Removal of Lead (II) from Aqueous Solution using Banana (Musa Paradisiaca) Stalk-Based Activated Carbon

O. O. Ogunleye [1*]   O. Adio[2]   T. O. Salawudeen[1]

1 Department of Chemical Engineering, Ladoke Akintola University of Technology, P. M. B. 4000, Ogbomoso
Nigeria

2 Centre for Entrepreneurship Development, Kwara State Polytechnic, Ilorin –Nigeria

*Corresponding Author's E-mail: ooogunleye@yahoo.com

Abstract

Banana Stalk Activated Carbon (BSAC) chemically prepared was used as adsorbent to remove Pb (II) from aqueous solution in a batch mode. BSAC was characterized using physicochemical properties, proximate analysis, pH_{pzc}, and Fourier Transform Infrared (FTIR) spectroscopy. Effects of initial concentration, contact time, temperature, adsorbent dose and pH on adsorption of Pb (II) were evaluated. FTIR showed that BSAC is rich in carboxyl, hydroxyl and phenolic functional groups. The maximum percentage removal of Pb (II) was 97.90% at equilibrium time of 120 minutes. The kinetic data of Pb (II) were analyzed using pseudo-first-order, pseudo-second-order and intra-particle diffusion models but the pseudo-second-order kinetic model gave the best fit. Langmuir, Freundlich, Temkin and Dubinin – Radushkevich (D–R) isotherm models were used to analyze the equilibrium adsorption data, but the Langmuir isotherm model provided the best correlation (R^2) of 0.998 and maximum adsorption capacity (q_{max}) of 200 mg/g. The thermodynamic properties of the adsorption process, such as the Gibbs free energy, enthalpy and the entropic change have been evaluated and established that the process was spontaneous, feasible and endothermic in nature. BSAC is efficient and effective in removing Pb(II) from its aqueous solution.

Keywords: Banana stalk, adsorption, kinetics, isotherm, equilibrium

1.0   Introduction

Economic and technological advancement all over the world brought about urbanization and industrialization that are accompanied by various forms of environmental pollutions (Yu, 2005). Prominent among these pollutants are the heavy metals, which are extremely toxic because of their solubility in water. This makes them readily absorbed into plant and animal tissues where they can eventually impair the functions of proteins and nucleic acids (Forstner and Wittmann, 1979). Unlike organic pollutants, which are susceptible to biological degradation, heavy metals do not degrade into harmless products (Yu, 2005). Industrial exposure and accidental childhood poisoning had been considered as the exclusive sources of heavy metals into human beings in the past, however, recent researches have linked other sources to products, industrial effluents and food stuffs (Khalid *et al*, 1996; Ryan *et al*,2004 and dos Santos *et al.,* 2011).

Lead is one of the heavy metals emanating from industries such as batteries manufacturing, smelting, paints, fertilizer and petrochemical industries, which are toxic even when in trace quantities (Rao *et al,* 2011). When inhaled or ingested into human body, its accumulation can cause monumental damage to kidney, nervous and reproductive system (Okoro and Ejike, 2007). Environmental protection and health issues requires that lead be removed from effluent in order not to compromise the World Health Organization's (WHO) maximum permissible limit (3 - 10µgL^{-1}) in drinking water (Needleman 1999; WHO 2000, Harvey and Chantawong, 2001; Pruss-Ustun et al. 2004). Adsorption has been the most adopted method of treatment of wastewater containing lead and other heavy metals because of its numerous advantages over others methods that are expensive and produce sludge that requires resources for treatment (Elsalah *et al*., 2002; Weirich *et al.*2002; Quadeer and Akhtar ,2005; Okoye *et al* ,2010; Alslaibi *et al.* 2013; Jeyakumar and Chandrasekaran, 2014). However, the relative costly nature of the commercial activated carbon used in adsorption brought about the development of adsorbents from low cost agricultural residues that are of no economic importance such as rice and wheat husks (Rao *et al*, 2009) and groundnut shells (Malik *et al*, 2007).

Numerous previous production of activated carbon from agricultural residues and other materials to remove Pb(II) from aqueous solution include *Eichhornia* (Shekinah *et al.,*2002), zeolites (Payne and Abdel-Fattah , 2004), palm shell (Issabayeva *et al*., 2006), *Euphorbia rigida* (Gercel and Gercel, 2007) , coconut and seed hull of the palm tree (Gueu *et al.,*2007). Other examples include *Militia ferruginea* plant leaves (Mengisite *et al*., 2008), *Eucalyptus camaldulensis Dehn.* back (Patnukao *et al.* 2008) , cow dungs (Eliagwu *et al* . , 2009), oil-palm fruit fibre (Bello *et al*., 2010), palm shell (Onundi *et al*., 2010), fluted pumpkin seed shell (Okoye *et al.*, 2010), lignite (Rao *et al*., 2011), groundnut shell (Isah and Yusuf , 2012) , palmyra palm nut (Nwabanne, and Igbokwe, 2012), waste biomass (Erdem *et al*. , 2013), watermelon shell and walnut shell (Moreno-Barbosa *et al.,* 2013),peanut shell (Tahiruddin and Rahman, 2013), olive stone waste(Alslaibi *et al*, 2013), carbon coated monolith (Teoh *et al*., 2013) and marine green algae(Jeyakumar and Chandrasekaran,

2014).

Due to the fibrous nature of banana stalk, it has been employed in the production of activated carbon for the treatment of dye related pollutants from aqueous stream with excellent performance (Bello *et al*, 2012). However, there is paucity of information on the application of Banana Stalk Activated Carbon (BSAC) for the adsorption of Pb(II) from aqueous solution. Therefore, this study investigated the use of banana stalk as a precursor for the preparation of activated carbon and to determine its adsorption capacity for Pb(II) from aqueous solution. The effects of initial lead ion concentration, temperature, contact time adsorbent dosage and solution pH on Pb(II) adsorption onto BSAC were investigated. Kinetic, isotherm and thermodynamic parameters governing the adsorption process were also studied and reported.

2.0   Materials and Methods
2.1 *Preparation of Adsorbate*
Adsorbate containing Pb (II) was prepared from the stock solution of 1000 mgL^{-1} Pb(NO$_3$)$_2$. Reagents used were of analytical grade and deionized water was used in solution preparation. Other concentrations (20 - 100 mg/L) were obtained from this stock solution by serial dilution. The concentration of Pb(II) in adsorbate was analysed by Atomic Absorption Spectrophotometer (model Pye Unicam SP-9 Cambridge, UK.)

2.2 *Adsorbent preparation and characterization*
Banana Stalks (BS) were washed thoroughly and then dried at 120 ^{o}C in an oven for 24 hours to constant weight. The dried samples were cut into small pieces, grinded   and sieved into desire mesh size of 300 -425µm. Dried BS of 100g was pyrolysed in the Gollenkamp Muffle furnace (model Tactical 308) at 600°C for 1hour. The char produced was cooled to room temperature and treated with phosphoric acid (H$_3$PO$_4$) at a ratio 1:1 (w/v). The mixture was dehydrated in an oven for 12 hours at 105°C and then carbonized in the absence of air at 800°C for 2 hours. The carbonized sample was cooled, filtered and   mixed with 0.1M HCl for 1 hour on magnetic stirrer**.** The sample was finally washed with hot de-ionized water until the pH of the washed solution reached 7.0 and then stored as BSAC. Proximate analysis, surface characteristics, physiochemical properties of the BSAC were carried out using ASTM (1991), ASTM (1996) and ASTM (2006) methods. Fourier transform infrared (FTIR) spectroscopic analysis was performed on the raw and BSAC using (FTIR – 2000, Perkin Elmer) and spectra were measured from 4000 to 400 cm^{-1}

2.3 *Batch Adsorption Equilibrium Experiment*
Batch equilibrium tests were carried out on the adsorption of Pb(II) on BSAC. The adsorption experiments were carried out in 250ml conical flasks with stopper on a mechanical shaker equipped with a thermostatic water bath operating at 120 rpm. The effect of initial metal ion concentration (50, 100,150,200 and 250mg/L), contact time (15, 30, 45, 60, 75, 90, 105, 120, 180 and 240 minutes), temperature (30, 40 and 50°C), solution pH (2, 4, 6, 8 and 10) and adsorbent dose (0.05, 0.1, 0.15, 0.20, 0.25, 0.30g.and 0.35g/100ml of Pb(II) solution)   were investigated. During the experiment, the parameter considered was varied while the other four were kept constant. The pH of the solution was adjusted to the desire pH by addition of 0.1M HCl or 0.1M NaOH and monitored using pH meter. Sample solutions were withdrawn and filtered using Whatman filter paper at time interval and equilibrium to determine residual concentrations. For equilibrium studies, the experiment was carried out for 240 minutes to ensure that equilibrium was reached. The concentrations of Pb(II) solution before and after adsorption were determined using Atomic Absorption Spectrophotometer (Model Pye Unicam SP-9 Cambridge, UK.) . The linear Beer–Lambert relationship between absorbance and concentration with the calibration curve was established by plotting the graph of absorbance versus concentration of the Pb(II) solution.

The adsorbed phase concentration (q$_t$, in mg/g) at time (t) was calculated using equation (1)

$$q_t = \frac{(C_o - C_t)V}{m} \tag{1}$$

Where, C$_o$ and C$_t$ are the initial and the final lead concentration (mg/L), respectively; V is the adsorbate volume (L) and *m* is the mass of adsorbent used (g).

The adsorption at equilibrium, q_e (mg/g), was calculated according to Equation (2)

$$q_e = \frac{(C_o - C_e)V}{m} \tag{2}$$

Where, C$_o$ and C$_e$ are the initial and the final (equilibrium) Pb (II) concentration (mg/L) respectively; V is the adsorbate volume (L); and *m* is the mass of adsorbent used (g). The percentage of Pb(II) removal was calculated using Equation (3) :

$$\text{Removal (\%)} = \frac{C_o - C_t}{C_o} \, X \, 100\% \tag{3}$$

3.0   Results and Discussion

3.1 *Characterization of BSAC*

The result of proximate analysis of adsorbent prepared from banana stalks are presented in Table 1. The BSAC has the highest value of fixed carbon contents of 79.31% which makes it well suitable for adsorption of Pb(II) than others and this is in agreement with Bello *et al* (2012). In addition, as observed from Table 2 where the physiochemical properties of the adsorbents are presented, BSAC has the highest iodine number of 820, which is due to greater surface area and available micropores for adsorption of iodine molecule on the surface. The higher value of the iodine number for the BSAC shows that it has well developed pore structure than the char and by implication higher surface area and adsorption capacity than the char. The bulk density of 0.34 g/cm^3 falls within the range (0.20 - 0.52g/cm^3) recommended by the American Water Work Association for activated carbon meant to be used for practical purpose (AMWA, 1991). The lower pH of the BSAC can be explained by the increase surface acidity of the adsorbent by chemical activation with H_3PO_4. This can be attributed to adsorption of (H$^+$) ions from desorption of (OH$^-$) ions from the sorbent surface (Ghazy and El-Morsy, 2007).

The FTIR spectroscopic characteristics for the Raw Banana Stalk (RBS) and BSAC are as shown in Figure 1a and 1b, respectively while the FTIR analysis indicating bands and peaks with their corresponding ascribed functional groups are on Table 3. There is a shift in bands, change in wave numbers, and absorbance difference between the RBS and BSAC samples, which indicate that chemical transformation would have taken place during chemical treatment and carbonization. The combined effects of chemical activation and carbonization on the RBS to produce BSAC resulted in enhancement and disappearance of some of the functional groups as well as shifting and lowering of wavelength numbers. The results of the surface characterization, which gave the quantification of the surface acidic and basic groups of the adsorbent, are presented in Table 4. pH_{PZC} of an adsorbent is important because it indicates the net surface charge of the carbon in solution. In this study, zero point charge was found to occur at 4.25 meaning that BSAC surface has a positive charge in solution up to pH of 4.25 and a negative charge above this pH. Oxygen functional groups with various acidic groups (carbonxyl, lactonic and phenolic) are found to be higher than the basic group (Table 4). This is consistent with the value of pH_{PZC} of 4.25 showing the dominance of acidic groups. The presence of the surface functional groups depicts the metal binding capacity of the adsorbent.

Table 1: Proximate Analysis of the Adsorbents

Sample	Moisture content (%)	Volatile content (%)	Fixed carbon content (%)	Ash content (%))
BS	14.45	70.53	8.57	6.45
Char	6.53	30.34	59.37	3.76
BSAC	2.79	12.48	79.31	5.12

Table 2: Physicochemical Properties of Adsorbents

Sample	Bulk density (g/cm^3)	Iodine number	pH
BS	0.21	Nil	8.06
Char	0.36	528	6.73
BSAC	0.34	6.73	3.78

(a)

(b)
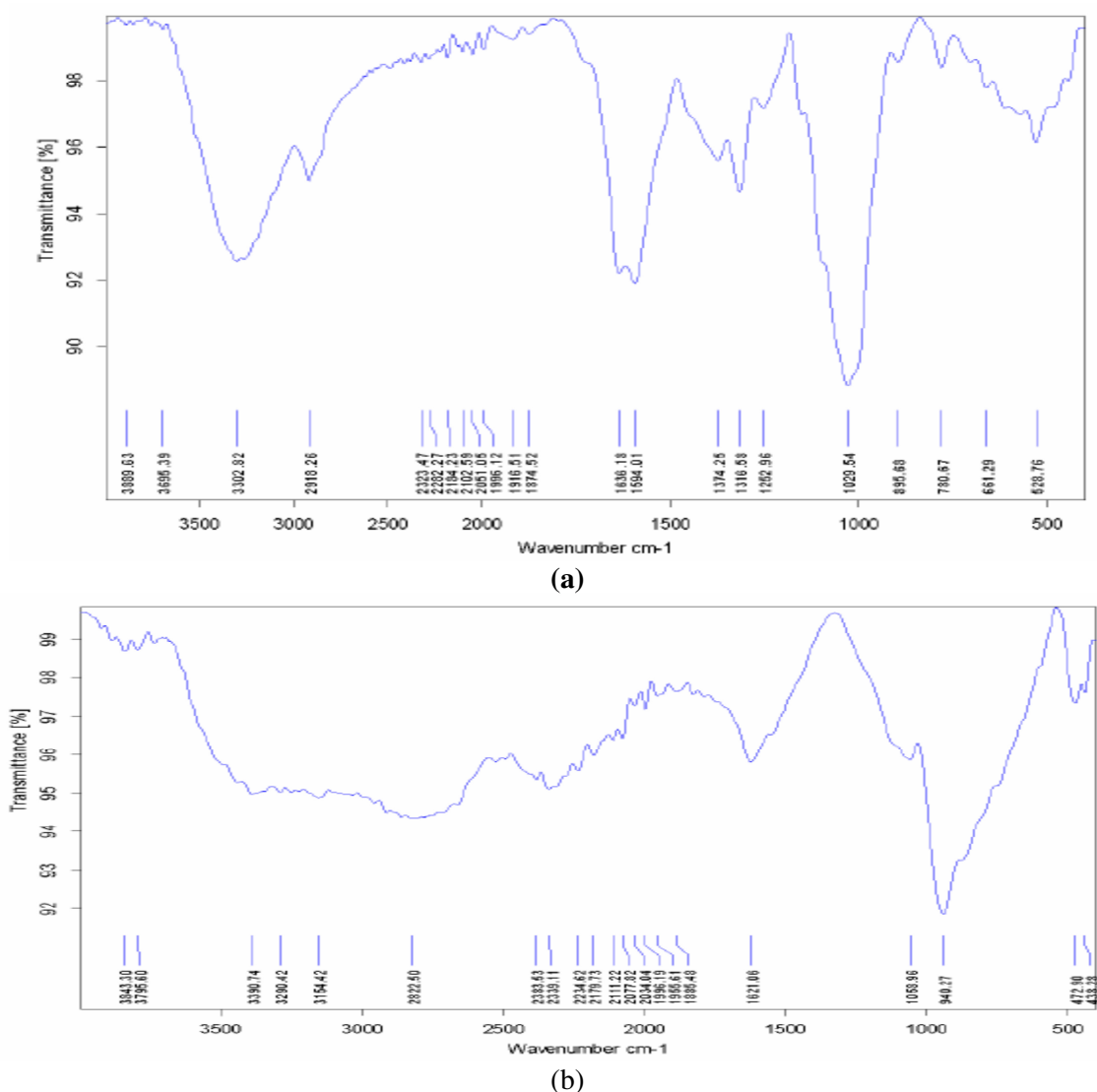
Figure 1: FTIR spectra for (a) RBS and (b) BSAC

Table 3: FTIR Spectra Characteristics

RBS		BSAC	
IR Spectra Peak (cm^{-1})	Functional groups	IR Spectra Peak (cm^{-1})	Functional groups
3889.63 – 3639	Bonded O-H group	3843.30 – 3797.60	O-H group
3302.82	O-H group of carboxylic acid	3390.74, 3290.42, 3154	O-H group of carboxylic acid
2918 - 2323.47	Aliphatic C-H group	2822.50 – 2383.53	Aliphatic C-H group
1636.16	Carbonyl stretching with aromatic Ring	1621	C=O stretching
1594.01	Amide group	1058	C=O=C stretching for ether or hydroxyl group
1316 - 1252.96	Nitrate (NO$_2$) symmetric stretching Vibration	980	β-glycolic linkages
1028	Si – O - Si asymmetric stretching	472-438	C=C stretching (lignin) and C-N stretching
661- 523.76	C-S stretching		

Table 4: Surface Characteristics of BSAC

BSAC	Surface Chemistry
Carboxylic (meq. g-1)	0.2152
Lactonic (meq. g-1)	0.2445
Phenolic (meq. g-1)	0.2816
Acidic (meq. g-1)	0.7413
Basic (meq. g-1)	0.1842
pH_{PZC}	4.25

3.2 *The effect of solution pH*

The effect of pH on the adsorption of Pb (II) from aqueous solution on BSAC, expressed in terms of percentage Pb (II) removal is as shown on Figure 2**.** The percentage removal of Pb (II) at pH (2) was 34.961% while at pH (4), it increased to 40.57%, which shows no appreciable difference in the amount of Pb(II) removed. However, as the pH increased above 4, the percentage removal was enhanced, reaching the maximum of 97.9% at pH of 8. This result is in agreement with   Kobya *et al.* (2005). At lower pH values, the surface charge of BSAC is positive, thus, Pb(II) adsorption is not favourable because of electrostatic repulsion between Pb(II) and BSAC surface. When pH was increased, the electrostatic repulsion between the Pb(II) and BSAC surface site decreased, the BSAC surface became negatively charged facilitating binding of the Pb(II) cation via electrostatic attraction, hence, lead uptake increased.
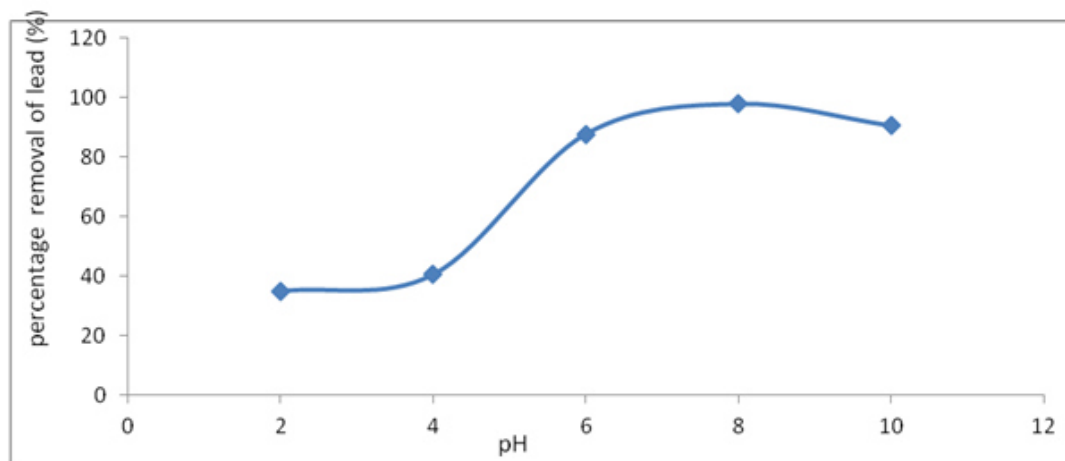

Figure 2: Effect of pH on the adsorption of Pb(II)

3.3   *Effect of adsorbent dose*

Adsorption capacity (qe) and percentage removal were plotted against adsorbent dose as shown in Figure 3. It was found that with increase in adsorbent dose, the percentage removal increased which is an indication of the presence of large surface area available for adsorption with the corresponding decrease in the maximum adsorption capacity, which is the amount, absorbed per unit mass of the adsorbent. The percentage of Pb (II) removed increased from 57 to 98.52% with the increase in adsorbent dose from 0.05 to 0.2g, while the adsorption capacity decreased from 114 to 49.26mg/g under the same condition. It clearly showed that for a fixed initial solute concentration, increasing the adsorbent dose provides a greater surface area or available adsorption sites increases and therefore result in the increase of the amount of Pb (II) adsorbed. The observed decrease in adsorption capacity, with increase in the adsorption site during the adsorption process can be attributed to the fact that the increasing adsorbent dose increased concentration of the adsorbent to an insufficiency of metal ions in solution with respect to available binding sites. This result is in agreement with what Pehliven *et al,* (2009) reported.
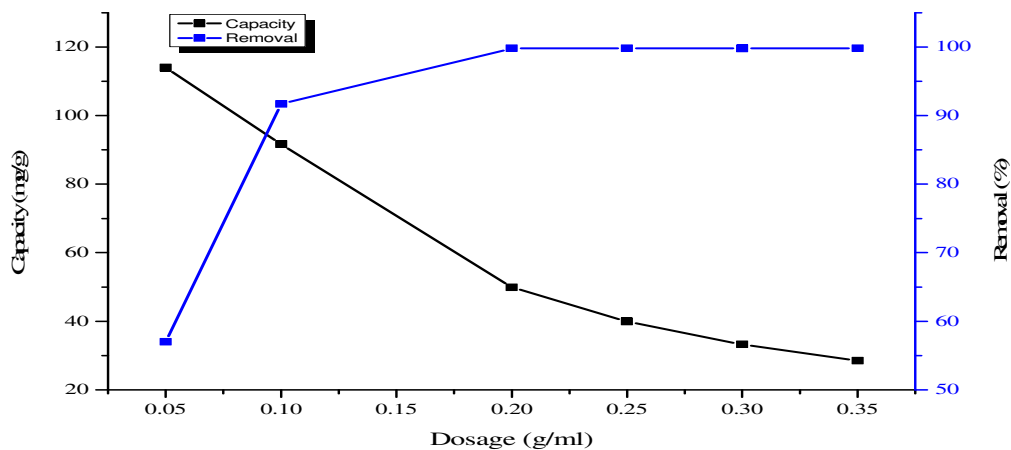
Figure 3: Effect of dose on Pb(II) removal at pH of 7.0 and at 30°C

3.4 *Effect of initial ion concentration and contact time*

The effect of initial ion concentration and contact time on the adsorption capacity of PB(II) onto BSAC is as presented in Figure 4. The percentage removal of Pb(II) increased with time and reached equilibrium at 120minutes. In addition, as the initial Pb (II) concentration increased from 50 to 250 mg/l, the loading capacity of the activated carbon increased from 23.5 to 106 mg/g. Thus, the adsorption capacity was enhanced with increased initial concentration. The removal of Pb(II) was rapid at initial stages and finally reaches constant value for a longer time and this initial high adsorption rate is due to abundance binding sites. The result indicate that up to 60% of the total amount of Pb(II) uptake was found to occur in the first 30 minute and thereafter the remaining 40% of maximum uptake was reached in the remaining time of 210 minutes which is in agreement with the findings of Teoh *et al*. (2013); Jeyakumar and Chandrasekaran (2014). Figure 4 can be divided into fast, slow and equilibrium portion corresponding to first 30 minutes, the portion between 30 and 120 minutes; and the portion between 120 and 240 minutes, respectively. The slow adsorption was due to the decrease in concentration gradient between the adsorbate in solution and adsorbate in sorbent surface due to accumulation of Pb (II) particles on the vacant sites. The equilibrium portion is characterized by practical non-sorption where rate of sorption may be equal to rate of desorption.

3.5 *Effect of Temperature*

A plot of adsorption capacity (q_e) of BSAC against initial concentration of Pb(II) at different temperatures was plotted and the result of the experiment data is presented on Figure 5. It is evident from Figure 5 that the value of maximum uptake capacity of lead increased with increased temperature, indicating a better adsorption at higher temperature. This is due to the increased surface activity, suggesting that adsorption of Pb(II) onto BSAC was an endothermic process as earlier presented by Bello *et al*, 2012.
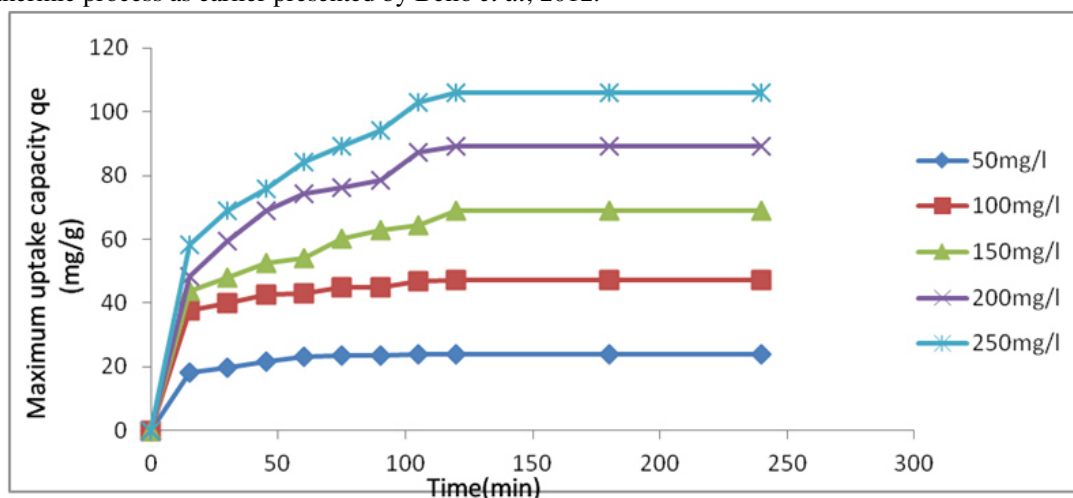

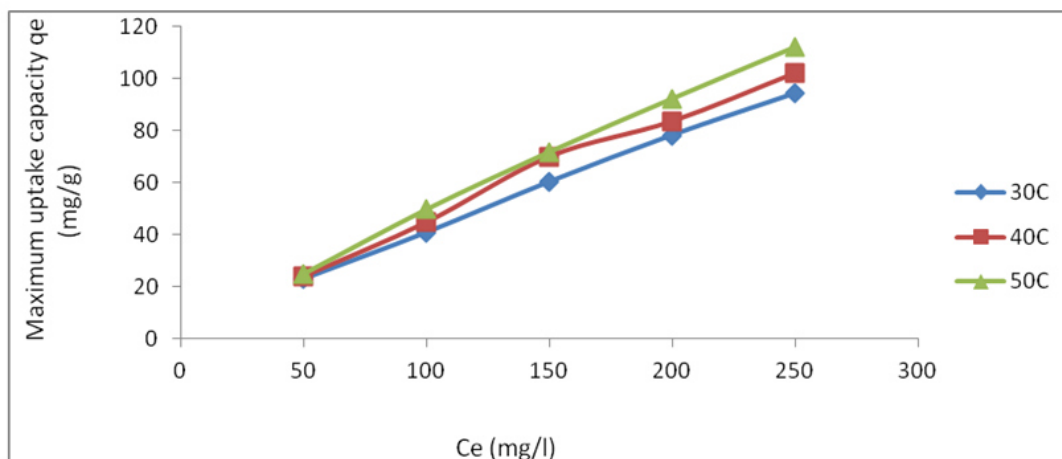**Figure 4: Effect of initial concentration and contact time on Pb(II) uptake by BSAC**

Figure 5: Effect of surface loading with temperatures

3.6   Adsorption kinetics

3.6.1   *The Pseudo- First Order Kinetic Model*

        The pseudo-first order equation is generally express as the integrated form of Langergren model (Lagergren, 1898)) as presented in equation 4:

$$\ln(q_e - q_t) = q_e - k_1 t \tag{4}$$

    Where q_e and q_t are the adsorption capacity at equilibrium and time *t*, respectively in (mg/g), k_1 is the rate constant for pseudo first order adsorption (min^{-1}); plot of ln(qe-qt) against *t* at various initial Pb(II) concentration (Figure 6), resulted in linear graph with negative slopes. k_1, and q_e were calculated from the slopes and intercepts, respectively. As shown on Table 5, although the correlation coefficient were high, the q_e (calculated) and q_e (experimental) values do not agree and therefore the adsorption of Pb(II) onto BSAC does not perfectly fit the pseudo first order kinetics.
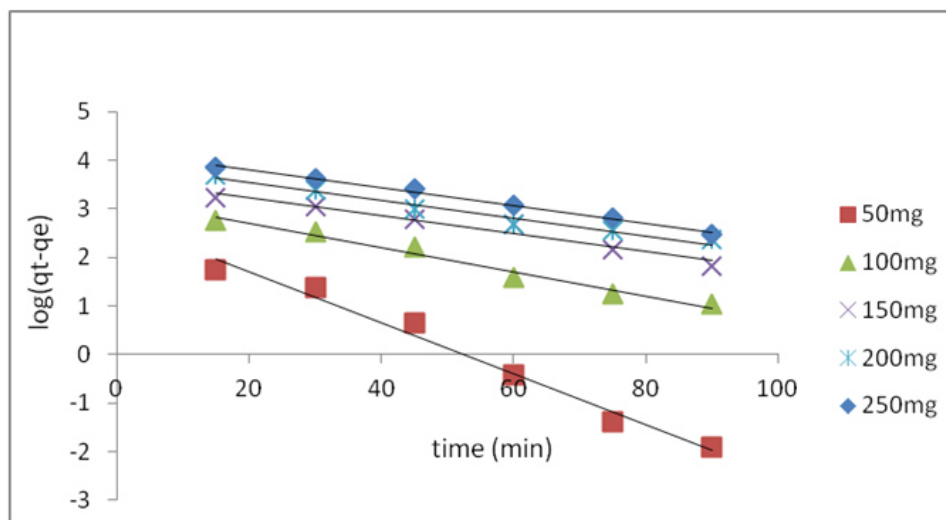

Figure 6 : Pseudo-first-order kinetic model fitted to the batch kinetic data of Pb(II) adsorption by BSAC at different initial concentrations

3.6.2   *The pseudo- second order kinetic model*

        The adsorption kinetics may also be described by a pseudo-second order equation (Ho and Mckay, 1999). The differential equation is the equation 5:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

Integrating the above Equation (5) and applying boundary conditions (q$_t$ = 0 when t = 0; and q$_t$ = q$_t$ at t = t, gives the equation 6

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

Equation (6) can be rearranged to obtain a linear form of equation 7:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \tag{7}$$

Where $h = k_2q_e^2$ (mgg^{-1}min^{-1}) can be defined as the initial adsorption rate as t→0 and k_2 is the rate constant of the pseudo – second order adsorption (g.mg^{-1}min^{-1})

   Plots of t/q_t versus t from Equation (6) gave a straight line (Figure 7) from which q_e, k_2 and h were determined from the slopes and intercepts of the plots. The computed results obtained from pseudo second order kinetic model are as shown in Table 5. The correlation coefficients obtained were greater than 0:99 for all initial concentrations studied and there were good agreement between $q_{e\ cal}$ and $q_{e\ exp.}$ The good agreement indicates that the pseudo-second-order kinetic model fits the adsorption system studied. A similar result was also obtained on the adsorption of malachite green dye onto BSAC (Bello *et al.,* 2012).
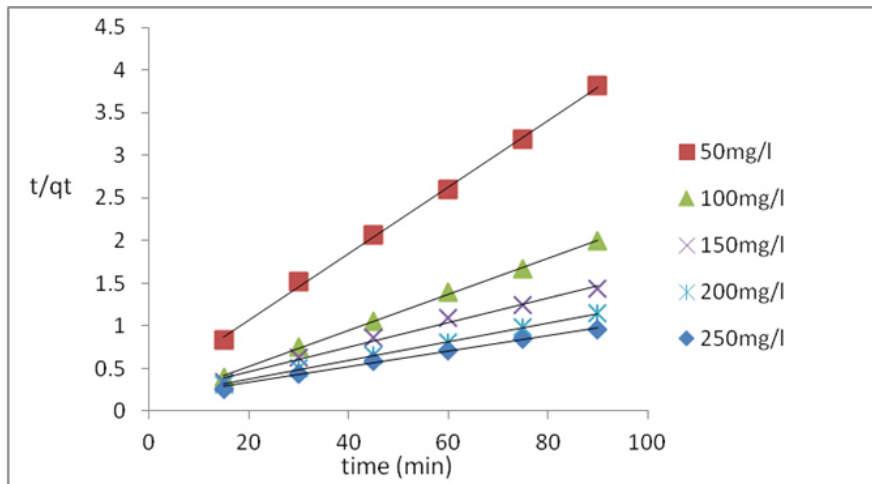

Figure 7 : Pseudo-second-order kinetic model fitted to the batch kinetic data of Pb(II) adsorption by BSAC at different initial concentrations

3.6.3 *Intraparticle diffusion model*
   The intraparticle diffusion equation (Weber and Morris, 1963) is given as equation 8:

$$q_t = k_{diff}t^{\frac{1}{2}} + C \qquad (8)$$

Where t is the amount of lead adsorbed (mgg^{-1}) at time t and K_{diff} (mgg^{-1}min^{-1}) is the rate constant for intraparticle diffusion. The value of C gives an idea about the thickness of the boundary layer, the larger the intercept the greater the boundary layer effect. Plot of uptake, q_t versus the square root of time, $t^{\frac{1}{2}}$ (Figure 8) should be linear if intraparticle is involved in the adsorption process, and if the line passes through the origin, then intraparticle diffusion is the rate controlling step. The rate constant k_{diff}, C and R^2 are shown in Table 5. The correlation coefficient (R^2) for intraparticle diffusion model are between 0.949 and 0.998, indicating that adsorption of Pb(II) onto BSAC may be controlled by intraparticle diffusion model. The plots do not pass through the origin in all cases. This is indicative of some degree of boundary layer diffusion

3.7 Adsorption Isotherms
3.7.1 *Langmuir isotherm model*
The linearised form of the Langmuir adsorption model (Langmuir,1918) is expressed as equation 9:

$$\frac{C_e}{q_e} = \frac{1}{k_Lq_m} + \frac{1}{q_m}C_e \qquad (9)$$

A plot of C_e/q_e against C_e (Figure 9) gave a straight line graph with a slope $1/q_m$ and intercept of $1/k_Lq_m$. Values of q_m and k_L are calculated from the graph and reported in Table 6. The q_m is the monolayer saturation at equilibrium whereas k_L is Langmuir constant. . To confirm the favorability of the adsorption process to Langmuir isotherm the essential features of Langmuir isotherm is the dimensionless equilibrium parameter (R_L) expressed by Equation 10
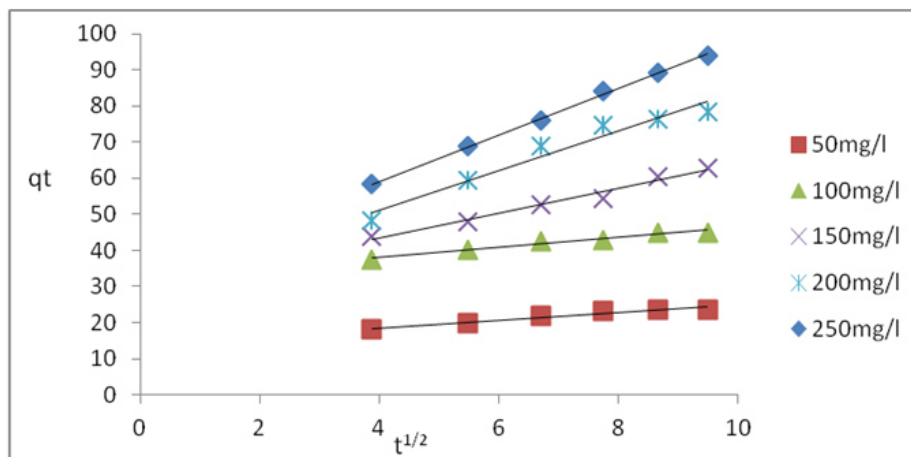
$$R_L = \frac{1}{1 + k_LC_o} \qquad (10)$$

Figure 8 : Intraparticle Diffusion kinetic model fitted to the batch kinetic data of Pb(II) adsorption by BSAC at different initial concentrations

Table 5: Pseudo first order, Pseudo second order, and Intraparticle diffusion Kinetic Parameter and Correlation coefficient obtained for adsorption of Pb(II) onto BSAC at different concentration

Model	Initial Pb(II) Concentrations (mg/L)				
	50	**100**	**150**	**200**	**250**
Pseudo first order					
q_{exp} (mg/L)	23.75	47.38	69.00	89.10	106.00
k_1 (min^{-1})	0 .052	0.020	0.018	0 .018	0.018
q_{cal} (mg/L)	2.767	2.573	3.579	3.905	4.173
R^2	0.981	0.962	0.955	0.970	0.995
Pseudo second order					
k_2 (g.mg^{-1} min^{-1})	0.00528	0.00428	0.00111	0.00078	0.00054
q_{cal} (mg/L)	25.64	47.62	71.43	90.90	111.11
h (mg. g^{-1}min^{-1})	3.4724	9.7101	5.6481	6.4103	6.7110
R^2	0.998	0.999	0 .990	0.998	0.992
Intraparticle diffusion					
k_{diff} (mg g^{-1}min^{-1})	1.065	1.376	3.412	5.489	6.423
C (mg. g^{-1})	14.19	32.62	29.75	29.28	33.47
R^2	0.949	0.971	0.976	0.958	0.998

Where C_o is the highest initial lead concentration in solution, is used to confirm the favorability of the adsorption process; that is the value of R_L indicate whether the isotherm is irreversible if ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$), unfavorable ($R_L > 1$) (Kadirvelu and Namasivayam, 2003). The value of R_L obtained for initial concentration of 250mg/L in this study as reported in Table 6 at various temperatures indicating that the adsorption of lead on to BSAC is favorable as the values lies between 0 and 1. The comparison of the q_{max} form the study (200mg/g) with previous study is as shown on Table 7.
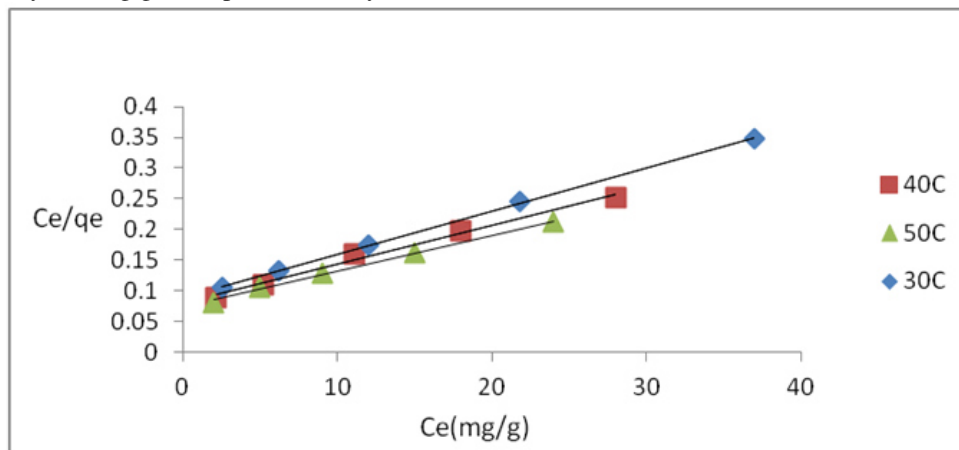

Figure 9: Langmuir isotherm fitted to the batch equilibrium data of Pb(II) adsorption by BSAC

3.7.2   *Freundlich Isotherm*

The linearized form of the Freundlich Isotherm equation (Freundlich, 1906) is given as equation 11

$$\log q_e = \frac{1}{n} \log C_e + \log k_F \qquad (11)$$

Where k_F and n are Freundlich constants, the characteristic of the system, K_F and n is the indicator of adsorption capacity and adsorption intensity, respectively. The ability of Freundlich model to fit the experimental data was examined. For this case, the plot of log q_e versus log C_e was carried out at different temperature (Figure 10). The values of k_F and 1/n were obtained, from the intercept and slope of the curve, respectively. The plots gave straight-line graphs with high R^2. Comparing the R^2 value of the Freundlich with Langmuir isotherms, adsorption data fits the Langmuir isotherms model better as indicated on Table 6. Values of n > 1 indicate the adsorption is favourable.
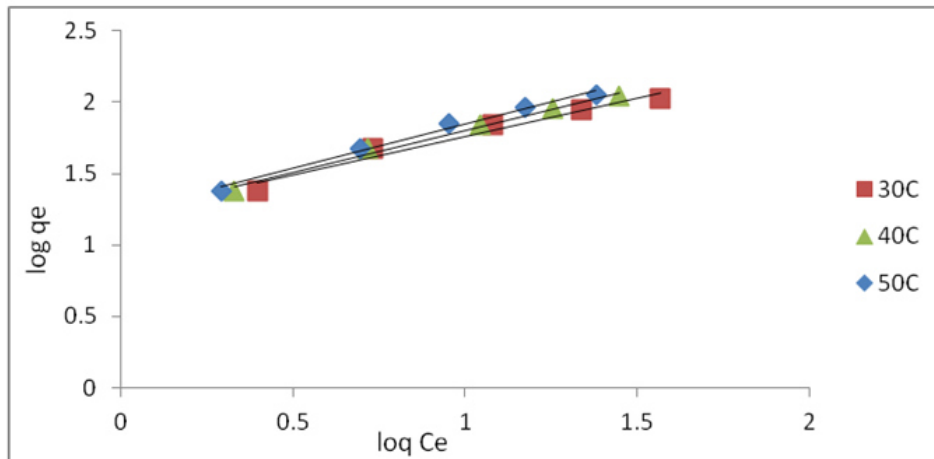

Figure 10: Freundlich isotherm fitted to the batch equilibrium data of Pb(II) adsorption by BSAC

3.7.3   *Temkin isotherm*

A linearised form of Temkin isotherm (Temkin and Pyzhev, 1939) can be written as equation 12

$$q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \log C_e \qquad (12)$$

Equation (12) can be simplified as equation 13:

$$q_e = B \ln A + B \ln C_e \qquad (13)$$

Where B = RT/b,   B is the molecular interaction parameter. A and B are the Temkin isotherm constants. A is the equilibrium binding constant corresponding to the maximum energy (L/mg), b is related to the heat of adsorption. B is the Temkin isotherm constant; T (K) is the absolute temperature and R is the ideal gas constant (8, 314Jmol^{-1} K^{-1}). A plot of ln C_e versus q_e gave a straight line(Figure 11) in which the constant A and B were obtained from the slope and intercept of the graph, respectively. The values of the Temkin constants A and b are presented in Table 6 for the different temperatures considered .The values of B were 30.46, 33.47 and 35.79 at 30°C, 40°C, and 50°C, respectively. The correlation coefficient obtained was greater than 0.98 for all the temperatures.
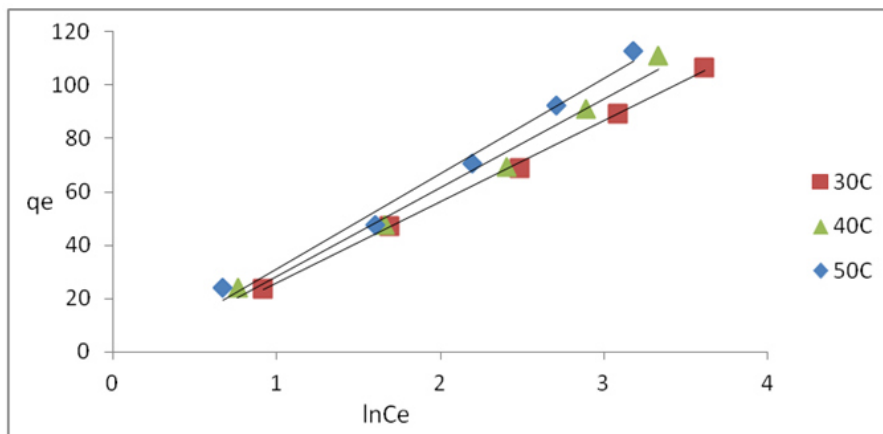

Figure 11: Temkin isotherm fitted to the batch equilibrium data of Pb(II) adsorption by BSAC

3.7.4 *Dubnin-Radushkevich (D-R) model*

The linearised D-R equation (Dubinin and Radushkevich, 1947) can be expressed as equation 14

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \qquad (14)$$

Where β is the free energy of sorption per mole of the lead as it migrate to the surface of BSAC from an infinite distance in the solution ($mol^2 kJ^{-2}$) qm is the maximum adsorption capacity and ε is the polarity potential ($Jmol^{-1}$), that is expressed as equation 15 :

$$\varepsilon = RT \ln \left(1 + \frac{1}{c_e} \right) \qquad (15)$$

Where R and T are the universal gas constant (8.314J/mol K) and the absolute temperature (K) , respectively and C_e is the equilibrium concentration of Pb(II). The plots of ln (q_e) against ε^2 (Figure 12) using Equation (14) for the BSAC at the range of temperatures considered are almost linear graphs with correlation coefficient range from 0.883 to 0.90. The D-R isotherm constants β and qm were calculated from the slopes and the intercepts of the plots respectively and were presented in Table 6. The mean free energy of adsorption (E) was calculated from the constant β using the relation in equation 16:

$$E = \sqrt{\frac{1}{2\beta}} \qquad (16)$$

It is defined as the free energy change when 1 mol of ion is transferred to the surface of the solid from infinity in solution. The values of E in this present study were found to be between 0.517- 0.675 kJ for all the temperature considered which is less than 8.kJ/mol indicating that the adsorption process is physical in nature.
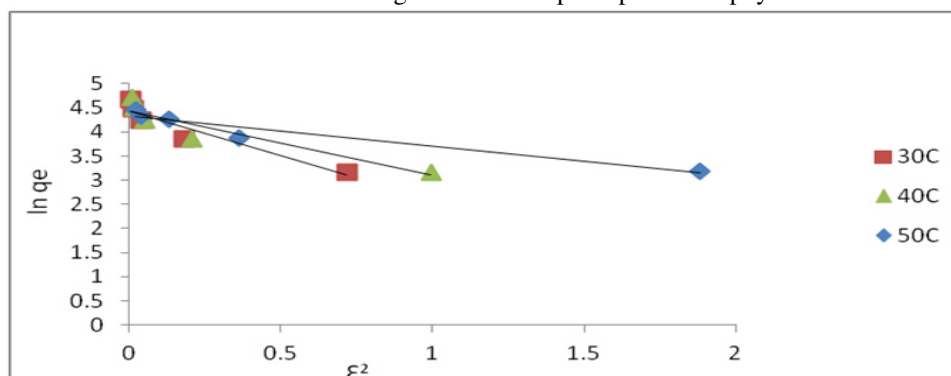

Figure 12: Dubinin–Radushkevich isotherm fitted to the batch equilibrium data of Pb(II) adsorption by BSAC

Table 6: Isotherm constant and correlation coefficient for the adsorption of lead (II) onto BSAC at different temperatures

Models	Temperatures		
	30°C	**40°C**	**50°C**
Langmuir isotherm			
q $_{max}$ (mg/g)	142.8600	166.6700	200.0000
k_L(L/mg)	0.0787	0.0800	0.0980
R_L	0.0509	0.0476	0.0392
R^2	0.9970	0.9950	0.9980
Freundlich isotherm			
k_F	16.4800	16.2900	16.7100
1/n	0.5420	0.5910	0.6240
N	1.8450	1.6920	1.6025
R^2	0.9620	0.9890	0.9890
Temkin isotherm			
A	0.8586	0.8511	0.8782
B	30.4600	33.4700	35.7900
B	0.0827	0.0778	0.0750
R^2	0.9980	0.9830	0.9840
Dubnin –Radushkevich isotherm			
q_o(mg/g)	84.8598	84.8400	86.4000
β (mol^2/kJ^2)	1.8650	1.3410	1.0980
E (kJ/mol)	0.5170	0.6106	0.6748
R^2	0.9000	0.8620	0.8550

Table 7: Comparison of adsorption capacities of activated carbons from various sources on Pb(II)

Adsorbent	Adsorptive capacity (Q_o in mgg^{-1})	Reference
Eichhornia	16.61	Shekinah *et al.*(2002)
Zeolites	121.95	Payne and Abdel-Fattah (2004)
Euphorbia rigida	279.72	Gercel and Gercel (2007)
Coconut and seed hull of the palm tree	4.56	Gueu *et al.*(2007)
Militia ferruginea plant leaves	3.30	Mengisite *et al.* (2008)
Eucalyptus camaldulensis Dehn. back	184.41	Patnukao *et al.* (2008)
Oil-palm fruit fibre	588.24	Bello *et al.*(2010)
Palm shell	1.34	Onundi *et al.* (2010)
Fluted pumpkin seed shell	14.29	Okoye *et al.* (2010)
Lignite	35.00	Rao *et al.*(2011)
Groundnut shell	86.25	Isah and Yusuf (2012)
Palmyra palm nut	142.85	Nwabanne, and Igbokwe (2012)
Waste biomass	476.20	Erdem *et al.* (2013),
Watermelon shell and walnut shell	126.80	Moreno-Barbosa *et al.*(2013)
Olive stone waste	22.37	Alslaibi *et al* (2013)
Carbon coated monolith	71.95	Teoh *et al.* (2013)
Marine green algae	22.93	Jeyakumar and Chandrasekaran (2014)
Banana stalk	200.00	This Study

3.8   *Thermodynamic study*

The thermodynamic parameters, which characterize the equilibrium state of a system, are the Gibbs free energy change (ΔG). The enthalpy change (ΔH) and the entropy change (ΔS). These parameters were determined to investigate the feasibility, spontaneity and the nature of the interaction of the adsorption process. This was achieved by using equation (17) to (20) (Faust and Aly, 1987):

$$K_c = \frac{C_{Ae}}{c_e} \qquad (17)$$

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \qquad (18)$$

$$\Delta G = -RT \ln K_c \qquad (19)$$

$$\Delta G = \Delta H - T\Delta S \qquad (20)$$

Where Kc is the equilibrium constant, Ce is the equilibrium concentration in solution (mg/l) and C_{Ae} is the solid-phase concentration at equilibrium (mg/l).ΔG, ΔH and ΔS are change in Gibbs, free energy, (kJ /mol),enthalpy(kJ mol) and entropy (kJ/ mol) of adsorption respectively. R is the universal gas constant (8.314 J/K/ mol) and t is the temperature (K). Batch adsorption studies were carried out with Pb (II) at varying temperature (30°C,40°C, 50°C) and optimum adsorbent dose. A Von't Hoff graph was plotted, taking ln(k) against 1/T (Figure 13) for initial concentration. Values of ΔH and ΔS were calculated from the slope and intercept of von't Hoff plots, respectively and is as presented in Table 8. From Table 8 the values of ΔG are negative for all the temperatures considered. The negative values of ΔG indicate that the adsorption of the Pb(II) on to BSAC was spontaneous and thermodynamically favoured. The positive value of ΔH suggested that the process is endothermic in nature and positive value of ΔS indicates that there was increased randomness at solid liquid interface during adsorption of lead onto BSAC, which increased with increase in initial Pb(II) concentration as shown on Table 8.
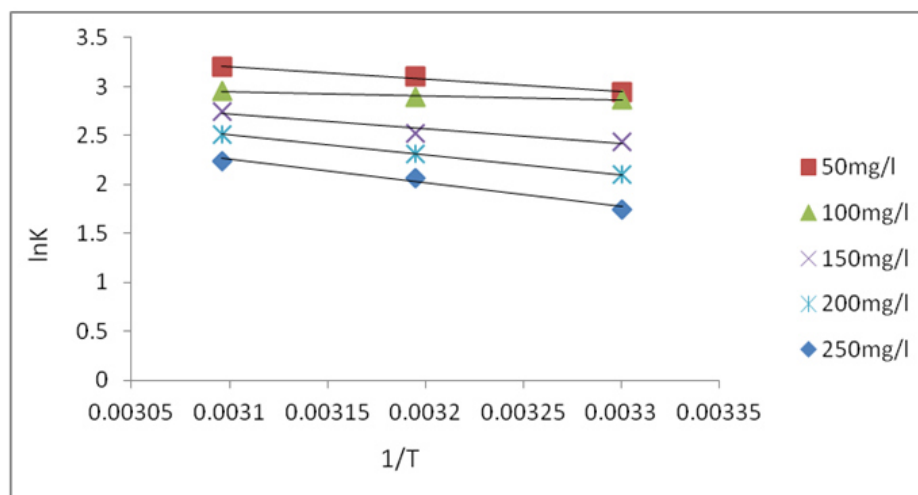
Figure 13: Von't Hoff plot for adsorption of Pb(II) by BSAC at different initial concentrations

Table 8 Thermodynamic parameter for the adsorption of Pb(II) onto BSAC at different   temperature

Parameter		Initial concentration				
		50mg/l	100mg/l	150mg/l	200mg/l	250mg/l
ΔH (kJ/mol)		10.185	3.509	12.513	16.678	20.054
ΔS (J/mol K)		59.014	35.360	61.400	72.510	80.930
	30°C	-7.697	-7.205	-6.091	-5.292	-4.468
ΔG (kJ/mol)	40°C	-8.287	-7.558	-6.705	-5.277	-5.277
	50°C	-8.877	-7.912	-7.319	-6.74	-6.086

4.0 Conclusions

BSAC produced from banana stalk possessed adequate adsorptive properties for Pb(II) removal from aqueous solution. The adsorption of Pb(II) onto BSAC depended on the initial Pb(II) concentration, temperature, contact time, pH and adsorbent dosage. Adsorption capacity decreased with increase in adsorbent dosage but increased with increase in initial Pb(II) concentration, contact time, temperature and pH. The maximum adsorption capacity was 200mg/g at pH (8) and 250mg/L initial concentration. The adsorption process was a fast kinetic process reaching equilibrium at 120minutes. The data were analyzed using pseudo first order, pseudo second order and intra particulate models, the result showed that the adsorption kinetic best fitted the pseudo second order model. Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherm models were used to analyze the equilibrium adsorption data, but the Langmuir isotherm model provided the best correlation (R^2) of 0.998. Thermodynamic parameters (ΔG, ΔH, and ΔS) showed that the adsorption process was spontaneous, endothermic and the randomness at the solid-solution interphase increased during the adsorption process. BSAC is efficient and effective in removing Pb(II) from its aqueous solution

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