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# **Comparative Studies on the Adsorption Efficiency of Activated Carbon Derived from Cattle Waste Parts for Removal of Heavy Metal Ions from Aqueous Solution**

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### **ABSTRACT**

*This study covers the production of activated carbon from cattle waste parts and used for the comparative study on the adsorption efficiency for some heavy metal ions from aqueous solutions. The physicochemical properties of the activated carbon such as bulk density, moisture content, ash content and surface area of the various adsorbents and the influence of pH, concentration, adsorbent dosage and contact time on the adsorption capacities of lead and nickel ions by the activated carbons were determined. The various adsorption data were fit into various isotherms with a view to determining the isotherm that best fits the data and the order of reaction. The adsorption data obtained from this study on the effect of concentration on the adsorption of the two metal ions revealed that adsorption rate increased with increase in concentration by all the adsorbents. The rate of adsorption increased as the pH of the solution increased from 2 - 8 and a slight decrease as it approached the pH of 10. It was observed generally, from the study that the rate of adsorption decreased with increase in adsorbents' dose with 0.2g having the highest values of (22.50 > 22.35 > 15.55 > 10.30 mg/g) respectively for TA, BA, HRA and HFA for lead ion.*

**Keywords:** Cattle wastes, adsorption, isotherms,

### **INTRODUCTION**

This study covers the carbonizatiOver the years, the bodies of natural waters have been polluted by man due to industrialization, population growth, uncontrolled methods of wastes disposal or management and other natural phenomena. Many of these pollutants include heavy metals, insecticides, pesticides, herbicides, fertilizers, organics, poly-aromatic hydrocarbons, domestic and industrial wastes amongst others (Bhatia, 2008). Water is a vital substance to all forms of lives and in its purest form; it is odourless and tasteless. However, whenever it is polluted, some of the aforementioned properties due to the presence of heavy metals pollutants may not be there. Indeed polluted water bodies pose a great threat to all forms of lives and heavy metals in particular, because they are not biodegraded and often tend to bio-accumulate in aquatic organisms such as fish, crabs, etc. and soil environment (Bhatia, 2008; Nagham, 2010; Rane *et al.,* 2010).

These heavy metals include metals such as lead, chromium, iron, nickel, mercury and arsenic to mention but a few. Their presence come from various sources such as metal plating, mining activities, iron smelting, batteries manufacturing, tanning of leathers, petroleum refining, agricultural activities, paint manufacturing, printing and photographic industries amongst others (Mukeshparmar and Singh, 2013; Appenroth, 2010). They often find their way into the aquatic and soil environments through industrial effluent discharge and storm water runoff. If such water is supplied directly without treatment, may not be used by the consumers due to psychological, aesthetic or physiological reasons and waterborne epidemics may be spread by supply and use of such water (Bhatia, 2008). Water pollution as a result of heavy metal has been considered to be more serious than other types of water pollution as it causes serious ill effects to the environment such as ground water pollution and soil pollution or contamination (Bhatia, 2008; Rajendran *et al*., 2011). Although, some heavy metals such as zinc, iron, copper, molybdenum, are required by most living organisms in small or trace amount for normal functioning of the system and healthy growth; although, they become toxic when they exceed their permissible limit. But even when these limits are not exceeded, there is still the possibility of a long term poisoning, since they are known to bio-accumulate within biological systems and soil environments (Bieby *et al*., 2011). According to the World Health Organization (WHO), heavy metals are known to be dangerous even at very low concentration and their presence can cause various forms of diseases (Lourie *et al*., 2010; Beesley*et al*., 2014). It has been reported that the presence of these potentially toxic metals in water and wastewaters have created enormous challenges to public health due to their negative impact and their carcinogenic nature (Duffus, 2002; Rafeah e*t al*., 2009).

According to Siegel (2002), the WHO concentration limit in drinking water for cadmium is 0.003 mg/L, copper is 1.0 mg/L, lead is 0.0015m/L, mercury is 0.001 mg/L , nickel, is 0.02mg/L and zinc 5.0mg/L. Thus, if these limits are exceeded, there is bound to be problem. Correspondingly, effective treatment of water/waste water containing heavy metals and proper management of wastes is essential for the protection and preservation of human lives

and aquatic ecosystem. Several methods and techniques have been employed by some researchers for the treatment and removal of heavy metal ions from aqueous solutions. Techniques such as chemical precipitation, oxidation, reduction, adsorption, coagulation and flocculation, solvent extraction, electrochemical treatment, membrane separation and reverse osmosis among others have been used (Moronkola *et al*., 2016). However, there are some economic challenges faced in trying to implement these technologies in small scale industries due to huge capital investment.

Coagulation, flocculation and chemical precipitation have been reported to be the most widely used techniques. However, they have the problem associated with difficulty in the disposal of sludge generated from the process and also the diminished effectiveness when treating low levels heavy metal presence in water or effluents (Ikhuoria and Okieimen, 2000). Some of these techniques suffer from low removal efficiency, particularly when treating large volumes of waste water containing low levels of heavy metal pollution (Ikhuoria and Etiuma, 2005; Cochrane *et al.,* 2006).

According to Li *et al*., (2012), many countries have guidelines and regulations forthe presence and exposure to heavy metals pollution as well as remediation and treatment options. The concentration limits to which these methods are economical and become ineffective or too expensive to treat is concentration of 100mg/L or below. This growing awareness of the potential health hazard presented by the accumulation of heavy metals in industrial and agricultural waste water streams has gained prominence and drawn the attention of some workers (Ekpo and Eddy 2009; Ikhuoria and Okieimen, 2000; Moronkola *et al*., 2016).Several non – conventional techniques have been used and adsorption has been proven to be an economically feasible alternative method as other conventional methods such as ion–exchange, precipitation, amongst others are becoming increasingly expensive. In continuation of the search for efficient and cost effective method to abate heavy metals pollution, adsorption technique uses materials that are naturally occurring and abundant, cheap and eco-friendly, have good adsorption properties and materials that have little or no economic values to the inhabitants (Moronkola et al., 2016). Also, it offers a wide range of advantages over the other conventional processes. It is said to be effective, economical, has low residual generation, ease of heavy metal removal and possibility for the reuse of the adsorbent (Moronkola *et al*., 2016).

The aim of this study is to carry out comparative studies on the adsorption efficiency of activated carbon derived from cattle waste parts for some heavy metal ions from aqueous solutions. Hence, the objectives of this study are to:

Prepare activated carbon from cattle waste parts (horn, teeth, hoof and bone) by carbonization in a muffle furnace at 600°C; Modify the activated carbon with acid (ammonium chloride) and base (sodium hydroxide) at different concentrations; Characterize and determine the physicochemical properties of the activated carbon such as bulk density, moisture content, ash content and surface area of the various adsorbents (horn, teeth, hoof and bone); Determine some important reaction parameters such as influence of pH, concentration, adsorbent dosage and contact time on the adsorption capacities of Pb and Ni ions by the activated carbons and fit the adsorption data into various isotherms with a view to determining the isotherm that best fits the data and the order of reaction.

### **METHODS**

### *Carbonization and chemical activation*

The cattle waste parts (horns, hooves, bones, and teeth) were collected from an abattoir in Oghara Community, located in Ethiop West Local Government Area of Delta State.

The adsorbents were prepared as described by (Ikhuoria and Onojie, 2007; Ikhuoria and Etiuma, 2005; Okuo and Ozioko, 2001; Ekpo and Eddy, 2009; Wartelle and Marshell 2001) with slight modifications. The cattle waste parts were thoroughly washed with water and rinsed with distilled water to remove dirt and other impurities. They were then air dried for four hours to remove moisture and taken to a muffle furnace for carbonization at a temperature of 600°C for a period of 4hrs. The cattle hooves were oven dried at a temperature of 105°C before carbonization. These various materials that were carbonized were pulverized differently to fine powered carbon. Thereafter, 510g of each of the powered carbons were weighed into eight (8) different containers. Four (4) of the containers were treated or modified with 50% ammonium chloride and the remaining four (4) containers were also treated or modified with 10% sodium hydroxide in the ratio of 2:1 (adsorbent to activating agent) and kept for an incubation period of two days. The samples were then washed several times with water and rinsed with distilled water to a constant pH in other to remove the unreacted activating agents that may be present. Thereafter, the washed samples were then oven dried at a temperature of 105°C for 24 hours and ground into powdered form using ceramic mortar and pestle.

### *Characterization of the activated carbon*

The various physicochemical properties associated with the activated carbons were characterized by following standard procedures;

### **Bulk Density**

The bulk densities of the powdered activated carbons were determined by weighing 10g each into 8 different clean dried 10ml measuring cylinders. The cylinders were then carefully tapped on the bench for the powder to fill the empty spaces. When it was observed that the continuous tapping yielded no further reduction in volume, the volume at this point was taken and recorded. The bulk density was then calculated from the relationship,

Bulk density

 $(BD) = \frac{mass\ of\ sample\ (g)}{4}$ Volume  $(cm^3)$ (2.1) This experiment was repeated twice and the mean bulk density computed (Aloko*, et al.,* 2007).

#### **Pore Volume**

2g of the powdered activated carbon was engrossed in H<sub>2</sub>O. It was then carefully heated to boiling point for about 15 minutes. Care was taken to ensure air was totally released from the pore. Then the samples werequickly oven dried at 105°C and new weight taken. The increase in weight divided by the volume of water gave the pore volume (Aloko, *et al.,* 2007).

 $p$ ore volume  $=$   $\frac{initial\ weight - final\ weight}{volume\ estimate}$ volume of water used (2.2)

#### **Ash Content**

The ash content of the samples was determined according to the method described by Eugene *et al*., (2015). 3g of the dried samples were placed into porcelain crucibles which initially was weighed and moved into a preheated muffle furnace at a temperature of 550°C. The furnace was left on for 4 hours after which the crucibles and their contents were moved to a desiccator and allowed to cool. The contents were weighed again and aptly recorded. The percentage ash contents were then calculated from the relationship.

Ash content  $\left(\% \right) = \frac{W_{ash} \times (100)}{W_{off}}$  $W_0$  of sample  $(2.3)$ 

*Wash* = content weight after final drying.

 $W<sub>o</sub>$  = the dried weight of the sample

### **Moisture Content**

1.5g of each of the samples were weighed into a crucible and dried in an oven continuously. The dried samples were constantly re-weighed at 10 minutes intervals until a constant weight was obtained. The ratio of the change in weights to the original weights expressed in percentage gave the moisture contents (Eugene *et al*. 2015).

moisture content  $=\frac{(W_0-W_{dry})\; \; x\; 100}{W}$  $W_0$  $(2.4)$ 

Where  $W<sub>o</sub>$  = weight of crucible plus weight of sample

*Wdry* = weight of sample after drying plus weight of crucible.

### **Volatile Content**

2g of the various samples were heated at 900°C for 10 minutes in anincompletelysealed porcelain crucible which has been previously weighed, and placed in a muffle furnace. The crucible and its contents wererecovered and cooled in desiccators, there after re-weighed. The differences in their weights were recorded as the percentage volatile content (VC) determined from the expression:

$$
VC = \frac{W_0^1 - W_1 \times 100}{W_0^1} (2.5)
$$

 $W_0^1$  = oven weight of the sample

 $W_1$  = weight of sample after heating at 900<sup>o</sup>C for 10 minutes.

### **Surface Area**

The iodine number method was used in the determination of the surface area of the powdered activated carbons and was done as described by Mianowski *et al.,* (2007), with minor adjustments. 0.5g of each of the samples were transferred into reagent bottles and 25ml of 0.05M iodine solution was added. Then the reagent bottles were corked and shaken for thirty minutes, after which they were allowed to stand vertically for about two hours (2hrs). Thereafter, the contents of the bottles were carefully decanted into different conical flasks.

10ml of the samples aliquots were pipetted into conical flasks and titrated against a standard solution of sodium thiosulphate until a pale yellow colour persisted. At this point 2ml of starch solution was added and the titration continued until a drop of the sulphide made the dark blue colouration turned colourless.

A blank titration (which is one that involved titrating iodine solution that was not treated with the sample) was carried out, and the iodine number (IN) calculated from the relationship.

$$
IN = \frac{Y - X \times V \times M (126.91)}{Y \times W}
$$

 $X =$  Volume of sodium thiosulphate used for sample free aliquot.

Y = Volume of sodium thiosulphate used for blank titration.

 $W = Weight of activated carbon sample$ 

 $M =$ Molarity of iodine solution used

### $V =$  Volume of iodine solution used

#### $IN =$ Iodine number

The surface area was calculated from the relationship



This experiment was done in triplicate and the mean as well as the standard deviation was calculated.

### **pH Determination**

1g of the different activated carbon was weighed into 250 ml clean dry beaker containing 100ml of the respective metal ion solutions and the mixtures stirred in a thermostat shaker bath for 1hour and subsequently filtered. The pHof the metal ion solutions were controlled by using 1 M HCl and 1 M NaOH to adjust the pH to (2, 4, 6, 8, 10, and 12)with a pH meter which was initially calibrated with standard buffer solutions 4 and 7, thereafter, the solutions were analyzed for the presence of lead and nickel ions (Aloko *et al.,* 2007; Wartelle and Marshell, 2001; Ekpo and Eddy 2009).

### *Preparation of Standards*

1000ppm of lead and nickel metal ion solutions were prepared from their respective metal salts by weighing 1.599g and 4.95g of lead nitrate and nickel nitrate hexahydrate respectively. These metal salts were then dissolved in about 1000ml distilled water in two different standard volumetric flasks. Each flask contents were made up to mark with distilled water. Thereafter, from the 1000ml of metal ion Solutions different concentrations ranging from 10, 20, 30, 40 and 50ppm of the two metal ions were prepared by simple dilution from their respective 1000ppm solutions. These solutions were stored in clean reagent bottles and adequately labeled in preparation for the analysis. These various standard solutions are the aqueous solutions used for the analysis.

### *Metal ions determination*

Adsorption studies were carried out for the following metal ions: lead (Pb<sup>2+</sup>) and nickel (Ni<sup>2+</sup>) according to the methods described (Ikhuoria and Okieimen, 2000; Ikhuoria and Onojie, 2007) with slight modifications. The batch adsorption studies were conducted at room temperature by mixing various weights (0.2g, 0.4g, 0.6g, 0.8g and 1.0g) of each of the activated carbon sample, with 100ml solution of the nickel and lead metal ion solutions (Adsorbate) previously prepared in plastic bottles. In each case the mixtures were put in an orbital shaker for a contact period of one hour. The respective solutions were then centrifuged at a speed of 240rpm and allowed to stand for a period of 30mins while the supernatants were subsequently decanted carefully and kept for the various metal ion analysis.

### *Equilibrium studies.*

Equilibrium sorption of lead and nickel ions on the powered activated carbon was examined at 29°C at different initial metal ion concentrations of 10ppm, 20ppm, 30ppm, 40ppm and 50ppm, from standard solutions of the two metal ions respective salts (lead nitrate and nickel nitrate hexahydrate). The effect of contact time on the adsorption of the metal ions were also studied ranging from 20 min, 40 min, 60 min, 80 min and 100 min respectively. The adsorbent dosage on the adsorption of lead and nickel ions from aqueous solutions (solution of the metal ions) were also evaluated as described by Ikhuoria and Etiuma (2005). The dosages used are 0.2g, 0.4g, 0.6g, 0.8g and 1.0g. The pH of the solutions of the metal ions were controlled by using 1MHCl and 1MNaOH to adjust the pH to 2, 4, 6, 8, 10 and 12 as described by Ekpo and Eddy (2009).Generally, equilibrium is achieved when the capacityof the adsorbents are saturated, thus making the rate of adsorption equals the rate of desorption (Payne and Abedel-Fattah, 2004).

### **RESULTS**









**BB**<sub>A</sub>(bone acid), **BB**<sub>B</sub>(bone base), **HF**<sub>A</sub> (hoof acid), **HF**<sub>B</sub>(hoof base).





 $HR_A$  (horn acid),  $HR_B$  (horn base),  $TT_A$  (teeth acid),  $TT_B$  (teeth base),  $BB_A$ (bone acid),  $BB_B$ (bone base),  $HF_A$  (hoof acid),  $HF_B$  (hoof base).

**Table 3: Effect of concentration on the amount of lead ion adsorbed.** 

Concentration	TA	TB	<b>HRA</b>	<b>HRB</b>	<b>HFA</b>	<b>HFB</b>	BA	BB
(ppm)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
10	0.86	0.650	0.900	0.270	0.880	0.820	0.830	0.470
20	1.77	1.730	1.798	0.960	1.440	1.690	1.690	1.730
30	2.64	2.499	2.691	2.361	1.770	2.580	2.679	1.920
40	3.60	3.572	3.580	2.940	3.580	3.460	3.572	3.020
50	4.48	4.220	3.700	3.750	4.400	4.370	4.460	4.020

 $HR_A$  (horn acid),  $HR_B$  (horn base),  $TT_A$  (teeth acid),  $TT_B$  (teeth base),  $BB_A$ (bone acid),  $BB_B$ (bone base),  $HF_A$  (hoof acid),  $HF_B$ (hoof base).

**Table 4: Effect of adsorbent dosage on the amount of Ni ion adsorbed.**

Dosage	TA	TB	<b>HRA</b>	<b>HRB</b>	<b>HFA</b>	<b>HFB</b>	BA	BB
(g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)	(mg/g)
0.2	11.00	15.250	6.200	5.900	10.70	9.250	12.55	15.50
0.4	7.313	8.375	5.450	7.750	6.125	5.025	6.525	9.275
0.6	5.333	7.078	2.500	3.067	4.417	7.483	4.433	7.033
0.8	4.719	5.549	1.938	1.625	3.025	3.525	3.675	5.425
1.0	3.925	4.456	1.140	2.750	2.470	3.670	2.990	3.130

 $HR_A$  (horn acid),  $HR_B$  (horn base),  $TT_A$  (teeth acid),  $TT_B$  (teeth base),  $BB_A$ (bone acid),  $BB_B$ (bone base),  $HF_A$  (hoof acid),  $HF_B$ (hoof base).

### **Table 5: Effect of adsorbent dosage on the amount of lead ion adsorbed.**





 $HR_A$  (horn acid),  $HR_B$  (horn base),  $TT_A$  (teeth acid),  $TT_B$  (teeth base),  $BB_A$ (bone acid),  $BB_B$ (bone base),  $HF_A$  (hoof acid),  $HF_B$ (hoof base).



 $HR_A$  (horn acid),  $HR_B$  (horn base),  $TT_A$  (teeth acid),  $TT_B$  (teeth base),  $BB_A$ (bone acid),  $BB_B$ (bone base),  $HF_A$  (hoof acid),  $HF_B$ (hoof base).



 $HR_A$  (horn acid),  $HR_B$  (horn base),  $TT_A$  (teeth acid),  $TT_B$  (teeth base),  $BB_A$ (bone acid),  $BB_B$ (bone base),  $HF_A$  (hoof acid),  $HF_B$ (hoof base).

### **Table 9: Effect of pH on the amount of Lead adsorbed.**

**Table 7: Effect of contact time on the amount of lead ion adsorbed**.

**Table 8: Effect of the pH on the amount of Nickel ion adsorbed.** 





HRA (horn acid), HRB (horn base), TTA (teeth acid), TTB (teeth base), BBA(bone acid), BBB(bone base), HFA (hoof acid), HFB(hoof base).

### **Table 10: Freundlich and Langmuir adsorption isotherms**



### **Table 11: Temkin adsorption isotherm**





### **Table 12: Kinetics of adsorption of nickel and lead by activated carbon.**

### **DISCUSSIONS**

### *Ash Content*

According to Bansal *et al.*, (1998), all activated carbons have a porous structure containing up to 15% of minerals matter in the form of ash content. Comparing the acid activated and base activated carbon, teeth and bone had more ash contents of 95% and 80% respectively for theacid modified activated carbon as against 84.5% and 70.5% respectively obtained for the base modified, while the horn had (30.5% and 15.5%) and hoof had the least (03% and 08%) for both acid and base modified activated carbon respectively. The importance of ash content is that it gives an idea of the amount of mineral elements present and content of organic matter in a sample. The percentage ash content is of the order: teeth> bone> horn> hoof for both the acid and base activated carbon (95>80>15.5>03) and (84.5>70.5>30.5>08) percent respectively. The teeth enamel can be described as a strong tissue; it is the most mineralized tissue in the body (Pilar and Reyes-Gasga, 2003).

### *Volatile Organic Matter (VOM)*

Organic matter may be defined as a material that is capable of decay or the product of decay (humus), or both. Usually, the matter will be the remains of recently living organisms, and may also include organism that is still living. According to Malik *etal*., (2006), VOM is responsible for the decomposition of the organic materials that release volatiles as well as produce micro porous assemblies. Olowoyo and Orere, (2012), also reported that low volatile content infers high porosity of the adsorbents. This is so as high volatile matter may block the carbon pores. The VOM, is of the order: Hoof>Horn>Born>Teeth for the acid modified carbon (97%, 84.5%, 20% and 5%) respectively, and for the base it is in the same order as in the acid activated (92%, 69.5%, 29% and 15.5%) respectively. Low volatile matter was recorded for both teeth and bone in this study as compared with the hoof and horn. The results from this study therefore indicate that the two materials "bone and teeth" will be better adsorbents than the hoof and the horn with the teeth being the best.

### *Moisture Content (MC)*

Moisture content is the quantity of water contained in a material. The percentage moisture contents of the activated carbon in this study for both the acid and base modified are in this order: horn > bone > hoof > teeth (20.07, 11.33, 8.67 and 4.24) percent respectively for the acid modified and for the base, horn > bone >hoof > teeth (28. 80, 16.16, 6.80 and 5.91) percent respectively. From the result of the study, horn and bone contain higher MC as compared to the hoof and teeth.Moisture content, according to Aziza *et al.,* (2008) has a relationship with porosity of a given carbon. According to them, adsorbent with high moisture content will swell less, thereby retarding pore size expansion for adsorbent uptake. Again, making the teeth the best.

### *Bulk Density (BD)*

Bulk density may be defined as the weight of fiber per unit volume, often expressed as g/ml and is a good index of structural changes (Sreeama *et al*., 2009). The weighty subject of bulk density relates simply to the ratio of solid material (e.g. sand, silt, and clay particles) to pore space (porosity) in a given sample of that material. The relationship between bulk density and porosity is reciprocal; bulk density increases as porosity decreases. Generally, the density of a generated activated carbon significantly affects the adsorption capacity of the adsorbent.According to Jibril, *et al*., (2007), higher density carbons have the capacity to hold more adsorbate per unit volume. From the result of the analysis in Table 3.1, BD is of the order: teeth> bone>horn>hoof for the acid activated  $(1.010g/cm^3, 0.875g/cm^3, 0.700g/cm^3$  and  $0.699g/cm^3$ ) respectively. The B.D of the bone was in accordance with what was obtained by Abdul-Rahman *et al.,* (2016), who reported that B.D of bone was 0.81g/ml. Also, from this result it has demonstrated that the teeth will be the best adsorbents as compared to the other parts examined. As reported by Jibril, *et al*., (2007), higher density carbons hold more adsorbate per unit volume.

### *Pore Volume (PV)*

The high adsorptive capacities of activated carbons are highly related to porous characteristics such as surface area, pore volume and particle size distribution. Pore volume may be defined as the ratio of a porous material's air volume to that of a porous material's total volume or the total volume of very small openings in a bed of adsorbent. Adsorption pores are the only regions within an activated carbon particles with sufficient adsorption forces to adsorb impurities. They are the smallest pores within the particles. The pore volume is of the order: teeth>bone>horn>hoof.

### *Surface Area (m<sup>2</sup> /g)*

Surface area is related to particle size, particle morphology, surface texture and porosity. It is one of the important characteristics of solid materials that highly determines the properties and performance of catalysts, sorbents etc. An ordinarily dense solid is unsuitable as a catalyst because its surface area is quite low. The high surface area results from the many small connected particles. The result obtained for the surface area was found to be Horn>bone>hoof>teeth (49.12 m<sup>2</sup>/g, 42.34 m<sup>2</sup>/g, 11.92 m<sup>2</sup>/g and 5.61 m<sup>2</sup>/g,) respectively for the acid activated. It is in the same order with the base also, but with different values. From literature, it has been reported that variations in the surface area of material may be due to the mode of activation and nature of the chemical used.

### *METHOD OF ADSORPTION*

The amount of metal ion adsorbed was calculated using equations 1 and 2 below:

$$
Q_e = \frac{V(C_o - C_e)}{W}
$$
  
\n
$$
Q_t = \frac{V(C_o - C_t)}{W}
$$
\n(1)

Where,  $Q_e(mg/g)$  is the amounts of adsorbent uptake at equilibrium,  $C_o(mg/l)$  and  $C_t$  are the adsorbate concentrations at initial stage and at time (t),  $C_e(mg/l)$  is the equilibrium concentrations, W(g) dry weight of the adsorbent and V (L) is the volume of the solutions respectively.

### *Effect of Concentration*

Figures 1 and 2 below show the effect of concentration on the amount of nickel and lead ions adsorbed. The effect of the initial metal concentration was studied at room temperature (25°C) at varied concentrations of 10, 20, 30, 40 and 50ppm respectively. The results obtained, showed that there was a general increase in the amount of the two metal ions adsorbed by all the adsorbents. The TB was observed to have the highest value of 4.423mg/l representing (88.46%) at the concentration of 50ppm, followed by BB with a value of 3.12mg/g representing (78%) at 40ppm while the least value 0.77mg/l representing (19.25%) was observed for HRB at the same concentration for Ni for the base modified adsorbents. For lead, TA had 4.48mg/l representing (89.60%) and BA, 4.46mg/l (89.2%) adsorption at concentration of 50ppm while the least value of 0.27mg/l (27%) was observed for HRB at the initial concentration of 10ppm for the acid modified adsorbents. Generally, the base activated carbon was observed to have the highest values for Ni ion and the acid activated ones was observed to have the highest values for Pb ion adsorbed. Ni ion adsorption, there was an increase in the amount of metal ion adsorbed at concentrations range of 10 – 30ppm, but at concentrations above 30ppm, irregular trend was observed in all the adsorbents except for TB and TA where the quantity adsorbed continued to increase with increase in the concentration of the adsorbent. According to Ekpo and Eddy (2009), adsorption of metal ions from aqueous solution depends on several factors such as pH of the solution, surface area of contact, chemical composition of the material, temperature of the solution, ionic character of the metal ion and, molecular weight of the metal ion. The percentage extraction by the activated carbons is of the order: TB > BB > HFB >HRB respectively for nickel base and TA >HFA>HRA >BA for lead acid respectively at concentration of 40ppm. The higher values obtained for lead may be due to its high molecular weight as compared to that of nickel.



*Figure 1: Effect of concentration on the amount of nickel ion adsorbed.*



*Figure 2: Effect of concentration on the amount of lead ion adsorbed*

### *Effect of Adsorbent Dose*

Figures 3 and 4 below show the effect of adsorbent dosage on the amount of nickel and lead ions adsorbed by the activated carbons. Lead ion was most adsorbed onto the activated carbons generally by all the adsorbents as compared to the nickel ion. From the Figures, the amount of metal ions adsorbed increased with decrease in the adsorbent dose, this might be as a result of aggregation of the adsorbents and consequently, the available adsorption site might decrease.

Also, it might be attributed to the fact that adsorption capacity of the adsorbents available was not fully utilized at higher adsorbent dosage in comparison to lower adsorbent dosage, a trend in line with previous studies (El-Ashtoukhy *et al*., 2008). He explained that at low concentrations metals are adsorbed by specific sites, while with increasing metal concentrations specific sites are saturated and the exchange sites are filled.

At 0.2 doses for lead, amount adsorbed is of the order: Teeth > Bone>Horn> Hoof (22.50>22.35>15.55>10.30 mg/g) respectively for the acid activated. For the acid activated, it is in the same order too, Bone > Teeth> Hoof> Horn (12.55 > 11.00 > 9.25 > 6.20 mg/g) respectively for Ni as presented in Tables 4 and 5 in the appendix. Adsorption amount (not capacity) decrease with increase in adsorbent dose simply because they have an inverse relationship, that is, removal efficiency (expressed in %) improves if the dosage is increased. However, removal capacity (expressed in mg/g) decrease as the dosage is increased. Researchers have attributed this to the availability of the active sites/ surface area for the adsorption of the metal ion. Result from this study show that at lower adsorbent dosage, the number of nickel and lead ions adsorbed were relatively higher, as compared with the higher dose. Sofia *et al.*, (2014), reported that an adsorbent dose of 0.1 g is sufficient for optimal removal of metal ions from aqueous solution



**Figure 3: Effect of adsorbent dosage on the amount of nickel ion adsorbed.**



*Figure 4: Effect of adsorbent dosage on the amount of lead ion adsorbed.*

### *Effect of Contact Time*

The effect of contact time on the adsorption process of the metal ions are shown in Figures 3.5 and 3.6, the data are presented in Tables 6 and 7. In any adsorption study, effect of contact time plays a vital role apart from other experimental parameters affecting adsorption kinetics and thermodynamics. This study was carried out at different contact time at constant initial concentration of lead (II) and nickel (II) ions with fixed adsorbent dose. From the results, the amount of metal ions adsorbed approached equilibrium within the first 40 min of contact time by HFB Ni (4.49 mg/g) on Ni ion and TA (4.50  $mg/g$ ) on Pb ion, thereafter, the amount adsorbed increased slightly until complete equilibrium was established within 60 – 100 min by all the adsorbents for both metal ions (Ni and Pb). Instantaneous adsorption process recorded by the activated carbons demonstrated that these materials have strong affinity for Ni and Pb ions. This study shows that the different metal ions attained equilibrium at different times by all the adsorbents, with the base modified adsorbing more of the nickel ion and the acid modified adsorbing more of the lead ion in most cases. The amount adsorbed by the activated carbons is of the order: BB> TB> HFB > HRB (4.27, 3.80, 2.58, and 1.30 mg/g) for base modified respectively for nickel and TA>BA > HRA > HFA (4.48, 4.47, 4.40 and 2.70 mg/g) for acid modified respectively for lead at the initial time of 20 min.



*Figure 5: Effect of contact time on the amount of nickel ion adsorbed.*



*Figure 6: Effect of contact time on the amount of lead ion adsorbed.*

### *Effect of pH*

The pH is a controlling factor for any kind of metal ion adsorption process from aqueous solution (Martinez*et al.,* 2003). The result from the study as presented by Figures 3.7 and 3.8 below, and also shown in the Tables 8 and 9. Generally, it was observed that the amount of the metal ions adsorbed increased with increasing pH in the range of 2-8 and decreased slightly in the pHrange of 10-12. The highest value was recorded by TB (0.978 mg/g), and the least value was (0.342 mg/g) for HFB for Ni. For lead it is of the order (1.228 mg/g) for BB and the lowest was (0.310 mg/g) for HRA at pH 8.

As explained by Martinez *et al.,* (2003), adsorbents with pH 6 – 8 are conventionally accepted in most applications generally. Lead ion was found to be more readily adsorbed than the Ni ion by the activated carbons, attaining maximum values of (1.228 mg/g) for Pb and (1.189 mg/l) Ni ions at of pH 8. This is an indication that adsorption was more favourable using the base modified carbon as compared to the acid modified carbon in this study. This result compared favourably with the explanation of Hasan, *et al* (2008). He explained that any sorbent surface creates either positive or negative charge on its surface; in acid medium adsorbent surface is highly protonated, which may not be too favourable for positively charged metal ion uptake, but at higher pH values the adsorbent surface begins to acquire a net negative charge making the solution electrostatically favourable for metal ion uptake. The lower values recorded by the adsorbents in acidic conditions (pH <7) could probably be due to the presence of high concentration of Hydrogen ions (H<sup>+</sup>) on adsorbent surface competing with the metal ions at the adsorption site (Ekpo and Eddy, 2009; Hynda and Rachinda., 2008). Adsorption is of the order bone > teeth > horn > hoof for Pb ion uptake for acid modified and teeth > bone > horn > hoof for Ni ion uptake for the base modified at pH of 8 respectively.



*Figure: 7: Effect of pH on the amount of nickel ion adsorbed.*



*Figure 8: Effect of pH on the amount of lead adsorbed.*

### *Adsorption isotherms*

In order to determine the adsorption capacity and potential for selecting the adsorbent for the removal of metal ions, the study of adsorption isotherm is essential in selecting the adsorbent for the removal of metal ions. The adsorption data obtained from the study was subjected to Langmuir, Freundlich and Temkin isotherm models in order to verify the adsorption performance. It was found that Langmuir isotherm had the best fit when compared to the Freundlich and Temkin isotherms (Guo *et al.,* 2017).

### **Langmuir Isotherm**

The linearized form of Langmuir equation is represented by eqn 3.3 below

$$
\frac{c_e}{q_e} = \frac{1}{b q_m} + \frac{c_e}{q_m} \tag{3}
$$

Where,  $Q_e$  = amount adsorbed per unit mass of the adsorbent (m/g),

 $C_e$  = the equilibrium concentration of the adsorbate (m/L),

 $Q_m$  = the equilibrium adsorption capacity for complete monolayer (mg/g) and

b = Langmuir adsorption equilibrium constant related to the energy of adsorption.

Using equation 3.3, the plots of log ( $C_e/Q_e$ ) versus log  $C_e$  (the graphs shown below were linear with very high  $R^2$  values.











**Figure 9c**

![](_page_15_Figure_3.jpeg)

The data of Langmuir adsorption parameters deduced from the plots are presented in table 10 with high  $R^2$  values ranging from (0.8021 – 0.9999). Essentially, the vital components of the Langmuir adsorption isotherm can be presented in the form of a dimensionless constant designated as the separation factor. It is also referred to as the equilibrium parameter  $(K_L)$ . It can be defined as:

$$
k_{L} = \frac{1}{1 + KC_{0}}\tag{4}
$$

Where,  $C_0$  is initial concentration of the adsorbate. The significance of equation (3.4) is that, when  $K_L > 1$ , the adsorption is unfavourable; when  $0 < K_L <$ l, the adsorption is favourable and when  $K_L = 0$ , the adsorption is irreversible. About (97%) of the values of  $K_L$  obtained in this study (Table 3.10) were within the range of 0 and unity for most of the adsorbents except in few cases for HRA Ni (2.419), HFA Ni (3.120) and BA Ni (3.295) that were above unity. Generally, these values that were between zero and less than unity  $(0.9999 > 0.9790 > 0.8954 > 0.8439)$  suggesting that the adsorption of Pb<sup>2+</sup> and  $Ni<sup>2+</sup>$  onto the AC is favourable.

### **Freundlich Isotherm**

Freundlich adsorption isotherm can be represented according to equation(3.5) which can also be written as equation (3.6) respectively below:

![](_page_15_Picture_302.jpeg)

Where, K<sub>r</sub>and n are Freundlich equilibrium constants relating to adsorption capacity and adsorption intensity, respectively. The values of K<sub>f</sub> and n can be obtained from the intercept and slope respectively and the logarithmic plot of  $Q_e$  versus  $C_e$  Where;

Qe= amount adsorbed per unit mass of adsorbent.

 $C_e$  = adsorbate equilibrium concentration.

The graphs of Freundlich adsorption isotherm for the adsorption of Pb(II) and Ni (II) ions from aqueous solution onto the AC are presented below. Values of adsorption parameters deduced from Freundlich adsorption isotherm are also recorded in table 10 with the  $R^2$  values ranging from (0.006 – 0.949). Although, from the result, it was seen that values of n are less than unity indicating that the experimental equilibrium data can inadequately be described by the Freundlich model. Some of the graphs are presented below:

![](_page_16_Figure_1.jpeg)

![](_page_16_Figure_2.jpeg)

![](_page_16_Figure_3.jpeg)

![](_page_16_Figure_4.jpeg)

![](_page_16_Figure_5.jpeg)

### **Temkin Isotherm**

This isotherm contains a factor that clearly takes into account of adsorbent- adsorbate interactions. By ignoring the extremely low and large value of concentrations, this model assumes that heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmic with coverage (Guo et al., 2017).From the equation below, its derivation is characterized by uniform distribution of binding energies was carried out by plotting the quantity adsorbed  $q_e$  against lnC<sub>e</sub> and the constants were determined from the slope and intercept from the equation given below:

### **Temkin equation:**

$$
Q_e = B\ln K + B\ln Ce
$$

B= heat of adsorption

 $K =$  equilibrium binding constant

Ce = concentration at equilibrium.

A plot of Temkim adsorption isotherm presented below.

![](_page_17_Figure_1.jpeg)

*Figure 11: Plot of Temkim adsorption isotherm*

### *Kinetics of adsorption.*

In this study, the adsorption mechanisms were determined using the pseudo-first order and pseudo-second order models. The non-linear forms of the pseudo-first order model (Lagergrens, 1998)and pseudo-second other model (Blanchard *et al*., 1984), are expressed mathematically by the equations 7 and 8 below:

$$
\ln(q_e - q_t) = \ln q_e - k_1 t(3.7) \tag{7}
$$

Where  $k_1$  is the pseudo-first order rate constant and  $q_e$  and  $q_t$  are the adsorption capacities of the adsorbents at equilibrium and time t, respectively for Pseudo-first order model. The pseudo-second order model can be expressed as follows:

(9)

$$
q_t = q_e (1 - e^{-k_1 t})
$$
\n
$$
q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t}
$$
\n(8)

Where  $k_2$  (g/mg) is the rate constant for pseudo-second –order.

 $Q_e$  and  $q_t$  are the amount of adsorbates uptake per mass of the adsorbent at equilibrium and at any time t (min) respectively.

The values of the first and second order rate constants along with their R<sup>2</sup>-values are presented in table 12.

Generally, the pseudo-second order model fitted more than that of the first order as they presented very high  $R^2$  values. The range is between (0.012 – 0.547) for TA (Ni) and HRA (Pb) respectively for first order and (0.999 – 1.000) for HFA (Ni) and TA (Pb) respectively for second order model expect  $0.6528$  for HFA (Ni) which is a little lower than the other values. Also, the (q) calculated values for the pseudo second order are not too far from the (q) experimental values as compared to that of the first order as presented by table 12.

Below are some of the graphs showing the plots of the first and second order adsorption kinetics.

![](_page_18_Figure_1.jpeg)

![](_page_18_Figure_2.jpeg)

![](_page_18_Figure_3.jpeg)

![](_page_19_Figure_1.jpeg)

**Figure 12c**

![](_page_19_Figure_3.jpeg)

**Figure 12d Figures 13 (a)-(d): Plots of first order kinetics**

![](_page_20_Figure_1.jpeg)

![](_page_20_Figure_2.jpeg)

![](_page_20_Figure_3.jpeg)

![](_page_20_Figure_4.jpeg)

**Figure 14b**

![](_page_21_Figure_1.jpeg)

**Figure 14d Figures 14 (a)-(d): Plots of second order kinetics.**

### **Findings**

The following were the findings from the study:

1. The alkaline modified adsorbent was found to be more effective in the removal of the metal ions than the acid modified in most cases for some of the adsorbents.

- 2. Lead ion was more readily adsorbed onto these adsorbents than the nickel ion.
- 3. The amount of metal ion adsorbed increased with increase in pH of the solution attaining a maximum value at pH of 8.
- 4. The Langmuir isotherm had the best fit for the adsorption than the Freundlich and Temkim isotherms.
- 5. The pseudo- second order model fitted the experimental data better ascompared to the pseudo- first order.
- 6. Adsorption capacity of the adsorbents was generally observed to be of the order: Teeth > bone > hoof > horn.

### **Conclusion**

In this study, activated carbon was prepared from cattle waste parts (hoof, horn, teeth and bone) through carbonization. It was characterized and used as adsorbents for the removal of Pb (II) and Ni (II) ions from aqueous solutions. These cattle waste parts which are usually available in abattoirs constitute nuisance to the environment, and are considered fit only for disposal. The activated carbon so produced from the cattle waste parts were subjected to physicochemical analysis. The results obtained showed that these materials are good source of adsorbents for the removal of lead (II) and nickel (II) ions from aqueous solutions with the teeth being the best as it has the highest bulk density. Higher density carbon holds more adsorbate per unit volume (Jubril, *et al.,* 2007). Again, the teeth have the lowest moisture content as compared with the others. Moisture content according to Aziza *et al.,* (2008), has a relationship with porosity of a given carbon as adsorbents with low moisture content will adsorb more as compared to the one with higher moisture content. The adsorption data obtained from this study on the effect of concentration on the adsorption of the two metal ions revealed that adsorption rate increased with increase in concentration by all the adsorbents. At concentration of 50 ppm for example, adsorption is of the order: Teeth > bone > hoof > horn (4.48, 4.460, 4.400 and 3.700 mg/g) respectively for Pb ion. The rate of adsorption also increased as the pH of the solution increased from 2 to 8 and a slight decrease as it approached the pH of 10, according to Hasan, *et al* (2008), in acidic medium adsorbent surface is highly protonated, which may not be too favourable for positively metal ion uptake, but at higher pH the adsorbent begins to acquire a net negative charge making the solution electrostatically favourable for metal ion uptake. Adsorption attained equilibrium within the first 40 min of contact time. It was observed generally, from the study that the rate of adsorption decreased with increase in adsorbents' dose with 0.2g having the highest values of  $(22.50 > 22.35 > 15.55 > 10.30$ mg/g) respectively for TA, BA, HRA and HFA for lead ion. Sofia *et al* (2014), reported that adsorbent dose of 0.1g is sufficient for optimal removal of metal ions from aqueous solutions. The three adsorption isotherms used for this study are the Langmuir Freundlich and Temkim. The Langmuir had the highest regression  $(R^2)$  values, hence the best fit. The data obtained from kinetics studies also revealed that the adsorption was of the second order as the data obtained had very high  $R^2$  values and also, the values of the q<sub>e</sub> calculated are closer to the q experimental as compared to that of the first order. It has been established in this study that cattle waste parts can be converted to useful products one of such is activated carbon. This will help in reducing their negative impacts on the environment and also serve as a source of wealth creation thus reducing poverty.

### **REFERENCES**

Abdolali, A., Guo, W.S., Ngo H.H., Chen, S.S., Nguyen, N. C. and Tung, K. L. (2014). Typical lingo-cellulosic wastes and by-products for biosorption process in water and wastewater treatment: A critical review. *Bio-resource Technology*. 160: 1-15.

Abdul-Raham, A., Latiff, A.A.A., Daud, Z., Ridzuan, M. B., N.F.M.D. and Jagaba A.H. (2016). Preparation and Characterization of Activated Cow Bone Powder for the Adsorption of Cadmium from Palm Oil Mill Effluents. *IOP Conf. Series: Material Science and Engineering.*136:1-5.

Ademiluyi, F. T. and David-West, E. O. (2012). Effect of Chemical activation on the Adsorption of Heavy Metals using Activated Carbons from Waste Materials. *International Scholarly Research*. 12 (3):321-49

Afshin, M. and Masoud, A.Z., (2008). Heavy metals in selected edible vegetables and estimation of their daily intake in sandbag, Iran. *Southeast Asian Journal Tropical Medical Public Health.* 39(2): 335-34.

Agunsoye, J. O., Talabi, S. I., Awe, O. and Kelechi, H. (2013). Mechanical Properties and Tibological Behaviour of Recycled Polyethylene/ Cow Bone Particulate Composite. *Journal of Material Science Research*. 2(2):41 -50.

Aloko, D. F. and Abebayao, G.A. (2007). Production and characterization of activated carbon from agricultural waste. *Medwel Journal*. 2:440-444.

Alosman, M., Yang, F. and Massey, I. (2019). Exposure routes and health effects of heavy metals on children. *Journal of BioMetals.* 32 (10): 193-195

Ananda, S. (2003). "Zinc Deficiency". *British Medical Journal*. 326: 388-409.

Aniket, E., Kale, M. B., Mandake, V. D. and Chitodkar. (2017). Removal of Heavy Metals using Adsorption Process- A Review. *International Journal of Advance Engineering and Research Development.*4: 123-334.

Appenroth, K.J. (2010). Definition of heavy metals and their role in biological systems. *Acta Physiol Plant*. 32:615-619

Aswin, K. R. and Baskar S. (2018). A Review on Adsorption of Nickel and Mercury from Aqueous Solution Using Nanoparticles*. International Journal of Civil Engineering and Technology (IJCIET)*. 9: 1246–1255.

Aziza, A., Odidiakosa, A., Nwajei, G. and Orodu, V. (2008). Modification and Characterization of Activated Carbon derived from sawdust. *Conference proceeding, CSN Delta Chem. 235 - 243.* 

Azzi, R.R., Denio, E. A., Ilza, D., Silvio, F.V.B., Claudio, L.D. and Rochel, M.L. (2003). Tailoring activated carbon by surface chemical modification with O, S and N containing molecule. *Journal of Material Research*. 6: 1439-1516.

Bansal, R.C., Donnet, J. B and Stokeli, H. F. (1988). Active Carbon. Marcel Dekker, New York. 134-138

Bansode, R.R., Losso, J.N., Marshall, W.E., Rao, R.M and portier, R.J. (2003). Adsorption of volatile organic compounds by pecan shell and Almond shell Based Granular Activated Carbons. *Bio-resource Technology*. 90: 175-184.

Beesley, L., Inneh, O.S., Norton, G.J., Moreno-Jimenez, E., Pardo, T., Clemente, R. and Dawson, J.J. (2014). Assessing the influence of compost and biochar amendments on mobility and toxicity of metals and Arsenic in a naturally contaminated mine soil. *Journal of Environmental pollution*. 186: 196- 202.

Bhatia, S.C. (2008). Water pollution; Environmental Chemistry. CBS Publishers and Distributors. Ganji, New Delhi., India. 80 – 82.

Bhattacharya, K.G., Gupta, S. S. and Sarma, G.K. (2015). Kinetics, equilibrium isotherms and thermodynamics of adsorption of cargo red onto natural and acid treated kaolinite and montmorillonite*.Journal of Desalination and water treatment.* 78: 530-540

Bieby, V. T., Siti-Rozaimah, S. A., Hassan, B., Mushrifah, I., Nurina, A. and Muhammad, M. (2011). A Review on Heavy Metals (As, Pb, and Hg) Uptake by Plants through Phytoremediation. *International Journal of Chemical Engineering*. 939:1-31.

Blanchard, G., Maunaye, M. and Martin, G. (1984). Removal of heavy metals from waters by means of natural zeolites. *Journal of Water Research*. 18 (12): 1501-1507.

Braun, C. L., Sergei, N. and Smirnov, N. (1993). ["Why is water blue?".](http://www.dartmouth.edu/~etrnsfer/water.htm) *Journal of Chemistry Education*. 70 (8): 612.

Bulut, K. and Tez, O. (2007). Investigating some unconventional methods and low cost materials for scavenging heavy metals ions from industrial waste water. *Journal of Water Management*. 214: 95-100.

Chen, L., Helevenius, J. and Kangus, A. (2005). Meat bone as Nitrogen and Phosphorous Fertilizer. *DIC Association of Agricultural Scientists Journal*. 5(2): 2-16.

Cheung, C.W., Porter, J. F. and Mackay G. (2001). Sorption kinetics analysis for the removal of cadmium ions from effluents using bone char. *Journal of Water Research.* 158: 605 – 612.

Cochrane, E. L., Lu, S., Gibb, S. W. and Villaescusa, I. (2006). A comparison of low-cost biosorbents and commercial sorbents for the removal of copper from aqueous media. *Journal of Hazardous Materials*, 137(1): 198-206.

Costa, L. M., Araujo, K., Sapag, M., Sardella, H., Silva, C., Deiana. and Lago, R. M. (2005). High surface area functional carbon briquettes: A novel adsorbent for metals from water. *Journal of Brazilian Chemical Society*. 16(5): 899-902.

Demirezen, D and Ahmat, A. (2006). Heavy metals levels in vegetables in Turkey are within safe limits for Cu, Zn, Ni and exceeded for Cd and P. *Journal food Quality*. 29:252-265.

Duffus, J.H. (2002). "Heavy Metals": A meaningless term?. *Pure and Applied Chemistry Bulletin*. 74(5) 793-807.

Edmund, T. Rolls. (2005). *"Emotion Explained*". Oxford University Press, Medical. London. 1<sup>st</sup> Edition.

Eichler, H. J., Eichler, J. and Lux, O. (2018). Adsorption and Emission of Light: Basics, Advances and Applications. 29-49

Ekpo, A.S. and Eddy, N.O., (2009). Adsorption of  $Pb^{2+}$ ,  $Zn^{2+}$ , and  $Ni^{2+}$ , from Aqueous Solution by Helix *aspera* Shell. *E-Journal of Chemistry*. 6(4): 1029 – 1034.

El-Ashtoukhy, E. S. Z., Amin, N. K. and Abdelwahab, O. (2008). Removal of lead (II) and copper (II) from aqueous E.S.Z. solution using pomegranate peel as a new adsorbent. *Desalination*. 223: 162-173.

Eneh, O. (2007). Improving the access to portable water in Nigeria. *African Journal of Science*. 8. 1962-1971.

Eugene, N., Onyeike, Ernest A., Anyalogbu, Micheal. O. Monunu, (2015). Effect of Heat processing on the proximate composition and Energy values of African Elemi (Canarium *Schweinfurthii*) Consumed as masticatories in Nigeria. *International Journal of Scientific and Technology research*. 4: 12- 36.

Fonseca, R.B., Haiter-Neto, F., Fernades-Neto, A.J., Barbosa, G. and Soars, C. J. (2004). Radio density of enamel and dentin of human, Bovine and Swine Teeth. *Archives of Oral Biology*. 49: 919-222.

Fornstedt, T. (2010). Characterization of adsorption processes in analytical liquid-solid chromatography. *Journal of chromatography*. 12 (17):792-812

Greenwood, Norman. N., Earnshaw, Alan. (1997). Chemistry of the Elements (2nd ed.). Butterworth-Heinemann. New York. London..8:36-45.

Guo, W., Ayawei, N., Ebelegi, A. N. and Wankasi, D. (2017). Modelling and Interpretation of Adsorption Isotherms. *Journal of Chemistry*. 9(4):243- 254

*Hasan, S. H., Singh, K., Prakash, T. M. and Hoc, Y. S. (2008). "Sorption equilibrium of mercury onto ground-up tree fern". Journal of Hazard Master. 152: 356-365.*

*Hynda, Y. and Rachida, M. (2008). Biosorption of lead (II) ions from aqueous solutions by Biological Activated Dates Stems. Journal of Environmental Science and Technology. 1: 201-213.*

*Ikhuoria, E. U. and Etiuma, R. A. (2005). Adsorption efficiency of activated carbon from palm kernel shells for Zn and Ni ions. African Journal of Environmental Pollution and Health. 3(2): 63- 70.*

*Ikhuoria, E. U. and Okieimen, F. E. (2000). Scavenging cadmium, copper, lead, nickel, and Zinc ions from aqueous solution by modified cellulosic sorbent. International Journal of Environmental studies. 57(4): 401 -409.* 

*Ikhuoria, E. U. and Onojie, O. C. (2007). Binding Nickel and Zinc ions with activated carbon prepared from sugar cane fibre (Saccharum Offiinarum L.). Journal of Applied Sciences. 7(6): 862-829.*

Jibril, B., Maamari, R., Houache, O., Aamri, M. and Qalhati, M. (2007). Effect ofH<sub>3</sub>PO<sub>4</sub> and KOH on Pyrolysis of Bituminous Coal in Preparation of Activated Carbon. *Journal of Applied Sciences Research*. 3 (11): 1343 – 135.

Jürgen, U. K. and Reiner, S. (2005). Adsorption Isotherms. In: Gas Adsorption Equilibria. Springer, Boston, MA. 178-189

*Kosnett, M. J. (2006). "Lead" in Olson, K. R. Poisoning and Drug Overdose. McGraw-Hill Professional,5th ed, 238.* 

Lagergrens, S., (1998). The theory of so-called adsorption of soluble substances. Kungliga Svenska Vetenskap-sakademiens. Handlingar. 24(4): 1-39

*Li, Q., Xu, X. T., Cui, H., Pang, J. and Wei, Z. B. (2012). Comparison of two adsorbents for the removal of pentavalent arsenic from aqueous solutions. Journal of Environmental Management. 98: 859-860.*

*Lourie, E., Patil, V. and Gjengendal, E. (2010). Efficient purification of heavy metals- contaminated water by microalgae- activated pine bark. Journal of Water Air Soil Pollution. 201: 493-500.* 

*Lourie, E., Patil, V. and Gjengendal, E. (2010). Efficient purification of heavy metals- contaminated water by microalgae- activated pine bark. Journal of Water Air Soil Pollution. 201: 493-500.* 

*Lua, A. C. and Gua, J. (2001). Micro porous oil – palm shell A.C prepared by physical activation for gas phase adsorption. Langmuir Journal. 17: 7112- 7117.*

*Malik, R., Ramteke, D. and Water, S. (2006). Physico-chemical and surface characterization of adsorbent prepared from groundnut shell by ZnCl<sup>2</sup> activation and its ability to adsorb colour. Indian journal of chemical Technology. 13: 329-333*

Marsh, H., Yan, D.S., O'Grady,T. M.and Wennerberg, A. (1984).Formation of Activated carbons from cokes using potassium hydroxide. *Journal of Carbon Research*. 22: 603-611.

*Martinez, M. L., Moiraghi, L., Agnese, M. and Guzman, C. (2003). Making and Some Properties of Activated Carbon Produced From Agricultural And Industrial Residues From Argentina. The journal of the Argentine Chemical Society. 91(416): 103-108.*

*Medellin-Castillo, N. A., Leyva- Ramos, R., Padilla-Ortega., Ocampo- Perez., Flores-Cano, J. V. and Berber-Mendoza, M. S. (2010). Adsorption capacity of bone char for removing fluoride from water solution. Role of hydroxyapatile content, adsorption mechanism and competing anions. Journal of Industrial and Engineering Chemistry. 16: 4014-4021.*

*Mianowski, A., Owczarek, M and Marecka, C. (2007). Surface Area of Activated Carbon Determined by the Iodine Adsorption Number. Journal of Energy Sources. 29(9):839-850*

Mokri G., Modrishala, N., Behnajady, M. A. and Vahid, B. (2015). Adsorption of C.I Acid Red 97 dye from aqueous solution onto walnut shell. Kineics, thermodynamics parameters isotherms.*International Journal of Environmental Science and technology.*22: 1401-1408.

Monisha J., Tenzin T., Naresh, A., Blessy, B., Mathew, K. N. and Beeregowda . (2014). Toxicity, mechanism and health effects of some heavy metals. *Journal of Interdisciplinary Toxicology*. 7(2): 60-72.

Moronkola, B.A., Giwa-Ajeniya, A. O., Alegde, M. J. and Eshilokun. A.O. (2016). Adsorption of Divalent Metal Ions from aqueous Media Using Unmodified Orange Peel (Musa sapientum) as Adsorbent. *Journal of Organic & Inorganic Chemistry*. 2(6): 2472-1123.

Mukeshparmar, L. and Singh T. (2013). Adsorption of heavy metals (Cu<sup>2+</sup>Ni<sup>2+,</sup> and Zn<sup>2+)</sup> from synthetic waste water by tea waste adsorbents. *International Journal of Chemical and Physical Sciences*. 2(6): 6-19.

Nagham, A.A. (2010). The use of local saw dust as an adsorbent for the removal of copper ion from wastewater using Fixed Bed Adsorption. *Journal of Environmental Science.*28: 859-860.

Ogunwande, I. A., Adefila, E. O. and Onwordi, C.T. (2010). Level of Metals uptake on vegetable planted on poultry droppings dump site. *Archives of Applied Science Research.* 2(1): 347-353.

Okieimen, C. O., Okieimen F. E. and Egbuchunam, T. O. (1999). Preparation and surface area determination of asluminium gels. *Nigeria Journal of Applied Science.* 17:56-63.

Okuo, J. M. and Ozioko, A.C. (2001). Adsorption of lead and mercury ions on chemically treated periwinkle shells. *Journal of Chemical Society of Nigeria.*26: 60-65.

Olayemi, E.A., Adeyemi, A. F. and Olabanji, I.O. (2012). Removal of Pb<sup>2+</sup> and Cd<sup>2+</sup> ions from waste waters using palm kernel shell charcoal. Research Journal in Engineering and applied sciences. *Research Journal in Engineering and Applied Sciences.* 1(5): 308-313.

Olowoyo, D. N. and Orere, E. E. (2012). Preparation and characterization of A.C made from palm kernel shell, coconut shell, groundnut shell and Obechi wood. Investigation of apparent density, total ash content, moisture content and particle size distribution. *International Journal of Research in Chemistry and Environment*. 2(3): 32-35.

Oremusova, J. (2007). Manuals for laboratory practice in physical chemistry for students of pharmacy. Department of physical chemistry; Faculty of pharmacy, Comenius University, Bratislava, in Slovak.*Pharmzie*. 62(4):273-277

Osasoma, I., Adebayo, A.O. and Ajayi, O.O. (2013). "Biosorption of cadmium, Copper, Lead and Zinc by inactive Biomass of Pseudomonas Putida".*Journal of Analytical and Bio-analytical Chemistry*. 376(1): 26-32.

Oviawe, P. A., Unuigbe, A. C., Ukpebor, E., Ikhuoria, U. E. (2006). A Text Book of Physical Chemistry. Seevon Prints, 3, Ekewan Road, Benin City. 314-320.

Payne, B. K. and Abedel-Fattah, M. T. (2004). Adsorption of divalent lead ions by zeolites and activated carbon: effects of pH, temperature, and ionic strength. *J. Environment Sci. Heal A,* 39:251 – 255.

Pilar, G. and Reyes-Gasga, J. (2003). Microhardness and Chemical Composition of Human Tooth. *Material Research*. 6(10):15-90.

Rafeah, W., Zainab, N. and Veronica, U. (2009). Removal of Mercury, lead and copper from aqueous solution by activated carbon of palm oil empty fruit bunch. *World Journal of Applied Sciences*. 5:84-91.

Rajendran, A., Ragupathy, D., Priyadarshini, M., Magesh, A., Jaishanker, P., Madhavan, N.S., Sajitha,K. and Balaji, S. (2011). Effective Extraction of heavy metals from their effluents using some potential ionic liquid as green chemicals. *E-Journal of Chemistry*. 8(2): 697-702.

Rane, N.M., Sapkal, V.S., Pati, M. B. and Shewale, S.P. (2010). Use of naturally Available Low Cost Adsorbents for Removal of Cr (VI) from wastewater. *Journal of Chemical Sciences and Applied Sciences*. 1: 65-69.

Raveesh, A., Mona, C. and Jayveer, S. (2015). Waste Management Initiatives in India for Human Well Being. *European Scientific Journal*. 36: 1857- 7881.

Reza, M. T., Lynam, J. G., Uddin, M. H. and Coronella, C. J. (2013). Hydrothermal carbonization: Fate of inorganics. *Biomass and Bioenergy*. 49:86-94.

Richard, O. P. and Rodolfo, T. (2003). Structural colouration of avian skin: convergent evolution of coherently scattering dermal collagen arrays. *The Journal of Experimental Biology*. 206: 2409-2429.

Samara, S. (2009). Heavy metal toxicity. Differential diagnoses and Workshop. 5-10.

Seema, T., Tripathi, I. P. and TiwariH. L. (2013). Effects of Lead on Environment. *International Journal of Emerging Research in Management and Technology*. 2(6): 34-5.

Siegel, F.R. (2002). Contaminant/Natural Background Values: Timing and Processes. Environmental Geochemistry of Potentially Toxic Metals. *Springer article*: 77-101.

*Smith, S. B. and Hieftje, G. M. (1983). A New Background- correction method for Atomic Absorption Spectrometry. Sage Journals. 37:419 – 427.*

Soetan, K. O., Olaiya C.O. and Oyewole O. E. (2010). The importance of mineral elements for humans, domestic animals and plants: A review. *African Journal of Food Science.* 4(5): 200-222.

Sofia, M., Sodeh, S. and Mohammad, O. (2014). Removal of heavy metals from aqueous solution using platinum nanoparticles/Zeolite-4A. *Journal of Environmental Health Science and Engineering*. 12(7):1-15.

Sreeama, Y.N., Sashikala, V. B. and Pratape, V.M.(2009). Expansion properties andultrastructure of legumes: effect of chemical and enzyme pretreatment. *Journal of Food Science and Technology*. 42: 44-49.

Stephanie, J. B., Fretham, E., Carlson, S. and Michael, G. K. (2011). The Role of Iron in Learning and Memory. American Society for Nutrition. *Journal of Advance Nutrition.* 2: 112–121.

Subodh, K. R. (2008). Occupational health risks among workers employed in leather tanneries at Kanpur. *Journal of Occupational Medicine*. 12:132- 135.

Syunyaev, R. Z., Balabin, R. M., Akhatov, I. S. and Safieva∥, J. O. (2009). Adsorption of Petroleum Asphaltenes onto Reservoir Rock Sands Studied by Near-Infrared (NIR) Spectroscopy. *Journal of Energy Fuels*. 23(3): 1230–1236.

UNICEF. (2006). Solid and liquid waste management in rural areas. Technical note.Retrieved from http//www.unicef.org/solid&liquidwaste//123/.hmtl.Accessed October 22, 2017.

USEPA. (1993). Standard Methods for the Examination of Water and Wastewater. *American Public Health Assoc. US.* 8:10-21

Wang, Y., Qiu, L. and Zhu, M. (2019). Comparative Evaluation of Hydrothermal Carbonization and Low Temperature Pyrolysis of *Eucommia ulmoisdes* Oliver for the Production of Solid Biofuel. *Sci Rep.* 9: 5535.

Wartelle, L. H. and Marshell, W. E. (2001). Nutshell as granular activated carbon: physical, chemical and adsorptive properties. *Journal of Chemical Technology and Biotechnology.* 16: 451 – 455.

WHO. (2006). *WHO Guidelines for the safe use of wastewater, Excreta and Grey water – Volume IV: Excreta and grey water use in Agriculture Archived 17 October 2014 at the way back machine.* World Health Organisation (WHO), Geneva, Switzerland.