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Kinetics of Palm Kernel Shell in Heavy Metal Ion Sorption

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Abstract:
The adsorptive capacity of activated 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. Batch adsorption studies were also carried out under varying experimental conditions of pH of the solutions, contact time and initial concentration of Pb^{++} and Fe^{++} solutions. The results showed that the highest percentage removal of 98.74 occurred at pH = 8 by APKS on Pb^{++} and the lowest % removal of 20.72 for iron at a PH of 4, though a PH of 7 is recommended. On the effect of contact time, it was found that the equilibrium time for the sorption was at 60mins with the percentage removal of 74.84 on Fe and 65.55 on lead. 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 the increase in initial conc. The Langmuir and Freundlich adsorption models were used for the mathematical description of adsorption equilibrium as well. It was deduced from the plot that Langmuir isotherm fitted for modeling the adsorption by APKS on Pb^{++} and Fe^{++} while the Freundlich isotherm was inadequate for modeling the APKS.

Keywords: *kinetics, palm kernel, adsorption, heavy metals*

1. Introduction

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.

Jumasiah and others, 2005. Reported that activated palm kernel shell (APKS) can be used as a low-cost adsorbent for waste water treatment containing dye. Palm kernel shell activated with Phosphoric acid (H_3PO_4) and potassium hydroxide (KOH) has also shown the ability of adsorbing Lead II ion and Chromium III ion in the work of Muah, 2013. Mokhlesur, M. and others , 2014; has shown that APKS and activated coconut shell could be used in water purification because of their ability to absorb heavy metals even at low concentration of the metal ions,(Lead, Nickel and Chromium VI ions). Were the activating agent was phosphoric acid. Emmanuel, Oluyemi and Iyabo, 2012, has also reported that activated palm kernel shell posses the ability to remove Lead II and Cadmium II ion from polluted water close to mining site or pollution that may occur due to industrial effluents.

Lots of work on activated palm kernel shell has been done, but this study, kinetics of palm kernel shell in heavy metal ion sorption, with Zinc chloride as the activating agent was not found. The objective of this work is to determine the extent or ability of activated palm kernel shell on heavy metals (Lead II and Chromium II ions) by using Zinc chloride as the activating agent.

2. Materials and Method

The palm kernel shell was collected from Ibagwa-Aka in Igbo-Eze south local government of Enugu State. The collected palm kernel shell was washed thoroughly with clean water for several times to remove dirt's, thereafter; it was air-dried for 48 hours. The dried palm kernel shell was carbonized in a muffle furnace at $600^{O}C$ for two hour which thereafter was impregnated with zinc chloride of suitable concentration and heated again at $800^{O}C$ for 2:30mins 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 where 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 palm kernel shell into a beaker, and 100ml of deionized water was also measured into the beaker. The solution was stirred for 5mins and allowed to stabilized, an electrode was inserted into the beaker containing the solution and the reading was taken. The Activated carbon was washed several times and process repeated until a stabilized pH reading was taken.

2.3. Determination of the Porosity of the Activated Carbon

- 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 Carbon

- 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% H_2 SO_4.

A known concentration of Iodine solution was prepared; also a known of molarity Sodium thiosuiphate was prepared too. 1g of the activated carbon was weighed in a conical flask and 50m1 of iodine solution was added. The sample was 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 l000mg/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 0.1M 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 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/I was taken in stopper plastic conical flask and are agitated with 1.0g of activated 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 sample was allowed to settle down before filtering, and the left out concentrations of the filtrate/solution was 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 of activated palm kernel shell 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/1 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. 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 APKS

Equilibrium studies were carried out by contacting 1.0g of 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
1	PH	7.67
2	Iodine number (mg/g)	620
3	Particle size (un sieve)	0.375
4	Bulk density (g/cm^3)	0.127
5	Volume of void	58.14
6	Porosity (n)	0.91
7	Specific gravity	0.78
8	Moisture content %	54.09

Table 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

The effect of pH on the adsorption of Fe2+ and Pb2+ was carried out at the Ph solution range of 2-8 and the percentage of the metal ions adsorbed is shown below.

This shows that the removal of metals from aqueous solution by APKS 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 sample. 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. We recommend that PH = 7 should be perfect because of consumable produce.

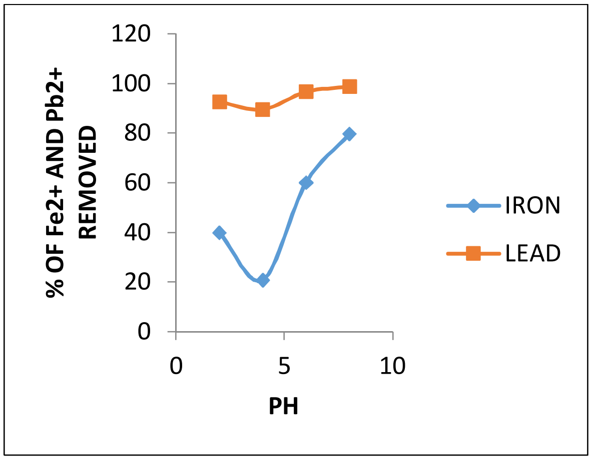

Figure 1: Effect of PH on percentage removal of iron and lead

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

The adsorption data for the uptake of metals versus contact time at initial concentration of 70mg/l is presented in Figure 2. The result showed that time required for the adsorption of metals onto APKS was almost l20mins (2hrs). However, for subsequent experiments, the sample was 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 to l hour.. The higher sorption rate at the initial period (30 - 60rnins) 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 the where the adsorption equilibrium is attained, where sorption and desorption is tending to be equal.

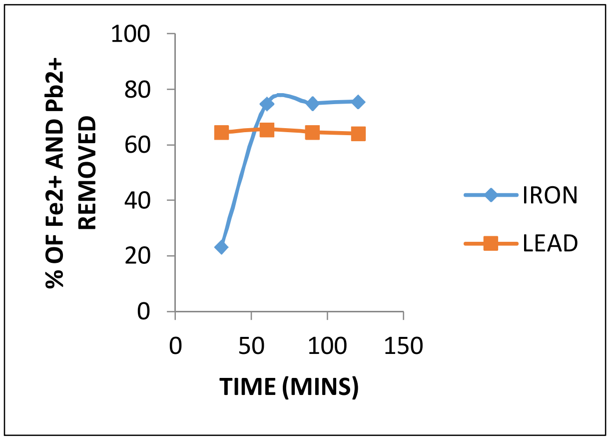

Figure 2: Effects of contact time on the percentage removal of Iron and Lead

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 3 and 4 In (Figure 3 & 4), 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/1 by APKS. 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 sample at 40mg/1 and 60mg/1 and 99.66% at 100mg/1. 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.

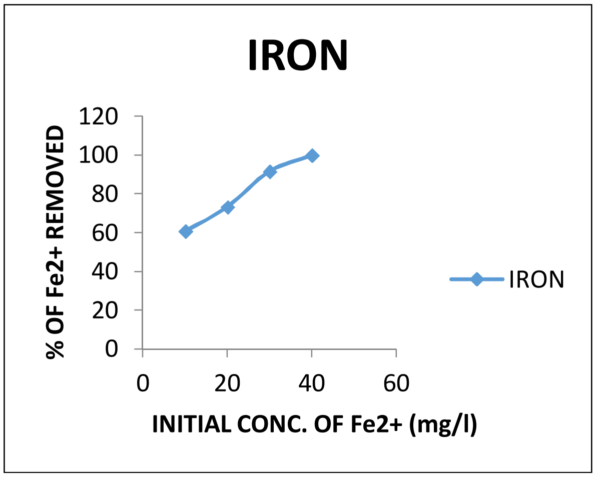

Figure 3: Effects of initial concentration of Iron

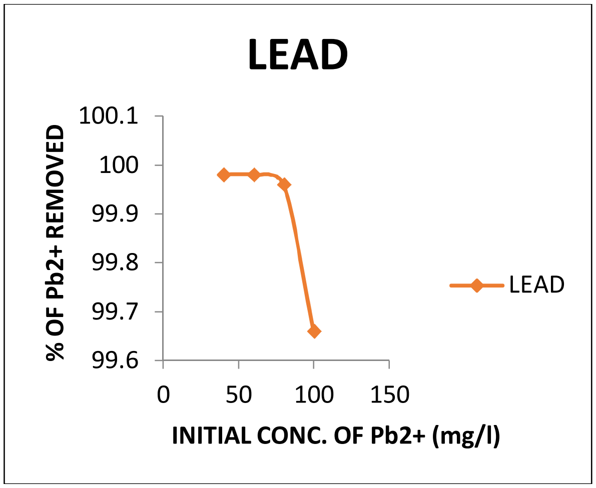

Figure 4: Effects of initial concentration of Iron

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 4.5 - 4.8 shows the Langmuir and Freundlich plots for Pb^{++} and
Fe^{++} adsorbed by APKS.

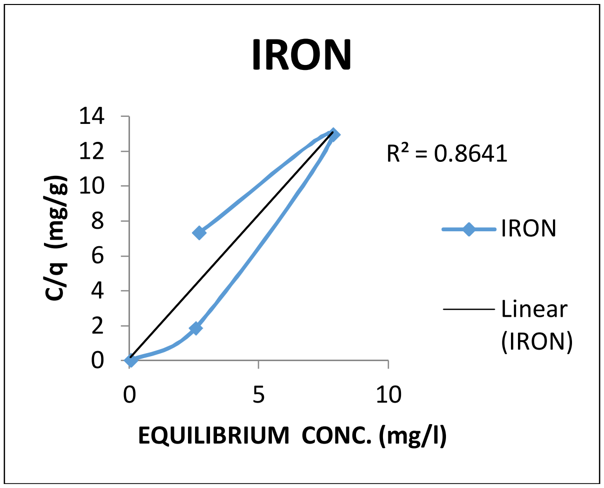

Figure 5: Langmuir isotherm for Iron

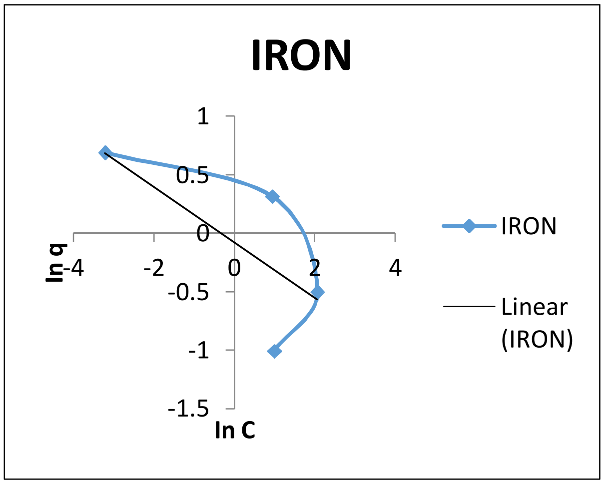

Figure 6: Freundlich isotherm for Iron

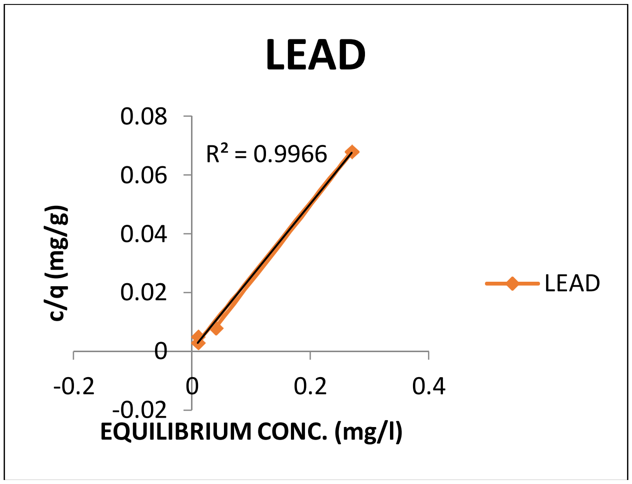

Figure 4.7: Langmuir isotherm for lead

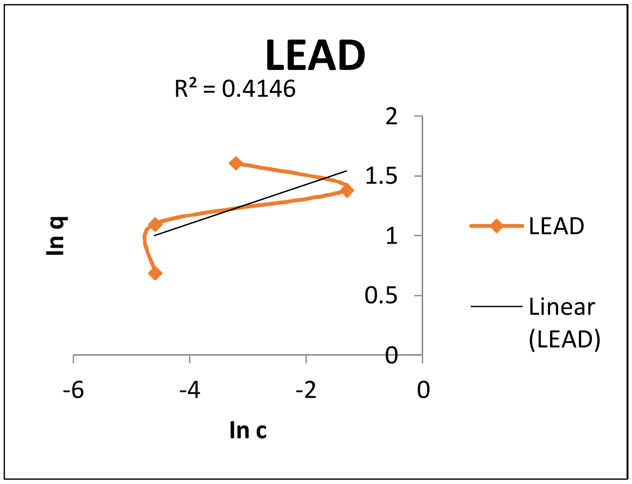

Figure 8: Freundlich isotherm for lead

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. The Langmuir model was fitted for the adsorption of iron and lead on APKS with the correlation coefficient of 0.864, 0.996 respectively. The Freundlich model was not adequate for modeling the APKS on any of the metal ions.

APKS		
Constants	**Iron**	**Lead**
a	1.91	3.34
b	1.36	0.681
R^2	0.864	0.996

Table 2: Langmuir Constants

APKS		
Constants	**Iron**	**Lead**
n	0.461	6.12
K_f	0.926	5.79
R^2	0.512	0.414

Table 3: Freundlich Constants and Correlation

From the Table 2, a model can be developed using the Langmuir equation, the Langmuir constant and the correlation coefficient that suited to the Langmuir isotherm.
For Fe^{++} adsorbed by APKS
$x/m = (abC_e) / [1 + (bC_e)]$
$x/m = 2.60C_e / [1 + (1.36C_e)]$
For Pb^{++} adsorbed by APKS
$x/m = (abC_e) / [1 + (bC_e)]$
$x/m = 2.27C_e / [1 + (0.681C_e)]$

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

In this research work, activated carbons for removal of heavy metals were produced from palm kernel shell; some of the properties of activated carbon that enhances adsorption were determined under pH, iodine number, moisture content, particle sizes and bulk density. The results showed that palm kernel shell has a pH of 6.36, iodine number of 510mg/g, and particle size of 0.375mm, and moisture content of 14.31%.

A batch adsorption experiment was also carried out under the conditions of pH, contact time and initial concentration of the metals, a mathematical expression of the percentage adsorption were carried out and the results show that the adsorption is pH dependent, the percentage adsorption of both metals (Lead & Iron) are higher at ph = 8, APKS adsorbed 79.71% of iron, and 98.74% for lead at the same pH. Under the condition of contact time, the adsorbent have a higher adsorption at 60mins of contact at which APKS adsorbed 74.84 of iron and 93.64% for lead. Langmuir and Freundlich model was applied and the results show that the adsorption fitted to the Langmuir model for iron and lead onto APKS, with the correlations coefficient of 0.864, and 0.996.

5. Conclusion

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

- That the use of APKS as an alternative, inexpensive adsorbent could, drastically reduce the cost of wastewater treatment.
- That the use of APKS as adsorbents could equally reduce the environmental problem that may be created by palm kernel shell. 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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