Full Length Research Paper

Lead removal in aqueous solution by activated carbons prepared from *Cola edulis* shell (Alocacée), *Pentaclethra macrophylla* husk (Mimosaceae) and *Aucoumea klaineana* sawdust (Burseraceae)

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Three activated carbons prepared from vegetable matters of Gabonese biomass are being investigated as adsorbents for the removal of Pb (II) ions from aqueous solutions by means of batch technique. The equilibrium adsorption level was determined to be a function of pH, contact time, temperature and adsorbent dosage. The experimental adsorption data are well applicable to both Freundlich and Langmuir models with the correlation coefficients higher than 0.9. The adsorption process followed the pseudo second order kinetics ($R^2 > 0.9$). The enthalpy change [ΔH = 41.237 kJ for activated carbon prepared from *Cola edulis* shell (CAo°), -3.963 kJ/mol for activated carbon prepared from *Pentaclethra macrophylla* husk (GAo) and -1.6 kJ/mol for activated carbon prepared from *Aucoumea klaineana* sawdust (QAo)] implied that the adsorption was endothermic and exothermic for CAo and GAo or QAo, respectively.

Key words: Vegetable carbons, surface functional group, adsorption capacity, Pb(II) ions, isotherms.

INTRODUCTION

Lead is a highly toxic heavy metal which adversely affects the red blood cells of the human's nervous system and kidneys (Potgieter et al., 2006). It has become one of the major environmental pollutants (Susmita et al., 2005) because of its presence in the atmosphere as gases, generated from combustion of fuel lead content, in waters and soils through the effluents of lead smelting, mining and battery manufacturing, paint, paper and pulp industries. It is necessary for lead to be removed before the wastewaters are reversed to the rivers.

The treatment of rich heavy metals aqueous solutions is realizable using many methods such as: ion exchange, chemical precipitation, ultra filtration and electrochemical deposition, among which adsorption on activated carbons is one of the most efficient in terms of simplicity, feasibility, low consumption of energy and high level in

heavy metals adsorption. The activated carbons have been previously used to remove lead from aqueous effluents. Mostafa (1997), Gomez et al. (1998) and Gueu et al. (2007) used activated carbons from coconut shell and seed hull of the palm tree to adsorb 4.38 and 3.77 mg/g of Pb(II) ions from aqueous solution at 60°C, respectively. Sekar et al. (2004) showed that an activated carbon of coconut shell allows the uptake of 26.5 mg/g of lead from aqueous solution at 65°C.

The purpose of this study is to investigate the possible use of *Cola edulis* shell, *Pentaclethra macrophylla* husk and *Aucoumea klaineana* sawdust activated carbons for lead removal, with reference to isothermal, thermodynamic and kinetics of the adsorption process.

MATERIALS AND METHODS

Activated carbons preparation

In this study, activated carbons are prepared in one step only. It

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consists of heating and cleaning of the small hydrated pieces of wood at 700°C for 5 h. Then, the activated carbon was cooled in a desiccator (Avom et al., 2001; Mukana and Kifuana, 2000; Guo and Luo, 1998; Hussein et al., 1996). CAo represents the sample obtained from *Cola edulis* (Alocacée) shell, while GAo and QAo were obtained from *Pentaclethra macrophylla* (Mimosaceae) husk and *Aucouméa klaineana* (Burseraceae) sawdust, respectively (Raponda-Walker and Sillans, 2003).

Activated carbon characterization

Acidity groups on the surface

The acid groups covering the carbon surface were quantified by using Bohem (1994) titration method, which was widely employed in works on activated carbon. For this study, the bases used are sodium hydroxide (NaOH), sodium hydrogen carbonate (NaHCO$_3$) and sodium carbonate (Na$_2$CO$_3$). The following procedure is described by Rockstraw (2000).

Surface area

It was performed according to the method of methylene blue adsorption described by Santamarina et al. (2002).

Ash content

This analysis was performed according to an ASTM method (American Standard Method Technology). Each sample was charred at 750°C in the calcinations furnace until no further weight loss was detectable. The samples were weighed before and after calcinations. The ash content for each sample was calculated according to the following formula:

$$\text{Ash content} = \frac{m_1 - m_2}{m_1} \times 100 \qquad (1)$$

m_1 and m_2 is the weight of the sample before and after calcinations, respectively.

After cooling, the samples were then crushed and the fraction passing through a tamis of 63 µm were used in the adsorption experiments.

Chemical reagent

The analytical grade salt of Pb(NO$_3$)$_2$ (Prolabo) was used without further purification. All the experiments employed the de-ionised water.

Instrumentation

An atomic absorption spectrometer GBC AAS AVANTA AES was employed to measure residual Pb (II) concentrations with uncertainty of 1 mg/L. The pH of the solution was measured with a Tacussel pHmeter model (mini 80) using a glass electrode with an uncertainty of 0.01. The water-bath bioblock scientific model 18201 was used to control the temperature with an uncertainly of 0.1°C. An analytical balance model Mettler Toledo (PB 602-5) was used for weighing the activated carbons and Pb salt samples with an uncertainty of 0.1 mg. The temperature of activation was obtained with an incertitude of 3°C by using bioblock furnace model Nobertherm.

Adsorption procedure

The known amounts of activated carbons were placed in different Erlenmeyer glass flasks of 250 ml capacity, containing 50 ml of Pb (II) ions solution of the known concentration and pH. All experiments were carried out at pH 6 (except when the effect of pH was studied). The solutions were shaken vigorously for a given time period to reach equilibrium. The agitation speed was kept constant for each run to ensure equal mixing. After completion of a pre-selected shaking time, the flasks containing the sample were withdrawn from the shaker, while the suspension was then filtered using filter paper, and the supernatant solution in each flask was analyzed by an atomic spectrometer for its residual Pb content. The experiments were carried out by varying the pH of the solution, the initial concentration of Pb (II), the amount of the adsorbent, the interaction time adsorbent-adsorbate and temperature.

Calculations

The amount of adsorbed Pb (II) ions (qt) was calculated using the equation:

$$q_t = \frac{C_0 - C_t}{m} \times v \qquad (2)$$

where C$_o$ and C$_t$ are the initials, and at any interaction time, the concentration of Pb(II) ions solution (v and m) are the volume of Pb(II) ions solution and the mass of the activated carbon in the suspension, respectively.

RESULTS AND DISCUSSION

Activated carbon characterization

According to the data presented in Table 1, the rates of ash remain relatively weak (lower than 5%), that is, the characteristics of carbon obtained from vegetable matters constitute an advantage from the point of view of their use in the wastewater treatment. The sample of CAo is more porous, because it has weaker ash content and also a relative higher surface area, with the essential parameter for the adsorbent activity of the activated carbon as it was reported by Gueu et al. (2007). The acidity neutralized by NaHCO$_3$, on the surface of carbon CAo, GAo and QAo are 0.225, 0.125 and 0.1 meq/g, respectively. This indicates the presence of the carboxylic groups to the surface of coals, which can play a significant role in adsorption. The neutralization of the acids on the surface with NaOH and Na$_2$CO$_3$, translated the presence of the functional group, such as –OH, -C = O and -COOH (Boehm, 1994). The values of the obtained surface area are relatively weak in comparison with those given in the literature (Mukana and Kifuana, 2000).

Table 1. Characteristics of the activated carbon.

Activated carbons	Ash (%)	Acidity neutralizations (meq/L)			Surface area (m^2/g)
		NaOH	NaHCO$_3$	Na$_2$CO$_3$	
CAo	1.3	0.8	0.225	0.2	46.27
GAo	4.6	0.9	0.125	0.175	30.749
QAo	3.17	0.875	0.1	0.15	46.65
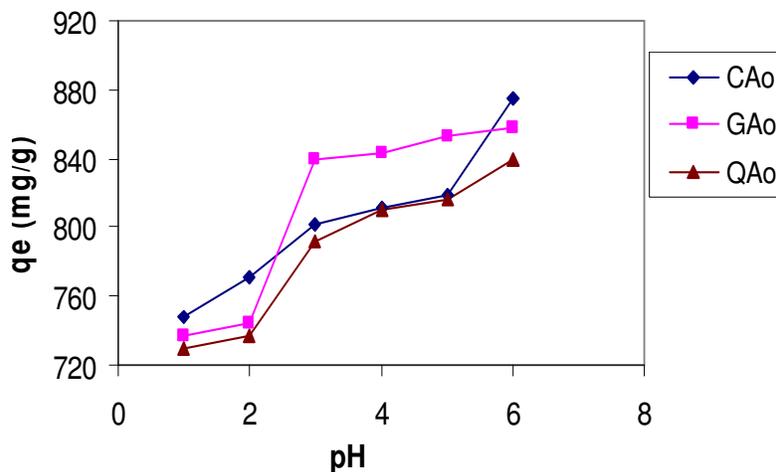
Figure 1. Amounts of Pb(II) ions adsorbed per unit mass (qe) on activated carbons at different pH (308K, interaction time 120 min, initial Pb(II) ions concentration 2000 mg/L, activated carbon 2000 mg/L).

Effect of the solution pH

According to Figure 1, the adsorption of Pb (II) ions on CAo increased continuously in the pH ranges (1 to 6) that were investigated. Those of GAo and QAo increase slowly from pH 1 to 3, substantially from pH 3 to 6. It seems that the amount of adsorption (qe) is affected by the surface change on the adsorbent, which in turn, is influenced by the pH (Ayari et al., 2007). As the pH changes, the surface change also changes, and the adsorption of the changed species is affected (Coetzee et al., 2003). At low pH, where there is an excess of H_3O^+ ions in the solution, the low amount (qe) of lead ions adsorbed may be explained by the competition existing between proton and cation for the available adsorption sites.

$$\left.\begin{array}{l} MOH + H^+ \quad \rightarrow MOH_2^+ \\ 2MOH + Pb^{2+} \rightarrow (MOH)_2 Pb^{2+} \end{array}\right\} \quad (I)$$
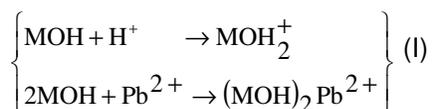
As the solution for the pH increases, the number of negatively charged sites increases. As a consequence, the positively charged metal ion is adsorbed more in the solution.

$$2MOH + 2OH^- \xrightarrow{\quad Pb^{2+} \quad} (MO)_2 Pb + 2H_2O \quad (II)$$
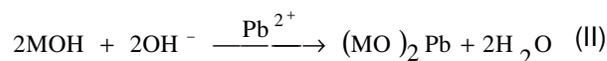
The amount of Pb^{2+} adsorbed on CAo, is larger than GAo, which in itself is superior to that of QAo. The difference in the amount of Pb^{2+} adsorption between these three distinguished activated carbon is dependent on their equilibrium constants obtained from Equations I (at weak pH) and II (at high pH).

Effect of reaction time

As it is shown in Figure 2, the amounts of Pb (II) ions adsorbed increased with the increasing time of equilibration. The removal equilibrium of lead (II) was obtained at about 25 min for CAo, 35 min for GAo and 25 min for QAo. After that, contact time has no significant effect in the removal and uptake of the metal (Bedoui et al., 2008), that is, the quantity of Pb(II) adsorbed ions increase weakly against contact time. Very high adsorption rates were observed at the beginning, because of a great number of sites available for the sorption operation and adsorption equilibrium which were then gradually achieved.
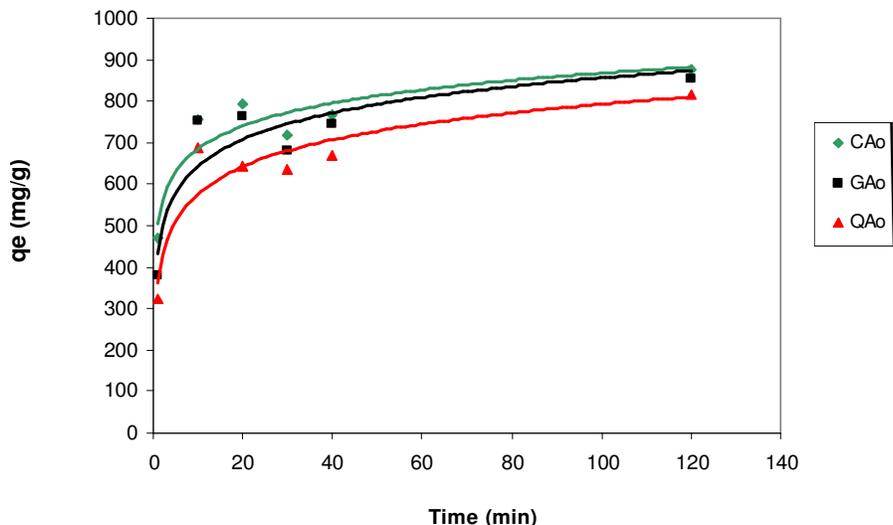
Figure 2. Effect of reaction time on the amount of Pb(II) ions adsorbed (pH 6, 308K, interaction time 120 min, initial Pb(II) ions concentration 2000 mg/L, activated carbon 2000 mg/L).

Effect of adsorbent mass

The amount of Pb (II) ions adsorbed per unit mass of activated carbon increased with high activated carbon loading (Figure 3). Similar results have been reported by other authors [for example, Cu(II) and Pb(V) by sawdust (Ahmad et al., 2009); Pb(II) by manganese oxide-coated carbon nanotubes (Wang et al., 2007). This may be attributed to two reasons: (i) the increase in the mass of the adsorbent surface area and (ii) several sites of adsorption are thus available to ensure a more significant retention of Pb (II) ions.

Adsorption isotherm studies

The adsorption experimental data were submitted to the test of the Langmuir and Freundlich models, with the aim of determining what model can accurately describe the adsorption results. The satisfactory agreement between the experimental data and the model predicted was expressed by the correlation coefficient (R^2) as reported by Sasmita et al. (2008). The model developed by Langmuir (1916) is represented by the following linearized equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m \times b} + \frac{C_e}{q_m}$$

(3)

Where q_e is the equilibrium quantity of Pb (II) ions adsorbed (mg/g), C_e is the equilibrium concentration of Pb (II) ions in aqueous medium, q_m is the maximum saturation capacity of the activated carbon (mg/g) and b

is the equilibrium constant (L/g). The Freundlich (1906) isotherm, in its linearized form, is expressed by this equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

(4)

Where K_F and n are the Freundlich adsorption capacity and the Freundlich coefficient relative to the adsorption intensity, respectively. The plots C_e/q_e as a function of C_e and log q_e as a function of log C_e, were reported in Figure 4, while in Figure 5, the applicability of the Langmuir and Freundlich models was illustrated.

Freundlich model (Table 2) is found as the most suitable to explain the experimental data ($R^2 > 0.99$). The Freundlich coefficient n remains between 1.035 and 1.485 with respect to the interaction of Pb (II) ions and the requirement of n > 1.0. The Freundlich adsorption capacity K_F is large for GAo (155.95 mg/g) compared to that of QAo (4.58) and CAo (0.82 mg/g). This result indicates that the surface of GAo is more heterogeneous in comparison with that of QAo and Cao, respectively. The Langmuir isotherm is applicable to the correlation coefficient which remained between 0.854 and 0.999(Table 2) when the initial concentration of Pb(II) ions are lower than 4000 mg/L. Over this value (4000 mg/L), the linear correlation coefficients became small (inferior to 0.8). The surface of CAo is more homogeneous when compared to that of QAo and Gao, respectively.

Kinetics studies

Assuming a pseudo-second order kinetic (Ho et al., 1999), the plots of t/q_t as a function of t (min) are linear
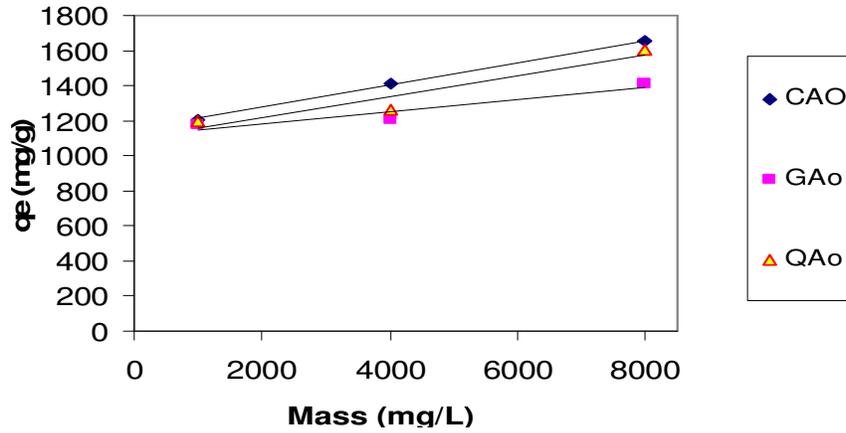
Figure 3. Amounts of Pb(II) ions adsorbed on the activated carbon for different activated carbon mass (Pb(II) ions concentration 2000 mg/L, interaction time 120 min, 308K and pH 6).
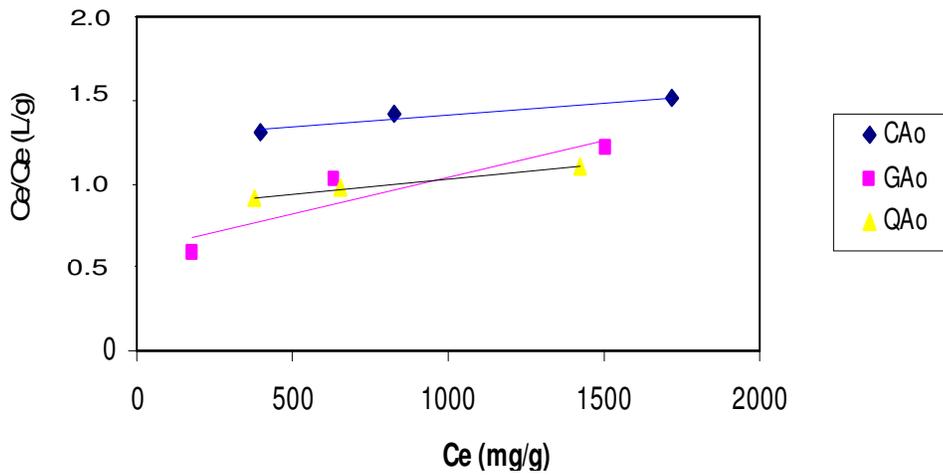
Figure 4. Langmuir plots for Pb(II) ions adsorbed on activated carbons (pH 6, 308K, activated carbon 2000 mg/L, interaction time 120 min).
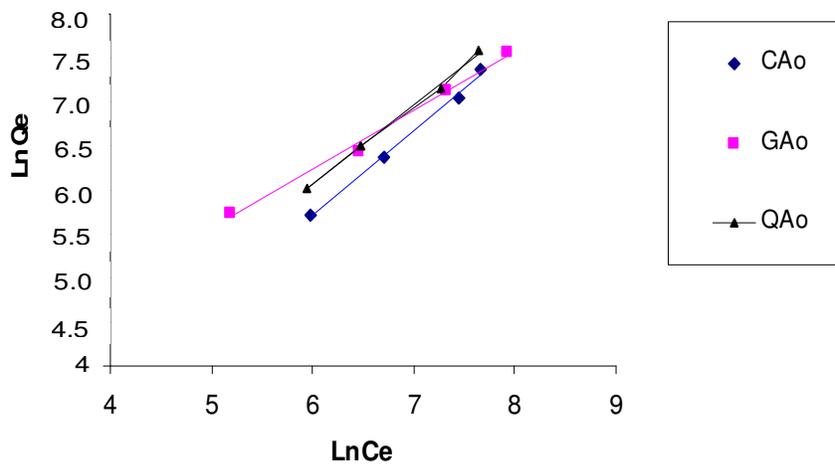
Figure 5. Freundlich plots for Pb(II) ions adsorbed on activated carbons (pH 6, 308K, activated carbon 2000 mg/L, interaction time 120 min).

Table 2. Freundlich and Langmuir parameter for adsorption of Pb (II) ions at 308K (activated carbon 2 g/L; initial Pb (II) ions concentration for 1000, 2000, 4000 and 6000 mg/L; pH 6 and time 120 min).

Activated carbons	Freundlich coefficients			Langmuir cœfficients		
	K_F (mg/g)	n	R^2	B (L/g)	q_m (mg/g)	R^2
CAo	0.82	1.035	0.99	7.82*10-3	100	0.96
GAo	155.95	1.485	0.99	4.349*10-2	33.3	0.854
QAo	4.58	1.10	0.99	2.336*10-2	50	0.99
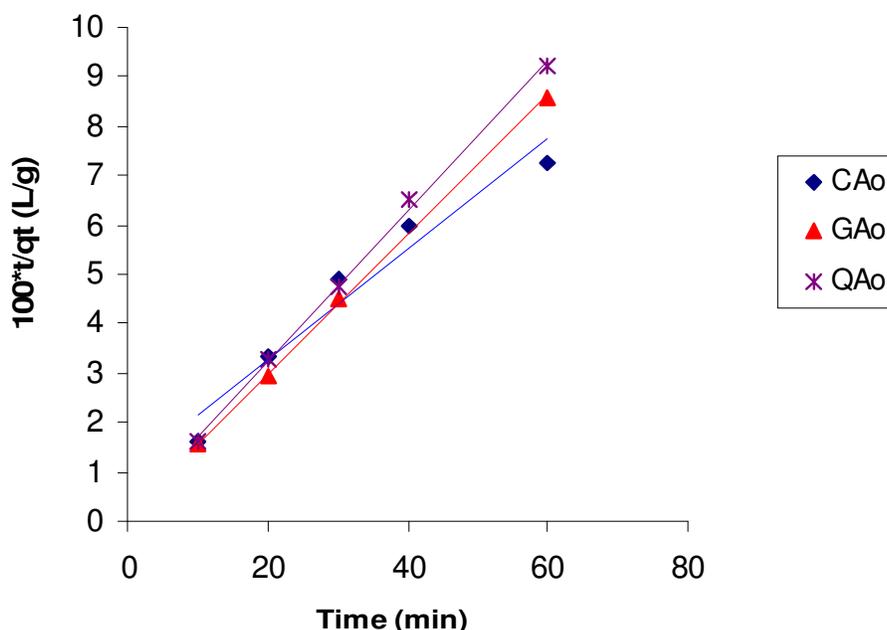
Figure 6. Pseudo second order plots for Pb(II) ions adsorbed on activated carbons (pH 6, 308K, activated carbon 2000 mg/L, initial Pb(II) ions concentration 2000 mg/L).

(R^2 varied from 0.95 to 0.99) (Figure 6). The second order rate constant k2 obtained from these plots varies from 3.31×10^{-2} g/mg.min for CAo to 3.99×10^{-2} g/mg.min for QAo and to 9.11×10^{-2} g/mg.min for GAo. From the consideration of the carbon-metal interaction, the second order rate constant are in the order of GAo > QAo > CAo. The comparison of q_e values (experimental and those obtained from the slopes of the second order plots) yields differences with deviations ranged from +6.8% for CAo to +5.66% for GAo and to +4.3% for QAo. The deviations existing (Table 3) may be due to the uncertainty inherent in obtaining the experimental qe values and also due to the actual process which is not exactly in conformity with the second order of the kinetic as reported by Gupta et al. (2005).

Thermodynamic study

The adsorption capacity of GAo and QAo activated carbons decreased as the temperature increased from 308 to 328K, thereby corresponding to an exothermic process (Gupta et al., 2008; Yadava et al., 1991). In opposite, the amounts of Pb (II) ions adsorbed on a CAo activated carbon followed a different behavior because it increased with the increase of temperature from 308 to 328K. This is a characteristic of an endothermic process as reported by Ahmad et al. (2009) and Karapinar et al. (2009). Thermodynamic parameters such as change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were determined using the following equations (Karapinar and Donat, 2009):

$$\ln K_0 = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{5}$$

and

$$K_0 = \frac{q_e}{C_e} \tag{6}$$

Table 3. Pseudo second order kinetics parameter of adsorption of Pb (II) ions on activated carbon CAo, Gao and QAo (activated carbon 2000 mg/L, initial Pb (II) ions concentration for 2000 mg/L, pH : 6 and 308 K).

Activated carbon	Initial concentration of Pb^{2+} solution (mg/l)	qe (mg/g) computed from the second order plots	Experimental qe (mg/g)	Deviation (%)	$k2*102$ (g*mg^{-1}*min^{-1})	R^2
CAo	2000	801.14	750	+6.8	3.31	0.96
GAo	2000	709.2	671	+5.66	9.11	0.99
QAo	2000	656.17	629	+4.3	3.99	0.99
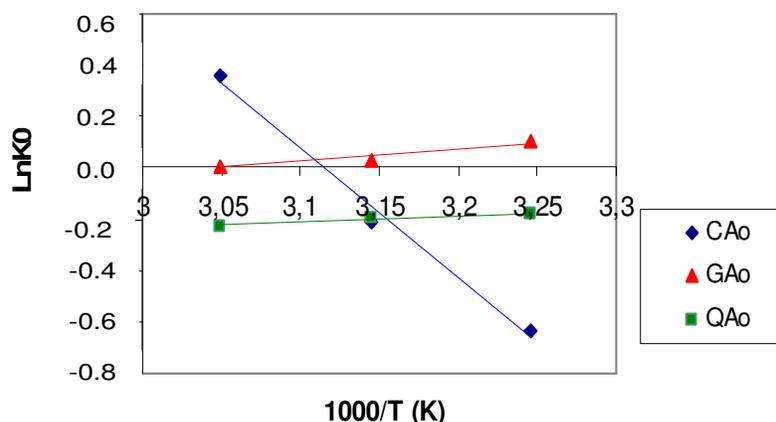
Figure 7. Plots of LnK0 as a function of 1/T (K) (pH 6 and initial concentration of Pb(II) ions for 2000 mg/L).

Table 4. Thermodynamic parameters for the adsorption of Pb^{2+} ions on activated carbons CAo, GAo and QAo (activated carbon amount 2000 mg/L, pH6 and initial Pb (II) ions concentration 2000 mg/L).

Activated carbon	ΔH (kJ/mol)	ΔS (J/mol/K)	ΔG (kJ/mol	T(K)	R^2
CAo	41.237	128.363	1.699	308	0.98
			0.416	318	
			-0.868	328	
GAo	-3.963	-12.085	-0.241	308	0.94
			-0.120	318	
			0	328	
QAo	-1.629	-6.763	0.45	308	0.89
			0.52	318	
			0.588	328	

where, R is the gas constant (in JK^{-1}mol^{-1}), T is the temperature (in Kelvin) and K_0 is the equilibrium constant.

The plots of logK$_0$ against 1/T (Figure 7) give effectively a linear relationship with the determinated correlation coefficients (R^2) which remained between 0.98 for CAo, 0.94 for GAo and 0.89 for QAo. The values of enthalpy (ΔH°) and entropy (ΔS°) were determined from the slopes and intercepts of logK0 vs 1/T plots. Gibbs free energy (ΔG°) was calculated from the expression:

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \qquad (7)$$

The values of thermodynamic parameters are reported in Table 4. Gibbs free energy ΔG^0 for CAo decreases with the increase in temperature, passing from positive (308 and 318K) to negative values, which is an indication that the reaction is spontaneous and more favorable at a higher temperature. The positive value of the entropy charge indicates that the process is irreversible. Gibbs

free energy of GAo and QAo increase in the same variation of temperature. With respect to CAo and QAo, the numeric values of their ΔG^0 are negative and positive, and they correspond to the spontaneous and non-spontaneous processes. The entropies change for GAo and QAo present negative values and indicate an order arrangement of Pb (II) ions on the adsorbent surface comparatively to the chaotic distribution in the solution state.

Conclusion

Activated carbons CAo, GAo and QAo are capable of removing Pb (II) ions from aqueous solution. The maximum adsorption capacity (qm) of CAo is higher than that for QAo and GAo. Adsorption increases with pH and temperature for CAo, and decreases as the temperature increases for GAo and QAo. Isotherm models of Langmuir and Freundlich are both applicable to explain the adsorption experimental data obtained. Adsorption process follows the pseudo second order Kinetic and the interactions adsorbent-adsorbate which is spontaneous for GAo, while at higher temperature, it is spontaneous for CAo and non-spontaneous for QAo.

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