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Comparative Study on the Adsorptive Capacity of Water Hyacinth and Palm Kernel Shell on Heavy Metals

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Abstract:

The adsorptive capacity of activated water hyacinth (AWH) and palm kernel shell (APKS) on lead (Pb^{++}) and iron (Fe^{++}) was studied. The zinc chloride activated carbons were characterized under pH and iodine number, moisture content, particle size, specific gravity, bulk density, porosity and volume of void. The results showed that APKS has a pH of 6.36 with iodine number of 510mg/g, where as the AWH has a pH of 7.67 and iodine number of 620mg/g.

Batch adsorption studies were also carried out under varying experimental conditions of pH of the solutions, contact time of the carbons and metal ions, and initial concentration of Pb^{++} and Fe^{++} solutions. The results showed that the highest percentage removal of 99.85 occurred at pH = 8 by AWH on Fe^{++} and the lowest percentage removal of 3.026 by AWH on the same metal. On the effect of contact time, it was found that the equilibrium time for the sorption was at 60mins with the percentage removal of 99.59 by AWH on Fe and lowest % removal of 23.27 by APKS on Fe^{++} . On the effect of initial concentration, the results showed that the adsorption of Fe increases with the initial concentration, while that of Pb^{++} decreases with increase in initial concentration. The Langmuir and Freundlich adsorption models were used for the mathematical description of adsorption equilibrium as well. It was deduced from the plot that the Langmuir isotherm fitted for modeling the adsorption by APKS on Pb^{++} and Fe^{++} while the Langmuir and Freundlich model for lead by AHW gave relative close correlation coefficient of 0.692 and 0.771 respectively, but was totally inadequate for modeling that of iron.

Keywords: capacity, comparative, palm kernel, water hyacinth, heavy metals

1. Introduction

The awareness of increasing water pollution has necessitates studies concerning water treatment and the removal of heavy metals from industrial waste water and drinking water (ground water).

Heavy metals are natural components of the earth's crust; they cannot be degraded or destroyed. They can enter a water supply by industrial and consumer waste, or even from acidic rain or through the everyday soil releasing heavy metals into streams, lakes, rivers and ground water, and to small extent our bodies through food, drinking water and the air. Sequel to these effects, the need for waste water treatments comes into play especially by using natural materials for the heavy metal removal. Some of these natural materials are available in large quantity and in some instance are waste from agricultural operation, capable of causing environmental pollution if not dispose properly. Hence, they are very cheap to purchase or free given by nature in abundance.

However, the application of low-cost natural adsorbent including carbonaceous materials, agricultural products and by products has been investigated in many studies (Nguyen and Da, 2001; Singh and others, 2005; Abdel-Ghani and others, 2007). Several studies have shown that non-living plant biomass materials are effective for the removal of trace metals from the environment (Mofa, 1995; Lujan "and others", 1994; Gardea "and others", 1996) and (Abia "and others", 2002).

Palm kernel shell is an agricultural waste produced in large quantities in some countries like Nigeria and Malaysia both locally and industrially. These shells, if not utilized or dispose properly, tend to be of environmental concern. In some rural areas in Nigeria, it serves as a biomass fuel for domestic use. Because of its availability, it becomes a cheap product that can easily be acquired, and research are ongoing as to its usefulness as an adsorbent in purification processes.

Water hyacinth (*Eichornia crassipes*) is a floating aquatic plant that grows in all type of fresh water. It is a native of America and was introduced into the Amazon Basin of U.S in 1884. The spread throughout the world has taken place over the last 100 years or so, although the actual cause of its spread is poorly documented.

Studies have shown that both activated water hyacinth (AWH) and activated palm kernel shell (APKS) are good low-cost material for adsorption processes.

Jumasiah A. and others, 2005. Reported that activated palm kernel shell (APKS) can be used as a low-cost adsorbent for waste water treatment containing dye. Mokhlesur, M. "and others ", 2014; showed that APKS and activated coconut shell could be used in water purification because of their ability in adsorbing heavy metals at low concentration of the metal ions. Buasri and other (2012), reported that water hyacinth could be a low cost absorbent for heavy metals and also is efficient in removal of CU (II) and Zn (II) ions from aqueous environment. Uddin, Islam and Abedin (2007) showed that water hyacinth ash can be used in the adsorption of phenol from aqueous solution.

The literature is littered with various works on the adsorption of heavy metals using various carbonaceous plants. However, comparative study on the adsorptive capacity of water hyacinth and palm kernel shell on heavy metal was not found in the any literature.

The objective of this work is to compare AWH and APKS to determine the one with a higher sorption capacity.

2. Materials and Method

The water hyacinth was collected from the Swani River beside Swani Market of Yenegoa in Bayelsa State, while the palm kernel shell was collected from Ibagwa-Aka in Igbo-Eze South Local Government of Enugu State. The collected water hyacinth and palm kernel shell were washed thoroughly with clean water for several times to remove dirt's. The water hyacinth was cut into smaller bits and air – dried for 168 hours, while the palm kernel shell was air-dried for 48 hours. The dried water hyacinth and palm kernel shell were carbonized in a muffle furnace at 300°C and 600°C for one and two hours respectively. The carbonized material was thereafter impregnated with zinc chloride of suitable concentration and heated again at 450°C for 1:30mins for water hyacinth and 800°C for 2:30 mins. for palm kernel shell in a muffle furnace (Carbolite, LMF 4. Sheffield, England) at plant anatomy laboratory Ofrima, University of Port Harcourt (UNIPORT)).

2.1. Characterization of the Activated Carbons

The zinc chloride treated activated carbons produced were characterized under the properties of pH, pore sizes, moisture contents, bulk density, volume of void and specific gravity. The processes of the characterizations are described below.

2.2. Determination of Ph of the Activated Carbons

Apparatus; Activated carbons, distilled water, beaker and pH meter. The pH was determined by weighing 1g of activated carbon from both water hyacinth and palm kernel shell into different beakers, and 100ml of de-ionized water was also measured into the beakers. The solutions were stirred for 5mins and allowed to stabilized, an electrode was inserted into the beaker containing the solutions and the readings were also taken. The Activated carbons were washed several times and processes repeated until a stabilized pH reading was taken respectively.

2.3. Determination of the Porosity of the Activated Carbons

Apparatus: Cylinder, Vernier caliper, spatula, oven, density bottle, mortar & pistil, glass funnel and weighing balance.

The diameter and mass of the cylinder were measured then the samples were allowed to cover the surface of cylinder and both end of the cylinder trimmed. The mass of the cylinder with the samples were recorded and oven dried, they were allowed to cool and reweighed to know the mass of the dried samples. Then, the specific gravity was determined together with other parameters.

2.4. Determination of the Iodine Numbers of the Activated Carbons

Apparatus: Burette, measuring cylinder, standard flask, conical flask, Weighing Balance, Mechanical Shaker, Filter Paper, Funnel.

Reagent: Sodium thiosuiphate, (standard Thiosuiphate titrate, iodine solution, starch indicator, 20% H₂ SO₄).

A known concentration of Iodine solution was prepared; also a known of molarity Sodium thiosuiphate was prepared too. 1g of the activated carbons each were weighed in a conical flask and 50ml of iodine solution were added. The samples were agitated with a mechanical shaker for 1hr and then filtered; the filtrate was titrated against standard sodium thiosuiphate solution to the end point using starch indicator. The end point was read when the blue colored solutions changed to colorless solution.

2.5. Batch Adsorption Process

The batch adsorption process of the metal ions were carried out under the condition of the effect of pH of the solution to the adsorption, the effect of contact time of the metal ions on the activated carbons, and the initial concentrations of the metal solutions.

2.6. Chemicals

The stock solutions of 1000mg/l of Lead (ii) chloride and Iron (ii) chloride were prepared by dissolving 1.0g of analytical reagent grade of the metallic salts in 1L of de-ionized water. The test solutions of desired concentrations were then prepared by diluting the stock solution. A 0.1 M of HCL and KOH used to adjust the pH to the required value were also prepared.

2.7. Determination of the Effect of Ph on the Adsorption of Pb^{++} and Fe^{++} BY APKS and AWH

The effect of pH on the amount of Iron (II) chloride and Lead (II) nitrate removal was analyzed over the pH range of 2 to 8. In this study, 50ml of the metal solutions of 100mg/l was taken in stopper plastic conical flask and are agitated with 1.0g of activated water hyacinth and palm kernel shell using a mechanical shaker (Stuart flask shaker, Industrial chemistry research Laboratory) at room temperature. Agitations were made for 2hrs:30mins at constant oscillations of 300osc/min. The samples were allowed to settle down before filtering, and the left out concentrations of the filtrate/solution were analyzed using Atomic Absorption spectrophotometer (Buck Scientific Atomic Absorption/Emission Spectrophotometer 205).

2.8. Determination of the Effect of Contact Time

The effect of contact time activated water hyacinth on the amount of removal of heavy metal solutions of Iron (II) chloride and lead (II) nitrate were also obtained by contacting 100ml of the solutions of initial concentration of 70mg/l with 1 .5g of the adsorbents at constant pH and room temperature. The samples were agitated for the time of 30mins, 1hour, 1.30mins, and 2hours respectively in plastic conical flask at a constant oscillation of 300osc/min. The picture 3.1 below shows the shaking process of batch adsorption. Then, the samples were allowed to settle down after in which it is filtered and the left out concentration of the solutions were analyzed as before.

2.9. Determination of the Effect of Adsorption Equilibrium of Pb^{++} and Fe^{++} on AWH APKS

Equilibrium studies were carried out by contacting 1.0g of activated water hyacinth and activated palm kernel shell with 100ml of lead solution of different initial concentrations (40,60,80,100mg/L) and also 100ml of iron solution of different concentrations (10,20,30,40 mg/L) respectively in 150ml plastic conical flask. The samples were then shaken at a constant oscillation of 300osc/min for 2.30mins. After equilibrium, the concentrations were analyzed as before.

3. Results and Discussion

S/N	PARAMETERS	AWH	APKS
1	PH	7.67	6.36
2	Iodine number (mg/g)	620	510
3	Particle size (un sieve)	0.375	0.141
4	Bulk density (g/cm ³)	0.127	0.723
5	Volume of void	58.14	35.99
6	Porosity (n)	0.91	0.56
7	Specific gravity	0.78	1.45
8	Moisture content %	54.09	14.39

Table 4.1: Summary of results from characterization carbons

The properties of activated carbons are a function of the material from which the activated carbon is made of, as it can be seen from the table above that the specific gravity of water hyacinth is less than 1.0 confirms its floatation in water.

3.1. The Effect of P^h on the Adsorption of Fe^{2+} and Pb^{2+} by APKS and AWH

The effect of pH on the adsorption of Fe^{2+} and Pb^{2+} was carried out at the Ph solution range of 2-8 and the percentage of the metal ions adsorbed is shown below.

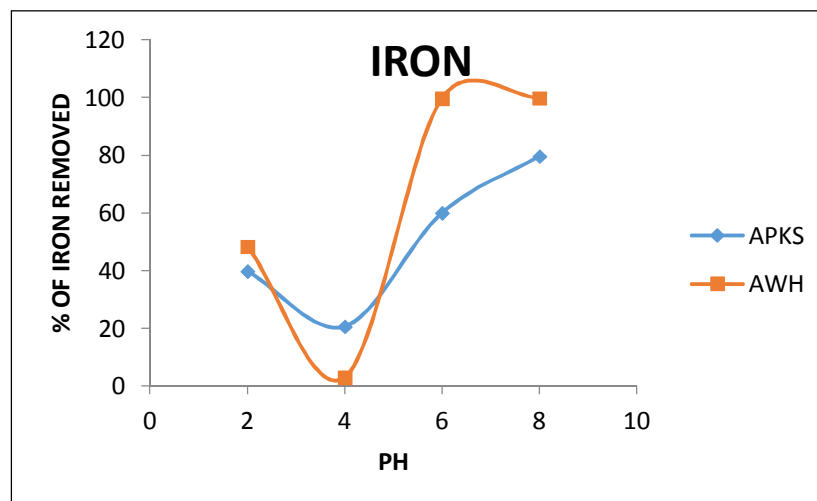


Figure 1: Effects of PH on percentage removal of AWH and APKS on Iron

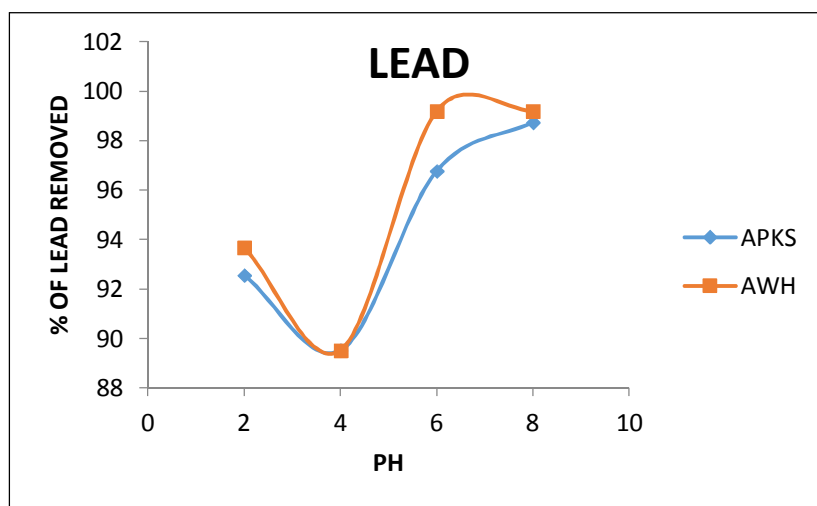


Figure 2: Effects of PH on percentage removal of AWH and APKS on Lead

This shows that the removal of metals from aqueous solution by APKS and AWH is PH dependent. This is because that pH affects the surface charge of the adsorbents degree of ionization, this influence of pH on the adsorption of metals ions was highest at pH = 8 for the both metals by the samples. It is generally believed to be that this effect is due to the exchange of hydrogen atoms in the substrate by metals ions (Okieirnen and others, 1988). It is thought that the presence of a relatively high concentration of H^+ in the medium would influence this exchange from the substrate as decreasing solution pH increases H^+ concentration in the solution which will coordinate with OH^- groups to form OH_2^+ and thereby reducing the number of negative sites on the adsorbent causing the repulsion of metal ions (Ofomaja and others, 2005). On the other hand, increasing pH reduces the amount of H^+ in and promotes ionization OH^- groups. Again, as can be seen in the table above that the uptake capacity of AWH on Fe^{++} is higher than that on Pb^{++} , this differential sorption of different ions may be attributed to the differences in their ionic sizes. The smaller the ionic size, the bigger its affinity to reactive sizes (Horsfall Jnr and others, 2003). We recommend that PH = 7 should be perfect because of consumable produce.

3.2. The Effect of Contact Time on the Pb^{++} and Fe^{++} by APKS and AWH

The adsorption data for the uptake of metals versus contact time at initial concentration of 70mg/1 is presented in Figure 3 and 4. The results showed that time required for the adsorption of metals onto AWH and APKS was almost 120mins (2hrs). However, for subsequent experiments, the samples were left for 150mins to ensure equilibrium. These results also indicated that up to 96 - 99% of the metals ions uptake by the adsorbents occurred in between the first phase of 30mins and 1 hr after in which it is found to be relatively constant for the rest of the time. The higher sorption rate at the initial period (30 - 60mins) may be due to an increased number of vacant sites on the adsorbent available at the initial stage; as a result, there exist increase concentration gradients between adsorbents in solution and adsorbate on adsorbent surface (Uddin and others, 2007). It is also believed that at 90 and 120mins is where the adsorption equilibrium is attained, where sorption and desorption is tending to be equal. Evidently at every time, the percentage removal of the metal ions AWH is always greater than that by APKS.

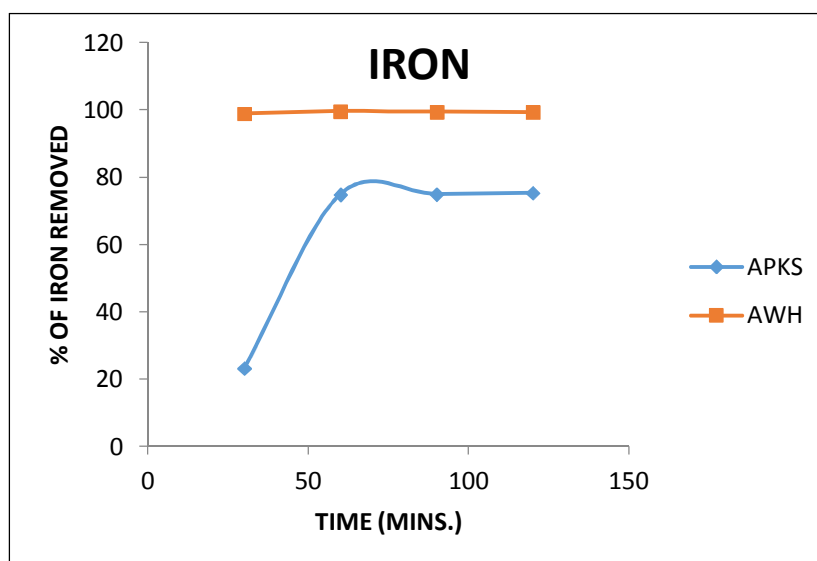


Figure 3: Effects of contact time of AWH and APKS on Iron

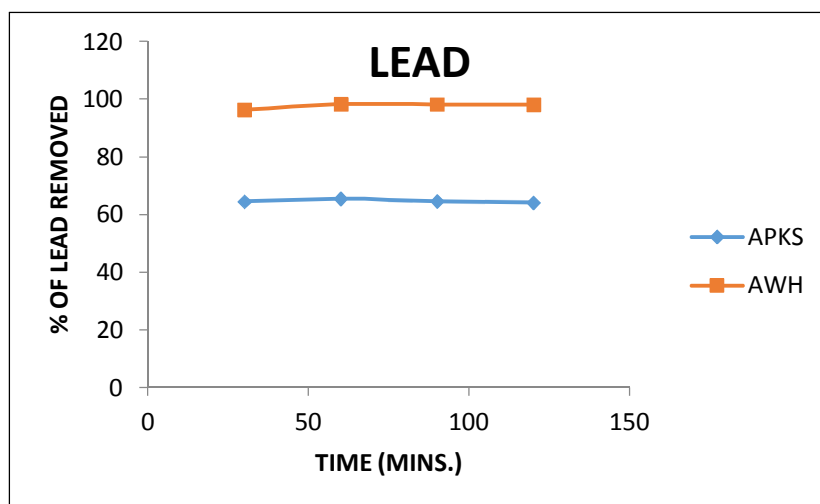


Figure 4: Effects of contact time of AWH and APKS on Lead

3.3. The Effect of Initial Concentration of the Metal Ions

The effect of initial concentrations of the metal ions were determined and the data obtained were plotted as shown in Figure 5 and 6

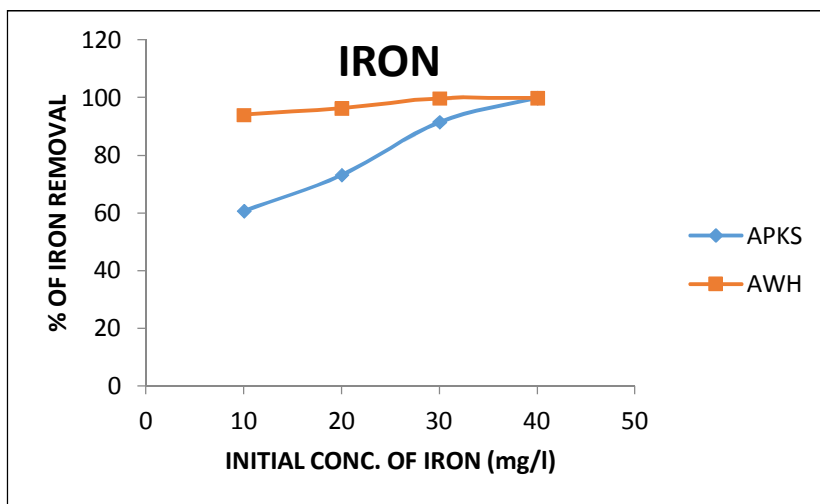


Figure 5: Effects of initial concentration of Iron on AWH and APKS

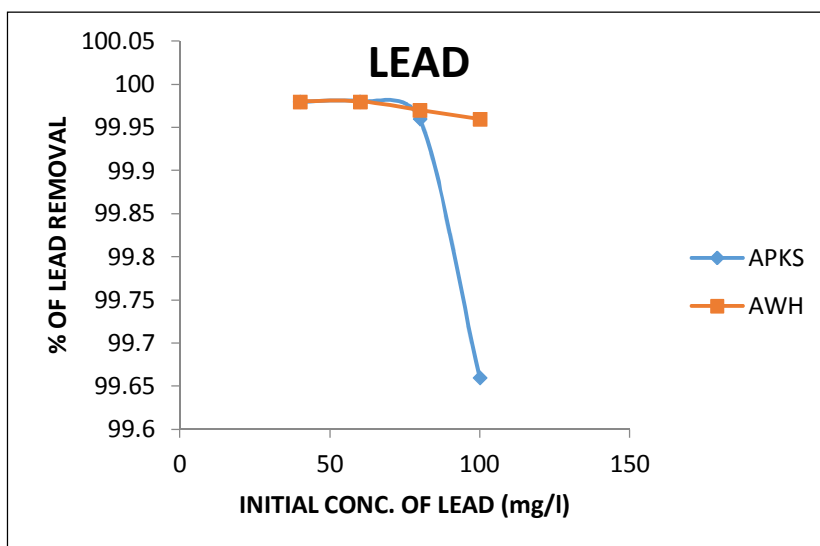


Figure 6: Effects of initial concentration of Lead on AWH and APKS

From (Figure 5 & 6), it can be seen that the percentage of removal of Fe^{++} increases as the concentration of the solution increases with the highest percentage removal of 99.90% at the concentration of 40mg/l by APKS, this was followed by 99.80% at same concentration by AWH. This shows that at high concentration of Fe^{++} the carbon has more affinity with the Fe solution and that the active sites is more active when the concentration is high than when it is at low concentration, which may be due to its low ionization sizes. However, the percentage removal of Pb^{++} decreases with increases in concentration, as can be seen that the highest percentage removal of 99.98% by the two samples at 40mg/l and 60mg/l. and 99.66% by APKS at 100mg/l. This shows that the active site of the carbon takes up the available ion faster at low concentrations and as the concentration increases the binding site gradually become saturated. Also, in both Figure 5 and 6, the average percentage removal of AWH was higher than APKS.

3.4. The Effect of Adsorption Equilibrium

Equilibrium study on adsorption provides information on the capacity of the adsorbent. An adsorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorptive capacities of the pollutants.

The Figures 7 - 14 shows the Langmuir and Freundlich plots for Pb^{++} and Fe^{++} adsorbed by AWH AND APKS.

From the figures above, it is observed that not all the equilibrium data gave a linear graph, but it was able to obtain the Langmuir and Freundlich constants and the correlation coefficients. As its showing in Table 4.2 and 4.3, the Langmuir model was fitted for the modeling of lead and iron on APKS with the correlation coefficient of 0.996 and 0.864 respectively. Whereas the model was not fit for modeling AWH on any of the metals, though it has a close proximity for lead with a correlation coefficient of 0.692. The Freundlich model was not also fit for any of the sample on the metals, but has a close range of correlation coefficient of 0.771 for the lead by AWH. It was also observed that the maximum sorption capacity (q_{max}) of the carbons for the metals was found to be 6.67mg/g on the sorption of lead by AWH. (Table 2).

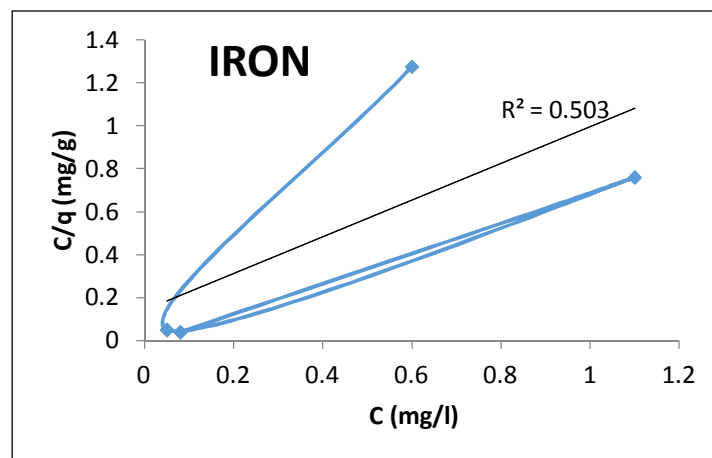


Figure 7: Langmuir model for Iron by AWH

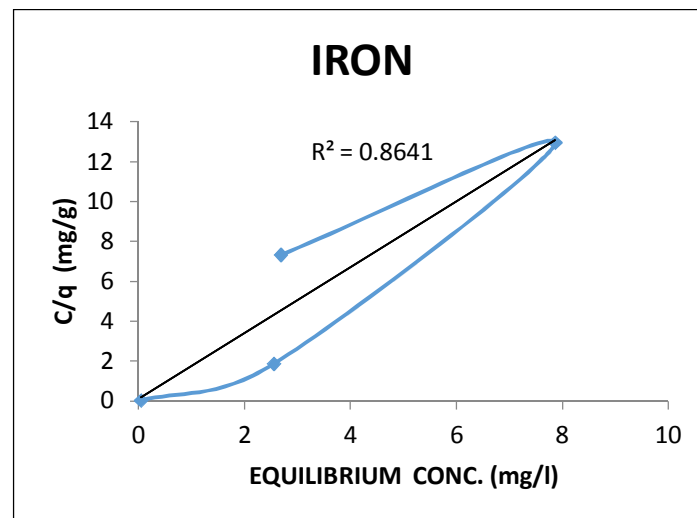


Figure 8: Langmuir model for iron by APKS

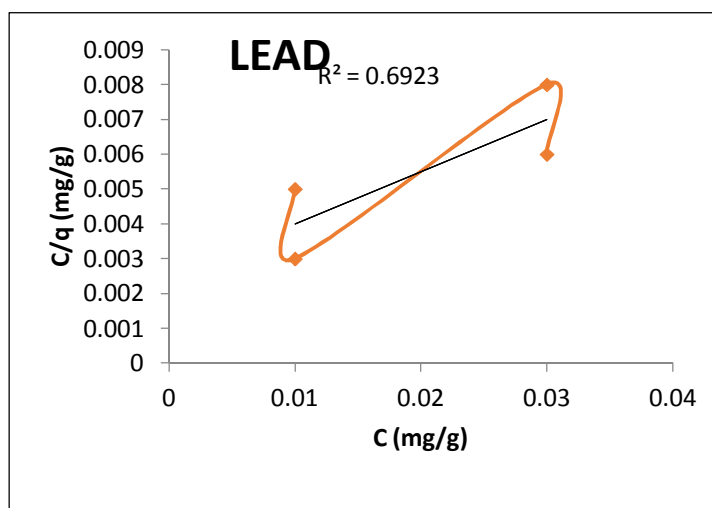


Figure 9: Langmuir model for Lead by AWH

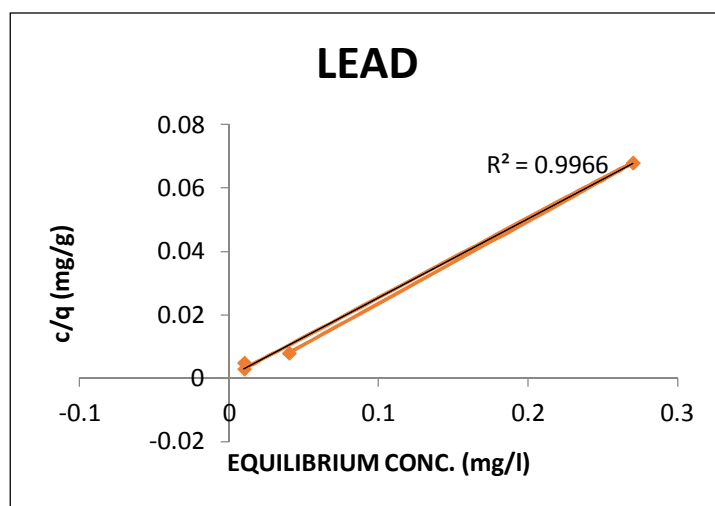


Figure 10: Langmuir model for Lead by APKS

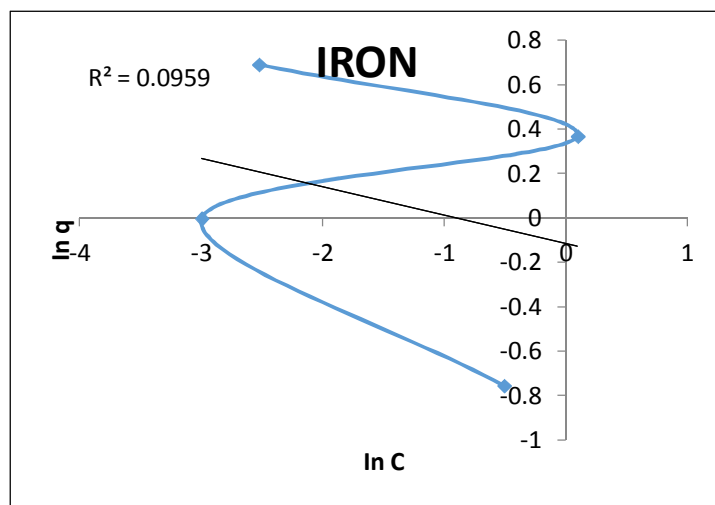


Figure 11: Freundlich model for Iron by AWH

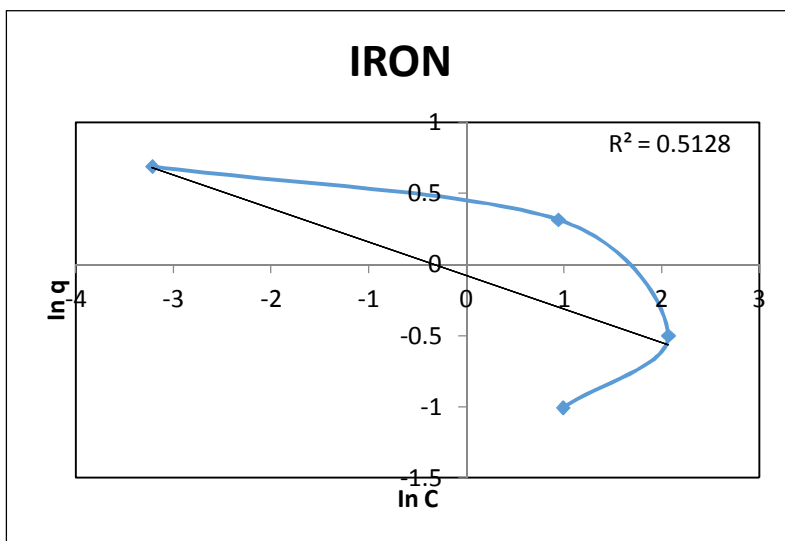


Figure 12: Freundlich model for Iron by APKS

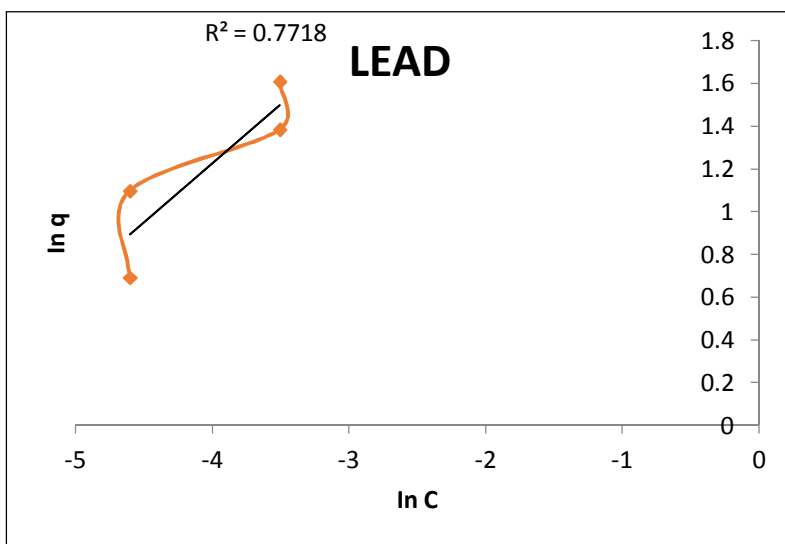


Figure 13: Freundlich model for Lead by AWH

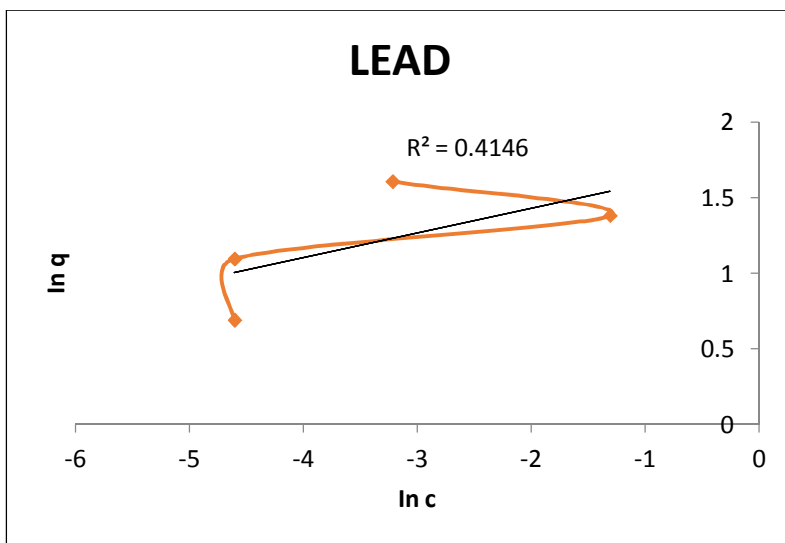


Figure 14: Freundlich model for Lead by APKS

APKS			AWH	
	Iron	Lead	Iron	Lead
a	1.91	3.34	3.47	6.67
b	1.36	0.681	0.66	-27.26
R²	0.903	0.9936	0.062	0.6923

Table 2: Langmuir Constants

APKS			AWH	
	Iron	Lead	Iron	Lead
N	0.461	6.12	0.963	1.82
K_f	0.926	5.79	0.126	30.57
R²	0.5228	0.4146	0.2046	0.7709

Table 3: Freundlich Constants and Correlation

4. Summary and Conclusion

The main objectives of drinking water treatment are to produce high quality water that has aesthetic appeal, safe for human consumption and is also economical in production. For this reason, activated carbon has been a source for drinking water purifications, hence the need for a PH of 7.0

Langmuir and Freundlich model were applied, the results shows that the adsorption fitted to the Langmuir model for iron and lead onto APKS, with the correlations coefficient of 0.864, and 0.996, but for AWH, the adsorption was not fitted for both the Langmuir and Freundlich isotherm. This shows that the Langmuir and Freundlich cannot be used for modeling the adsorption.

5. Conclusion

Based on the results of this study, the following conditions can be drawn;

- That the use of AWH and APKS as an alternative, inexpensive adsorbent could, drastically reduce the cost of wastewater treatment.
- That the use of AWH and APKS as adsorbents could equally reduce the environmental problem that may be created by water hyacinth and palm kernel shell.
- That AWH is more efficient than the APKS for the removal of heavy metals, this may be because of its higher iodine number, lower particle size which enhances adsorption, because the higher the iodine number the higher the adsorption capacity. Again its basicity characteristics indicate that it may have a high adsorption capacity on cation more than APKS, which is acidity in character. But in a situation that the AWH is not available, APKS can be used in place of AWH as can seen in the above Tables that it also has a high adsorption capacity.

Therefore, it is now recommended that government should encourage this kind of research works by recommending it to the users of the activated carbon. This will help boost the economy of the country as a domestic product and a major way of adopting the integrated waste management method of recovering resources from waste.

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