Original Research Article

Study of kinetics of chemically activated carbon produced from palm kernel shell

Abstract

Palm kernel shells (PKS), waste product of oil mill industrials, were used to produce activated carbon by chemically activating with $ZnCl_2$. The shells were carbonized at temperature ranging from 500℃ to 800℃, for an hour and activated with 10%, 20% and 30% concentration of $ZnCl_2$. The effect of carbonization temperature and concentration of $ZnCl_2$ were studied. Batch adsorption studies on adsorption of Cu^{2+} by 'PKS 700℃ activated', 'PKS 700℃ non activated' and 'PKS 500℃ activated' were also carried out. Langmuir and Freundlich isotherms fit the data from the experiment. The adsorption capacities of the samples were studied. Results of single component kinetic studies on the samples revealed that about 93% of the metal ion removal occurred in the first 30 minutes. The adsorption rate constant for the samples at adsorption temperature of 15℃, 25℃ and 50℃ were '0.0462, 0.0654, 0.125', '0.0343, 0.0395, 0.070' and '0.281, 0.0313, 0.054' (min^{-1}) respectively. The result shows that PKS 700℃ activated had the highest adsorption capacity. The entropy and energy of activation were also determined and it was found out that adsorption is an exothermic and a reversible process. The reaction was found to be first order reaction with respect to $ZnCl_2$.

Key words: Adsorption column, Adsorption rate constant, Equilibrium time, Granular activated carbon.

1.0 Introduction

As industrialization keep increasing, efficient waste management poses a serious challenge to industrialist and environmental practitioners. Most effluents are containing traces of heavy metal ions, whose resultant effects might be detrimental to living organisms and environment. Elements having atomic weights between 63.5 and 200.6g/mol. and specific gravity greater than 5.0g/cm^3 are regarded as heavy metals [1, 2]. These heavy ions are of great concerns as they do not degrade into harmless end-products [3]. Different technologies such as precipitation, membrane process and ion exchange have been and are still in use for the treatment of large volumes of dilute metal ion containing solutions. A major drawback in the use of some of these technologies is the high cost of their implementations. Carbon materials such as activated carbon are attractive as adsorbent due to its low cost, wide availability, high thermal stability, and low sensitivity to moisture [4, 5]. Activated carbon can be in powder, granular or pellet form. It is useful for wide variety of processes including filtration, deodorization, decolourization, purification and separation. It is a non-polar material with high affinity for non-polar compounds. These compounds are bound to the surface of the activated carbon by adsorption process, which utilizes van der Waal forces. Since adsorption is a surface phenomenon, the adsorption capacity is directly related to the pore structure and surface area. Activated carbon adsorption potential is as a result of adhesion of the adsorbate to the internal surface constituting the walls of the pores. Therefore, the greater the adsorption surface available, the better the adsorption function [6]. The use of activated carbon as adsorbent is mainly due to its capacity for adsorption from both gas and liquid phases [7, 8]. The raw material used, processing parameters and activation process determine the properties and the performance characteristics of the activated carbon. In this work, a low cost adsorbent from palm kernel shell was produced. The properties and kinetic studies of the activated carbon were considered to provide for reaction rate, rate constant and other data essential in the design of adsorption column.

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2.0 Materials and Methods

Palm kernel shells (PKS), obtained from local farm in Awka, Anambra State of Nigeria were washed with distilled water and air dried for one week by natural convection. Preliminary size reduction was carried out and the sized samples were carbonized at 500^0C, 600^0C, 700^0C and 800^0C for an hour in a limited supply of air using carbolite furnace, model CF 1200. After cooling, 100g of the carbonized PKS were separately soaked with 10%, 20% and 30% zinc chloride and allowed to stay for 24hours after which they were filtered and washed with distilled water to a pH close to neutrality as indicated by universal pH indicators. The washed samples were dried in an oven at 120^0C for 90 minutes, cooled, stored in plastic containers and labeled. A sample of non-activated PKS carbonized at 700^0C was also stored and labeled. The sample were reduced into a smaller size and made to pass through 2mm stainless sieves.

0.2g, 0.4g, 0.6g, 0.8g and 1.0g of activated carbon were measured into five corked plastic containers. 50ml of 5mg/l of Copper ion were pipetted into each container and the containers placed in a mechanical shaker and shook for 2hours. Each of the samples was filtered and the filtrate stored in refrigerator prior to analysis. The residual copper concentrations were also determined using atomic absorption spectrophotometer (AAS).

5mg/l solution of lead ion and 5mg/l of solution of copper ion were prepared from lead nitrate and copper II sulphate-5-hydrate salt respectively. 50ml of the copper solution was pipetted into six corked containers (for competitive adsorption studies, the two ions were mixed). 1g of activated carbon was measured and introduced into each of the 50ml solution and the contents were shook using mechanical shaker. After shaking, one sample was removed from the shaker, filtered and filtrate stored in a refrigerator prior to analysis. The residual concentrations of Pb^{2+} and Cu^{2+} were determined using Atomic absorption spectrophotometer at 15^0C, 25^0C and 50^0C.

Finally, 500ml each of 5mg/l of copper ion and lead (II) ion were mixed in a volumetric flask. 50ml of the solution was pipetted into six corked plastic containers. 1g of activated carbon was measured and introduced into each of the 50ml solution. The containers with their contents were shaken using a mechanical shaker at 5, 10, 15, 30, 60, 90 and 120minutes. One sample was removed from the shaker, filtered and filtrate stored in a refrigerator prior to analysis. The residual concentrations of Pb^{2+} and Cu^{2+} were determined using atomic adsorption spectrophotometer (AAS). The iodine number, pH and bulk density of the activated carbon were also determined.

3.0 Results and Discussions

Samples of activated carbon were produced from palm kernel shell (PKS) with 10%, 20% and 30% concentration of $ZnCl_2$ as the activating agent at 500^0C, 600^0C, 700^0C and 800^0C carbonization temperature. A non-activated 700^0C carbon was also produced. The samples produced enabled the effect of carbonization temperature and chemical activation to be studied. Preliminary studies revealed that carbon activated with 30% $ZnCl_2$ at 700^0C carbonization temperature had better adsorption characteristics for copper and as a result, was used for further studies. The properties of the granular activated carbon (GAC) produced showed that PKS 700^0C activated, PKS 700^0C non-activated and PKS 500^0C activated had iodine number of 90.01, 62.58, 55.07 mgl_2/g while their pH values were 6.94, 9.03, and 6.79 respectively.

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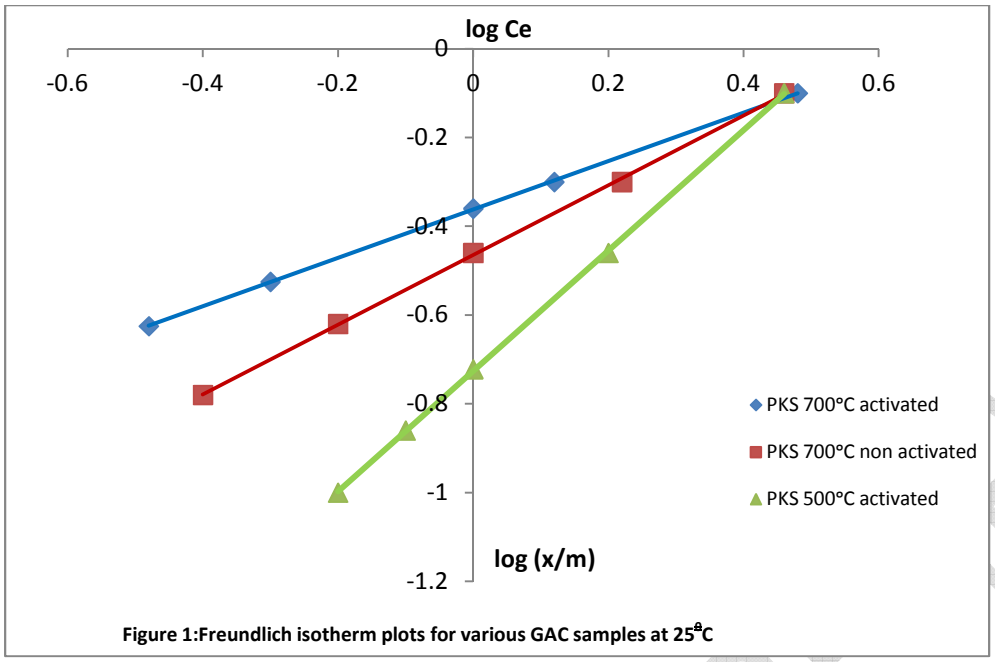

Figure 1:Freundlich isotherm plots for various GAC samples at 25°C

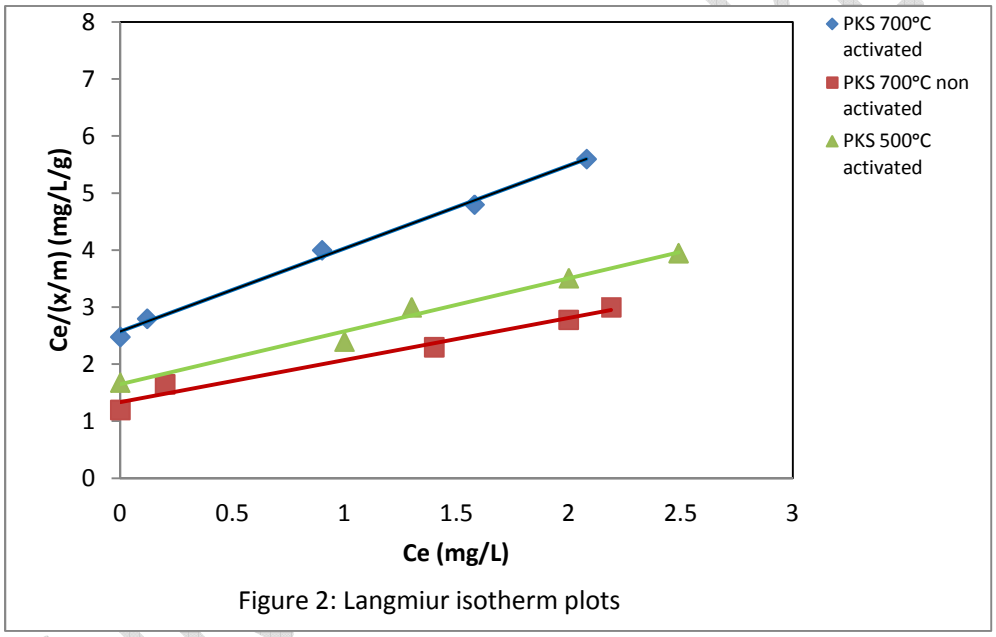

Figure 2: Langmiur isotherm plots

Equilibrium adsorption isotherms or capacity studies are of fundamental importance in the design of adsorption system since they indicate how the metal ions partition themselves between the media and liquid phase with increasing concentration at equilibrium. Figures 1 and 2 are plots showing linearized Freundlich and Langmuir isotherms. The isotherm constants and coefficients of correlation obtained using different samples are presented in the Table 1; from the plots, the equilibrium capacity for PKS 700^{0}C activated, 700^{0}C non- activated and PKS 500^{0}C activated were found to be 1.25, 1.22 and 1.095 mg/g from the Langmuir isotherm. Freundlich isotherm is given as

$$\frac{x}{m} = kC_e^{\frac{1}{n}} \qquad (1a)$$

This can be transformed into

$$log\frac{x}{m} = logk + \frac{1}{n}logC_e \quad (1b)$$

The Freundlich isotherm constants were obtained from equation (1b), where log k is the intercept and 1/n is the slope of Figure 1.

Table 1: Determination of isothermal constants

Sample	Freundlich		Langmuir	
	k	n	a (mg/g)	b (1/mg)
PKS 700°C activated	0.347	1.30	1.220	0.468
PKS 700°C non activated	0.437	1.75	1.33	0.667
PKS 500°C activated	0.217	0.72	10.076	0.0291

Langmuir model is given as:

$$\frac{abC_e}{1+bC_e} = \frac{x}{m} \quad (2a)$$

This can be transformed into

$$\frac{C_e}{\left(\frac{x}{m}\right)} = \frac{1}{ab} + \frac{1}{a}C_e \quad (2b)$$

The Langmuir isotherm constants 'a' and 'b' are obtained from equation (2b) where 1/a is the slope and 1/ab is the intercept of Figure 2. Langmuir model represent the physical adsorption of adsorbates to cover monolayer on the surface of absorbent [9]. The higher adsorption capacity of PKS 700^{0}C activated over PKS 700^{0}C non activated is as a result of chemical activation which improves the surface chemistry of activated carbon to bind metal as well as oxidize non carbonaceous impurities from the pores. The higher capacity of PKS 700^{0}C activated over PKS 500^{0}C activated as seen from Langmuir isotherm is as a result of temperature of activation. The duration of carbonization invariably increases the pore volume leading to a better adsorption capacity [10, 11]. These linearized isotherms are merely empirical expression for representing experimental data in a mathematical convenient form and describing the extent of adsorption.

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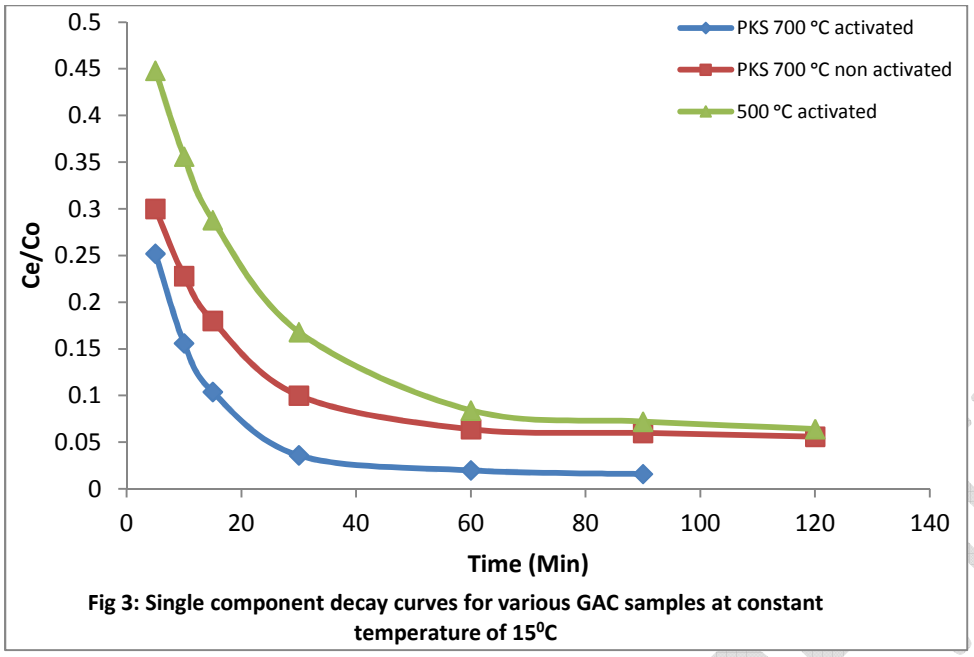

Fig 3: Single component decay curves for various GAC samples at constant temperature of 15^{0}C

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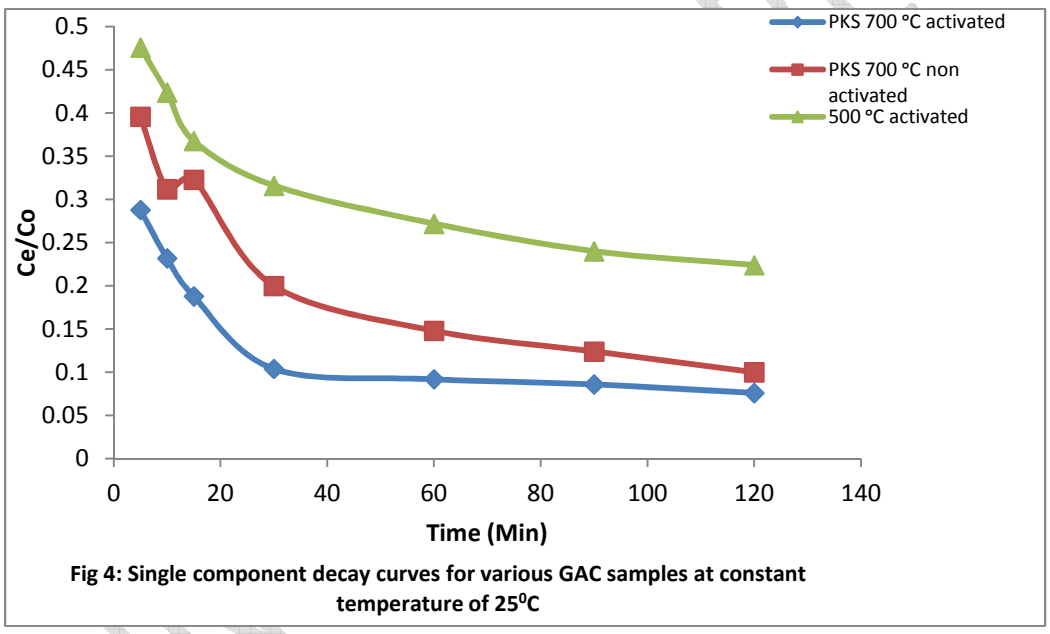

Fig 4: Single component decay curves for various GAC samples at constant temperature of 25^{0}C

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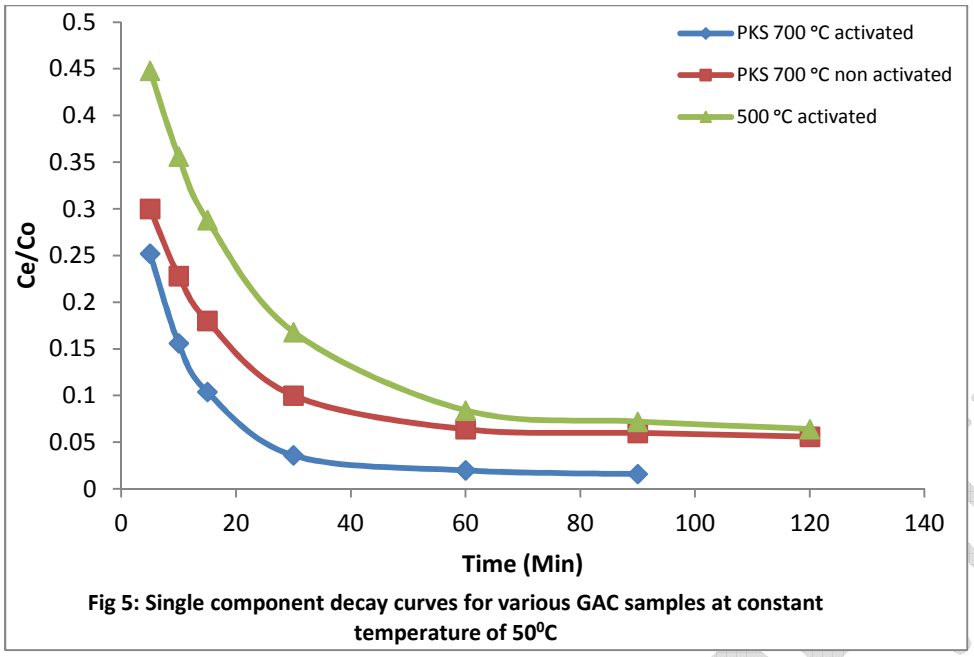

Fig 5: Single component decay curves for various GAC samples at constant temperature of 50^{0}C

The rate at which adsorption takes place is an important factor in establishing the time dependence of contaminant capture under specified process conditions. Single component decay curves obtained by batch contact time studies for PKS 700^{0}C activated, PKS 700^{0}C non-activated and PKS 500^{0}C activated for the adsorption of Cu^{2+} were plotted in figures 3-5. These figures show that most of the uptake occurred in the 1st 5-30 minutes, for all metal – media combination, and then the uptake showed as equilibrium was reached. These results agree with the previous work by [12] where it was reported that most of the metal uptake of peanut hull occurred in the first 10-20 minutes. By implication, in the design of adsorption column, contact time in the range of 5-30 minutes would be adequate. Contact times are fixed by the flow rate and contactor dimensions.

It was observed that an equilibrium time of 120 minutes was assumed for the three carbon samples. This is the time after which adsorption rate remains constant. The equilibrium time and concentration was applied in the Lagergren equation which is a first order rate expression and the adsorption rate constants K_{ad} determined. The linearized Lagergren pseudo first order equation is given as [13]

$$log(q_e - q_t) = logq_e - \frac{K_{ad}t}{2.303} \quad (3)$$

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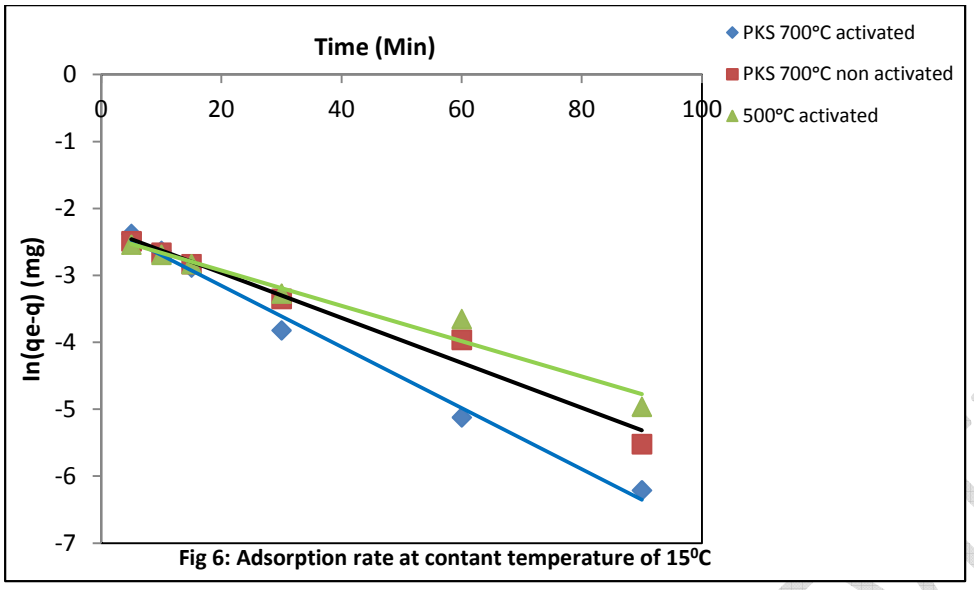

Fig 6: Adsorption rate at contant temperature of 15^{0}C

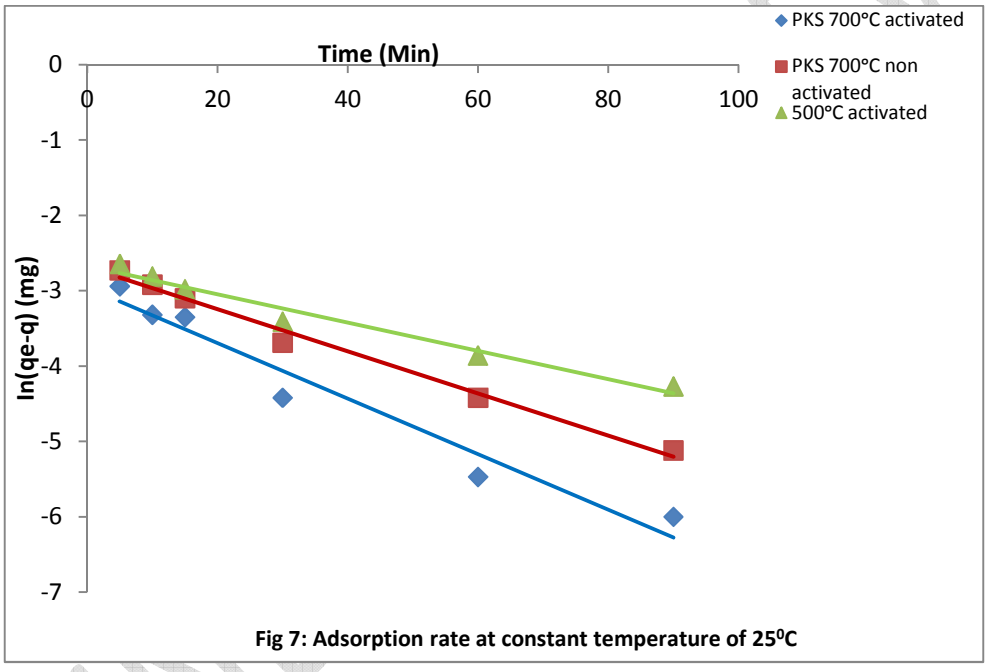

Fig 7: Adsorption rate at constant temperature of 25^{0}C

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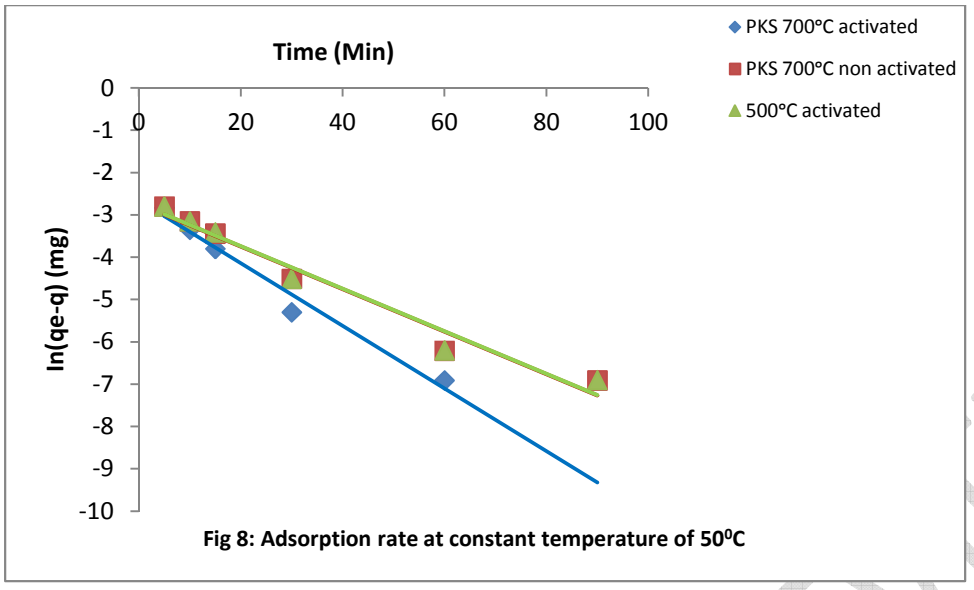

Fig 8: Adsorption rate at constant temperature of 50^{0}C

Plots of Lagergren equation are shown in figures 6-8. From the plots, the adsorption rate constant for PKS 700^{0}C activated, PKS 700^{0}C non-activated and PKS 500^{0}C activated were found to be 0.0313min^{-1} , 0.0395min^{-1} , 0.0654min^{-1} at 25^{0}C adsorption temperature, 0.06min^{-1}, 0.07min^{-1}, and 0.125min^{-1} at 50^{0}C adsorption temperature, and 0.0281min^{-1}, 0.0343min^{-1} and 0.0462min^{-1} at 15°C adsorption temperature. These results were expected as carbon content and surface increase with temperature. These results also showed that chemical activation improves rate of adsorption.

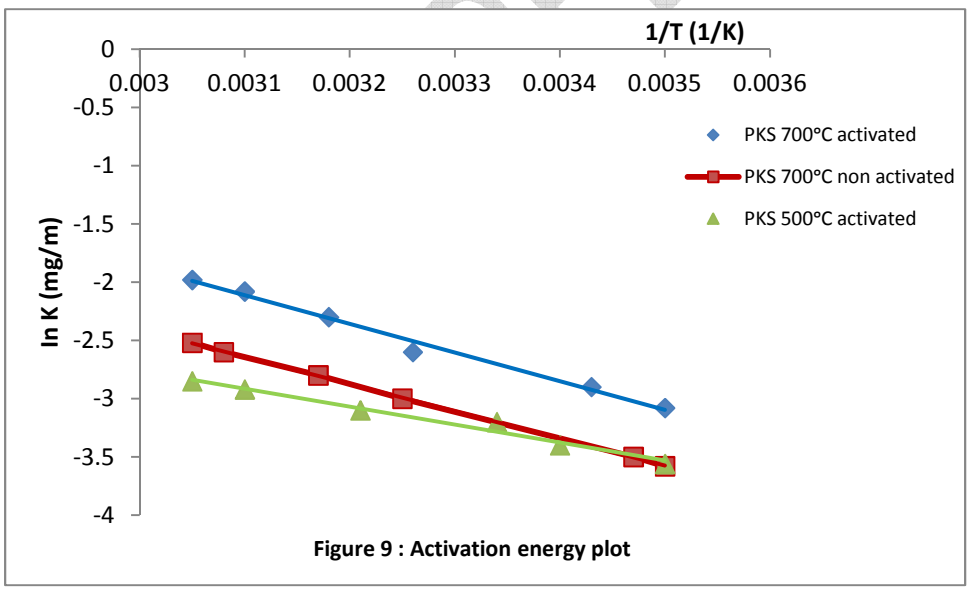

Figure 9 : Activation energy plot

Energy of activation which is the minimum energy which the molecules must absorb before the reaction can take place was also determined. Rashidi et al [5] suggested that magnitude of the activation energy is important in any adsorption process, as it provides insight information on the mechanism of the adsorption process. The activation energy can be determined from the Arrhenius equation

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$$In\ K = \frac{-E_a}{RT} + In\ K_o \quad (4)$$

Figure 9 is plot of In K against 1/T. It is a straight line with $-E_a/R$ as the slope and In K_o as the intercept. The results shown that PKS 700°C activated, 700°C non -activated and 500°C activated have activation energies of 441.56 cal, 372.56 cal and 350.5 cal respectively.

The entropy and enthalpy of the system was also calculated and both found to be negative as shown in Table 2. The negative sign of the enthalpy shows that adsorption is an exothermic reaction while that of entropy shows that the reaction is a reversible reaction. These results were expected because in every adsorption process, there will be a time when desorption starts to take place. The enthalpy and entropy were evaluated using the following relationships

$$\Delta H = \Delta G + T\Delta S \quad (5)$$

$$\Delta G = -RT \ln K_e \quad (6)$$

$$K_e = \frac{k_{ad} N_a h}{RT} \quad (7)$$

$$A = \frac{RT}{N_a h} e^{\Delta S/R} \quad (8)$$

$$A = \frac{k_{ad}}{e^{-(Ea/RT)}} \quad (9)$$

where A is Arrhenius constant

Table 2: Entropy and Enthalpy Data

Sample	T°C	15	25	50
700°C activated	ΔS	-27.306	-28.829	-27.948
	ΔH	-6974.717	-7090.296	-6013.819
700°C non activated	ΔS	-28.164	-27.591	-26.578
	ΔH	-7216.628	-6709.862	-5544.263
500°C activated	ΔS	-29.427	-29.35	-26.55
	ΔH	-7596.807	-2269.184	-5619.894

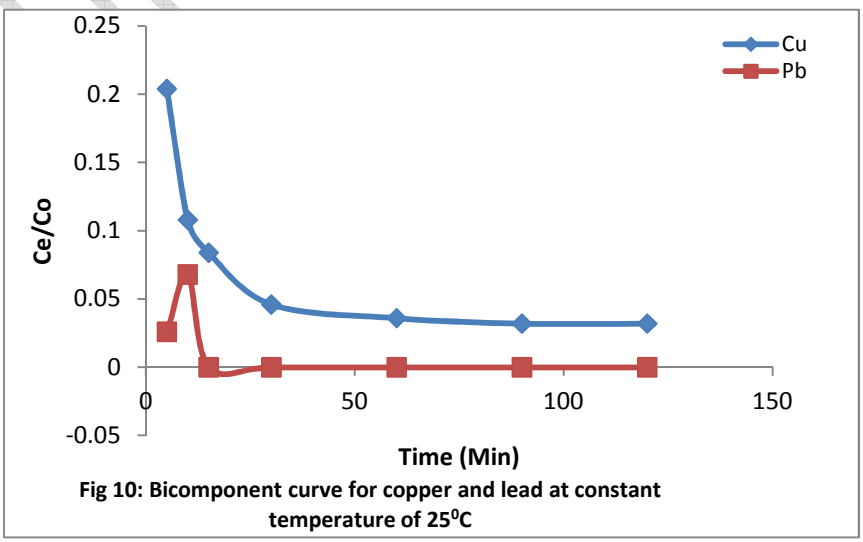

Fig 10: Bicomponent curve for copper and lead at constant temperature of 25°C

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Bi-component kinetic study between Cu^{2+} and Pb^{2+} was also conducted using PKS 700^0C activated. Since both ions are divalent, they would be competing for the same sites. The results are shown in figure 10 from where it is seen that the carbon adsorbed lead better than copper as indicated by the drop in concentration with time.

The single component kinetics studies data was regressed using time in minutes as the independent variable and C_e/C_o as the dependent variable. The equation that fitted the data gave

$$\frac{C_e}{C_o} = a \exp(-bt) \quad (10)$$

The regression results gave the values of "a" to be 0.3819, 0.313, and 0.23, and "b" to be -0.015, -0.025 and -0.0317 at 15^0C, 25^0C and 50^0C respectively.

4.0 Conclusion

Palm kernel shells, which are waste product of oil mill industries, have potential for use in the production of activated carbon for adsorption of metals, Cu^{2+} and Pb^{2+} for instance, from aqueous solution. The activated carbon produced had a higher affinity for Pb^{2+} than Cu^{2+}. Higher temperature of activation enhances pore development and improves surface area resulting in higher adsorption capacity for such carbon, though it depends on the time of carbonization (if the temperature is too high, the time should be reduced, else the carbon burns to ashes). Chemical activation also improves adsorption of heavy metals by carbon but the effect is less glaring when compared to that of carbonization temperature.

Kinetic studies have shown that sorption of Cu^{2+} with activated carbon produced from PKS is first order reaction with respect to $ZnCl_2$. The average rated constant for 700^0 C activated is $0.0654 min^{-1}$ at 25^0C and the reaction rate is a function of the initial concentration of Cu^{2+}. The studies also showed that over 93% of metal ion removal occurred within the first 30 minutes of contact.

Nomenclature

a = Langmuir isothermal constant (mg/g)

b = Langmuir isothermal constant (1/mg)

C_e = Liquid phase metal concentration (mg/l)

C_o = Initial concentration metal ion solution (mg/l)

E_a = Activation energy

h = Plank's constant, 6.626×10^{-27} erg/sec

k & n =Freundlich isothermal constants

k_{ad} = Adsorption rate constant (min^{-1})

N_a = Avogadro's constant, 6.023×10^{23} mole

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q_e = Amount of metal adsorbed per gram of carbon at equilibrium (mg/g)

q_t = Amount of metal adsorbed per gram of carbon at time t (mg/g)

R = Universal gas constant (1.987 calorie/mol°C)

T = Temperature (^{0}C)

$\frac{x}{m}$ = Metal adsorbed per gram of carbon (mg/g)

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