

THERMAL REGENERATION OF SPENT COCONUT (COCOS NUCIFERA) SHELLS ACTIVATED CARBON FOR Pb²⁺ ADSORPTION

Itodo A.U.^{1*}, Aisagbonhi N.B.² and Itodo H.U.¹

¹Department of Chemistry, University of Agriculture, Makurdi, Nigeria

²Department of Chemistry, Kebbi State University of Science and Technology, Aliero, Nigeria.

ABSTRACT. Activated carbon was prepared from *Cocos nucifera* shells using chemical activation, for Pb²⁺ adsorption. Thermal Regeneration study was carried out on the spent Carbon. Recovered adsorbent was then used for the adsorption of Lead (Pb²⁺) from simulated lead solution (effluent) at 60, 120, 180, 240, 300 and 360 minutes interval following AAS runs. Adsorption of Pb²⁺ using derived powdered activated carbon gave high removal efficiency than that of the regenerated carbon with %RE of 82.95, 73.85, 94.31 and 81.24% at time 60, 120, 300, and 360 respectively. Comparative study was based on both coefficient of determination (R²) and kinetic adsorption parameters. Data obtained from the analyses followed the pseudo second order kinetics (R² of 0.963). The rate constant for the adsorption of Pb²⁺ onto Derived and Regenerated PAC is as low as 0.0048 mgg⁻¹mm⁻¹ and 0.0007 mgg⁻¹mm⁻¹ respectively. The intraparticle diffusion as the verified mode of transport has R² value of 0.959.

Keywords: Regeneration, Activated Carbon, *Cocos nucifera*, Kinetics, intraparticle

INTRODUCTION

It is an established fact that safety in world environment has been continuously threatened by increased in industrialization and human activities (Koffi et al., 2010; Friday et al., 2012). Pollution is the introduction of contaminants into the natural environment that causes adverse change. Pollutants are waste materials that pollute air, water or soil; three factors determine the severity of pollutants: its chemical nature, the concentration and the persistence. A contaminant however is regarded a pollutant when it exerts detrimental effects. (Satyanarayana and Chakrapani, 2010).

Heavy metals are elements having atomic weights between 63.546 and 200.590 and a specific gravity greater than 4.0 i.e. at least 5 times that of water. They exist in water in colloidal, particulate and dissolved phases (Adepoju et al, 2009) with their occurrence in water bodies being either of natural origin (example eroded minerals within sediments, leaching of ores deposit and volcanism extruded products) or of anthropogenic origin (example solid waste disposal, industrial or domestic effluents, harbor channel dredging) (Marcovecchio et al, 2007). Lead poisoned food, when ingested causes kidney failure, CNS breakdown, affects red blood cell, liver and bone marrow and induces stunted growth (Dekhil et al., 2011). The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction Friday et al., 2012). These methods are somewhat less effective, expensive (Dekhil et al., 2011) and do not remove metals at the microgram scale. The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to adsorption, based on metal binding capacities. Adsorption is the process of transferring material from a fluid phase to a

solid phase. Activated carbon (carbo activatus) is an amorphous form of carbon with large internal surfaces and pores. On account of this adsorption, activated carbon is extensively used in the purification-- of water sewage treatments, dry cleaning, refrigeration, food, and beverage industries, pharmaceutical industries e.t.c. (Foster and Leshe, 1980). Adsorption by activated carbon, by far, has become a method of choice to offset this problem. Adsorption becomes a preferred choice than other physico-chemical techniques of heavy metal remediation due to its simplicity, cheap, easy to scale-up and most importantly able to remove low concentration substance even at part per million levels with high efficiency (Kurniawan et al., 2006). Raw materials for activated carbon generation are numerous. Authors have exploited biomasses such as bagasse, sorghum, and millet straws (Lori et al., 2008), poultry wastes and droppings (Itodo et al., 2011) and host of others. This present work utilizes *Cocos nucifera* shells.

The proposed Adsorption study is the kinetics adsorption study were interaction is made using different time interval, also allowing the use of different kinetic model such as Pseudo first and second order. Intraparticle diffusion, Mass transfer and Film diffusion models are the explored modes of transport. A research on regeneration of spent activated carbon was carried out by Rahat and Hao, (2000). This research work made use of the effect of the different temperature and concentration of HCl and H₃PO₄ on the regeneration of spent activated carbon for iodine and Methylene blue solutions. The result revealed that the decolouring efficiency of the product increased with increasing temperature and concentrations. Freundlich adsorption isotherm was adopted for soil phosphorus requirement wherein it gave a good match (Naseri et al., 2012). In similar study, Onweremadu et

*Correspondence: Dr. Adams Udoji Itodo, Department of Chemistry, University of Agriculture, Makurdi, Nigeria . TEL: +234(0)8039503463 Email: itodoson2002@gmail.com;
 Article published: March 2014

al., (2007) ascertained sorption characteristics in highly weathered soil, relating components to soil P-sorption capacity. Atomic Absorption Spectroscopy (AAS) is a spectroanalytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state (Walsh, 1999). In adsorption studies, the technique is used for determining the initial and equilibrium phase concentration of a particular element or metal (the sorbate analyte) in a sample to be analyzed.

Regeneration of Spent Activated Carbon

The regeneration of activated carbons involves restoring the adsorptive capacity of saturated activated carbon by desorbing adsorbed contaminants on the activated carbon surface. During removal and adsorption of various impurities, active carbon loses its sites which are responsible for adsorption. The spent carbon may be regenerated by off-site and on-site regeneration (Jahangir et al, 1995). Over a long period of time, a number of regeneration processes have been tested, evaluated and applied. These include the thermal, chemical and biological processes (Clark and Dorsey, 1987). Thermal Regeneration: The most common technique practiced in regeneration is the thermal volatilisation in which adsorbed substances are desorbed by volatilization and oxidation at high temperature (Martin et al, 1984). This thermal regeneration technique is characterized by the loss of carbon (10-15%) due to oxidation and attrition, and by the cost of energy in treating the carbon to around 800-900°C (Guymont et al., 1980).

Wet oxidation: Is a form of hydrothermal treatment. It is the oxidation of dissolved or suspended components in water using oxygen as the oxidizer. It is referred to as "Wet Air Oxidation" (WAO) when air is used. The oxidation reactions occur in superheated water at a temperature above the normal boiling point of water (100°C), but below the critical point (374°C). **Electrochemical regeneration:** involves the removal of molecules adsorbed onto the surface of the adsorbent with the use of an electric current in an electrochemical cell restoring the carbon's adsorptive capacity. Once the adsorptive capacity of the activated carbon bed has been exhausted by the adsorption of pollutant molecules, the carbon is transferred to an electrochemical cell (to either the anode or the cathode) in which electrochemical regeneration can occur (Narbaiz et al, 1994, and Mehta et al, 1997).

Adsorption Kinetics Studies: Kinetics of adsorption is one of the important characteristics defining the efficiency of the adsorption and consequently the efficacy of the adsorbent. Kinetics is an adsorption dynamics which describes the solute uptake rate and evidently control the resident time of adsorbate and possibilities of desorption (Dermibas et al., 2002).

The first and second-order kinetic models, generally given are described in equation below:

$$dq_t/dt = k_n(q_e - q_t)^n \quad (1)$$

Where k_n is the rate constant for the n th order adsorption. k_n units are min^{-1} and $\text{gm}^{-1} \text{min}^{-1}$ for first order, $n=1$. This generalized model is simplified by the Lagergren model proposed in 1898 (Dermibas et al., 2002) to assume first order kinetics, which is linearly represented as equation 2 :

$$\log(q_e - q_t) = \log q_e (kt/2.303) \quad (2)$$

The integral rate law for the pseudo second order reaction is given as equation

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \quad (3)$$

Equation 3 can be written as equation 4:

$$t/q_t = 1/h + (1/q_e)t \quad (4)$$

where h is the initial adsorption rate and is given as:

$$h = k_2 q_e^2 \quad (5) \text{ (Hameed, 2009).}$$

Intraparticle Diffusion Model:

The adsorption process is described in terms of mode of transportation or diffusion as an empirical functional relationship relating uptake of adsorbate to $t^{1/2}$ rather than with the contact time as represented:

$$q_t = k_{id} t^{1/2} + C_i \quad (6)$$

where k_{id} ($\text{mg}^{-1} \text{min}^{-1/2}$) is the rate parameter of state I and is obtained from the slope of the straight line graph of q_t versus $t^{1/2}$. C_i is the intercept (Hameed 2009; Horsefall and Spiff, 2005).

This present research is carried out for the purpose of converting agricultural waste into useful adsorbent, Regeneration of the already spent carbon and to investigate by comparison, the adsorption phenomenon of lead uptake onto both derived and regenerated activated carbon using kinetics study approach. Hence, the study is generally that of detoxification, purification, sorbent re-use and performance assessment.

MATERIALS AND METHODS

This study was conducted at the chemistry laboratory of Kebbi state University, Aliero, Nigeria between May and October, 2012. It was designed as part of the recommendation from a PhD thesis being carefully followed. The work is also a requirement to actualizing derivation of homemade adsorbent for treatment of different adsorbates (Itodo et al., 2011), with an attempt to improve the ecological system.

Sampling: The coconut shells were obtained from Aliero township in Kebbi State, Nigeria. Washing was carried out with plenty of water to remove the surface impurities after which it was sundried and later oven dried at 100°C overnight (Omonhenle et al., 2006). The dried shells were pounded followed by sieving with a <2mm mesh size sieve, the less than 2mm samples were kept in airtight container. Reagents used in this research (viz; hydrochloric acid, sodium hydroxide, Phosphoric Acid and Lead Acetate) were of analytical grades except otherwise stated.

Carbonization Process: Crucibles were washed and dried in the oven to a constant weight and the weight was taken. 5g of the grinded coconut shell was taken into each crucible, the furnace was fired to 550°C, and the weighed samples were introduced into the furnace and removed after 10 minutes, which was

immediately poured into ice bath containing ice for rapid cooling. The sample was first washed with water, rinsed with 0.1M NaOH solution to remove residual ash, this was also rinsed again with distilled water, sun dried and oven dried and the final weight was taken (Gimba et al., 2012). The process was repeated until much sample was obtained. %burn off on carbonization was estimated.

Activation Process: The two ways activation scheme was adopted. 3g of already carbonized sample was weighed into a crucible, and impregnated with 3cm³ of 1M H₃PO₄ and was allowed to stand for some time, then the furnace was fired up to 800°C and the sample was introduced for 5 minutes being a predetermined activation time. The sample was washed with water, then with 0.1M NaOH solution (Fan et al., 2003) to remove surface ash, followed by warm and cold water rinsing to remove residual acid (Rahman et al., 2002). The sample was sun dried and then oven dried after which the weight was taken. The process was repeated in order to obtain much activated carbon.

Characterization of the Activated carbon: Also estimated were bulk density, Moisture contents, ash contents and pH.

Bulk Density: A 100ml measuring cylinder was filled to a given volume with the produced *Cocos nucifera* shells carbon. The cylinder was tapped for at least 2 minutes to compact the carbon and then weighed. The bulk density was calculated as (Ahmedna et al., 2000)

Bulk density(g/cm³)= weight of dry activated carbon (g)/Volume of packed dry material(cm³)

Ash content: Copper crucibles were heated in a furnace at 550°C, then cooled in a desiccators and weighed. The oven dried samples from the previous section were placed in the crucible and transferred into the Muffle furnace at 800°C for 10min. The samples were removed and poured into ice water bath. Excess water was drained. The crucibles/content were allowed to cool in a desiccators and then weighed to obtain the weight of the ash. The ash content was expressed as percentage of the oven dry weight.

pH: The standard test method for determination of pH was used. 1.0 g of activated carbon (PAC) was weighed and transferred into a beaker. 100 ml of distilled water was measured and added and stirred for one hour. The samples were allowed to stabilize before the pH was measured using a pH meter. (Ektepe and Horsefall, 2011).

Batch Kinetics Adsorption Test: Experiments on adsorption using the batch test was conducted in 250cm³ Erlenmeyer flasks. 0.5g of derived activated carbon was mixed with 10ml of 10ppm concentration of the Pb solution in 6 different flasks for each experimental set. These solutions were shaken in a mechanical shaker for equilibration using an orbital shaker at 150 rpm (Ismail et al., 2009) and allowed to stand for 60,120,180,240,300 and 360 minutes contact

time. Mixtures were filtered using Wattman No.42 filter paper (Abdulrahman et al.,2009; Odeunmi and Okeola, 2001). Equilibrium phase heavy metal concentrations (mg/L) were measured using the Atomic Adsorption Spectrophotometer.

Thermal regeneration of Spent activated carbon: Thermal regeneration was carried out on the spent activated carbon. The used activated carbon was first washed with water, then with 0.1M NaOH and rinsed with distilled water and left to dry in the oven, after which the weight was taken. The activation process was repeated on the pretreated spent carbon and was washed with water and 0.1M NaOH (Fan et al., 2003) to remove surface ash, followed by warm and cold water rinsing to remove residual acid (Rahman et al., 2002). The sample was then dried in an oven at 105°C overnight, stored and ready for use.

Regeneration Efficiency (Reg.E %): The regeneration efficiency was judged on the basis that the adsorbent recovered its sorption capacity on derivation. The following method of calculation was used to measure the extent of the recovery (Martin et al., 1984). The formula for calculating regeneration efficiency is expressed as:

$$\text{Reg. E\%} = \text{Ar}/\text{Ao} \times 100 \quad (7)$$

Where Ar is the adsorption capacity of the regenerated adsorbent, Ao is the adsorption capacity of the fresh adsorbent and Reg.E% is the regeneration efficiency of the regenerated or derived activated carbon. The same batch adsorption process was repeated using the regenerated activated carbon as adsorbent. On the same fashion, lead removal was calculated using equation 8.

$$\text{R(\%)} = (\text{Co} - \text{Ce})/\text{Co} \times 100 \quad (8)$$

Where Co and Ct are the initial and final Pb²⁺ concentration in solution respectively (Koffi et al., 2010; Dekhil et al., 2011).

RESULTS AND DISCUSSIONS

Physicochemical parameters

The result from the table of physicochemical parameters (Table 1) clearly shows that the regenerated activated carbon has higher bulk density (0.583) and a lesser %burn off (10.0) compared to those of their corresponding derived activated carbon which presented 0.48 and 34.4 respectively. The low value of %burn off upon thermal regeneration is an indication that most of the organic component has been volatilized during the initial Pyrolysis. This is the reason why the %burn off of carbonized carbon (60.7) is greater than the derived activated carbon (34.4) which is in turn greater than the regenerated activated carbon (10.00). The high value of ash content is an indication that the final product is tending towards graphene carbon while the low value of moisture content is an indication that the received sample was already air dried followed by oven drying.

Table 1

Results of Physicochemical parameters.

| Sample | Bulk density (g/cm ³) | %Burn off | %Moisture | %Ash | pH |
|------------|--------------------------------------|-----------|-----------|------|-------|
| Raw sample | 0.517 | N/A | 1.70 | 95.6 | NA |
| CS | 0.543 | 60.7 | NA | NA | NA |
| DAC | 0.480 | 34.4 | NA | NA | 2.406 |
| RDAC | 0.583 | 10.0 | NA | NA | 2.065 |

Keys: CS- Carbonized Sample, DAC- Derived activated carbon, RAC- Regenerated activated carbon, NA- Not applicable

Table 2 highlights the experimental data of Pb adsorption onto regenerated powdered activated carbon (RPAC), the equilibrium concentration with the least value of Ce is the interaction at 240 min, this implies that 240s it the equilibrium time in this run. It thus,

gave the highest %Removal of 93.750%, the highest equilibrium constant of 15.000 with a more spontaneous adsorption as indicated by a more negative ΔG value (-6754.419).

Table 2

Experimental data of Pb²⁺ adsorption onto Regenerated Powdered Activated Carbon (Co, 10ppm).

| Samples | Ce(ppm) | Ca(ppm) | q _e (mg/g) | %RE | Kc | ΔG |
|-----------------|---------|---------|-----------------------|--------|--------|-----------|
| RPAC/Pb/60min | 5.230 | 4.770 | 0.095 | 47.700 | 0.912 | 229.754 |
| RPAC/Pb/120 min | 2.729 | 7.271 | 0.145 | 72.710 | 2.664 | -2443.889 |
| RPAC/Pb/180 min | 2.274 | 7.726 | 0.155 | 77.260 | 3.398 | -3050.533 |
| RPAC/Pb/240 min | 0.625 | 9.375 | 0.188 | 93.750 | 15.000 | -6754.419 |
| RPAC/Pb/300 min | 3.240 | 6.760 | 0.135 | 67.600 | 2.086 | -1834.358 |
| RPAC/Pb/360 min | 3.581 | 6.419 | 0.128 | 64.190 | 1.793 | -1455.666 |

Keys: RPAC/Pb/60 min – Adsorption of Pb onto regenerated powdered activated Carbon at 60 min. contact time, Co – Initial concentration of Pb, Ce - Equilibrium Metal concentration, Ca – Adsorbed concentration, q_e – Amount of adsorbate adsorbed per unit mass, RE – Removal efficiency, Kc – Equilibrium constant, ΔG – Gibbs free energy

Table 3 is a study result for Pb uptake onto regenerated granular activated carbon (RGAC). The %RE at the equilibrium time is high with values greater

than 93%. It however took the adsorption of Pb onto GAC a higher time to equilibrate. This explains the role played by surface area.

Table 3

Experimental data of Pb adsorption onto regenerated Granular Activated Carbon (Co, 10ppm).

| Samples | Ce(ppm) | Ca(ppm) | q _e (mg/g) | %RE | Kc | ΔG |
|-----------------|---------|---------|-----------------------|--------|--------|-----------|
| RGAC/Pb/60 min | 2.103 | 7.897 | 0.158 | 78.970 | 3.755 | -3300.121 |
| RGAC/Pb/120 min | 2.672 | 7.328 | 0.147 | 93.280 | 2.743 | -2516.337 |
| RGAC/Pb/180 min | 0.739 | 9.261 | 0.185 | 92.610 | 12.532 | -6306.009 |
| RGAC/Pb/240 min | 1.023 | 8.977 | 0.179 | 89.770 | 8.775 | -417.218 |
| RGAC/Pb/300 min | 3.069 | 6.931 | 0.139 | 69.310 | 2.258 | -2031.906 |
| RGAC/Pb/360 min | 0.625 | 9.375 | 0.188 | 93.750 | 15.000 | -6754.419 |

Keys: RPAC/Pb/60 min – Adsorption of Pb onto regenerated powdered activated Carbon at 60 min. contact time, Co – Initial concentration of Pb, Ce - Equilibrium Metal concentration, Ca – Adsorbed concentration, q_e – Amount of adsorbate adsorbed per unit mass, RE – Removal efficiency, Kc – Equilibrium constant, ΔG – Gibbs free energy

The effect of contact time on Removal efficiency

The effect of contact time on the amount of Pb adsorbed was investigated at the optimum initial concentration of Pb (Table 2). The extent of removal (in terms of %RE) of Pb by the activated carbon was found to linearly increase until it reaches a maximum value with increase in contact time after which desorption sets in. The removal efficiency %RE was calculated using the following equation;

$$\%RE = (C_0 - C_e) / C_0 \times 100 \quad (7)$$

The adsorbed concentration, Ca was calculated using the formula;

$$C_a = C_0 - C_e \quad (8)$$

The adsorption capacity was calculated from the equation as follows,

$$q_e = (C_0 - C_e) \times V / W \quad (9)$$

FTIR Spectra of Commercial, Derived and Regenerated Activated Carbon

Characterization of derived activated carbon using FTIR was once presented by Biswajit et al., (2013). Generally, resemblance of the biomass used as raw materials in the two adsorbents, their level of purity,

residual functional groups as a result of unwashed reagents and possible adsorption site functional groups were investigated using FTIR. The FTIR Spectra for the derived and regenerated activated Carbons showed different peaks along the functional group region (figure 2 and 3). These several peaks were seen in the FTIR Spectra of the commercial activated Carbon (figure 1). A 3429.55 peak of the commercial activated Carbon Spectra represents N-H amine functional group or N-H amide functional group. This may result from experimental reagents, raw material and environment of production of the commercial activated Carbon. Also the several peaks showing within 2294.40, 2917.43 and 3221.23 to 3909.84 range may also be as a result of an expelled residual chemical during experimental process. The derived activated carbon spectra showed several peaks along the functional group region (figure 2) while less numbers of peaks was observed from the FTIR spectra of the regenerated activated carbon (figure 3). This observation may be as a result of the additional washing stage in regeneration process.

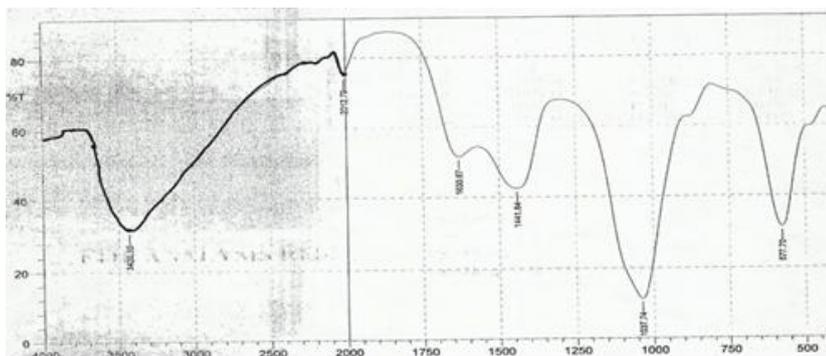


Fig. 1: FTIR spectra for Commercial Activated Carbon

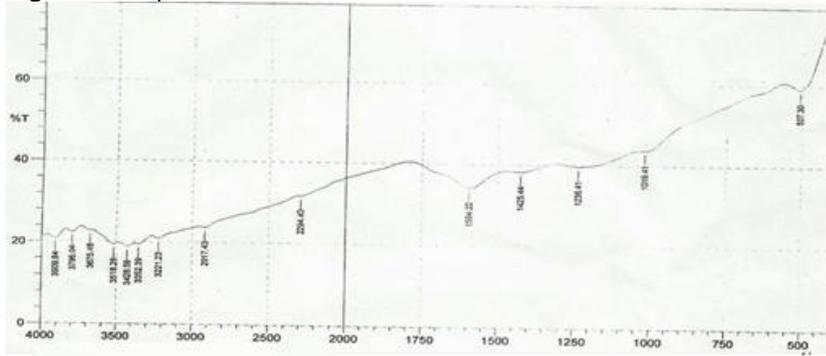


Fig. 2 : FTIR Spectra for Regenerated Cocos nucifera shell derived activated carbon

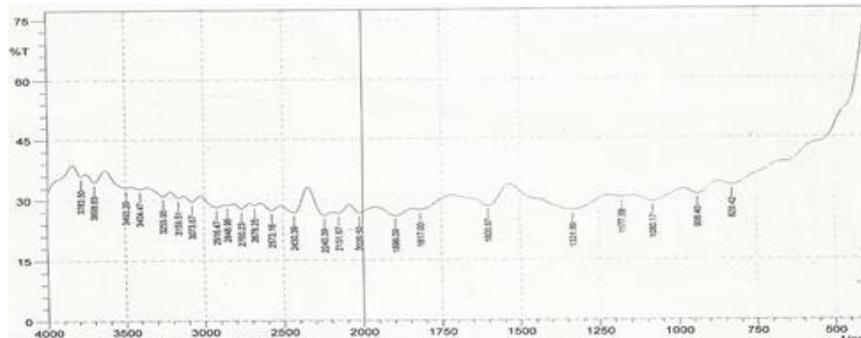


Fig. 3: FTIR Spectra for Cocos nucifera shell Regenerated Activated carbon

Table 4

Kinetic Studies Experimental data for Pb uptake onto regenerated powdered activated cocos nucifera shells

| Samples | t(min) | q _t | Log(q _e -q _t) | t/q _t | t ^{1/2} | C _t |
|-----------------|--------|----------------|--------------------------------------|------------------|------------------|----------------|
| RPAC/Pb/60min | 60 | 0.095 | -1.032 | 631.579 | 7.746 | 5.230 |
| RPAC/Pb/120 min | 120 | 0.145 | -1.367 | 827.586 | 10.954 | 2.729 |
| RPAC/Pb/180 min | 180 | 0.155 | -1.481 | 1161.290 | 13.416 | 2.274 |
| RPAC/Pb/240 min | 240 | 0.188 | 0.000 | 1276.596 | 15.492 | 0.625 |
| RPAC/Pb/300 min | 300 | 0.135 | -1.276 | 2222.222 | 17.321 | 3.240 |
| RPAC/Pb/360 min | 360 | 0.128 | -1.222 | 2812.500 | 18.974 | 3.581 |

KEYS: RPAC/Pb/60 min adsorption of Pb onto regenerated powdered activated Carbon at 60 min, q_e = q_t - Amount of adsorbate adsorbed per unit mass, C_t – Equilibrium Metal concentration, t(min) – time of interaction in min.

Table 5

Kinetic Studies Experimental data for Pb uptake onto Regenerated Granular activated cocos nucifera shells

| Sample | t(min) | q _e | q _t | Log(q _e -q _t) | t/q _t | t ^{1/2} | C _t |
|-----------------|--------|----------------|----------------|--------------------------------------|------------------|------------------|----------------|
| RGAC/Pb/60min | 60 | 0.188 | 0.158 | -1.523 | 379.747 | 7.746 | 2.103 |
| RGAC/Pb/120 min | 120 | 0.188 | 0.147 | -1.387 | 816.327 | 10.954 | 2.672 |
| RGAC/Pb/180 min | 180 | 0.188 | 0.185 | -2.523 | 972.973 | 13.416 | 0.739 |
| RGAC/Pb/240 min | 240 | 0.188 | 0.179 | -2.046 | 1340.782 | 15.492 | 1.023 |
| RGAC/Pb/300 min | 300 | 0.188 | 0.139 | -1.309 | 2158.273 | 17.321 | 3.069 |
| RGAC/Pb/360 min | 360 | 0.188 | 0.188 | 0.000 | 1914.894 | 18.974 | 0.625 |

KEYS: RPAC/Pb/60 min – Adsorption of Pb onto regenerated powdered activated Carbon at 60 min, q_e = q_t - Amount of adsorbate adsorbed per unit mass, C_t – Equilibrium Metal concentration, t(min) – time of interaction in min.

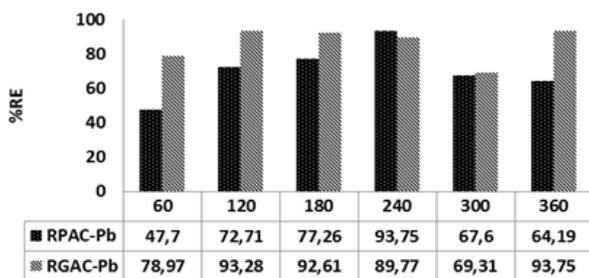


Fig. 4: Effect of Contact time on removal efficiency for adsorption of Pb onto Regerated powdered and Regenerated Granular Activated Coconut Shells Carbon

Removal Efficiency Studies

Figure 4 is a chart showing the comparative study on the adsorption Pb using regenerated powdered and granular derived activated coconut shells carbon. From the chart, it is evident that Pb adsorption using powdered regenerated activated coconut shells carbon has its highest adsorption at time 240s with (%RE=93.75) and also Pb adsorption by granular regenerated activated coconut shells carbon has its highest adsorption at time 360s with (%RE=93.75). The result shows that adsorption of Pb using granular regenerated activated coconut shells carbon is more efficient. There is a linear relationship in percent removal at lower contact time (60 to 140 minutes) for

both regenerated PAC and GAC, the equilibrium time for PAC (240 mins; %RE of 93.75%) differs from that of GAC (180 min ; %RE of 92.61%). highest value of Pb Pb²⁺removal onto GAC (300 min ; %RE of 93.75%) arises after a characteristic desorption at the 300th minute.

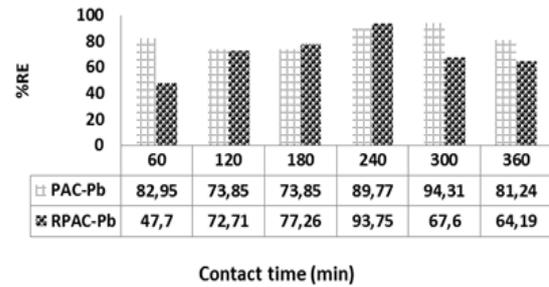


Fig. 5: Estimation of Removal efficiency for Pb adsorption onto Derived and Regenerated Powdered Activated Coconut Shells Carbon

Figure 5 is a chart showing a comparative study on adsorption of Pb using derived powdered activated coconut shells carbon and regenerated powdered activated coconut shells carbon. From the chart, it is seen that adsorption of Pb²⁺ using derived powdered activated coconut shells carbon is more efficient than its corresponding regenerated powdered activated coconut shells carbon as adsorption using derived powdered activated coconut shells carbon is higher at time 60, 120, 300, 360s with (%RE= 82.95, 73.85, 94.31, 81.24) respectively. Generally, a non uniform adsorption with contact time was presented for the derived PAC affinity for Pb²⁺. The adsorption is however highest at 300 minutes contact time with a removal efficiency of 94.31% as against the low value of 67.6% estimated for RPAC– Pb²⁺.

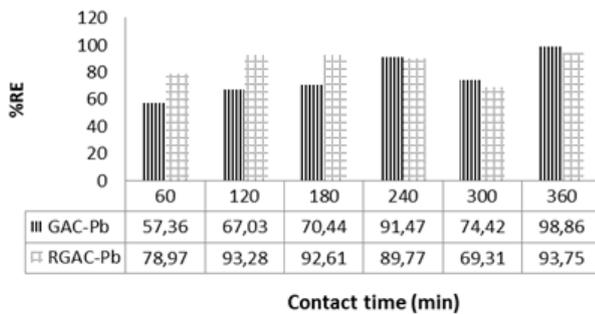


Fig. 6: Estimation of Removal efficiency for Pb adsorption onto Derived and Regenerated Granular Activated Coconut Shells Carbon

Figure 6 is a chart showing the comparative study on the estimation of adsorption efficiency of Pb²⁺ onto derived and regenerated granular activated coconut shells carbon. From the chart, both derived granular activated carbon gave the highest adsorption of Pb at time, 360min with the derived granular carbon having the highest value (%RE= 98.86).On the contrary, Pb²⁺ adsorption at initial contact time(60 minutes) is more favourable using RGAC (%RE= 78.97) as against the use of DGAC (%RE= 57.36).

Kinetic Studies

Screening and adoption of the best fit kinetic model entail the comparison of the coefficient of

determination value, R² as well as the precision test, utilizing the extent of agreement between the experimental and calculated q_e values. R² values depict the extent of suitability or applicability of a given kinetic model.

Figure 7 for the linear first order plot with R² of the range of 0.899 to 0.904 as well as figure 8 for the pseudo first order kinetic plot (R² of 0.233 to 0.632) were presented as unsuitable kinetic models for modeling the adsorption phenomenon in this study.

Figure 9 as clearly interpreted in Table 6 is typical of the result obtained for the pseudo second order kinetic plot. The R² values are of the range of 0.963 (for derived carbon) to 0.913 (for regenerated carbon). It should be noteworthy that this model by the implication of high R² value is the best fit model for interpreting the rate of Pb²⁺ uptake onto derived and regenerated *Cocos nucifera* shell activated carbon.

The rate constant was therefore deduced from the second order kinetic plot (Figure 9) and interpreted in Table 6 as k₂ = 0.0048 for DPAC and 0.0007 for RPAC. It therefore follows that the rate of adsorption of Pb²⁺ onto DPAC (which is simply a speed study in terms of adsorption capacity other than concentration) is higher than the adsorption onto RPAC. In a research by Koffi et al., (2010), k value ranges between 0.0290 to 0.0720 for Pb²⁺ sorption onto sawdust.

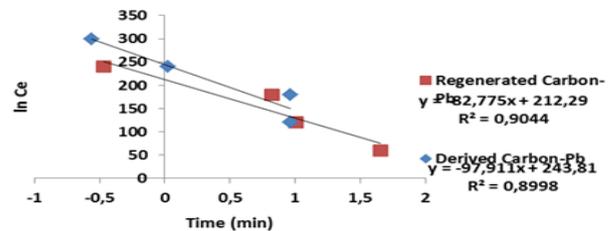


Fig.7: Compare Linear First Order Adsorption Plot for Pb adsorption onto derived and Regenerated powdered Cocos nucifera Activated Carbon

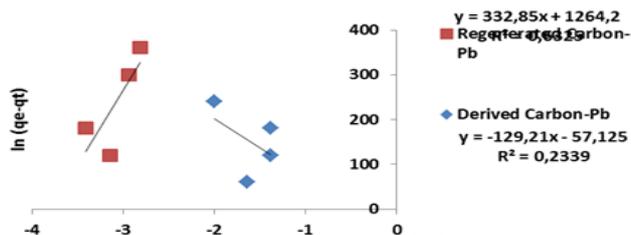


Fig. 8: Compares Pseudo First Order Adsorption Plot for Pb adsorption onto derived and regenerated powdered Cocos nucifera Activated Carbon

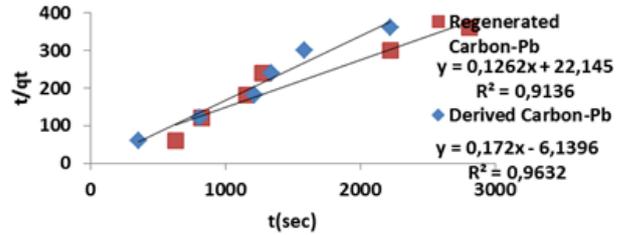


Fig.9: Compares Pseudo Second Order Adsorption Plot for Pb adsorption onto derived and regenerated powdered Cocos nucifera Activated Carbon

Table 6

Pseudo second order experimental constants for Pb adsorption onto derived and regenerated powdered and granular activated cocos nucifera shells carbon.

| Adsorbent | Linear equation y = | R ² | K ₂ | q _{e cal} | q _{e exp} |
|-----------|---------------------|----------------|----------------|--------------------|--------------------|
| DPAC | 0.172x – 6.139 | 0.963 | 0.0048 | 0.189 | 5.8139 |
| RPAC | 0.126x +22.14 | 0.913 | 0.0007 | 0.188 | 7.9365 |

Mode of Transport

The modes of transport of the adsorbates (Pb) onto the adsorbent (DPAC and RPAC) surfaces were also investigated. The intraparticle diffusion plot (Figure 10; R² = 0.853 for DPAC and 0.959 for RPAC) is acceptable for interpreting the transport process. This plot is more acceptable than those of least applicability like mass transfer plot (Figure 11; R² = 0.709 for DPAC and 0.899 for RPAC) and for the film diffusion plot (Figure 12; R² = 0.231 for DPAC and 0.632 for RPAC). It was to this regards that this research work predicted the intraparticle diffusion as the mode of transport of Pb²⁺ adsorption onto both derived and regenerated *Cocos nucifera* shell activated carbon. It thus implies that at the occupation of adsorption site, the adsorbent can still attract adsorbates passing through already adsorbed solids.

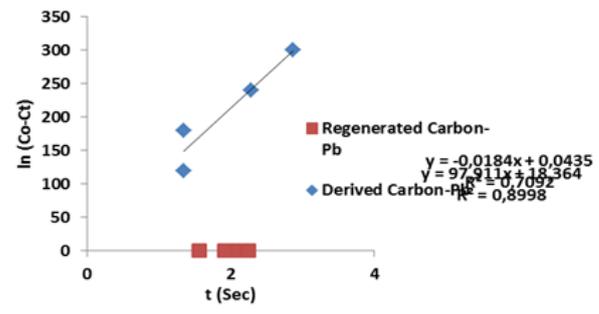


Fig. 11: Compares Mass Transfer Equation Plot for Pb adsorption onto derived and Regenerated powdered Cocos nucifera Activated Carbon

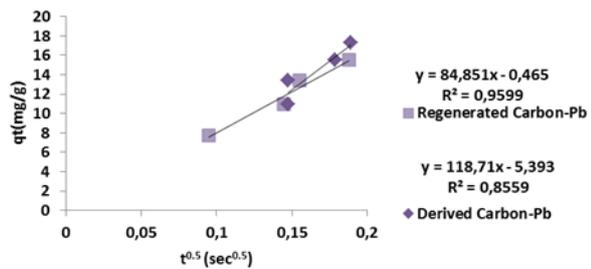


Fig. 10: Compares Intraparticle Diffusion Plot for Pb adsorption onto derived and regenerated powdered Cocos nucifera Activated Carbon

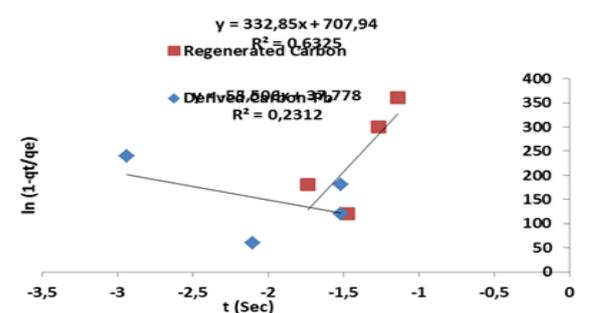


Fig. 12: Compares Film Diffusion Equation Plot for Pb adsorption onto derived and Regenerated Powdered Cocos nucifera Activated Carbon

CONCLUSION

The activated carbon derived from *Cocus nucifera* shells was found to be very efficient in the adsorption of heavy metals. It was evident from the findings of this work that Pb²⁺ was successfully adsorbed to an extent, using the regenerated *Cocos nucifera* shells activated carbon. Form the result; it was observed that

adsorption increases with increase in contact time. The low value of %burn off upon thermal regeneration is an indication that most of the organic component has been volatilized during the initial Pyrolysis. The physicochemical result also showed that the *Cocos nucifera* shells has high ash but low moisture content. The data gotten from the experiment was found to follow Pseudo second order kinetics with higher R² values. This research work has shown that agricultural waste can be converted into useful products that can help improve and protect the environment.

REFERENCES

- Abdulrahman FW, Hassan LG, Itodo AU and Maigandi SA, Freundlich adsorption isotherm of the adsorbent from H₃PO₄ and ZnCl₂ treated irish potatoe peels, Nigerian Journal of pure and applied science 16(2), 256-261, 2009.
- Adepoju AA, Ojomolade OO, Ajoola GA, Coker HB, Quantitative analysis of some toxic metals in domestic water obtained from lagos metropolis. The Nig. J. Pharm.,42(1), 57-60, 2009.
- Ahmedna M, Marsha W, Rao M, Production of granular activated carbon from selected Agric by-products. Bioresources Technology, 71(2), 113-123, 2000.
- Biswajit D, Naba KM, Palas R, Soumya C, "Equilibrium, Kinetic and Thermodynamic Study on Chromium(VI) Removal from Aqueous Solution Using Pistia Stratiotes Biomass," Chem Sci Trans, 2(1), 85-104 , 2013.
- Clark RM, Dorsey P, Operating variables influences cost of GAC treatments. Water and sewage works, R-36, 1987.
- Dermirbas E, Kobiya M, Oncel S, Sencan S, Removal of Ni(ii) from solution by adsorption unto hazenut shells activated carbon, Bioresource Technology 84, 291-293, 2002.
- Dekhil AB, Hannachi Y, Ghorbel A, Boubaker T, Comparative Study of the Removal of Cadmium from Aqueous Solution by using Low-cost Adsorbents. Journal of Environmental Science and Technology, 4, 520-53, 2011.
- Ekpete OA, Horsfall MJNR, Preparation and Characterization of Activated Carbon derived from Fluted Pumpkin Stem Waste (*Telfairia occidentalis* Hook F). Research Journal of Chemical Sciences. 1(3), 10-17, 2011.
- Fan M, Marshall W, Daugard D, Brown C, Steam activation of vchars produced from oat hulls. Bioresource Technology 93(1), 103-107, 2003.
- Friday O, Bamidele IO, Kayode OA, Kinetics and Thermodynamic Adsorption of Pb(II) and Cd(II) Ions from Used Oil onto Thevetia neriifolia Nutshell Active Carbon. Current Research in Chemistry, 4, 26-40, 2012.
- Foster DS, Leslie SE, Encyclopedia of industrial chemical Analysis. John Wiley and Sons inc., New York, p. 557, 1980.
- Gimba CE, Odike OJ, Peter AE, Turoti M, Emmanuel EA, New raw material for activated carbon. I. Methylene blue adsorption on activated carbon prepared from Khaya senegalensis fruits. Global Journal of Pure and Applied Sciences 7, 265-267, 2012.
- Guymont FJ, The effect of capital and operating costs on GAC adsorption system design, Activated carbon adsorption of organics from the aqueous phase(c) Annabor science, 1980.
- Hameed BH, Evaluation of papaya seed as a non conventional low cost adsorbent for removal of MB. Journal of Hazardous Material 162, 939-944, 2009.
- Horsefall M, Spiff AI, Kinetics Studies on the sorption of lead and cadmium ions from aqueous solution by caladium bicolor biomass. Journal of chemical society 19(1), 89-102, 2005.
- Jahangir MA., Martin R, Mirajuddin J, Biological regeneration of exhausted activated carbon-2. Sarhad J. Agric. 11, 205-17, 1995.
- Ismail BS, Sameni M, Halimah M, Adsorption, Desorption and Mobility of 2,4-D in Two Malaysian Agricultural Soils. Asian Journal of Agricultural Research, 3, 67-77, 2009.
- Itodo AU, Abdulrahman FW, Hassan LG , Atiku FA, Itodo HU, GCMS Prediction of Organochlorine Herbicide Sorption Rate: A Batch Kinetic Studies. Trends in Applied Sciences Research, 6, 451-462, 2011.
- Koffi LC , Adouby K., Wandan E.N, Yao B, Kotchi K.P, Sorption and Desorption of Pb(II) from Aqueous Solution using Triplochiton scleroxylon Sawdust as Sorbent. Journal of Applied Sciences, 10, 1536-1544, 2010.
- Kurniawan TA., Chan GY, Lo WH, Babel S, Physico-chemical treatment techniques for wastewater laden with heavy metals, Chem. Eng. J. 118, 83-98, 2006.
- Lori JA, Lawal AO, Ekanem EJ, Adsorption Characteristics of Active Carbons from Pyrolysis of Bagasse, Sorghum and Millet Straws in Ortho Phosphoric Acid. Journal of Environmental Science and Technology, 1, 124-134, 2008.
- Marcovecchio JE, Botte SE, Freije RH, Heavy metals, major metals, trace elements. In: Handbook of water analysis .L.M. Nollet, Ed.2nd Edn. London: CRC press, pp 275-311, 2007.
- Martin MJ, Artola A., Balaguer MD, Rigola M, Activated carbon development from surplus sewage sludge for the removal of dyes from dilute aqueous solutions. Chem. Eng. J, 94, 231-239, 2003.
- Martin RJ, Nig WJ, Chemical regeneration of exhausted activated carbon-1, Water research 18, 59, 1984.

- Mehta MP, Flora JR, Effects of electrochemical treatment of granular activated carbon on surface acid groups and the adsorptive capacity for phenol, *Water Research*, 31 (9), 2171-2176, 1997.
- Narbaitz RM, Karimi-Jashni A, Removal of volatile organic compound by activated carbon fiber, *Carbon*, 42 (14), 2949-2962, 1994.
- Odebunmi E, Okela F, Preparation and characterization of activated carbon from waste material. *Chemical Society of Nigeria* 26(2): 49-155, 2001.
- Okoniewska E, Joanna L, Malgorzata K, Ewa N, The trial of regeneration of used impregnated activated carbons after manganese sorption, *Desalination* 223, 256-263, 2007.
- Omomnhenle S, Ofomaja A, Okieimen F, Sorption of Methylene blue by unmodified and modified citric acid sawdust. *Journal chemical society of Nigeria*, 30 (1 and 2), 161-164, 2006.
- Onweremadu EU, Predicting Phosphorus Sorption Characteristics in Highly Weathered Soils of South-Eastern Nigeria. *Research Journal of Environmental Sciences*, 1, 47-55, 2007.
- Rahat Parveen and Haq Nawaz, Regeneration of spent activated carbon, *Capricorn Publications*, Pakistan, 3(5), 866-876, 2000.
- Rahaman A, Saad B, Shaidan S, Rizal. S, Adsorption characteristics of malachite green on activated carbon derived from rice husks produced by chemical thermal process. *Bioresource technology* 90(14), 1578-1583, 2002.
- Rich. G, Cherry K, *Hazardous Waste Treatment Technologies*, Pudvan Publishers, New York, 1987.
- Satyanarayana U, Chakrapani U, *Biochemistry*. Arunabha Sen books and allied l.t.d, Kolkata. Third edition, pp 665-666, 2010.
- Walsh A., Welz B, Sperling M, *Atomic Absorption Spectrometry*, Wiley-VCH, Weinheim, Germany, 1999.