

Full Length Research Paper

Preparation, characterization and adsorption performance of the KOH-activated carbons derived from kenaf fiber for lead (II) removal from waste water

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In this study, activated carbon was prepared from kenaf fiber (KF) by using physiochemical activation method consisting of potassium hydroxide (KOH) impregnation with carbon dioxide (CO₂) gasification. Pore structure and physical characteristics of the prepared activated carbon were determined. Adsorption studies for divalent lead (Pb) were carried out to delineate the effect of contact time, temperature, pH and initial metal ion concentration. About 93.23% of Pb (II) was removed from 100 mg/l solution at pH 5.5. The experimental data followed pseudo second order kinetics which confirms chemisorptions. The linear plots of intra particle diffusion demonstrated that, the adsorption process is mainly governed by pore diffusion. The values of Langmuir dimensionless constant, R_L and Freundlich constant, $1/n$ were less than 1 representing favorable process for adsorption. Thermodynamic parameters such as ΔG° , ΔH° and ΔS° which are related to Gibbs free energy, enthalpy and entropy were evaluated. The research concluded that activated carbon from kenaf fiber (KFAC) has sufficient porosities and surface area and it has got good potential to remove Pb (II) from waste water.

Key words: Kinetics, isotherm, lead, thermodynamics.

INTRODUCTION

The adsorption process has been shown to be highly efficient method for the removal of inorganic and organic pollutants from waste effluents. Commercially available granular and powdered activated carbon has been frequently employed for thousands of years in many adsorption processes for removal of impurities from liquids and gases due to its excellent adsorption properties. It consists of numerous graphites like microcrystalline unit which are similar to that of carbon black (Do, 1996). The effectiveness of activated carbon as an adsorbent is due to its versatile properties, including highly developed internal surface area between 500-2000 m²/gm, favorable pore size and high degree of surface reactivity due to presence of surface functional

groups, especially, oxygen groups (Ismadji and Bhatia, 2001). In spite of its' extensive use in waste water treatment, commercial activated carbon remains an expensive material. This has lead many researchers to find out cheaper source to prepare activated carbon. Previously coal, lignite and wood which are carbonaceous sources are commonly used precursors for production of activated carbon. Recently, agricultural by-products such as jackfruit peel (Prahas et al., 2008), coconut shell (Hu and Srinivasan, 1999), coffee bean husk (Baquero et al., 2003), oil palm fiber (Hameed et al., 2008), rubber wood sawdust (Srinivasakannan and Bakar, 2004), chestnut woods (Gomez- Serrano et al., 2005), fruit stone (Puziy et al., 2005), bamboo waste (Ahmed and Hameed, 2010), grain sorghum (Diao et al., 2002), rattan sawdust (Ahmed et al., 2009), cassava peel (Sudaryanto et al., 2006), olive seed waste (Stavropoulos et al., 2005) have been successfully used to produce activated carbon due to their high carbon and low ash

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content for different application.

However, adsorptive removal of heavy metals including lead from aqueous streams by using agricultural and industrial waste products which are abundant in nature and requires little processing has received much attention in recent years (Zuorro and Lavecchia, 2010). Several adsorbent derived from low cost material such as: *zea mays* Tassel (Caliphs et al., 2010), sea mussel and white clay (Sakulphaemaruehai et al., 2010), *Spirogyra neglecta* (Modher et al., 2009), dried activated sludge (Soltani et al., 2009), palm oil ash (Chowdhury et al., 2011a). for treating waste water at the solid-solution interface have been reported.

Earlier review of the literature reflects that several types of adsorbents have been used to prepare activated carbon or after some processing employed for removal of heavy metals from waste water. But until now, no attempts have been made to produce activated carbon from KF by physiochemical activation, illustrate its surface features and consequently explore its feasibility for removal of Pb (II) from waste water. Kenaf (*Hibiscus cannabinus* L.) has similar morphological features like cotton and jute. In Malaysia, the National Kenaf Research and Development Program has been started to produce kenaf due to its expanded application in different industrial sector. The government has allocated around 12 million RM (Aber et al., 2009) for further development of the kenaf-based industry under the 9th Malaysia Plan (2006 to 2010). This research aims to determine the adsorption mechanisms including reaction kinetics, isotherm studies and evaluation of thermodynamic parameters for the sorption process of Pb(II) cation onto KFAC.

MATERIALS AND METHODS

Preparation of activated carbon

Kenaf fibers used in this research are supplied by MARDI (Malaysian Agricultural Research and Development Institute). Preliminary washing of the fibers with hot distilled water is essential to remove dust like impurities and inorganic matters onto their surfaces. After that, it was dried at 105°C for 24 h to remove all moisture. The dried samples were easy to cut into small pieces and were sieved to the size of 1 to 2 mm. Then stored in air-tight containers to protect them from moisture build up and fungi infections. 40 g of dried fiber samples were placed on the metal mesh located at the bottom of the tubular reactor under 150 cm³/min flow rate of purified nitrogen gas. During this period of semi carbonization, the heating rate was kept constant at 10°C/min respectively. The temperature was increased from room temperature to 400°C and kept constant for 2 h. The char thus produced was allowed to cool down at room temperature under nitrogen flow at the same flow rate and stored in air-tight containers. The impregnation ratio (IR) of 1.4 was used to prepare KFAC from the char. The specific amount of KOH pellets were crushed together with 40 g of char and 250 ml deionized water was added slowly in a 500 ml beaker with occasional stirring to dissolve all fragments of KOH pellets. The beaker containing char mixed with KOH and water was placed inside an oven overnight at temperature 105°C for dehydrating purpose. After the water is

evaporated it will leave behind only KOH onto the sample. The impregnation ratio was calculated by using equation (1):

$$\text{Impregnation ratio (IR)} = \frac{W_{\text{KOH}}}{W_{\text{Char}}} \quad (1)$$

Here, W_{KOH} is the dry weight of potassium hydroxide pellets and W_{char} is the dry weight of char.

Exactly weighted amount of KOH impregnated chars were placed inside the tubular furnace with nitrogen gas flow rate of 150 cm³/min and heating rate of 10°C/min. The temperature was increased from room temperature to 700°C. Once the activation temperature of 700°C was reached, the gas flow was switched to carbon dioxide at the same flow rate and kept constant for 1 h. The prepared activated carbon was cooled to room temperature under nitrogen gas flow maintaining the same flow rate mentioned above. Then the final product obtained was washed with hot deionized water for several times to remove remaining KOH. During the washing process, 0.1 M hydrochloric acid (HCl) was used until the pH of the washing solution reached to 6 to 7. The washed samples of activated carbon was dried at 105°C in an oven until it was completely dried and stored in air-tight container for further applications.

Preparation of stock solution

Lead (II) nitrate, Pb(NO₃)₂, sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Merck, Germany. Stock solution of Pb(NO₃)₂ having concentration of about 1000 mg/l was prepared by using double distilled water. Various concentrations of test solution of Pb(II) ranging from 50 mg/l to 100 mg/l were prepared by subsequent dilution of the stock solution while the initial pH was adjusted to 5.5 using a pH meter (Mettles Toledo, Model: Ross FE 20, USA). Fresh dilution of the stock solution was prepared for each adsorption study.

Batch adsorption study

Each of the batch experiment was carried out by adding 0.2 gm of KFAC with 50 ml of different concentration of Pb (II) solution at 150 rpm. The residual concentration of Pb (II) was analyzed after predetermined interval of time until the system reached equilibrium by using atomic absorption spectrophotometer (Perkin Elmer Model 3100).

For isotherm studies each experiment was carried out at 30°C in a thermo regulated water bath (Haake Wia Model, Japan) with shaker cover in order to prevent heat loss to the surroundings. The equilibrium adsorption amount (q_e) was calculated according to equation (2):

$$q_e = \frac{(C_i - C_e)}{W} V \quad (2)$$

Here, q_e represents the adsorption amount of metal ion (mg/g) at equilibrium contact time, W denotes the weight of adsorbent (g), and V is the volume of solution (ml). The removal efficiency of the metal ion was calculated by using following equation (3):

$$\text{Removal\%} = \frac{C_i - C_e}{C_i} \times 100 \quad (3)$$

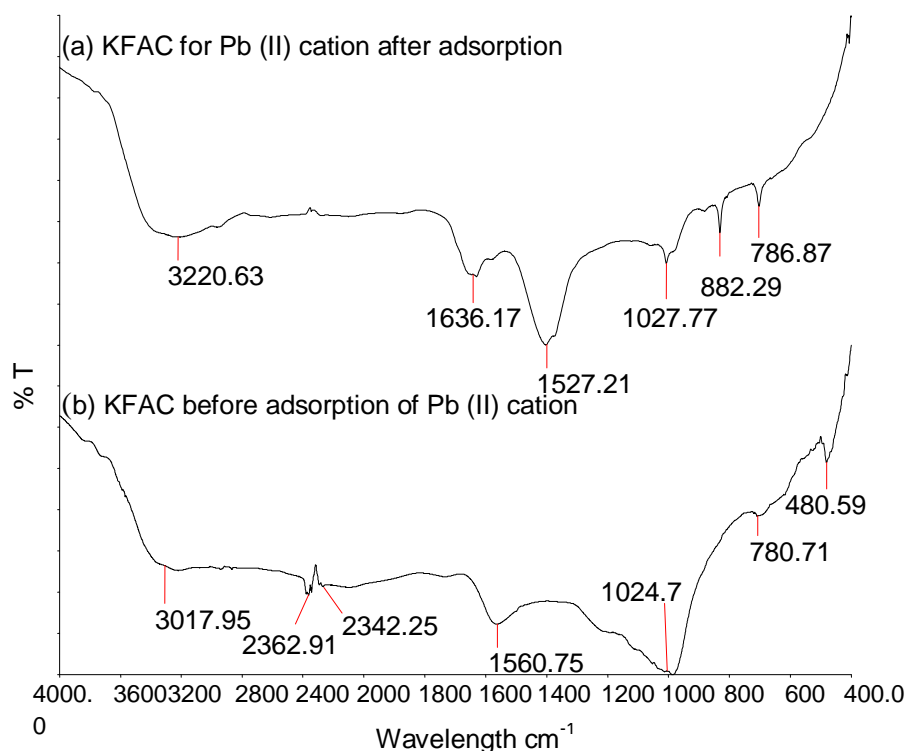


Figure 1. FTIR spectra of KFAC before and after adsorption of Pb (II) cation.

Physiochemical characterization of KFAC

Scanning electron microscope (Model Leo Supra 50VP Field Emission, UK) was used to study the pore structure and morphological features of KFAC. Surface area, pore volume and pore diameter of the prepared adsorbent was measured by Autosorb1, Quantachrome Autosorb Automated gas sorption system supplied by Quantachrome. Before performing the nitrogen gas adsorption, the activated carbon was outgassed under vacuum at temperature 300°C for 4 hours to remove any moisture content from the solid surface. Surface area and pore volume were calculated by Brunauer Emmett Teller (BET). Aforementioned procedure was automatically performed by software (Micropore version 2.26) available with the instrument. The surface functional group of the KFAC was detected by Fourier Transform Infrared (FTIR) spectroscope (FTIR-2000, PerkinElmer). The spectra were recorded from 4000 to 400 cm^{-1} .

RESULTS

Surface characterization of KFAC

FT-IR spectrum is an essential tool to identify the surface functional groups which can contribute significantly to enhance absorption efficiency of the activated carbon by surface complexation. Figure 1 shows the FTIR spectra of activated carbon before and after adsorption of lead from aqueous phase. Table 1 listed the major peaks recorded for both the sample. It clearly shows that many functional groups shifted or disappeared after adsorption

revealing possible involvement of those groups for uptake of Pb(II) cations.

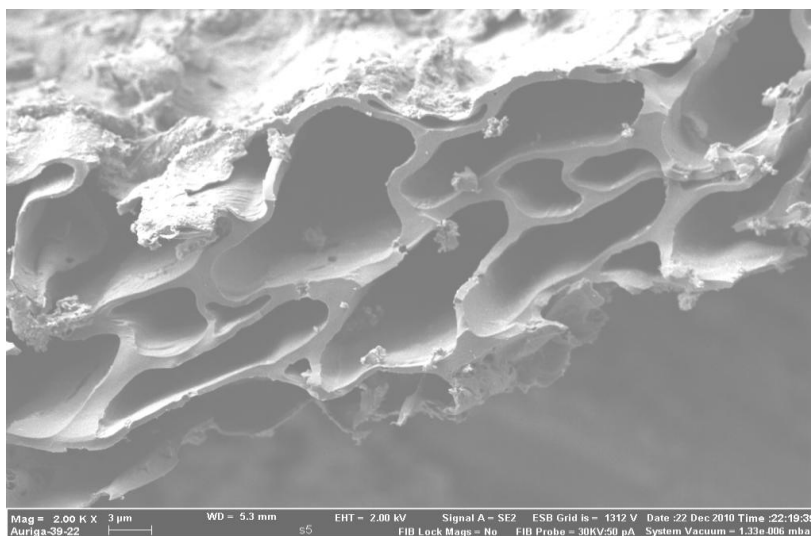
The porous texture of KFAC sample obtained from SEM image is shown in Figure 2. The figure clearly reveals that, significant number of pores with different structure was produced due to physiochemical activation of the raw fiber. It shows that the physiochemical activation process by using KOH and CO_2 was effective in creating well-developed pores on the surfaces having well defined walls surrounding the pores.

The SEM micrograph indicated that, the pore structure was made up of cylinder like tubes. The results were in agreement with the previous observation reported by the researchers for preparation of activated carbons from pistachio-nut shells, jute and coconut fiber (Lua and Yang, 2004; Phan et al., 2006).

The phenomenon of adsorption is mainly dependent on the surface area and pore size distribution and surface functional groups anchored onto it. The BET surface area of the prepared activated carbon was found 525.5 m^2/g . The Langmuir surface area was 624.4 m^2/g . It was found that the total pore volume was 0.322 cm^3/g with micro pore surface area of 610.2 m^2/g . However, according to the IUPAC classification, the average pore diameter of 2.49 \AA represents that the prepared activated carbon is of mesoporous type. BET surface area and total pore volumes increased significantly as the

Table 1. Analysis of FTIR spectra of KFAC before and after adsorption.

IR peak	Frequency (cm ⁻¹)		Peak Assignment
	Before adsorption	After adsorption	
1	480.59	-	C-H out-of-plane bending of benzene derivatives
2	780.71	786.87	C-H out-of-plane bending of benzene derivatives
3	-	882.29	C-H out-of-plane bending of benzene derivatives
4	1024.71	1027.77	C-O-C stretching of esters, ethyl or phenol groups
5	1560.75	1527.21	C=C ring stretching of benzene derivatives
6	-	1636.17	C=O stretching
7	2342.25	-	C=C stretching of -COOH group
8	2362.91	-	C=C stretching of -COOH group
9	3017.95	3220.63	O-H stretching vibration of hydroxyl functional groups including hydrogen bonding

**Figure 2.** SEM image of KFAC prepared for Pb (II) sorption.

activation process involved both chemical and physical activating agents of KOH and CO₂. However, the intermediate step of semi carbonization was important since it can enhance the distribution of KOH and CO₂ molecules into the pores and thus can enlarge the BET surface area and volume of the pore. Nevertheless, KOH is acting here as a dehydrating agent and during activation it can form K₂O which can react with CO₂ to produce K₂CO₃ by water shift reaction (Salman and Hameed, 2010). Mainly, intercalation of metallic potassium is the key factor for drastic expansion of surface area, pore volume and diameter of the prepared activated carbon from kenaf fiber.

Batch adsorption study

Figure 3 shows the effect of initial Pb(II) ion concentration

and uptake with equilibrium contact time. It can be visualized from the graph that, the amount of uptake q_t (mg/gm) increased with increasing contact time and after certain period of time; it reached to a constant value beyond which no further adsorption was observed. The trend of the graph showed that, the adsorption was fast at initial stage of contact period and after that when it was approaching towards the equilibrium time, it became relatively slower. The rate of uptake was initially high due to the availability of larger surface area of KFAC for adsorption. With the lapse of time, the surface adsorption sites were already occupied. The remaining vacant sites were difficult to be captured by residual Pb(II) ions due to repulsive forces between cations present in solid and bulk phases.

As the concentration of the cation was increasing, the sorption capacity by the prepared activated carbon was also increasing. The plot reflects that, very quick

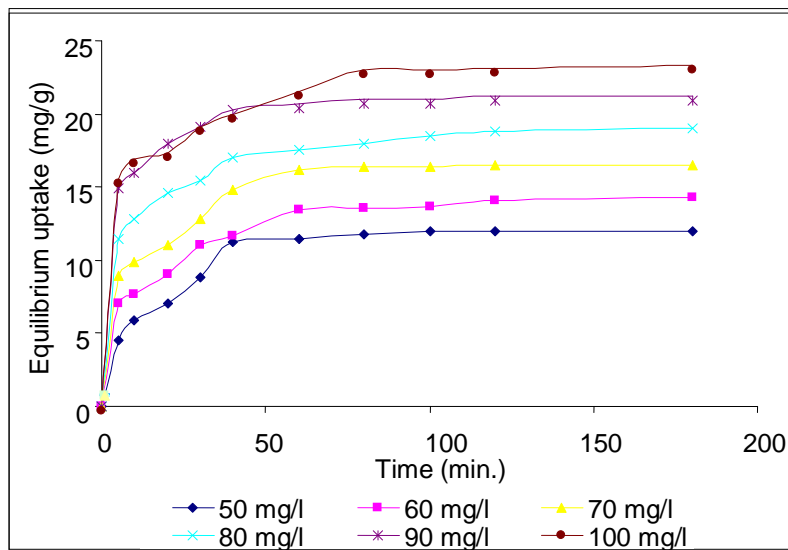


Figure 3. Effect of initial metal ion concentration on equilibrium uptake (mg/g) of Pb (II) cation from solution at 30°C temperature.

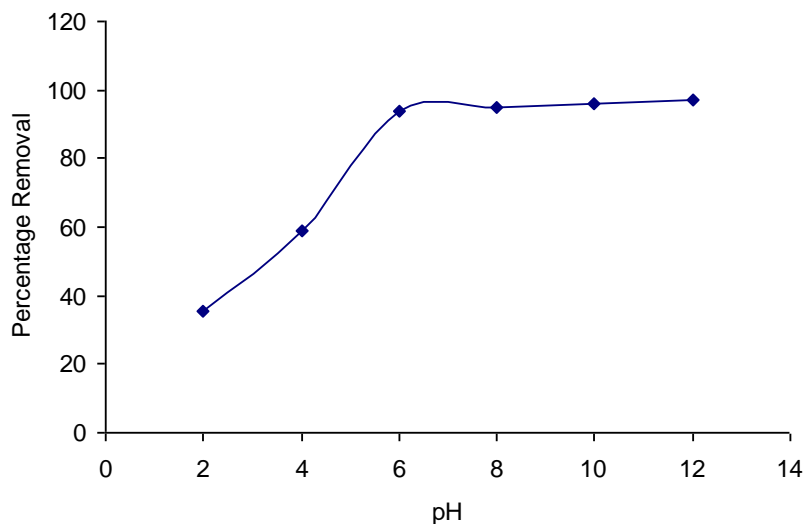


Figure 4. Effect of pH on of equilibrium uptake (mg/g) of Pb (II) cation from solution at 30°C temperature.

equilibrium of 60 min. was required for lower concentration range of 50 to 70 mg/l solution. On the other hand, almost within 80 min. the higher concentrated solution reached equilibrium and after that the adsorption did not change significantly. The experimental data were measured for 180 min. to ensure that full equilibrium was attained.

pH of the medium plays significant role in adsorption process. In order to study the effect of pH on uptake, the solution pH was varied from 2 to 12, while keeping the other variable constant. The bar graph in Figure 4 depicts the effect of pH on removal percentage of lead by

KFAC. It was found that adsorption of Pb(II) ions from aqueous solution was strongly pH dependent. At pH 2 the adsorption was reasonably low around 35.23% and it rapidly increased between pH 5 to 8 resulting greater removal efficiency. The maximum removal percentage obtained was 96.98% at pH 12. At pH less than 4, H^+ and H_3O^+ exist into the solution and they compete with positive metal ions for active binding sites on the surface of KFAC, which leads to fewer binding sites being available to bind Pb(II) ions resulting lower removal efficiency. As the pH increases, there were fewer numbers of H^+ and H_3O^+ available, the surface became

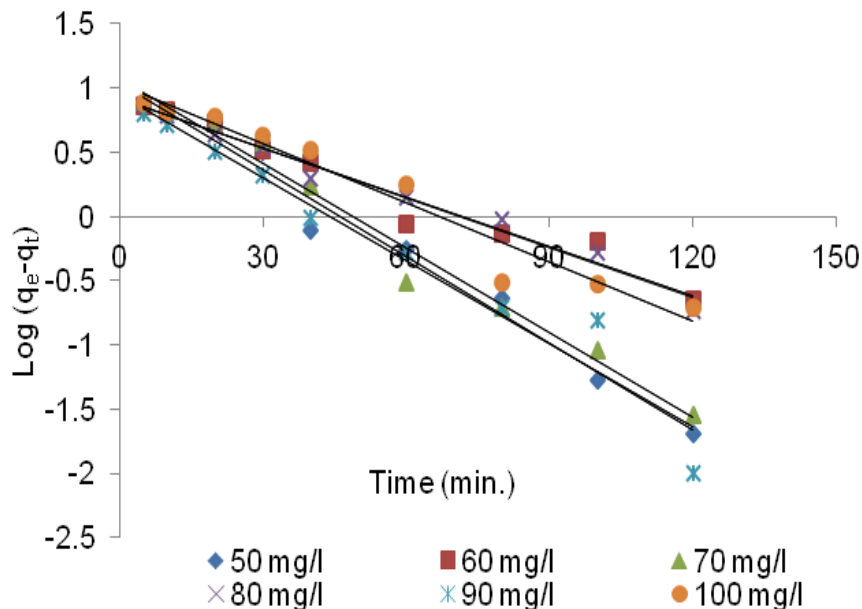


Figure 5. Pseudo-First Order Kinetics for adsorption of Pb (II) cation onto KFAC at 30°C temperature.

negative resulting greater electrostatic attraction between Pb(II) ions and the surface of KFAC.

Thus, the removal efficiency was increased between pH 4 to 12. However, it is well known that at basic pH heavy metals like Pb(II) starts to precipitate. Therefore to avoid collective effect of adsorption and precipitation, all the batch experiments were conducted in slightly acidic medium of pH 5.5.

DISCUSSION

Equilibrium kinetics study

For any adsorption system, study of chemical kinetics is very important so as to determine the rate constants for the reaction and to know how quickly or slowly the reaction is proceeding. In order to evaluate the kinetic parameters, Pseudo first order and Pseudo second order models were implemented to analyze the experimental data. The pseudo first order equation (Ong et al., 2010) can be expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (4)$$

Here, q_e and q_t represent the amount of adsorbed (mg/g) at equilibrium and at any time t , K_1 is the first order rate constant (min^{-1}). From the plots of $\log(q_e - q_t)$ versus t (Figure 5), K_1 can be calculated from the slope and theoretical q_e can be obtained from intercepts. Pseudo

second order equation can be given by (Sahu et al., 2010):

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

Here, K_2 is the rate constant of second order adsorption. The linear plots of t/q_t versus t determine $1/q_e$ as slope and $1/K_2 q_e^2$ as intercepts. The linear plots of pseudo second order model is shown in Figure 6.

The prediction of the rate-limiting step is a key factor to have insight about the adsorption mechanism. The most commonly used technique for identifying the mechanism involved in the adsorption process is by fitting experimental data with the intraparticle diffusion plot (Weber and Morris, 1962). The intraparticle diffusion coefficient K_{id} can be calculated by the equation:

$$q_t = K_{id} t^{0.5} \quad (6)$$

The plot of q_t versus $t^{0.5}$ is shown by Figure 7.

The slope of the plot has been defined to yield the intraparticle diffusion parameter K_{id} ($\text{mg/g-hour}^{0.5}$). On the other hand, the intercept of the plot reveals C , the boundary layer effect. It is assumed that, the larger the intercept, the greater the contribution of the surface sorption in the rate-controlling step. The calculated intraparticle diffusion coefficient K_{id} values are listed in Table 3.

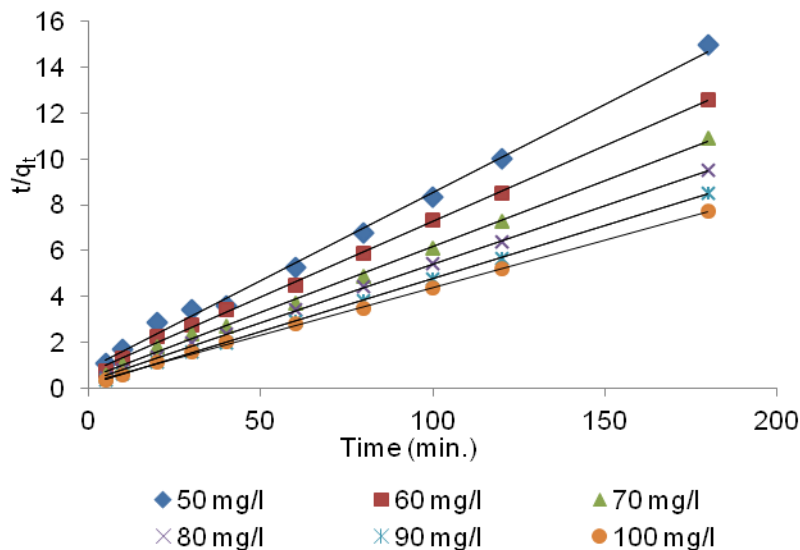


Figure 6. Pseudo-Second Order Kinetics for adsorption of Pb (II) cation onto KFAC at 30° C temperature.

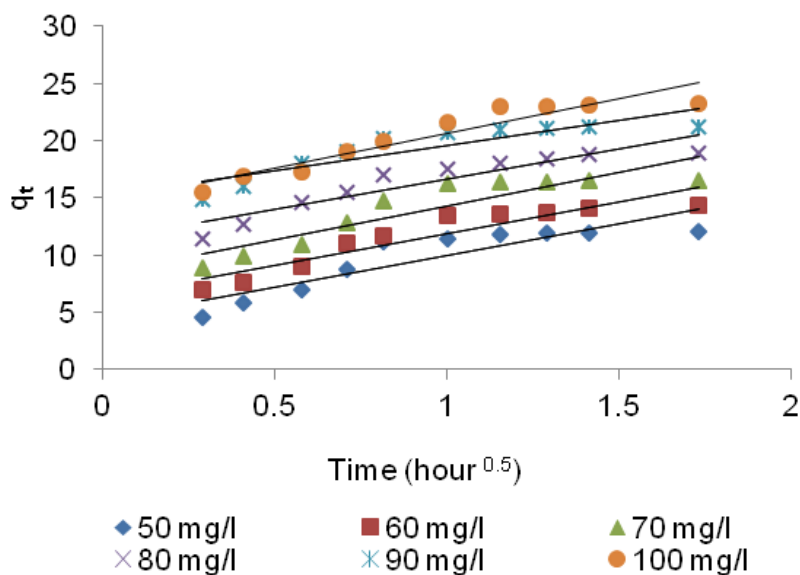


Figure 7. Intra-particle diffusion rate studies for adsorption of Pb (II) cation onto KFAC at 30°C temperature.

The correlation coefficient, R^2 of pseudo first order kinetics were between 0.95 to 0.98 but the calculated q_e (mg/g) values obtained from Pseudo first order kinetics did not agree well with the experimental q_e (mg/g) values. Thus it can be concluded that it is not appropriate to use the Pseudo first order kinetic model to predict the adsorption kinetics for Pb(II) onto KFAC for the entire sorption period.

On the contrary, the correlation coefficient, R^2 for the second order kinetic model were almost equal to unity for all the concentrations signifying the applicability of the

model. Moreover, the calculated q_e (mg/g) values obtained from Pseudo second order kinetics were in good agreement with the experimental q_e (mg/g) values. Thus it appeared that the system under study is more suitably described by pseudo second order kinetics which was based on the assumption that the rate limiting step may be chemisorptions concerning valency forces through sharing and exchange of electrons.

The plots of intra-particle diffusion showed that, the lines did not pass through the origin. This implied that the rate limiting process is not only governed by intra particle

Table 2. Comparison of pseudo-first order and pseudo-second order adsorption rate constant for different initial concentration at 30° C temperature.

C ₀ (mg/l)	Pseudo-first order kinetics				Pseudo-second order Kinetics		
	q _e (exp) (mg/g)	q _e (cal) (mg/g)	K ₁ (min ⁻¹)	R ²	q _e (cal) (mg/g)	K ₂ (min ⁻¹)	R ²
50	12.010	11.0918	0.05066	0.982	12.9870	0.00714	0.996
60	14.305	8.27942	0.02764	0.965	15.1515	0.00670	0.998
70	16.528	11.8304	0.04836	0.980	17.5439	0.00763	0.997
80	18.965	8.26040	0.02764	0.982	19.6078	0.00845	0.999
90	21.198	8.87156	0.04836	0.952	21.7391	0.00469	0.999
100	23.308	10.6905	0.03455	0.954	24.3902	0.00695	0.998

Table 3. Intra particle diffusion parameter at different initial concentration.

Initial concentration (mg/L)	C	K _{dif} (mg/gh ^{0.5})	Correlation coefficient, R ²
50	4.502	5.500	0.785
60	6.326	5.553	0.868
70	8.363	5.934	0.818
80	11.31	5.310	0.870
90	15.20	4.393	0.778
100	14.63	4.393	0.899

diffusion. Some other mechanism along with intraparticle diffusion was involved for the whole sorption process (Kalavathy et al., 2005).

Equilibrium isotherm study

Isotherm studies are essential to interpret the adsorption process adequately. The most commonly used isotherm models proposed by the researchers for explaining solid-liquid adsorption are the Langmuir, Freundlich, and Temkin isotherms. The Langmuir isotherm is based on monolayer adsorption and it assumes constant heat of adsorption for all the active sites present on the adsorbent (Langmuir 1918) and it is expressed by following equation:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \quad (7)$$

The linear form of the Langmuir isotherm can be given by:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{1}{q_{\max}} C_e \quad (8)$$

Where, q_e denotes the equilibrium cation concentration

on the adsorbent (mg/g), C_e is the equilibrium cation concentration in liquid phase (mg/l), q_{\max} reflects the maximum monolayer adsorption capacity of the adsorbent (mg/g), and K_L is the Langmuir adsorption constant (l/mg). When C_e/q_e is plotted against C_e , a straight line with slope $1/q_{\max}$ and intercept of $1/q_{\max} K_L$ is obtained. The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless factor, R_L which is given as:

$$R_L = \frac{1}{1 + K_L C_o} \quad (9)$$

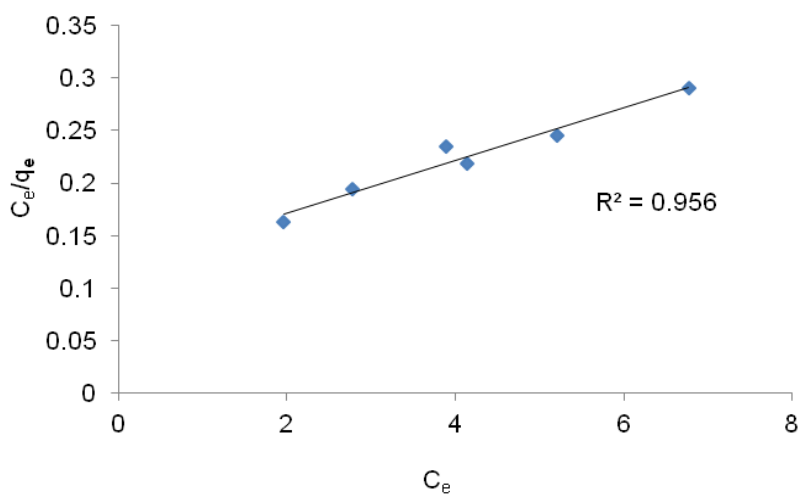
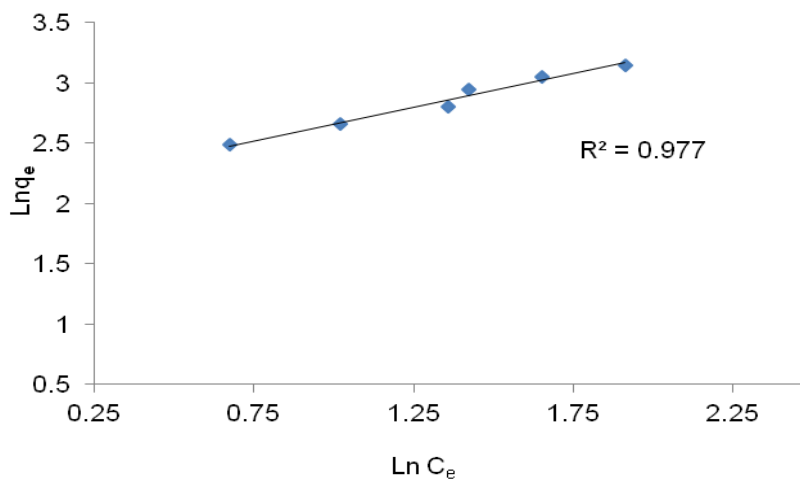
Where, C_o is the highest initial cation concentration (mg/l). The values of separation factor R_L can be summarized as shown in Table 4. The linear plot of Langmuir Isotherm at 30°C temperature is shown by Figure 8.

Freundlich isotherm gives the relationship between equilibrium liquid and solid phase capacity based on the multilayer adsorption properties consisting of heterogeneous surface of the adsorbent. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption (Freundlich 1906) and is expressed by:

$$q_e = K_f C_e^{1/n} \quad (10)$$

Table 4. Separation factor.

Value of R_L	Types of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

**Figure 8.** Langmuir Isotherm for adsorption of Pb (II) cation onto KFAC at 30° C temperature.**Figure 9.** Freundlich Isotherm for adsorption of Pb (II) cation onto KFAC at 30° C temperature.

The linear form of Freundlich isotherm is;

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (11)$$

Here, K_f (mg/g) and $1/n$ represent the multilayer adsorption capacity and intensity of adsorption respectively. The linear plot of Freundlich Isotherm at 30°C temperature is shown in Figure 9.

According to Temkin isotherm, the effects of the heat of

Table 5. Isotherm model parameters at 30°C, 50°C and 70°C temperature.

Temp. °C	Langmuir isotherm				Freundlich isotherm			Temkin isotherm		
	q_{\max} (mg/g)	K_L (l/mg)	R_L	R^2	K_F (mg/g) (l/mg) ^{1/n}	1/n	R^2	B	K_T (l/mg)	R^2
30	40.00	0.2066	0.05	0.956	8.190	0.557	0.977	9.469	1.70	0.967
50	37.04	0.3333	0.03	0.899	10.49	0.483	0.947	8.232	3.07	0.909
70	38.46	0.3250	0.03	0.839	10.51	0.509	0.929	8.631	2.95	0.874

Table 6. Thermodynamic parameters of Pb (II) sorption onto KFAC.

Temperature, °K °K	ΔG° (Kj-mol ⁻¹)	ΔH° (Kj-mol ⁻¹)	ΔS° (jK ⁻¹ mol ⁻¹)
303	-3.9726	10.02	0.2056
323	-2.9505		
343	-3.2051		

adsorption of all molecules in the layer would decline linearly with coverage due to the adsorbate and adsorbent interactions (Temkin and Pyzhev, 1940) and is expressed by:

$$q_e = \frac{RT}{b} \ln K_T C_e \quad (12)$$

Equation 11 can be linearized as:

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \quad (13)$$

Here, $RT/b = B$ (j/mol), which is Temkin constant related to heat of sorption whereas K_T (L/g) represents the equilibrium binding constant corresponding to the maximum binding energy. R (8.314 J/mol k) is universal gas constant and T° (K) is absolute solution temperature. However, present investigation attempted to analyze the above mentioned isotherm parameters at 30°, 50° and 70° C and the model parameters are listed in Table 5.

The validity of the Langmuir model here, recommended that the adsorption process was monolayer (Pruksathorn and Vitidsant, 2009) and adsorption of each molecule had equal activation energy. The R_L value obtained is between 0 to 1 indicating that the adsorption of Pb(II) onto KFAC is favorable. The Langmuir model was found to fit the data significantly better than Freundlich model, which showed the more homogeneous nature of KFAC. Freundlich exponent, $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity. The value $1/n$ below one reflects favorable adsorption of Pb(II) onto KFAC. The experimental data were further fitted with Temkin isotherm which showed a higher

regression coefficient, revealing the linear dependence of heat of adsorption at low or medium coverage. This linearity may be owing to repulsive forces between adsorbate species or for the intrinsic surface heterogeneity of KFAC. The regression coefficient of these models showed a strong affinity for the adsorption of Pb(II) onto KFAC.

Thermodynamic characterization

The thermodynamic parameters related to ΔG° , Gibbs free energy, ΔH° , change in enthalpy of reaction and ΔS° , change in entropy of adsorbate-adsorbent reaction can be calculated by using following equations:

$$\ln K_L = \frac{S}{R} - \frac{H}{RT} \quad (14)$$

$$\Delta G = RT \ln K_L \quad (15)$$

Here, K_L (l/mg) is the constant obtained from Langmuir Isotherm at different temperature; R is universal gas constant (8.314 j/ mol. K) and T is absolute temperature in Kelvin. The values of ΔH° and ΔS° can be determined from the graph of $\ln K_L$ versus $1/T$. However, the calculated values of thermodynamic parameters are listed in Table 6.

The value of enthalpy change, ΔH° obtained here is 10.02 kJ/mol. The positive value of enthalpy change confirms the endothermic nature of the adsorption process. The positive value of entropy, ΔS° represents an increase in the degree of freedom of the adsorbed species. The positive value of ΔS° also reflects that some changes occur in the internal structure of KFAC during

the adsorption process. Similar types of observation were reported previously for removal of lead from waste water by using activated palm ash (Chowdhury et al., 2011b). The magnitude of Gibbs free energy change, ΔG° obtained is negative demonstrating that the adsorption is rapid and spontaneous. The negative value of ΔG° ensures the feasibility of the process.

Conclusion

This study investigated the adsorption of Pb(II) from aqueous solution using activated carbon prepared from kenaf fiber by physiochemical activation method. The experiments were carried out at initial pH of 5.5 of the solution to ensure true adsorption. The adsorption was found to be strongly influenced by pH, contact time and initial metal ion concentration. However, the ability of KFAC to adsorb is the accumulated result of a number of mechanisms, including surface adsorption, chemisorptions, complexation, ion exchange, micro precipitation and metal hydroxide complexation. Pseudo second order gave better R^2 values confirming chemisorptions onto the surface. Equilibrium attained very quickly within 80 minutes. Both Freundlich and Langmuir model can be used to fit the data and estimate model parameters but the overall data is slightly better fitted by Freundlich isotherm at the studied temperature range reflecting surface heterogeneity of KFAC. The result indicates that, the findings will be helpful up to a great extent for treating Pb(II) contaminated effluents and at the same time it is economically feasible and environmentally friendly material which can be employed successfully for separation of Pb(II) in industrial scale.

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