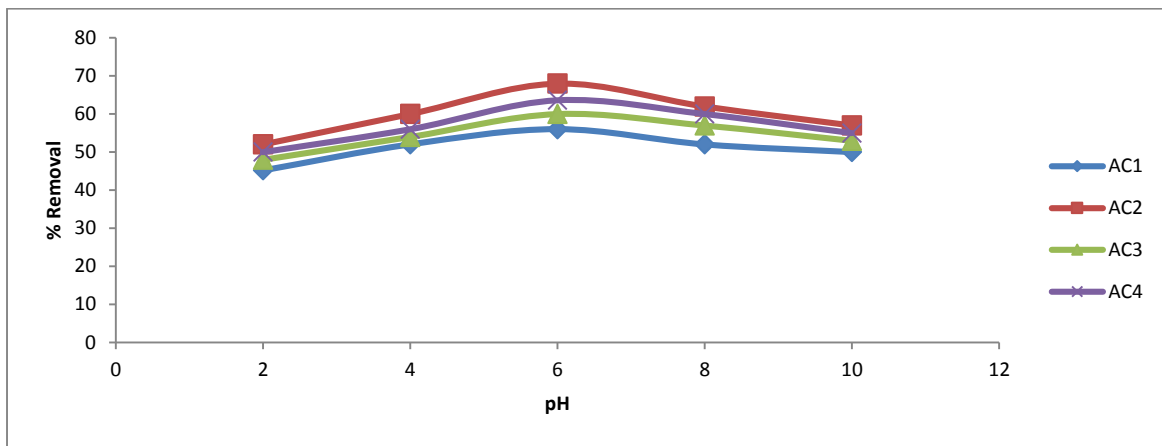

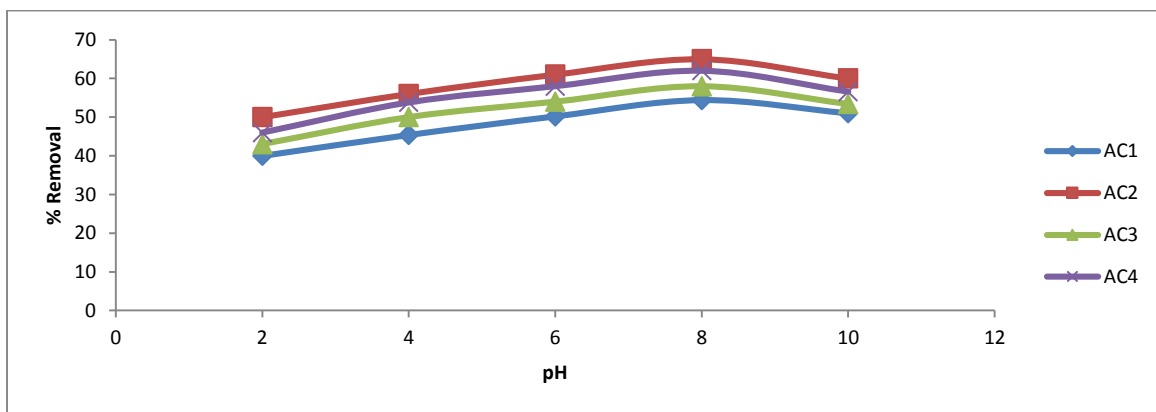**Fig. 3:** Effect of variation of pH on adsorption of Pb by the adsorbents

**Fig. 4:** Effect of variation of pH on adsorption of Cd by the adsorbents

Effect of pH of the solution on heavy metal adsorption

Figures 3 and 4 show the effect of pH on percentage removal of heavy metals. The hydrogen ion concentration is an important parameter in the adsorption of metal from waste water because it affects the solubility of the metal, the form in which the metal is present, the extent at which it ionizes in solution, and the charge on the surface of the adsorbent (Giwa *et al.,* 2013).

The effect of change in pH was studied at pH range of 2-10. Highest percentage removal of lead was 56, 65, 60 and 63.6% by AC_1, AC_2, AC_3 and AC_4, respectively at optimum pH of 6 after which the percentage removal decreases while the highest removal of Cd by AC_1, AC_2, AC_3 and AC_4 was at pH 8 after which the percentage removal decreases. Highest removal was 54.4, 65, 58, and 62%, respectively. The low removal of metal ion at low pH can be attributed to the fact that in highly acidic pH there is more H^+ in the solution and the active sites of the adsorbent becomes highly protonated, which competes with the metal ion for active sites. This reduces the attraction between the metal ion and the adsorbent site by repulsive forces (Ahamed and Begum,2012). As the pH increases the H^+ concentration decreases and are dissociated from the functional group of the adsorbent which result in increase in attraction between the metal ion and the active sites of the adsorbent (Chaturvedi and Sahu, 2014). Most heavy metal ions readily precipitate when the pH of the solution is raised forming their respective metal hydroxide precipitate.

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The decrease in percentage removal of Cd and Pb at higher pH may be due to the formation of metal hydroxide precipitate according to the equation:

$$M^{+n} + nOH^- \leftrightarrow M(OH)_n$$
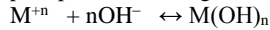
Effect of initial metal ion concentration

Figures 5 and 6 show the effect of variation of metal ion concentration from 10 to 20, 30, 40 and 50 mol/dm³on the uptake of Cd and Pb. The percentage removal decreases as the initial concentration increases to 50 mol/dm³. Highest removal of 58.4, 70, 61, and 66.6; was obtained for Pb and 49.5, 59, 52 56 for Cd at 10 mol/dm³by AC_1, AC_2, AC_3 and AC_4,respectively.At high concentration there is more molecules in the solution compared to the available sites and the exchangeable sites of the adsorbent become saturated which leads to the decrease in percentage removal. Also external mass transfer by the metal ion no longer holds at high concentration. The metal ion needs to diffuse to the available surface of the adsorbent by intraparticle diffusion, so a decrease in percentage removal is expected (Ibrahim and Jimoh, 2008; Tuama and Mohammed 2014).

Effect of temperature

Figures 7 and 8 show the effect of variation of temperature from 30through 40, 50, 60 and 70ºC on adsorption of metal ion. Percentage removal of lead increases up to 60ºC after which there was slight decrease in adsorption. While that of cadmium increases throughout the range of temperature studied. Highest removal of lead by the various adsorbents are 52.4, 65, 58 and 61 and cadmium was 56 65, 60.20 and 62.40.As the temperature increases, the kinetic energy of the metal ion increases and also there is enlargement of pore structure as energy in the form of heat is absorbed this lead to increase in adsorption (Shelkeet al., 2009). The decrease in percentage removal of lead at higher temperature may be attributed to the decrease in the thickness of the boundary layer, decomposition of the adsorbent-metal complex and weakness in the forces of attraction between the adsorbent and the metal ion (Horsfall and Spiff, 2005; Kailas, 2010).
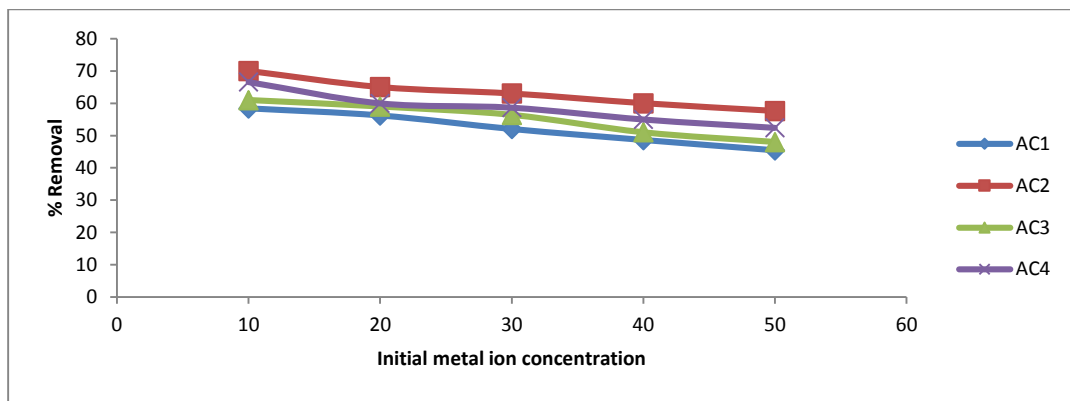

Fig. 5: Effect of variation of initial metal ion concentration on the adsorption of Pb by the adsorbents
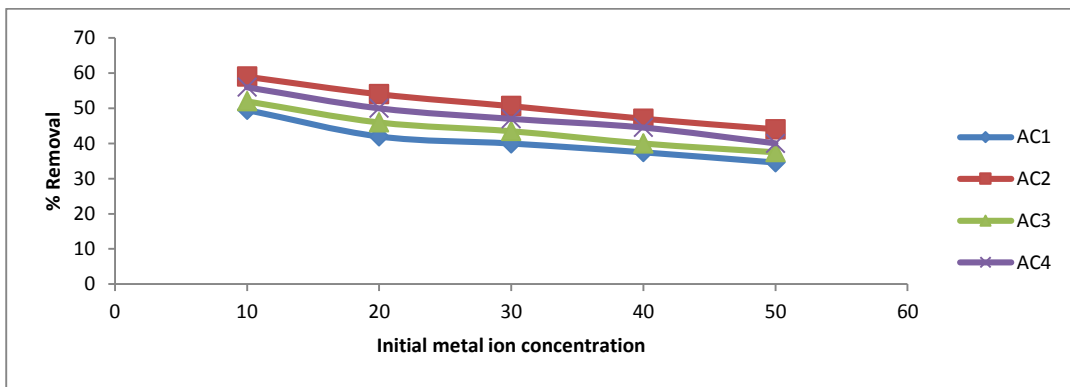

Fig. 6: Effect of variation of initial metal ion concentration on the adsorption of Cd by the adsorbents
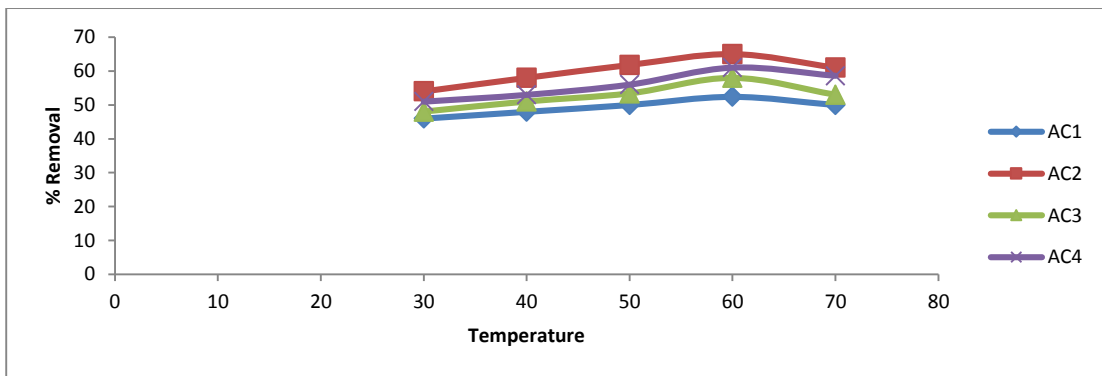

Fig. 7: Effect of variation of temperature on adsorption of Pb by the adsorbents

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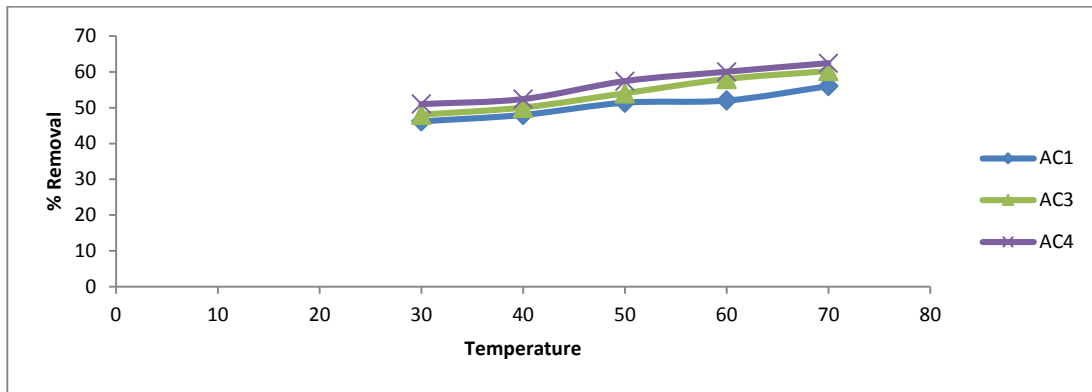
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Fig. 8: Effect of variation of temperature on adsorption of Cd by the adsorbents

Adsorption isotherm

The values of the adsorption isotherm constants are presented in Table 2. The value of the regression coefficient square (R^2) is normally used to check the fitness of an isotherm (Bansal*et al.,* 2009). R^2 value obtained for lead and cadmium showed that both isotherms give a good fit to the experimental data. Comparison of the R^2 values however shows that Freundlich isotherm has a slightly higher R^2 value than Langmuir isotherm indicating the applicability of Freundlich isotherm and a multilayer coverage (El-Batouti and Ahmed, 2014). This can be attributed to the fact that activated charcoal has large surface area; therefore a multilayer adsorption can occur on its surface.

Table 2: Adsorption isotherms parameters ofPb and Cd

Adsorbent	Heavy metal	Langmuir			Freundlich		
		q_m	b	R^2	K_f	N	R^2
AC$_1$		3682	0.036	0.997	0.176	1.388	0.991
AC$_2$		4.916	0.041	0.979	0.253	1.369	0.999
AC$_3$	Pb	3.817	0.039	0.984	0.195	1.389	0.984
AC$_4$		4.239	0.039	0.966	0.227	1.413	0.997
AC$_1$		2.721	0.031	0.964	0.129	1.461	0.998
AC$_2$	Cd	3.354	0.039	0.996	0.183	1.450	0.997
AC$_3$		2.926	0.033	0.987	0.142	1.446	0.998
AC$_4$		3.026	0.038	0.987	0.166	1.468	0.995

The Freundlich heterogeneity factor (n), used to measure the affinity of adsorbate on adsorbent should be in the range of 1-10, or 1/n should be less than 1, The n values obtained in this

present study ranged from 1.37-1.51 indicating a favourable adsorption and a formation of strong bond between the adsorbate and adsorbent (Patil*et al.,* 2006).

Adsorption kinetics

The kinetic involved in the adsorption of Pb and Cd onto AC$_1$, AC$_2$, AC$_3$ and AC$_4$, was evaluated using the pseudo-first order and pseudo-second order kinetic models. Table 3 shows the R^2 value and other kinetic parameters. The calculated equilibrium adsorptive capacity q$_e$ evaluated from the plots of pseudo-first order do not agree with experimental q$_e$. It is also evident from the Table that, the R^2 value obtained from pseudo-first order is very low. This suggests that the pseudo-first order model is not suitable for modeling the adsorption of the heavy metal ions onto the various adsorbents (Adeogun*et al.,* 2011).

The R^2 value obtained from pseudo-second order are in the range of 0.98–0.99 while the calculated equilibrium adsorptive capacity q$_e$ obtained are in close agreement with the experimental q$_e$. This indicate that the kinetic involve in the adsorption of lead and cadmium onto the various adsorbents is best described by pseudo-second order kinetic (Nassef, 2013). This suggests a chemical interaction involving valence forces due to sharing of electrons between the metals ion and the active sites of the adsorbents (Qaiser*et al.,* 2009) and also indicates that, the rate limiting step of the adsorption mechanism is chemisorption (Tuama and Mohammed, 2014).

Table 3: Kinetics properties of the different adsorbents on lead and cadmium

Adsorbent	Heavy metal	Pseudo -first order				Pseudo- second order		
		$q_e$exp	$q_e$cal	k_1	R^2	$q_e$cal	k_2	R^2
AC$_1$		0.240	0.039	0.001	0.011	0.198	4.126	0.996
AC$_2$		0.264	0.060	0.004	0.011	0.241	17.917	0.995
AC$_3$	Pb	0.226	0.053	0.003	0.007	0.209	17.560	0.994
AC$_4$		0.256	0.059	0.004	0.013	0.225	4.055	0.992
AC$_1$		0.208	0.035	0.004	0.011	0.172	0.861	0.984
AC$_2$	Cd	0.240	0.029	0.005	0.017	0.206	0.856	0.991
AC$_3$		0.216	0.027	0.006	0.021	0.181	0.850	0.988
AC$_4$		0.226	0.017	0.009	0.052	0.187	0.695	0.989

Table 4: Thermodynamics properties of different adsorbents on lead and cadmium

Adsorbent	Heavy metal	ΔH (kJ/molK)	ΔS (kJ/mol/K)	ΔG (kJ/mol/K)					
				303K	313K	323K	333K	343K	R^2
AC$_1$		4.378	0.013	-0.348	-0.215	-0.082	-0.051	-0.184	0.691
AC$_2$		7.691	0.027	-0.551	-0.823	-1.095	-1.367	-1.639	0.661
AC$_3$	Pb	6.043	0.019	-0.104	-0.092	-2.88	-0.484	-1.679	0.562
AC$_4$		8.204	0.027	-0.098	-0.372	-0.646	-0.920	-1.194	0.828
AC$_1$		8.159	0.026	-0.282	-0.022	-0.239	-0.499	-0.525	0.958
AC$_2$	Cd	10.099	0.035	-0.414	-0.761	-1.108	-1.455	-1.802	0.998
AC$_3$		11.307	0.036	-0.278	-0.086	-0.814	-0.814	-1.178	0.984
AC$_4$		10.726	0.036	-0.029	-0.384	-0.739	-1.094	-1.449	0.974

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Adsorption thermodynamics

The thermodynamic parameters values of the different adsorbents are shown in Table 4. ΔG values were negative at all studied temperature indicating that the adsorption process is feasible and spontaneous (Ge and Li, 2011). The positive values of ΔH confirmed the endothermic nature of adsorption and strong bond between adsorb ate and adsorbent which was also supported by the increase in the value of metal ion uptake as the temperature increases (Deosarkar, 2012). The positive value of ΔS shows increase in randomness of the system at the adsorbent – adsorbate interface during the adsorption process (Sarin and Pant, 2006). Generally, the adsorptive capacity of all adsorbents towards the metal ions is in the order $AC_2 > AC_4 > AC_3 > AC_1$ which shows that adsorption process is dependent on the nature of the adsorbent.

Conclusion

This result from this study showed that desert date and shea nut shell and their various blend ratios activated with 1 mol/dm³H_2SO_4 was effective for the removal of heavy metal ions from aqueous solution at low concentration in the range of 5 – 50 mg/dm³ and can be adopted in the removal of water contaminated by Pb and Cd. Operational parameters such as contact time, pH, initial concentration of metal ion and temperature influence the adsorption process. The adsorption process is simple, less expensive and can help in reducing the problem of heavy metal pollution in our environment.

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