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Adsorption of Heavy Metals Contaminants in Used Lubricating Oil Using Palm Kernel and Coconut Shells Activated Carbons

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Abstract: This research work investigated the adsorption of some heavy metals contaminants in used lubricating oil using chemically activated carbon adsorbents produced from palm kernel and coconut shells. The adsorption mechanism was able to remove some heavy metals such as zinc, chromium, cadmium and magnesium contaminants from the used lubricating oil to appreciable levels. For instance, zinc from initial concentrations of 16.475±0.950 ppm before to 10.375±0.171 ppm after filtration processes for used lubricating oil sample A. Also, for coconut shell from an initial concentration of 14.575±0.272 ppm to 5.450±0.3000 ppm after filtration processes. It was observed that the coconut shell activated carbons was effective in the removal of lead metals while palm kernel cannot. However, the activated carbons produced from palm kernel and coconut shells are not suitable for the removal of both copper and iron metals. For example, after the filtration process with the palm kernel shell activated carbon, the mean concentration of copper metal increases for virgin (C) 0.001± 0.000 to 0.075±0.013 ppm and used lubricating oil samples (A&B) from 0.150±0.008 to 0.400±0.018 ppm and from 0.220±0.096 to 0.230±0.008 ppm respectively. Also, in the case of the coconut shell activated carbon, the mean concentration of copper in virgin lubricating oil remains the same 0.001±0.000 whereas for used lubricating oils samples (i.e. A&B) it increases from 0.150±0.008 to 0.780±0.014 and from 0.220±0.096 to 0.790±0.026 respectively. Also, the equilibrium adsorption data were analysed using the Langmuir isotherm model. The fit of this isotherm model to the equilibrium adsorption data was determined, using the linear coefficient of correlation (R^2). The following R^2 values were obtained; Copper (0.8185), Cadmium (0.8347), Lead (0.9349), Chromium (0.9378), Iron (0.9927), Zinc (0.9953), and Magnesium (0.9997) respectively. From the results obtained and statistics point of view, it can be concluded that the Langmuir model shows a better fit due to the high coefficient of correlation ($R^2 \approx 1$). The recovered oil could be also re-used.

Keywords: Activated Carbons, Heavy Metals, Contaminants, Used Lubricating Oils, Adsorption, Langmuir Isotherm Model, Correlation Co-efficient

1. Introduction

Activated carbon has been known as the most effective, efficient, reliable and useful adsorbents for the removal of pollutants from polluted gas, liquid streams, wastewater, dyes, used lubricating oils etc. This is made possible because of the properties of activated carbons which have a large active surface area which can provide high adsorption capacity, well developed porous structures and good mechanical properties [1, 2]. Also, activated carbon is most widely used since most of its chemical (e.g. surface groups) and physical properties (e.g. surface area and pore size distribution) can be designed and adjusted according to the required application [3]. Besides, the adsorption on activated carbon appears to be most common techniques because of its simplicity of operation since the adsorbents material can be made highly efficient, easy to handle and in some cases they can be regenerated [4].

The most common precursors used for the preparation of activated carbons are organic materials that are rich in carbon content. Hence, the development of methods to recycle waste materials as activated carbons is greatly preferred and offers a promising future. Agricultural wastes, such as coconut shell and palm kernel shell are of importance to be converted into activated carbons because of their hardness and high strength in which these desired properties are due to its high lignin, high carbon content and low ash content of the materials [2, 5]. The most frequent method used for the preparation of activated carbon is the carbonization of the precursors at high temperature in an inert atmosphere followed by the activation process. The activation process is subdivided into physical and chemical. Physical activation process comprises treatment of char obtained from carbonization with oxidizing gases, generally steam or carbon dioxide at high temperature (400-1000°C) [6]. In the chemical activation process, the starting material is mixed with an activation reagent and the mixture is heated in an inert atmosphere [7-9]. This process is usually done at lower temperature and activation time, higher producing surface area and better porosity as compared to physical activation. The goal of this study is to prepare activated carbons from palm kernel shell and coconut shell by chemical activation with potassium carbonate (K_2CO_3) and sodium bicarbonate ($NaHCO_3$) to adsorb some heavy metals from used lubricating oil samples. The surface area of the impregnated activated carbons was analyzed using Brunauer, Emmett and Teller (BET). Therefore, in this study, palm kernel shell and coconut shell were selected as a precursor for the production of activated carbon since both of them are abundantly available in Nigeria and has extremely low market value. In other to further improve the adsorption efficiency of the activated carbons, this paper also aims to use the data obtained to model the heavy metal parameters.

2. Materials and Methods

Raw material

Among the agriculture waste materials, palm kernel shell (PKS) and coconut shell (CS) were selected for activated carbon preparation. PKS was collected from a palm oil mill that is located in Aluu, and CS was collected from the local community in Choba, all suburbs in Port Harcourt, Rivers State, Nigeria. The materials were thoroughly cleaned with tap water and distilled water several times to remove dust and impurities. The PKS and CS samples were later dried in the spray drying oven at 110°C for 24h to remove any surface moisture and were then ground to the desired size.

Chemical Activation and Activated carbon preparation

Activated carbons were prepared from the palm kernel and coconut shells using a chemical activation method used by [10, 11]. 30g of the powdered samples each (that is palm kernel and coconut shells) were impregnated with 1M solution of K_2CO_3 and $NaHCO_3$ and left in the room temperature for 3 hours. The samples were activated for 40mins at a carbonization temperature of 800°C using Carbolite Muffle Furnace. The activated carbons produced were washed with 0.5 M glacial acetic acid solution, rinsed thoroughly with distilled water until the pH's were within 6-7. The samples were sun-dried and sieved with 500 µm mesh. Portions of the activated carbons retained on the mesh were oven-dried for 1 h, removed and stored in airtight containers. According to the literature, the surface area of chemical activated carbons can range from 250 to 2500m^2g^{-1}, depending on the precursor and the type of treatment used for the production of the activated carbon. However, the most common values are around 600 to 1000m^2g^{-1} [12-14].

(a)

(b)

Figure 1. *(a) Palm kernel shell; (b) Coconut shell.*

Characterization of the Activated Carbon Samples.

Surface Area Determination by Brunauer, Emmett and Teller (BET)

The specific surface area of the chemical activated carbons from the palm kernel and coconut shells were determined including the pore size distribution by means of adsorption and desorption of nitrogen at 77 K using the method of Brunauer, Emmett and Teller (BET) with a model ASAP 2020 Micromeritics Analyser (Dublin, Ireland) [11].

Oil Samples Collection, Preparation, Digestion and Elemental Analysis

5 litres of used lubricating oil samples (total quartz 20 W 50) that have been used for 3 and 6 months were collected

from Total Service Stations at East-West Road, Port Harcourt, Rivers State, Nigeria. The 3 and 6 months old used lubricating oils were labels as sample A and B respectively. Also, 5 litres of fresh sealed lubricating oil (total quartz 20 W 50) were purchased from the same source and label as control sample C. Used lubricating oil samples A and B were stored for several days to allow large suspended particles and small particles to settle under gravity.

Preparation of Oil Samples

Filtration of the used lubricating oil samples A and B were carried out under gravity using Buchner funnel and filter paper to remove impurities such as sand, metal chips, micro impurities etc. that contaminated the lubricating oil. The used lubricating oils were allowed to settle for 24 hours and samples were further filtered.

Oil Samples Digestion and Elemental Analysis

According to the acid digestion method used by [11, 15, 16]. 0.5 g each of the fine oil samples were weighed into a Kdjedahl digestion flask and 5 mL concentrated H_2SO_4 was added to each of the oil samples and heated in a fume hood until the oil samples started to char. Then, 10 ml of H_2O_2 were added to the charred mixture and were heated for 5 min and the mixture turned colourless when the digestion was completed. The used and virgin lubricating oil (control) samples were digested using the same procedure. The each digested samples were transferred into a 100 ml volumetric flask and made up to the mark. The samples were then transferred into a cleaned plastic container for AAS analyses. The digested samples were analysed using Perkin Elmer Atomic Absorption Spectrophotometer model number Buck Scientific 210 at the Pollution Control and Environmental Management Limited, Port Harcourt, Nigeria.

Determination of Heavy Metals Present

Perkin Elmer Atomic Absorption Spectrophotometer model number buck Scientific 210 were used to determine the heavy metals that were present in the oil samples before and after analyses with the activated carbons.

Adsorption Isotherms

Adsorption isotherm reveals the relationship between the amount of a solute adsorbed at constant temperature and its concentration in the equilibrium solution. It provides essential physiochemical data for assessing the applicability of the adsorption process as a complete unit operation [17]. Langmuir isotherm models are widely used to investigate the adsorption process [18]. The model parameters can be construed further, providing understandings on sorption mechanism, surface properties, and an affinity of the adsorbent [19]. The Langmuir isotherm was developed on the assumption that the adsorption process will only take place at specific homogenous sites within the adsorbent surface with uniform distribution of energy level. Once the adsorbate is attached on the site, no further adsorption can take place at that site; which concluded that the adsorption process is monolayer in nature. The Langmuir adsorption model further based on the assumption that all the adsorption sites are energetically identical and adsorption occurs on a structurally homogeneous adsorbent. The linearized form of the Langmuir equation based on those assumptions is given as [20, 21].

$$\frac{1}{q_e} = \frac{1}{Q^o} + \frac{1}{bQ^oC_e}$$

Where q_e is the amount of solute adsorbed on the surface of the adsorbent (mmol g^{-1}), C_e is the equilibrium ion concentration in the solution ($mmol^{-1}$), Q^o is the maximum surface density at monolayer coverage and b is the Langmuir adsorption constant (L $mmol^{-1}$). The plots of $1/q_e$ versus $1/C_e$ give a straight line and the values of Q^o and b can be calculated from the intercept and slope of the plots, respectively. In general, the amount of this parameter is between 0.0 and 1.0, and the quality of fitting increases with the nearness of R^2 to 1.0. From the statistics point of view, it can be concluded that the Langmuir model shows a better fit due to the high coefficient of correlation ($R^2 \approx 1$). D. W. T. is another parameter considering the difference between the real and model amount in every point knowing as residual. This parameter determines the relation adsorption on both sizes of activated carbon.

Methods for Data Analysis and Presentation

IBM SPSS version 23 statistical analysis software [22] was used to analyse the data generated in the experiments. The results obtained were recorded in the below tables. Also, the constants of all models were obtained by an ordinary correlation coefficient of the parameter (least square method) using the Jan 15 (2018), XLSTAT version.1 [23]. With XLSTAT version.1 software Jan 15 (2018), several examinations were performed for analysing and fitting of data. The models are developed based on the statistical function such as coefficient of correlation (least square) parameter (R^2) and Durbin-Watson Test (D. W. T.).

3. Results and Discussion

Table 1. *Mean, ±SD, of virgin and used lubricating oil samples before filtration with palm and coconut shells activated carbons.*

Samples/Parameters	Control	Sample A	Sample B
Cu (ppm)	0.001±0.000	0.150 ±0.008	0.220±0.096
Fe (ppm)	1.502±0.092	4.650±0.159	3.350±0.289
Zn (ppm)	2.833±0.034	16.475±0.950	14.575±0.272
Cd (ppm)	0.020±0.008	0.020±0.008	0.030±0.008
Pb (ppm)	1.000±0.093	1.045±0.478	1.525±0.222
Cr (ppm)	0.410±0.051	0.400±0.065	0.445±0.039
Mg (ppm)	41.900±0.258	5.450±0.265	21.475±0.650

Table 2. *Mean, ±SD of virgin and used lubricating oil samples after filtration with Palm Kernel Shell Sample.*

Samples/Parameters	Control	Sample A	Sample B
Cu (ppm)	0.075±0.013	0.400±0.018	0.230±0.008
Fe (ppm)	1.150±0.129	8.500±0.258	3.400±0.183
Zn (ppm)	8.325±0.275	10.375±0.171	5.450±0.300
Cd (ppm)	0.000±0.000	0.018±0.009	0.000±0.000
Pb (ppm)	1.650±0.039	1.648±0.097	2.388±0.070
Cr (ppm)	0.065±0.013	0.210±0.026	0.135±0.013
Mg (ppm)	0.350±0.026	0.900±0.025	0.505±0.013

Table 3. *Mean, ±SD of virgin and used lubricating oil samples after filtration with Coconut Shell Sample.*

Samples/Parameters	Control	Sample A	Sample B
Cu (ppm)	0.001±0.000	0.780±0.014	0.790±0.026
Fe (ppm)	3.650±0.625	13.500±0.942	14.125±0.618
Zn (ppm)	0.6700±0.071	5.838±0.344	5.400±0.280
Cd (ppm)	0.001±0.000	0.001±0.000	0.001±0.000
Pb (ppm)	0.563±0.172	0.410±0.037	0.438±0.222
Cr (ppm)	0.348±0.049	0.388±0.046	0.528±0.055
Mg (ppm)	1.475±0.171	3.625±0.222	0.645±0.037

Table 4. *Analysis of Variance of Variables and Summary for all Y's for the various Heavy Metals.*

S/N	(Cu)	(Fe)	(Zn)	(Cd)	(Pb)	(Cr)	(Mg)
R^2	0.8185	0.9927	0.9953	0.8347	0.9349	0.9378	0.9997
F	15.2181	459.5948	715.9685	17.0436	48.4738	50.8595	11356.9041
Pr > F	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001	<0.0001
Filtration process	20.9543	864.8179	1058.5040	51.4600	164.4045	171.7839	26526.6506
	<0.0001	<0.0001	<0.0001	< 0.0001	<0.0001	<0.0001	<0.0001
Samples	13.1799	696.8264	978.8792	3.1714	17.1650	14.7779	5447.8007
	0.0001	<0.0001	< 0.0001	0.0579	<0.0001	<0.0001	< 0.0001
Filtration process*	13.3691	138.3674	413.2453	6.7714	6.1629	8.4382	6726.5826
Samples	<0.0001	<0.0001	<0.0001	0.0007	0.0012	0.0001	<0.0001

Table 5. *Brunauer, Emmett and Teller (BET) Summary.*

Parameters	Palm Kernel shell	Coconut shells
Surface area (m^2/g)	717.142	1177.524
Correlation coefficient (r)	0.9994	0.9963
Slope	3.063	2.121
Intercept	1.793e+00	8.361e-01
Constant	2.706	3.537

4. Discussions

Adsorption of Heavy Metals in Used Lubricating Oil using Palm Kernel and Coconut Shells as Adsorbents.

From the results obtained, it can be seen that for both the palm kernel and coconut shells were not suitable for the removal of copper metal in the fresh and used lubricating oil samples. Because, the initial mean concentrations of copper in virgin (C) and used lubricating oil samples (i.e. A &B) were 0.001±0.000 ppm, 0.1500±0.008 ppm and 0.220±0.026 ppm respectively before filtration processes. But after the filtration process with the palm kernel shell activated carbon, the mean concentration of copper metal increases for virgin (C) to 0.075±0.013 ppm and used lubricating oil samples (A&B) are 0.400±0.018 ppm and 0.230±0.008 ppm respectively. In the case of the coconut shell activated carbon, the mean concentration of copper also in virgin lubricating oil remains the same 0.001±0.000 whereas for used lubricating oils samples (i.e. A&B) it increases to 0.780±0.014 and 0.790±0.026 respectively. The increase in mean concentrations after the filtration processes with both the palm kernel and coconut shells activated carbons can be attributed to leaching of copper ions already present in the filter beds as ascertain in the physio-chemical characterization analysis of the filter beds by [11, 24]. Though, the percentage leached in palm kernel was small compared to that of coconut shells. Hence, there is the need to further search for better and potential raw materials for the production of activated carbons that can meet industrial needs of removal of copper metals in both fresh and used lubricating oil samples. However, [25] reported that date palm kernel can slightly reduce copper metals in used lubricating oils from 7mg/kg to 6mg/kg. But several works of literature have shown that chemical activated carbons from palm kernel and coconut shells are effective in the removal of pollutants in muddy water and colour from wastewater [26, 27]. Also, Kwakye-Awuah *et al.,* 2018 [28] reported that laboratory-synthesized zeolite types LTA and LSX successfully removed heavy metals, particularly lead, copper and iron that was in the spent oil.

Also, it can be observed from the results obtained that the concentrations of iron metal increases after filtration processes with both the chemically activated carbons produced from coconut and palm kernel shells. The concentrations of iron metal before the filtration processes were 1.502±0.092 ppm for virgin and 4.650±0.159 ppm and 3.350±0.289 ppm for both used oil samples A&B. However, after filtration processes with chemically activated carbons produced from palm kernel and coconut shells, the concentrations of the iron metal increases. For the palm kernel activated carbon, the values obtained are 1.150±0.129 ppm for virgin, 8.500±0.258 ppm for sample A and 3.400±0.183 ppm for sample B respectively. In the case of the coconut activated carbons, the observed values are 3.650±0.625 ppm for virgin, 13.500±0.942 ppm for sample A and 14.125±0.618 for samples B respectively. The level of increase was not much in palm kernel as compared to coconut shells. The concentration increase in iron metal after the filtration process with both the coconut and palm kernel shells might be due to leaching of the iron metal concentration already present in the filter beds by [11, 24]. According to their research works reported, chemically activated carbons produced from coconut and palm kernels contain a high amount of iron metal concentration. Though, the analyses of iron revealed that palm kernel shell activated carbon performed better followed by coconut shell activated carbon respectively. Because of this reason, activated carbons produced from palm kernel and coconut shells as adsorbents are not recommended for the removal of iron metals present in used lubricating oil samples. However, [28] reported that laboratory-synthesized zeolite types LTA and LSX successfully removed heavy metals, particularly lead, copper and iron that was in the spent oil.

In general, zinc is added to fresh lubricating oil as zinc diethyl dithiophosphate (ZDDP), zinc dithiophosphates, and zinc dialkyl dithiocarbamates. This was added to the base oil as part of multi-functional additives for improving oil's performance [28]. From all the tests conducted on the zinc before filtration with activated carbons produced from coconut and palm kernel shells the results were for virgin was 2.833±0.275 ppm and used lubricating oil samples A&B are 16.475±0.950 ppm and 14.57±0.272 ppm respectively. But after the filtration process with palm kernel shell activated carbon the values recorded were for virgin was 8.325±0.275 ppm and used lubricating oil samples A&B are 10.375±0.171 ppm and 5.450±0.300 ppm. For coconut shell activated carbon, the results obtained were for virgin was 0.670±0.071 ppm and used lubricating oil samples A&B are 5.838±0.344 ppm and 5.400±0.280 ppm respectively. Comparing the various results observed, it proved that coconut shell activated carbon has the best adsorption capacity followed by palm kernel shell activated carbon. lnegbenebor *et al.* 2012, conducted similar research using activated carbons from palm kernel and coconut shells for purification of polluted water for drinking but reported that palm kernel was rather effective than coconut shells. The disparity might due to the used lubricating oils sample instead of the polluted water for drinking. Kwakye-Awuah *et al.,* 2018 [28] reported that the recycling of the used oil with metakaolin and the zeolites as compared to that of the used oil led to a reduction in zinc content by 94.96%, 96.76% for zeolite LTA and 93.88% for zeolite LSX figure. This shows that coconut shell activated carbon produced can be used effectively and efficiently as an alternative to those prepared by other researchers.

Analysis of the heavy metal such as cadmium from tables 1, 2 and 3 revealed that both coconut and palm kernel shells activated carbons are very efficient and effective in the adsorption processes. Because the concentrations of cadmium metal before the filtration process with palm kernel and coconut shells activated carbons were for virgin 0.020±0.008 ppm and used samples A&B lubricating oils are 0.0200±0.008 ppm and 0.030±0.008 ppm respectively. But after the filtration with palm kernel shell activated carbon the concentrations of cadmium metal reduces, for lubricating oils; virgin 0.000±0.000 ppm and used samples A&B to 0.018±0.009 ppm and 0.000±0.000 ppm lubricating oils respectively. Also, with the coconut shells activated carbon after the filtration processes, they all drop in the concentrations of the cadmium metals, with lubricating oils; virgin 0.001±0.000 ppm and used samples are A&B the recorded values are 0.001±0.000 and 0.001±0.000 respectively. This affirmed what [25] had reported earlier that, date palm kernel powder was a good adsorbent for removal of cadmium metal in used lubricating oils.

However, [29] reported that coconut shell adsorbed Pb^{2+}, Cu^{2+} Cd^{2+} and As^{3+} ions from aqueous solutions and the concentration of the metal ions adsorbed increased with increase in concentrations, increase in contact time, increase in temperature and increases in pH for each metal. He concludes that coconut shell could serve as a cheap, readily available effective adsorbent for the removal of Pb^{2+}, Cu^{2+}, Cd^{2+}, and As^{3+} from wastewater as a way of treatment before discharge into the environment. From the literature findings reported earlier, it can be concluded that chemically activated carbons produced from both coconut and palm kernel shells are good adsorbents for removal of heavy metal such as cadmium from used lubricating oils.

From the analysis of chromium metal in tables 1, 2 and 3, it was observed that concentrations of chromium metal before the filtration processes with both palm kernel and coconut shells activated carbons were, for lubricating oils; virgin 0.410±0.051 ppm, used samples A&B are 0.400±0.065 ppm and 0.445±0.039 ppm respectively. But after filtration with palm kernel shells activated carbon, the values obtained were 0.065±0.013 ppm for virgin, 0.210±0.026 ppm for used sample A and 0.135±0.013 ppm for used sample B lubricating oils respectively. In the case of after filtration with coconut shell activated carbons, the values recorded are 0.348±0.049 ppm for virgin, 0.388±0.046 ppm for used sample A and 0.528±0.055 ppm for used sample B. From all the results obtained, it revealed that palm kernel shell activated carbon is a good adsorbent compared to coconut shell activated carbon. Because the palm kernel shell reduces the concentrations of chromium metal compared to coconut shell activated carbons. Babayemi, A. K, 2017 [30] revealed that palm kernel shell being an agricultural waste could be converted to useful and efficient adsorbent through the use of activating chemicals, particularly H_2SO_4. Also, [25] reported a similar phenomenon with chromium metal.

However, Hidayu and Muda, (2016) [9] reported that palm kernel and coconut shells can be used as the perfect raw material to prepare activated carbon with the high surface area for CO_2 adsorption rate. Also, [31] found out that palm kernel shell, an inexpensive and easily available material, was very effective to remove Cr (VI) from aqueous solutions. He reported that the tested activated carbon produced from palm kernel shells showed higher adsorption capacities compared to those of some coconut shell and other activated carbons found in the works of literature. Odisu *et al.,* 2019 [24] reported that palm kernel husks, coconut and groundnut shells could be used as an alternative to available commercial adsorbents for cement wastewater treatment. They also affirmed that the combination of physical and chemical treatment of these adsorbents could enhance their adsorption capabilities due to their resultant high surface area and increased depth of pore spaces.

From the tables 1, 2 and 3, the analysis of heavy metal such as lead (Pb) concentrations before filtration processes with both chemically activated carbons produced from palm kernel and coconut shells gave the following results for the lubricating oil samples; for virgin 1.000±0.093 ppm, used sample A 1.045±0.478 ppm and used sample B 1.525±0.222 ppm respectively. But after the filtration process with the chemically activated carbon prepared from palm kernel shells, the values recorded were as follows, for virgin 1.650±0.039 ppm, used sample A 1.648±0.099 ppm and used sample B 2.388±0.070 ppm lubricating oils in that order. However, with the chemically activated carbon produced from coconut shells, the results obtained after the filtration process were as follows, for virgin 0.563±0.172 ppm, used sample A 0.410±0.037 ppm and used sample B 0.438±0.220 ppm lubricating oils respectively. From all the test results recorded, it shows that coconut shell activated carbon as having the best adsorption capacity of lead metals after the filtration processes with various types of lubricating oil samples compared to palm kernel shells activated carbons. This proofed that coconut shell activated carbon was effective and efficient adsorbent. Therefore, it can be used as a suitable adsorbent for the removal of lead metal concentration in used lubricating oils. However, [9] reported that palm kernel and coconut shells can be used as the perfect raw material to prepare activated carbon with the high surface area for CO_2 adsorption rate. But usually, coconut shell is preferred to palm kernel shell activated carbons because of its large surface area as shown in table 5.

In the case of palm kernel shell activated carbon, the concentration of lead metals increases. This can be attributed to the high levels of lead concentration already present in the activated carbon [24] and the high contact time of the filtration process. Nabil *et al.,* 2010 [25], also reported an increase in lead metal concentration with activated carbon prepared from date palm kernel. Jodeh *et al.,* 2015 [32], found out that concentration of heavy metal lead in used lubricating oil is higher than the concentration of other metals and adsorption of lead increases with increase adsorbent dosage, temperature and time of contact.

Finally, the adsorption results obtained for magnesium heavy metal analysed indicated that activated carbons produced from the coconut and the palm kernel shells can be used as a high-performance adsorbent with higher adsorption capacity. It was worthy of note that from all the analysis performed, the magnesium metal contents of the used lubricating oil samples were generally far below the general range reported in the literature with both palm kernel and coconut shells activated carbons. From tables 1, 2 and 3, the results obtained for the analysis of magnesium concentrations before the filtration process was as follows for the various lubricating oils, for virgin was 41.900±0.258 ppm, used sample A was 5.450±0.265 ppm and used sample B was 21.475±0.650 ppm respectively. But after the filtration process with activated carbon produced from palm kernel shells, the values obtained for the respective lubricating oils were, virgin 0.350±0.026 ppm and used samples A&B are 0.900±0.025 ppm and 0.505±0.013 ppm in that order. In the case of the coconut shell activated carbon, the results recorded for the various types of lubricating oils are as follows, virgin 1.475 ±0.171 ppm, used sample A 3.625±0.222 ppm and used sample B 0.645±0.645 ppm respectively. Nabil *et al.,* 2010 [25] reported a similar trend of decrease in magnesium metal concentration from fresh to used lubricating oil samples with activated carbons prepared from date palm kernel powder. Also,[33] found that the increase of chitosan dosage from 0.5 to 1.0 g decrease the metals such as sodium, magnesium, calcium and zinc removal percentage in used lubricating oils. Furthermore, they observed that the increase of temperature from 30 to 70°C and the increase of contact time from 2 to 10 min resulted in a decrease of metals removal from used lubricating oils.

Adsorption Model

Table 4, shows that copper have the R^2 (0.8185), DW (1.4546) and Pr > F (< 0.0001). In this model, the amounts of R^2 are close to 1 for the adsorbate and D. W. T. is more than 1 for the solute which confirms the definition of modelling basis. Also, in the ANOVA, the lesser the Pr > F value, the more significant the results. The equilibrium isotherm for the heavy metals analysed was determined. The heavy metal copper analysed was found to conform to a straight line Langmuir adsorption isotherm [34]. The adsorption data obtained after the analysis fitted well to the Langmuir model and adsorptive surface area of 717.120 m^2/g palm kernel and 1177.524 m^2/g coconut shells were obtained for the activated carbons respectively as shown in table 5.

From the results in table 4, iron metal have R^2 (0.9927), DW (2.6443) and Pr > F (< 0.0001) respectively. R^2 is the most important parameter to obtain the model ability, in fitting for various conditions provided based on experimental data. In this model, the amounts of R^2 are close to 1 for the adsorbate and D. W. T. is more than 1 for the solute which confirms the definition of modelling basis. Also, in the ANOVA, the lesser the Pr > F value, the more significant the results. The iron metal revealed that it conforms to a straight line Langmuir adsorption isotherm [34].

The values recorded in table 4, zinc have R^2 (0.9953), DW (2.2315) and Pr > F (< 0.0001) respectively. R^2 is the most important parameter to obtain the model ability in fitting for various conditions provided based on experimental data. In this model, the amounts of R^2 (0.9953) are close to 1 for the adsorbate and D. W. T. (2.2315) was more than 1 for the solute which confirms the definition of modelling basis. Also, in the ANOVA, the lesser the Pr > F value, the more significant the results. Hence, the zinc metal was found to conform to a straight line Langmuir adsorption isotherm [34].

Also from the results obtained in table 4, cadmium has R^2 (0.8347), DW (2.7000) and Pr > F (0.0001). From the statistic point of view, R^2 is the most important parameter to obtain the model ability in the fitting of various conditions provided based on experimental data. For this model, the amounts of R^2 (0.8347) are relatively close to 1 for the adsorbate and D. W. T. (2.700) was more than 1 for the solute which confirms the definition of modelling basis. Also, in the ANOVA, the lesser the Pr > F value, the more significant the results. Therefore, these results showed that cadmium metal conforms to a straight line Langmuir adsorption isotherm

[34].

In table 4, lead recorded values of R^2 (0.9349), DW (2.3732) and Pr > F (< 0.0001) respectively. R^2 is the most important parameter to obtain the model ability in the fitting of various conditions provided based on experimental data. It can be seen from the results obtained in tables that, the Langmuir isotherm best fitted to the experimental data since it had a high value for the correlation coefficient R^2 (0.9349). This data has revealed that activated carbons produced from palm kernel and coconut which are agricultural waste, can be used as an adsorbent for lead metal [35].

From the results obtained in table 4, chromium has R^2 (0.9378), DW (2.1824) and Pr > F (< 0.0001). From the statistic point of view, R^2 is the most important parameter to obtain the model ability in the fitting of various conditions provided based on experimental data. Hence, the results recorded showed that chromium metal conforms to a straight line Langmuir adsorption isotherm [34]. The results obtained for chromium revealed that activated carbons produced from the coconut and the palm kernel shells can be used as a high-performance adsorbent with higher adsorption capacity [35, 36].

Finally, from table 4, magnesium recorded the following results R^2 (0.9997), DW (2.4396) and Pr > F (< 0.0001). R^2 is the most important parameter to ascertain the model ability in the fitting of various situations provided based on experimental data. In this model, the amounts of R^2 (0.9997) are close to 1 for the adsorbate and D. W. T. (2.4396) was more than 1 for the solute which confirms the definition of modelling basis. Also, in the ANOVA, the lesser the Pr > F value, the more significant the results. This revealed that magnesium metal conforms to a straight line Langmuir adsorption isotherm [34]. This result obtained for magnesium proofed that activated carbons produced from the coconut and the palm kernel shells can be used as a high-performance adsorbent with higher adsorption capacity [36]. The adsorption results obtained for some of the heavy metals analysed indicated that activated carbons produced from the coconut and the palm kernel shells can be used as a high-performance adsorbent with higher adsorption capacity.

5. Conclusions

The adsorption results obtained for some of the heavy metals analysed indicated that activated carbons produced from the coconut and the palm kernel shells can be used as a high-performance adsorbent with higher adsorption capacity. This research work further ascertained that the some of the heavy metal contents in the used lubricating oil samples were reduced considerably to appreciable concentrations through re-refining with the chemically activated carbons produced from both palm kernel and coconut shells. Particularly, magnesium, cadmium and chromium contents in the used lubricating oil samples respectively. However, the activated carbons produced from palm kernel and coconut shells were not suitable for the removal of both copper and iron metals. From the R^2 values obtained and statistics point of view, it can be concluded that the Langmuir model shows a better fit due to the high coefficient of correlation ($R^2 \approx 1$). Also, the recovered oil could be re-used. Finally, agriculture waste such as palm kernel and coconut shells can be converted to a high-performance adsorbent.

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