

KINETICS AND THERMODYNAMIC STUDIES OF ADSORPTION OF LEAD FROM PAINT EFFLUENT USING LOCALLY ACTIVATED CARBON

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ABSTRACT

Activated carbon produced from fluted pumpkin seed shells was utilized for the removal of lead (II) ion from paint effluent. The paint effluent was analyzed physically and chemically. The activated carbon produced was carbonized at 800°C for 2 hours and then chemically produced with 9M KOH solution. Adsorption data's were used for modeling the First order, Pseudo first order, Second order, Pseudo second order, Elovich and Intra-particle diffusion models. The linear regression coefficient R^2 of 0.997 for first order model, made the best fit. Thermodynamic parameters such as ΔH° , ΔS° , and ΔG° obtained indicated that the adsorption was not spontaneous. It is also exothermic and the degree of dispersion increased with increase in temperature.

Keywords: Activated carbon, Paint effluent, kinetic studies. Thermodynamic studies, Adsorption

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INTRODUCTION

Industrialization has introduced the metals contamination problem in the environment over the past decade. The effluents being released from various industries commonly include Cd, Pb, Cu, Ni and Co. These metals are not biodegradable and their presence in streams and lakes leads to

bioaccumulation in living organism causing health problems in animals, plants and human beings (Rafique et al, 2013). The rate at which effluents are discharged into the environment and water bodies, has been on the increase due to rapid growth of cities in the world. Generally, water bodies are major sites of heavy metal deposits due to the fact that streams and rivers flow through agricultural areas where pesticides and fungicides may have been used, through industrial districts where there may have been many metal waste deposits or direct discharge of effluents into these water bodies (Malakootian *et al.*, 2009). These metal pollutants are conservative contaminants that are not easily biodegradable chemically or biologically. They are therefore permanent chemical overload in the environment (El-Nady and Atta, 1996). Effluent from numerous industries such as paints and pigments, glass production, mining operations, metal plating and battery manufacturing processes are known to contain contained contaminants such as heavy metal. Heavy metals such as Pb(II), Cd(II), Hg(II), Ni(II), Zn(II), Cu(II) and Fe are present in industrial waste water(Mhemet et al, 2006).

Lead (Pb(II)) is one of the common heavy metals found in paint industrial waste water. Lead is one of the heavy metals with high toxicity when in excess. In children, lead causes a decrease in intelligent quotient (IQ) score, retardation of physical growth, hearing impairment, impaired learning, as well as decreased attention and classroom performance. In individuals of all ages, lead can cause anaemia, kidney malfunction, brain diseases and impaired function of peripheral nervous system, high blood pressure, reproduction abnormality, developmental defects, abnormal vitamin D metabolism, colic-like abnormal pains, dementia, madness and, in some situations, death (Okoro and Ejike, 2007).

Many researchers have reported the removal of these heavy metals using several physicochemical methods such as chemical precipitation, evaporation, ion exchange, and reverse osmosis (Ikhuoria and Omonmhenle, 2006). Agricultural by-products have been used as adsorbents in research work for removal of heavy metals from industrial effluents or other sources. This is due to the toxic effects of heavy metals and disadvantages of conventional methods of removal (Eze et al, 2013). The major advantages of an adsorption system for water pollution control are less investment in terms of initial cost and land, simple design and easy operation and no effect of toxic substances compared to conventional biological treatment processes (Markovska et al, 2006). Activated carbon is extensively used as an adsorbent due to its high level of effectiveness; this has led many researchers to search for inexpensive and locally available adsorbents so that the process can become economically feasible. In this study, fluted pumpkin (*Telfairia occidentalis*) seed shell was used as adsorbent for the adsorption of lead from paint effluent. This is investigated in the work in the laboratory. Kinetics and thermodynamic studies were also carried out in the study.

MATERIALS AND METHOD

MATERIALS

Preparation of activated carbon

The fluted pumpkin seed was collected from New market Enugu, Nigeria. The shell was separation and was dried for 6 days under the sun light to reduce the moisture content of the seed shells. After this, it was collected and stored in a glass jar until use. The dried fluted pumpkin seed shells were crushed to desired mesh size of 1-2mm and then carbonized at 800⁰C for 2hrs in a stainless steel vertical tubular reactor placed in a tube furnace. The char produced was crushed and sieved with 600nm sieve size. The char was soaked in 9M KOH solution with (1:1.5) char to KOH ratio. The mixture was then dehydrated in an oven at 105⁰C to remove moisture and then was activated under the same condition as carbonization, but to a different final temperature of 850⁰C for 1hrs. The activated product was then cooled to room temperature and washed with hot deionized water and 0.1 NHCL until P^H of washing solution reached 6.4. The preparation of the adsorbent was in accordance of the method used by (Tan et al; 2008) with slight modification.

Adsorbate

4 litres of effluent (waste water) was supplied by Buxtin Paint Ltd Uwani Enugu, Nigeria.

METHOD

Adsorption Kinetic Studies

The studies were carried out using 30ml each of 0.144 mg/L, 0.145mg/L, 0.146mg/L, 0.147mg/L and 0.148mg/L, 30ml of the waste water mixed with each of them, 0.1g, 0.2g, 0.3g, 0.4g and 0.5g of the adsorbent in a flask. The flask was agitated in a shaker incubator for a contact time of 20mins to 40mins to 60mins to 80mins to 100mins at a speed of 200rpm under room temperature. The adsorbent was separated from the solution by centrifugation and the filtrate was analyzed using UV visible spectrophotometer. The amount of lead adsorbed at each time interval per unit mass of the adsorbent, qt(mg/g), was calculated by

$$q_e = \left(\frac{C_0 - C_e}{w} \right) V \quad (1)$$

While removal efficiency will be calculated

Using the % removal

$$\left(\frac{C_0 - C_e}{C_0} \right) V \times \frac{100}{1} \quad (2)$$

KINETICS MODELS FOR BATCH ADSORPTION

First Order Model

The sorption kinetics may be described by a simple first order equation. The change in bulk concentration of the system using the following sample first order rate equation.

$$C_e = C_{oe}^{k/t} \quad (3)$$

Equation (3) can be rearranged to obtain a linear form:

$$\text{Log } C_e = \frac{K_1}{2.303} (t) \log C_0 \quad (4)$$

Where C_e and C_0 are the concentration of the isolate at time t and initial concentration (mg/L), respectively and K_1 is the first order rates constant, (min^{-1}). If the first order kinetics is applicable, to the system, then the plot of $\log C_e$ versus t of equation (4) will give a linear relationship with $k_1/2.303$ and $\log C_0$ as slope and intercept respectively.

Pseudo-First-Order Model

Lagergren (1898) presented a first order rate equation to describe the kinetic process of liquid-solid phase adsorption of oxalic acid and malonic acid onto charcoal, which is believed to be the earliest model pertaining to the adsorption rate based on the adsorption capacity. It can be presented as follows:

$$d q_t / dt = K P_1 (q_e - q_t) \quad (5)$$

Where q_e and q_t (mg/g) are the adsorption capacities at equilibrium and at time t (min), respectively k_p1 (min^{-1}) is the pseudo-first-order rate constant for the kinetic model integrating equation (5) with the boundary conditions of $q_t = 0$ at $t = 0$ and $q_t = q_t$, at $t=t$, yields, $\ln q_e - \ln (q_e - q_t) = k_p t$ (6)

This can be re-arranged to give;

$$\log (q_e - q_t) = \log q_e - \frac{K_p1}{2.303} (t) \quad (7)$$

If the Lagergren first-order kinetics is applicable to the system, then the plot of $\log (q_e - q_t)$ versus t of equation (7) will give a linear relationship with $K_p1/2.303$ and $\log q_e$ as slope and intercept respectively. To distinguish kinetic equations based on adsorption capacity from solution concentration, Lagergren first order rate equation has been called pseudo-first order.

Second-Order Model

The typical second-order rate equation in solution systems is as follows:

$$dC_t/dt = -K_2 C_t^2 \quad (8)$$

integrating equation (8) above with the boundary conditions of $C_t = 0$ at $t=0$ and $C_t = C_1$ at $t=t$ to yield; $1/C_t = K_2 t + 1/C_0$ (9)

Where C_0 and C_t (mg/l) is the concentration of solute at equilibrium and at time t (min), respectively, and k_2 (L/mg. min) is the rate constant of second order.

If the second-order kinetics is applicable to the system, then the plot of $1/C_t$ versus t of equation (9) will give a linear relationship with K_2 and $1/C_0$ as slope and intercept respectively.

Pseudo-Second Order Model

HO, (2001) described kinetic process of the adsorption of divalent metal ions onto peat. The driving force ($q_t - q_e$) is proportional to the available fraction of active sites.

$$\text{Then, it yields: } dq_t/dt = K_p^2 (q_e - q_t)^2 \quad (10)$$

Re-arranging equation (10) above as follows:

$$dq_t / (q_e - q_t)^2 = k_p^2 dt \quad (11)$$

integrating equation (11) with the boundary conditions of $q_t = 0$ at $t=0$ and $q_t = q_t$ at $t=t$, yields;

$$1/(q_t - q_0) = 1/q_e + k_p^2 t \quad (12)$$

This can be rearranged as follows to give;

$$t/q_t = 1/K_p^2 q_e^2 + 1/q_e (t) \quad (13)$$

Where $K_p^2 q_e^2$ (mg/ Cg min) means the initial adsorption rate. If the kinetics is applicable to the system, then the plot of t/q_t versus t to equation (13) will give a linear relationship with $1/q_e$ and $1/k_2 q_e^2$ as slope and intercept respectively.

The values of q_e and k_p^2 can be determined from the slope and intercept and there is no need to know any parameters beforehand. Similarly, Ho's second-order rate equation has been called pseudo-second-order rate equation to distinguish kinetic equations based on adsorption capacity from concentration of solution. The pseudo second-order kinetics model has been successfully applied to several bio-sorption systems.

Elovich Model

A kinetic equation of chemisorption was established by Zeldowitsch in 1934, and was used to describe the rate of carbon monoxide on manganese dioxide that decreases exponentially with an increase in the amount of gas adsorbed, the Elovich equation is as follows:

$$dq_t/dt = \alpha e^{-\beta q_t} \quad (14)$$

where q_t represents the amount of gas adsorbed at time t , α and β , known as the Elovich coefficients. Where α is the initial adsorption rate (mg/g, min) and β is the adsorption constant (g/mg) during an experiment. To simplify the Elovich equation, Chien and Clayton assumed $\alpha\beta \gg t$ and by applying the boundary conditions at $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$ the equation becomes;

$$q_t = 1/\beta \ln(\alpha\beta) + 1/\beta \ln(t) \quad (15)$$

If the Elovich's kinetics equation is applicable to the system, then the plot of q_t versus $\ln t$ of equation (15) will give a linear relationship with $1/\beta$ and $1/\beta \ln(\alpha\beta)$ as slope and intercept respectively.

Intra-Particle Diffusion Model

Besides adsorption at the outer surface, there is also possibility of intra-particle diffusion from the outer surface into the pores of the material. The adsorption mechanism of a solute onto the adsorbent follows three steps via: film diffusion, pore diffusion and intra-particle transport. Though there is a high possibility for pore diffusion to be the rate limiting step in a batch process, the adsorption rate parameter which controls the batch process for most of the contact time is the intra particle diffusion. Weber-Morris, 1962, found that in many adsorption cases, solute uptake varies almost proportionally with $t^{1/2}$ rather than with the contact time t .

$$q_t = k_{id} t^{1/2} + C \quad (16)$$

the logarithmic form of the above equation is:

$$\log q_t = \log k_{id} + 0.5 \log t \quad (17)$$

Where k_{id} is the intra-particle diffusion rate constant. According to equation (17), a plot of q_t versus $0.5 \log t$ should yield a straight line with a positive intercept for intra particle diffusion controlled adsorption process. For Weber-Morris model, it is essential for the plot of q_t versus $t^{1/2}$ to go through the origin if the intra-particle diffusion is the sole rate-limiting step. However, it is not always the case that adsorption kinetics may be controlled by film diffusion and intra particle diffusion simultaneously. Thus the slope is not equal to zero.

Adsorption Thermodynamics Modelling

The thermodynamic constants, Gibb's free energy (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) are calculated to evaluate the thermodynamics feasibility of the process and to confirm the spontaneous nature of the adsorption process.

The Gibb's free energy change of the process is related to equilibrium constant K_c by equation 30 below:

$$\Delta G = RT \ln Kc \quad (22)$$

The Gibb's free energy change is related to the enthalpy change (ΔH^0) and entropy change (ΔS^0) as:

$$\ln Kc = \Delta S^0/R - \Delta H^0/RT \quad (23)$$

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \quad (24)$$

Where R (8.314j/mol.k) is the gas constant, j(k) the absolute temperature, and kc (L/g) is the standard thermodynamic equilibrium constant defined by qad, eq/Ce. By plotting a graph of $\ln kc$ versus $1/T$, the values ΔH^0 and ΔS^0 can be estimated from the slopes and intercepts. The value of ΔG^0 determines the feasibility of the sorption process and the spontaneity of adsorption. A negative value of ΔG^0 indicates a spontaneous process and vice versa. The value of ΔH^0 obtained indicates an endothermic or exothermic nature of the process if positive or negative respectively. The value ΔS^0 indicate whether the adsorbent has affinity for the solute or not.

RESULTS AND DISCUSSIONS

Table 1: ANALYSIS OF PAINT EFFLUENT

S/N	Parameter Physical Analysis	Unit	Waste water
1	Temperature	⁰ C	30.4
2	Odour	-	-
3	Conductivity	Ns/Cm ³	468
4	p ^H	-	6.01
5	Turbidity	NuT	18.01
6	Acidity	Mg/L	Nil
7	Alkalinity	Mg/L	20
8	Total solid	Mg/L	0.5
9	Dissolved solid	Mg/L	0.2
10	Suspended solid	Mg/L	0.3
11	Copper	Mg/L	0.40

12	Iron	Mg/L	0.15
13	Zinc	Mg/L	Nil
14	Lead	Mg/L	0.148
15	Chloride	Mg/L	21.3
16	Sulphate	Mg/L	24.6
17	COD	Mg/L	12.4
18	DO	Mg/L	19.7
19	BOD	Mg/L	143.7
20	Phosphorus	Mg/L	0.029
21	Aluminum	Mg/L	Nil

The analysis was performed physically to ascertain its temperature, odour, conductivity, P^H and Turbidity. Also chemically to determine its acidity, alkalinity, total solid, dissolved solid, suspension solid, BoD, CoD, Do and presence of some metals such as Cu²⁺, Fe²⁺, Zn²⁺, Pb²⁺, Cl⁻, sulphate, phosphorus and aluminum.

Apparatus and Equipments used are as follows

conical flasks, beakers, P^H meter, weighing balance, crucible, electric shaker, sintered glass crucible, platinum crucible, muffle furnace, desiccators, graduated cylinders, thermometer, filter paper, Atomic Absorption Spectrophotometer, pipette, volumetric flask, shaker incubator, UV Visible spectrophotometer.

Table 2: Characterization of fluted pumpkin seed shells

S/N	Parameter	Unit	Raw fluted pumpkin seed shells	Activated fluted pumpkin seed shells
1	Bulk Density	g/ml	0.28	0.48
2	Ash Content	%	4.0	2.0

3	Moisture Content	%	8.1	6.6
4	Iodine Number	GI ₂ /100g	290.4	411.4
5	p ^H	-	6.4	6.4
6	Tapped Density	g/ml	0.32	0.52
7	Volatile matter	%	48.9	28.0
8	Fixed carbon	%	39.0	63.4

The fluted pumpkin seed shells were characterized based on its raw state and after activation.

Apparatus and Equipments used are as follows:

Stainless steel vertical tabular reactor, tube furnace, crusher, sieves and weighing balance

KINETIC STUDIES

In order to study the kinetics of the adsorption processes, the data shown in figure 1-6 were analyzed using various kinetic model equations which are, the first order kinetic model, Pseudo-first order kinetic model, second order model, Pseudo-second order kinetic model, Elovich model and Intra-particle diffusion model.

The mathematical linear forms of the equations were used.

The associated kinetic parameters for each of the kinetic models for the different lead concentration in the waste water have been evaluated from the slopes and intercepts of the respective linear plots and are shown in table 3.

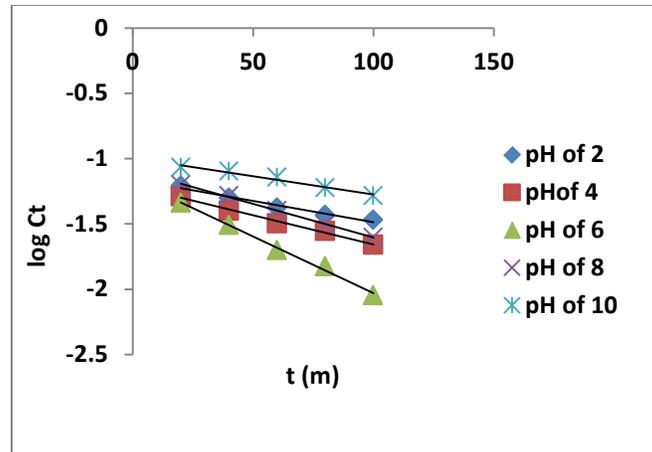


Figure 1: First Order plots for the Adsorption of different concentrations of Lead on FPSS Activated carbon.

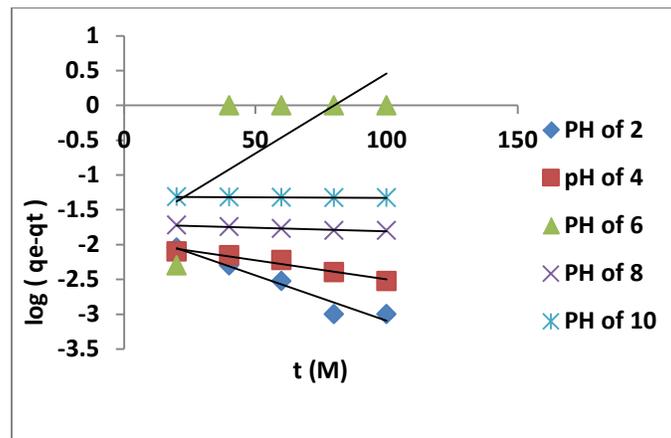


Figure 2: Pseudo-first order plots for Adsorption of different concentrations of Lead on FPSS Activated carbon.

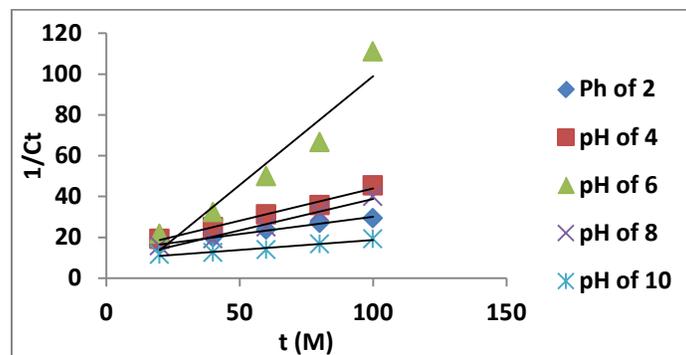


Figure 3: Second Order plot for the Adsorption of different conditions of Lead on FPSS Activated carbon.

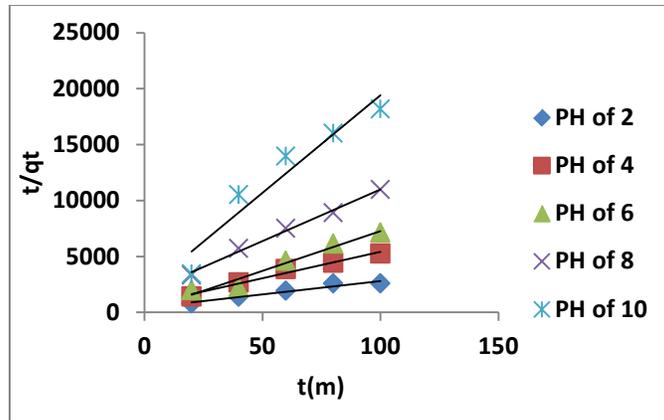


Figure 4: Pseudo-second Order plot for the adsorption of different concentration of Lead on FPSS Activated carbon.

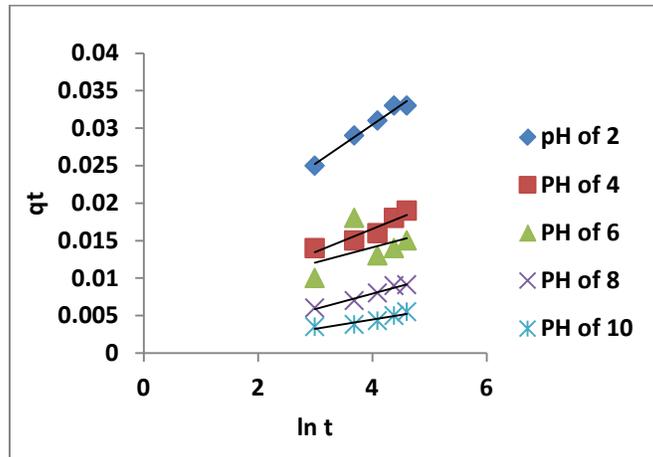


Figure 5: Elovich plot for the Adsorption of different concentration of Lead on FPSS Activated carbon.

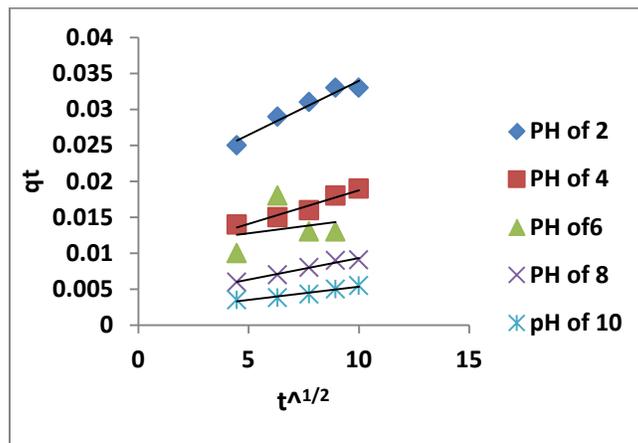


Figure 6: Intra-Particle diffusion Plots for the Adsorption of different concentration of Lead on FPSS Activated carbon.

Table 3: Kinetic Parameters for Pb²⁺ Adsorption on fluted pumpkin seed shells actuated carbon

KINETIC MODEL	P ^H	PARAMETERS	R ²
First order model	2	K ₁ = -0.007(min ⁻¹)	0.970
	4	K ₁ = -0.009(min ⁻¹)	0.991
	6	K ₁ = -0.018(min ⁻¹)	0.994
	8	K ₁ = -0.012(min ⁻¹)	0.997
	10	K ₁ = -0.005(min ⁻¹)	0.975
Second order Model	2	K ₂ = 0.168(L/mg.min)	0.991
	4	K ₂ = -0.315 (L/mg.min)	0.984
	6	K ₂ = -1.065(L/mg.min)	0.922
	8	K ₂ = -0.306(L/mg.min)	0.979
	10	K ₂ = -0.096(L/mg.min)	0.955
Elovich Model	2	β=200g/mg, α =1.4l/mg min	0.983
	4	β=333g/mg, α =1.02mglg min	0.897
	6	β=500g/mg, α =1.01mglg min	0.196
	8	β=500g/mg, α =1.0mglg min	0.971
	10	β=100g/mg, α =1.0mglg min	0.883
Intra -Particle Diffusion Model	2	K _{id} = 0.015(min ⁻¹), C = 0.361	0.976
	4	K _{id} = 0.007(min ⁻¹), C = 0.380	0.918
	6	K _{id} = 0.006(min ⁻¹), C = 0.404	0.254
	8	K _{id} = 0.0003(min ⁻¹), C = 0.551	0.982
	10	K _{id} = 0.001(min ⁻¹), C = 0.569	0.187

Pseudo-First Order					Pseudo-Second Order		
Ph	q _e (mglg)	q _{cal} (mglg)	K _{p1} (min ⁻¹)	R ²	K _{p2} (min ⁻¹)	Q _e (mglg)	R ²
2	0.034	0.016	0.029	0.945	4.2 x 10 ⁶	0.0419	0.945
4	0.014	0.011	0.012	0.955	6.4 x 10 ⁻⁷	0.0212	0.980

6	0.015	0.123	0.646	0.5	1.2×10^{-6}	0.0147	0.955
8	0.025	0.019	0.046	0.957	6.2×10^{-8}	0.0108	0.992
10	0.052	0.049	0	0.933	1.7×10^{-8}	0.0057	0.921

First order Model

To determine the controlling method of adsorption process of lead, such as transfer and chemical reaction, the first order kinetic model was used to test the experimental data. The value of the rate constant was determined from the slope of graphs plotted at figure 1. These values were tabulated in table 3. The correlation coefficient (R^2) obtained at different P^H values was in agreement with the first order model. This was in line with the work done by (Okoye et al, 2010). At P^H of 8, correlation coefficient R^2 obtained read 0.997, showing where first order model was best fitted.

Pseudo-first order Model

The linear plot in figure 2 shows the pseudo-first order plot for Pb^{2+} adsorption on fluted pumpkin seed shells activated carbon. The parameters at different P^H along side with their correlation coefficients R^2 are shown in table 3. The $q_{e, cal}$ values were derived from the slope of the plot using the mathematical formula. The pseudo second-order model was well fitted on P^H of 8 where R^2 which is the correlation value is equal to 0.957.

Second order Model

The plot on figure 3 shows the second order model. The parameters in line with its P^H values and correlation coefficients are tabulated on table 3. These R^2 values are closer to unity in all the P^H values.

The highest value 0.991 at P^H of 2 indicates that the model fits the experimental value well.

Pseudo-second order model

Figure 4 indicates the plot of $\log(q_e \text{ and } k_{p1})$ were obtained from the slope and intercept. The values of the rate constant correlation coefficients are shown in table 3.

From the results, it can be seen that the correlation coefficient for the linear plot increased from 0.921 to 0.992 at P^H of 8, which is higher than the correlation coefficients of all other P^H values studied. There is also a good relationship between the experimental q_e values. This implies that

the absorption kinetics is much more represented by the Pseudo-second order model. This was in agreement with the work done by (Andre et al,2011; Mehmet et al, 2011 and Okoye et al, 2010).

The high initial sorption rate obtained indicates that the adsorption was rapid. The adsorption of the adsorbate by adsorbent has been observed either in rapid and quantitatively predominant or slower and quantitatively insignificant (Sag et al, 1996; Umuabonah et al, 2009). The rapid adsorption of lead by this adsorbent is probably due to the abundant availability of active sites on the biomass and the perceived porous and mesh structure of the adsorbent which provides ready access and large surface area for the adsorption of lead on the binding site (Saced et al, 2005; Cheung et al, 2007).

Elovich Model

The Elovich equation has been applied to represent chemisorption processes and at low adsorption rate. The constants of the initial sorption rate constant α (mg/gmin) and parameter β that is related to the extent of the surface coverage and to the activation energy of chemisorption (g/mg) can be obtained from plot of q_t versus $\ln t$. The model parameters are presented in table 3 and the correlation coefficient (R^2) were still lower than that of first order model.

The graph of this result was shown in figure 5. The highest R^2 value, 0.983 at P^H of 2 signifies that the model fits the experimental values well. This research work was in agreement with the work done by (Okoye, 2010).

Intra-Particle Diffusion Model

The Intra particle diffusion model was developed to identify the adsorption mechanism and to predict the rate controlling steps. This models follows three steps. Firstly, the external surface adsorption or boundary layer diffusion. Secondly, the gradual stage of adsorption which is the Intra particle diffusion. If the plot of $\log q_t$ versus $0.5 \log t$ is a straight line with a positive intercept, then the Intra particle diffusion is the controlled adsorption process or rate controlling step (Mamound et al, 2012).

Thirdly, the final equilibrium stage in which the intra particle diffusion starts to slow down due to the extremely low lead concentration left in the solution (Cheung et al, 2007).

The plot in figure 6 shows that the linear plot did not pass through the origin which indicated that intra-particle diffusion was not only the rate controlling step but also that the boundary layer diffusion control the adsorption to some extent. (Cheung et al, 2007).

This deviation can be as a result of the difference in mass transfer rate in the initial and final stage of adsorption (Mamound et al, 2012).

The values of C and k_{id} are given in table 3. The values of the intercept C increased with an increase in P^H , which showed that boundary layer effect increased as P^H increases. The

correlation coefficients for intra particle diffusion were lower than that for the first order model. This was in line with the work done by (Tan et al, 2007). The correlation factor was highest at P^H of 8 (0.982) signifying that the model fitted well with intra particle diffusion.

A comparison of the various plots based on their linear regression coefficient (R^2) values shows that first order model best described the adsorption at all considered concentration. Therefore the adsorption of Pb^{2+} on fluted pumpkin seed shells activated carbon can best be described using first order model.

ADSORPTION THERMODYNAMICS

The results shown in table 4; indicate the thermodynamic constants used in confirming the spontaneous nature of the adsorption process. The plot of $\ln k_c$ versus $1/T$ is shown in figure 7

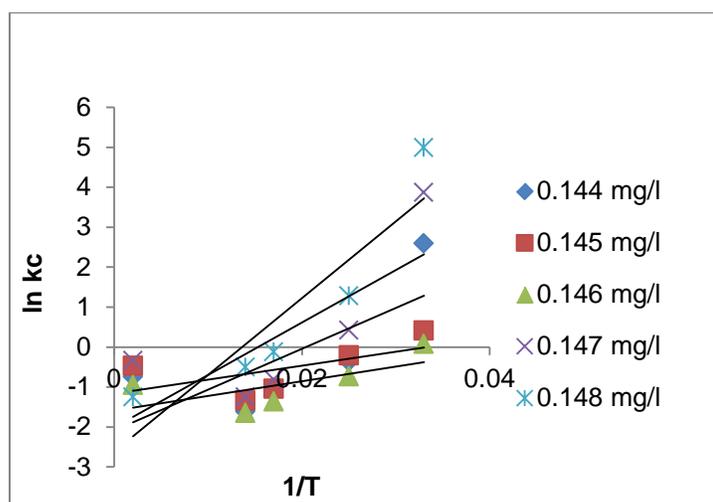


Figure 7 Adsorption Thermodynamics plots on Lead Adsorption on FPSS Activated carbon

Table 4: Thermodynamic Parameters for Lead Adsorption

Conc (mg/L)	ΔG (klmol)					ΔH (kJ/mol)	ΔS (j/mol/k)
	303k	313k	323k	333k	343k		
0.144	4505	3708	3693	3968	5608	-2.09	-7.4
0.145	4595	2745	3825	4135	5226	-292	-9.7
0.146	4421	2842	3957	4302	5444	-306	-13.2
0.147	4943	2939	4089	4469	5662	-1091	-16.7
0.148	5117	3036	4214	4636	5880	-1597.1	-21.8

The thermodynamic constants, Gibb's free energy (ΔG), enthalpy change (ΔH^0) and entropy change (ΔS^0) are calculated to evaluate the thermodynamic feasibility of the process and to confirm the spontaneous nature of the adsorption process (Auta, 2012).

The values of ΔS^0 and ΔH^0 were obtained from the intercept and slope respectively of plot of $\ln k_c$ against $1/t$.

The positive values of ΔG^0 in table 4 indicated that the process is not spontaneous and less feasible. The result also showed that both enthalpy and entropy values were negative at different concentrations, signifying that the adsorption process is exothermic and degree of dispersion increased with increase in temperature.

CONCLUSION

The result obtained from this work shows the possibility of production of activated carbon with good properties from fluted pumpkin seed shells. The kinetic model was best described using first order equation as it has the best R^2 values.

The thermodynamic properties such as ΔG^0 ; ΔH^0 and ΔS^0 studied, shows adsorption process as non spontaneous and exothermic in nature which is less favorable at high temperature.

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