

Full Length Research Paper

Removal of Pb (II) in aqueous solution using acid activated carbons prepared from *Cola edulis* shell (Alocaceae), *Pentaclethra macrophylla* husk (Mimosaceae) and *Aucoumea klaineana* sawdust (Burseraceae)

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The present research was undertaken to study the potential efficiency as adsorbents of three acid activated carbons, prepared from plant biomass of *Cola edulis* shell (CAH), *Pentaclethra macrophylla* husk (GAH) and *Aucoumea klaineana* sawdust (QAH), for the removal of Pb (II) ions from aqueous solution, by the means of batch technique. The study was managed using pH, concentration of lead solution, adsorption process equilibrium time and temperature as parameters. The adsorption increased with the increase in pH. The Pb (II) concentration to the equilibrium on the acid activated carbons surface for CAH (765 mg/g) is higher than for GAH (743 mg/g) and than of QAH (671 mg/g). The experimental data were found to fit both Freundlich and Langmuir isotherms. CAH (3.52 mg/g) was found to possess a more large heterogeneous surface capacity than GAH (2.19 mg/g) and QAH (1.43 mg/g) for Pb (II) ions adsorption, according to the Freundlich model. The testing of Langmuir model had given QAH (42.19 mg/g) higher monolayer surface capacity than GAH (27.25 mg/g) and CAH (22.62 mg). Adsorption kinetics was found to follow well the pseudo-second-order than the pseudo-first-order models. The adsorption process was found to be realized spontaneously between 308 and 318K.

Key words: Adsorption, lead (II), acid activated carbons, isotherm models, kinetic equations.

INTRODUCTION

It is known that some heavy metals dissolved in water resources, as industrial effluents, have been responsible for several health problems with animals, plants and human beings. Lead is one of these toxic heavy metals largely disseminated in atmosphere, soils and waters (Eba et al., 2011). Toxicological studies have shown that the ingestion and inhalation effects of Pb (II) on human health, includes red blood cells and nervous systems attack and kidneys damage as reported by Burriel et al. (1989), Moore et al. (1994), and Shujing et al. (2007). As Pb (II) does not degrade biologically, its removal from wastewaters remains an important challenge. Adsorption

of lead on appropriate adsorbents among other expensive methods such as chemical precipitation, ultrafiltration, electrochemical deposition, is highly efficient because of its simplicity of feasibility, low consumption of energy and great adsorption capacity for metal ions. The generalization in the entire world of the use of commercial activated carbons is knocked against their high cost. Therefore, to obtain activated carbons of low-cost and always available, many raw materials from the agricultural biomass and woodwork wastes were tested for their potential in the adsorption process. Activated carbons prepared from coconut shell (Gueu et al., 2006; Sekar et al., 2004; Manju et al., 1998; Gomez et al., 1998; Mostafa, 1997), rice husk (Srinivasan et al., 1988) seed hull of palm tree (Guo and Luo, 2000), sawdust (Avom et al., 2001; Kifuni et al., 2004)

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sugar-cane bagasse (Krishna and Anirudhan, 2003; Mukana and Kifuani., 2000) and from other inexpensive materials of different sources such as chitosan, clay materials, peat moss, fly ash, coal, natural oxide as reported by Sandya and Kurniawan (2003) have been used.

Cola edulis shell contains one almond. These almonds are largely consumed as food by Gabonese populations. The empty shell is released in the nature to be biodegraded. Cola edulis shell is a vegetable waste giving a very hard and not fibrous wood. Pentaclethra macrophylla husk is a vegetable product characterized by a tender and fibrous wood. Aucoumea klaineana is the main industrially tree exploited of Gabonese forest. Its wood is meanly tender and fibrous. The wood industries in Gabon release without valorization very high quantities of sawdust in the environment. This constitutes today a specific pollution in some cities area.

This study was undertaken as a contribution to lead (II) removal from aqueous solution by using low-cost adsorbents obtained as acid activated carbons from the preceding vegetable matters. The study was managed using various environmental conditions such as pH, concentration of lead solution, contact time between solution and solid and temperature of adsorption reaction.

MATERIALS AND METHODS

Activated carbons preparation

In this study, after impregnation into 3 M solution of H_3PO_4 for 24 h, the cleaned small pieces of wood are charred at 973K for 5 h. Then, the activated carbon is cooled in a dessicator. After cooling, the sample was rinsed several times with distilled water until obtaining flushing water whose pH range between 6 and 7. The wet sample was dried at 378K for 24 h. It was then crushed and passed through a sieve of 63 μm . only the particles of size inferior of 63 μm are employed in this study (Avom et al., 2001; Mukana et al., 2000).

Activated carbons characterization

Acidity functional groups on the surface

The acid groups covering the carbon surface were quantified by using Boehm titration method; which is widely employed in works on activated carbon. For this study, the bases used are: Sodium hydroxide (NaOH), sodium hydrogeno-carbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3). The followed procedure is described by Rockstraw (2000).

Surface area

The evaluation of surface area was performed according to the method of methylene blue adsorption described by Santamarina et al. (2002).

Ash content

The ash content was measured according to ASTM method (American Standard Method Technology). Each sample was

charred at 1023K 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:

$$\text{Ash content} = \frac{m_1 - m_2}{m_1} \times 100$$

m_1 and m_2 are the weights of the sample respectively before and after calcinations.

Chemical reagent

The analytical grade salt of $Pb(NO_3)_2$ was used without further purification. All experiments employed de-ionized water.

Instrumentation

An atomic absorption spectrometer Analyst 100 Perkin Elmer was employed to measure residual Pb (II) concentrations with uncertainty of 0.01 mg/L. The pH of solution was measured with a Tacussel pHmeter model mini 80 using a glass electrode with uncertainty of 0.01. Temperature of adsorption experiments has been realized with a Bioblock water-bath with an uncertainty of 0.1 °C. An analytical balance model Mettler Toledo PB 602-5 was used for the weighing of carbons and lead salt samples with uncertainty of 0.1 mg. The temperature of activation and calcinations were obtained with an uncertainty of 3 °C by using Bioblock furnace model Nobertherm.

Adsorption procedure

A known weight of activated carbons was equilibrated with 50 ml of the spiked lead (II) solution of known concentration, in stopped Erlenmeyer glass flasks. All experiments were carried out at a pH of 5 (except when the effect of pH was studied) and the Erlenmeyer flasks were shaken for given time to reach equilibrium. The agitation speed was kept constant for each run to ensure equal mixing. After the equilibrium time was attained, the Erlenmeyer flasks containing the samples were withdrawn from the shaker, the suspension was then filtered using filter paper and the filtrates were analyzed by an atomic spectrometer for their residual lead contents. The adsorption effect of parameters such as lead (II) solution pH, concentration of lead solution, interaction time and temperature were performed at adding 0.1 g of particle size (63 μm) of acid activated carbon to 50 ml of lead solution of 2000 mg/L and for the adsorption isotherm studies, lead initial concentrations were ranged between 10 and 60 mg/L.

The amount of lead (II) ions adsorbed at equilibrium was calculated by:

$$q_e = \frac{(C_0 - C_e) * V}{m}$$

where C_0 and C_e (mg/L) are the concentrations of lead at initial and equilibrium time respectively. V is the volume of the solution (L) and m is the mass of dry adsorbent used (g).

The kinetic experiments were realized with procedures basically identical to those of preceding equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations

Table 1. Characteristics of activated carbon.

| Activated carbon | Ash (%) | Acidity neutralizations (meq/g) | | | Surface area (m ² /g) |
|------------------|---------|---------------------------------|---------------------------------|--------------------|----------------------------------|
| | | NaOH | Na ₂ CO ₃ | NaHCO ₃ | |
| CAH | 1.02 | 3.249 | 0.399 | 0.228 | 137.279 |
| GAH | 3.88 | 2.88 | 0.171 | 0.456 | 49.443 |
| QAH | 2.83 | 3.15 | 0.171 | 0.114 | 62.985 |

of lead were similarly measured. The amount of adsorption at time t : q_t (mg/g) was calculated by:

$$q_t = \frac{(C_0 - C_t) * V}{m}$$

where C_0 and C_t (mg/g) are the concentrations of lead (II) at initial and any time respectively. V is the volume of the solution (L) and m is the mass of dry adsorbent used (g).

Theoretical foundation of results

The adsorption equilibrium is often described using an isotherm whose parameters present the surface properties and affinity of adsorbent to solute. In this study, the adsorption process has been tested by the use of Freundlich (Freundlich, 1906) and Langmuir (Eba et al., 2011) isotherm equations.

The linearized form of Freundlich equation is given by:

$$\ln q_e = \ln K_F + 1/n \ln C_e \quad (4)$$

where C_e is the equilibrium Pb(II) ions concentration (mg/g), q_e is the amount of Pb(II) ions adsorbed. K_F and n are the Freundlich constants corresponding to adsorption capacity and adsorption intensity respectively.

The Langmuir isotherm is expressed by the equation:

$$C_e/q_e = 1/b * q_m + C_e/q_m \quad (5)$$

where b and q_m are the Langmuir coefficients representing the adsorption equilibrium constant and the maximum monolayer capacity.

The slopes and intercepts to origin of the linear Freundlich plots $\ln q_e$ vs $\ln C_e$ and Langmuir plots C_e/q_e vs C_e give the Freundlich parameters k_F and n and Langmuir parameters, b , q_m and the separator factor, R_L .

The study of Langmuir model is completed by that of dimensionless constant R_L (Juang et al., 1997) given by:

$$R_L = 1/(1+b*C_0) \quad (6)$$

R_L values indicate the nature of adsorption. For favourable adsorption, $0 < R_L < 1$ and $R_L > 1$ or $R_L = 1$ represents respectively unfavourable or linear adsorption. When $R_L = 0$, the adsorption process is irreversible (Kadirvelu and Namasivayam, 2003).

Kinetics for adsorbent Pb (II) ions interaction was studied by applying the pseudo-first-order and pseudo-second-order kinetic models.

The pseudo-first-order model in the integrating form of Lagergren's equation (Lagergren, 1898; Ho, 2004) is given by the expression:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

and the linearized form of the equation of the pseudo-second-order kinetic (Ho and Mc Kay, 1999) model is:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (8)$$

where k_1 and k_2 are the Lagergren rate constant (min^{-1}) and the second order rate constant ($\text{g/mg}^2 \cdot \text{min}$) respectively, q_e (mg/g) and q_t (mg/g) are the amounts of Pb (II) ions adsorbed at the equilibrium and any time of interaction.

The kinetic models serve to determinate the adsorption rate constant, the equilibrium uptake of sorbate on sorbent surface and adsorption process mechanism.

The plots of $\ln(q_e - q_t)$ vs t and t/q_t vs t yield straight lines with the slopes and intercepts giving the values of pseudo-first-order and pseudo-second-order kinetic parameters respectively.

The thermodynamic parameters related to acid activated carbons-Pb (II) were determined from the equations (Eba et al., 2011):

$$\ln K_D = \Delta S/R - \Delta H/RT \quad (9)$$

$$K_D = q_e/C_e \quad (10)$$

From the slopes and intercepts values of plots of $\ln K_D$ versus $1/T$ are calculated

ΔH and ΔS .

Gibbs free energy is given by

$$\Delta G = \Delta H - T\Delta S. \quad (11)$$

RESULTS

Acid activated carbons characterization

The characteristics of activated carbons CAH, GAH and QAH concerning their ash content, surface specific area and acidity groups on the surface, are summarized in Table 1.

The rates of ash for acid activated carbons remain relatively weak (lower than 5%). These values are lower than those for activated carbons from Ntola (6.31%) and Lifaki (8.27%) wood sawdusts (Kifuani et al, 2004), which is a characteristics of carbon obtained from vegetable matters and constitutes an advantage from the point of view of their use in wastewaters treatment' (Gueu et al., 2007). In this case, the mineral species transfer from the adsorbent exchangeable sites to the solution during the adsorption process is limited to a very lower level. These

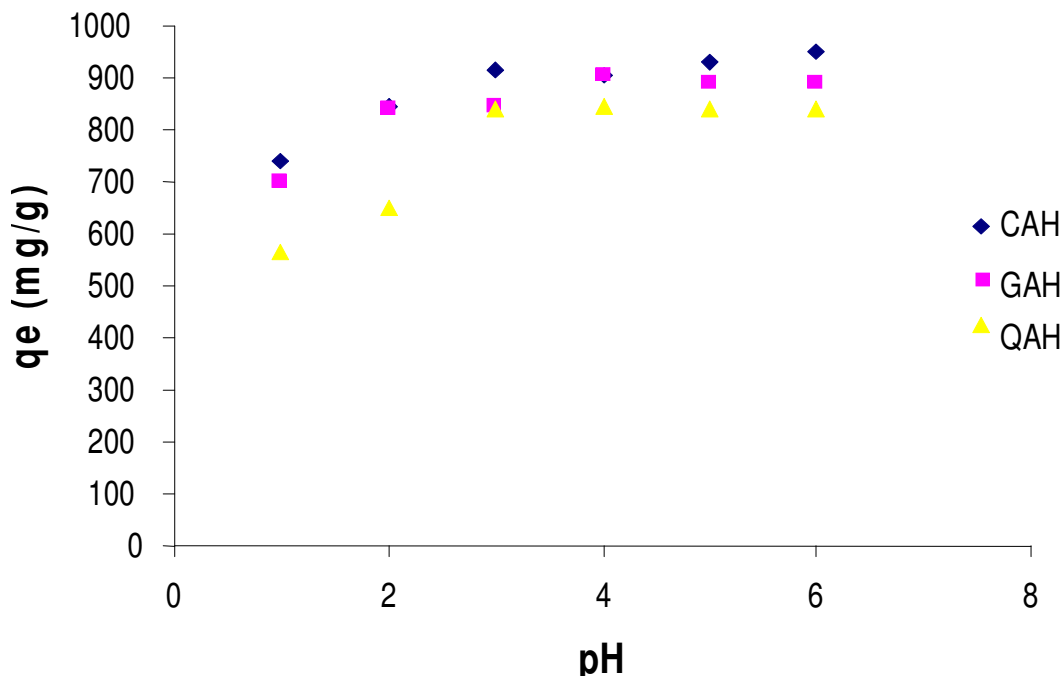


Figure 1. Amounts of Pb (II) ions adsorbed versus pH at 308K (activated carbon 2 g/L; Pb (II) 2 g/L).

weak values of the rates of ash are justified if it is considered that the mineral species which are lowly present in the vegetable matters form the constituents of ash. The porosity of activated carbon varies as well as the specific surface area as reported by Branka et al. (2009). The sample CAH seems more porous than GAH and QAH and also than those from coconut shell (98 m²/g) and seed shell (95 m²/g) of the palm tree (Gueu et al., 2006) and weaker porous than those of activated carbon hollow fibers (239 to 1440 m²/g) (Branka et al., 2009). The acidity neutralized by NaHCO₃ on the surface of activated carbon GAH (0.456 meq/g) is higher than those of CAH (0.228 meq/g) and QAH (0.114 meq/g). The acidity neutralized by Na₂CO₃ for CAH (0.399 meq/g) is higher than those for GAH (0.171 meq/g) and QAH (0.171 meq/g). The acidity neutralized using NaOH for CAH (3.249 meq/g) is higher than those of QAH (3.15 meq/g) and GAH (2.88 meq/g) are 0.228; 0.456 and 0.114 meq/g, respectively. The neutralization of the acids on the surface with NaOH, Na₂CO₃ and NaHCO₃ corresponded to the presence of carboxylic acid groups such as -OH, -COO⁻ and -COOH, respectively (Boehm, 1994). These acids play a significant role in adsorption. Values of surface area obtained are relatively weak in comparison with those given in literature 986.23; 980.31 and 576.99 m²/g for Ntola, Lifaki and Merck activated carbons respectively (Mukana et al., 2000). It is to be noted that specific surface area depends on particle size distribution, particle shape and number distribution of cracks and pores in the material, and therefore, cannot be presented as a general characteristics of a particular

type of material (Grim, 1968: 463-465).

Effect of the solution pH

The effect of the solution pH on the adsorption process is presented in Figure 1. Two types of behavior are observed: That of CAH is different from that of GAH and QAH. For the activated carbon CAH, the amount of Pb (II) ions adsorbed per unit mass increases continuously with the increase of pH from 1 to 6. Similar results have been reported by Gueu et al. (2006). The uptake of Pb (II) ions adsorbed on the acid activated carbons GAH and QAH surface increases only greatly from pH 1 to that of 4. Above pH 4, the adsorption by using these carbons as adsorbents was found increasing very weakly.

In the pH range lower than 3, the amounts of Pb (II) ions settled on the adsorbents were found weak compared to those fixed at pH higher than 4. Results with a similar behavior, reported by Ayari et al. (2007) and Gupta and Bhattacharyya (2008) are in good agreement with our results.

Effect of initial concentrations of Pb (II) solution

The amounts of Pb (II) ions adsorbed per unit mass of acid activated carbons increased with the increase in initial concentrations of Pb (II) aqueous solutions as shown in Figure 2. The increase of amount adsorbed of metal ions with the increase in metal ions concentration

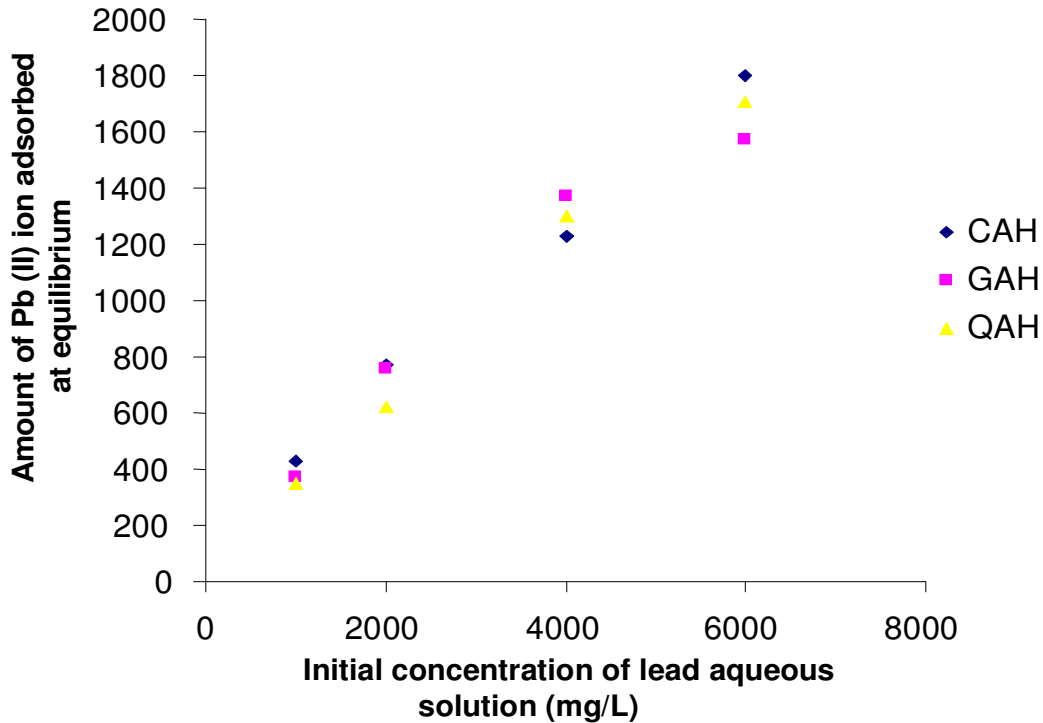


Figure 2. Amount of Pb (II) ions adsorbed on activated carbon for form different initial Pb (II) ions concentrations.

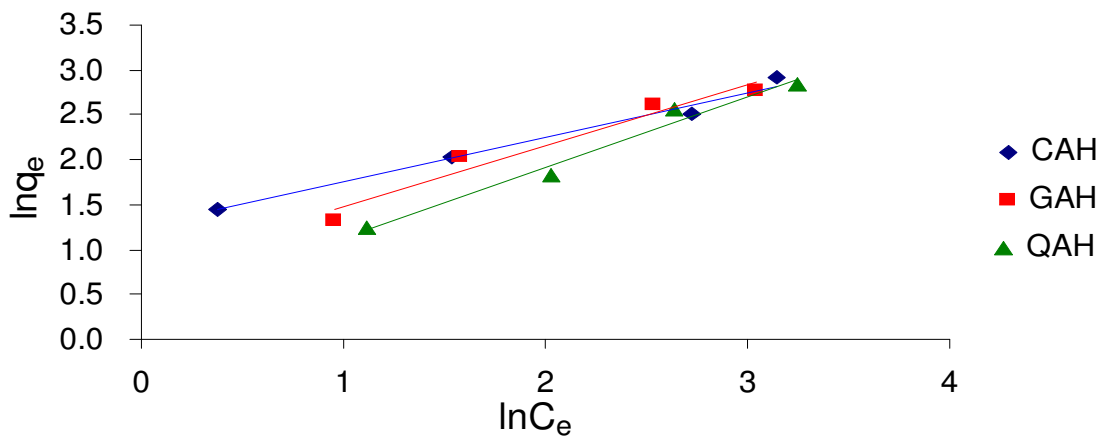


Figure 3. Freundlich plots for Pb (II) ions adsorbed on acid activated carbons (pH 5, 308K, activated carbon 2000 mg/L, interaction time 120 min, initial concentrations of lead solution: 10, 20, 40 and 60 mg/L).

has also been reported by Mukana et al. (2000) and Gueu et al. (2006).

Pb (II) adsorption isotherms studies

The equilibrium experimental data related to the adsorption of Pb (II) ions on acid activated carbons CAH, GAH and QAH were fitted in the empirical Freundlich (Freundlich, 1906) and Langmuir (Eba et al., 2010).

The Freundlich and Langmuir plots obtained by tracing

(i) $\ln q_e$ versus $\ln C_e$ (Figure 3) and (ii) $\frac{C_e}{q_e}$ as function of

C_e (Figure 4) are linear. The slopes and intercepts to origin of the preceding plots, are used to calculate Freundlich constants, n and K_F respectively and Langmuir parameters, b , q_m and the dimensionless parameters R_L with their respective correlation coefficients (Table 2).

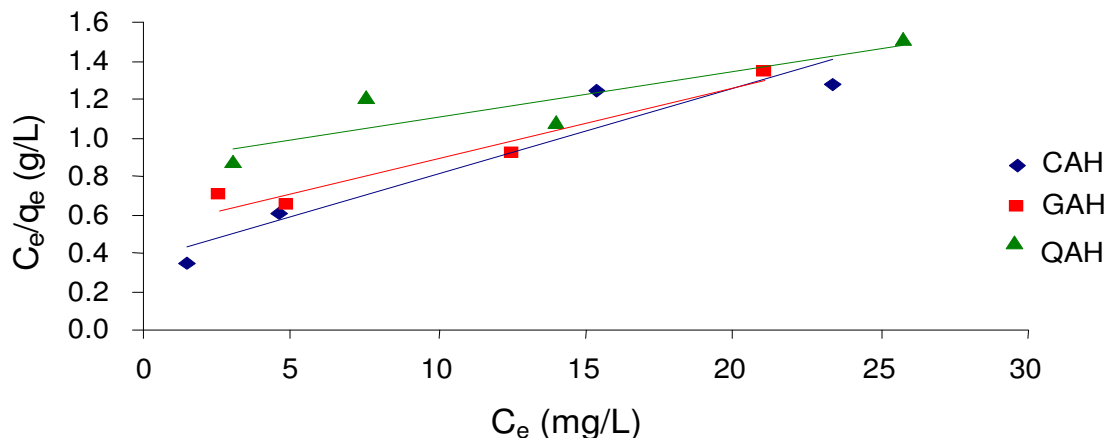


Figure 4. Langmuir plots for Pb (II) ions adsorbed on acid activated carbons (pH 5, 308K, activated carbon 2000 mg/L, interaction time 120 min, initial concentrations of lead solution: 10, 20, 40 and 60 mg/L).

Table 2. Freundlich and Langmuir constants and correlation coefficients for adsorption of Pb (II) on acid activated carbons at 308K and pH 5.

| Activated carbon | Freundlich Isotherm | | | | Langmuir Isotherm | | | |
|------------------|---------------------|--------------|--------|--------|-------------------|-----------|--------------|--------|
| | q_{exp} (mg/g) | K_F (mg/g) | $1/n$ | R^2 | q_m (mg/g) | b (L/g) | R_L | R^2 |
| CAH | 4.27 to 18.32 | 3.52 | 0.4973 | 0.9844 | 22.62 | 1.19 | 0.12 to 0.45 | 0.9016 |
| GAH | 3.7 to 15.7 | 2.19 | 0.6855 | 0.9502 | 27.25 | 0.7 | 0.19 to 0.58 | 0.9425 |
| QAH | 3.48 to 17.1 | 1.43 | 0.7811 | 0.9768 | 42.19 | 0.27 | 0.38 to 0.78 | 0.7745 |

The value of Freundlich adsorption capacity, K_F for CAH (3.52 mg/g) is higher than for GAH (2.199 mg/g) and QAH (1.45 mg/g). The other Freundlich constant, n , related to adsorption intensity is found with all values higher than the unity, 1.2 for CAH ($R^2 = 0.9844$), 1.48 for GAH ($R^2 = 0.9502$) and 1.28 for QAH ($R^2 = 0.9768$). Freundlich adsorption capacity values in similar ranges have been reported by other workers. Wenji et al. (2007) from studies of adsorption of Cd (II) on activated palygorskite found K_F between 4.32 and 12.95 mg/g ($R^2 = 0.99$); Mellah and Chegrouche (1997) reported K_F as 8.44 mg/g ($R^2 = 0.99$) with the adsorption of Zn (II) on natural bentonite. K_F values given by Gueu et al. (2007) for the adsorption of lead on coconut shell and seed hull of palm tree activated carbons seem lower, because it ranged between 0.0605 to 0.1417 mg/g ($R^2 = 0.99$) when temperature increased from 303 to 333K.

In term of adsorption efficiency of sorbents for Pb (II) ions on acid activated carbons, the Freundlich isotherm model gives CAH as having a more large multilayer heterogeneous surface than GAH and QAH, whence adsorption capacity of CAH>GAH>QAH.

The Langmuir monolayer adsorption capacities, q_m , were found with very high values. QAH (42.19 mg/g) possesses a greater monolayer surface for the adsorption of Pb (II) ions than CAH 22.62 and GAH 27.25 mg/g.

The Langmuir equilibrium constant, b , has its values varying from 0.234 L/g for QAH ($R^2 = 0.07745$), to 0.769 L/g for GAH ($R^2 = 0.9425$) and to 1.078 L/g for CAH ($R^2 = 0.9016$). Values of Langmuir maximum adsorption capacities in similar ranges have been reported by other workers. Gupta and Bhattacharyya (2008) from studies of adsorption of Pb (II) on montmorillonite and on kaolinite found adsorption capacities, q_m , as 31.1 mg/g ($R^2 = 0.99$) and 11.5 mg/g ($R^2 = 0.98$), respectively.

The R_L values of this work have been obtained in conformity with the requirement, $0 < R_L < 1$ of favorable adsorption (Juang et al., 1997; Kadirvelu and Namasiyama, 2003).

Kinetics studies

The experimental variations of adsorption capacities as a function of time were subjected to the pseudo-first-order and pseudo-second-order kinetic models. The slopes and intercepts values of linear plots $\ln(q_e - q_t)$ versus t ($R^2 = 0.96$ for CAH, 0.92 for GAH and 0.85 for QAH) (Figure 5) and t/q_t versus t ($R^2 = 0.75$ for CAH, 0.99 for QAH or GAH), (Figure 6) serve to determine the adsorption rate constants and equilibrium uptake of Pb(II) ions on sorbent surface for the pseudo-first-order and pseudo-second-order kinetic models. The results are shown in

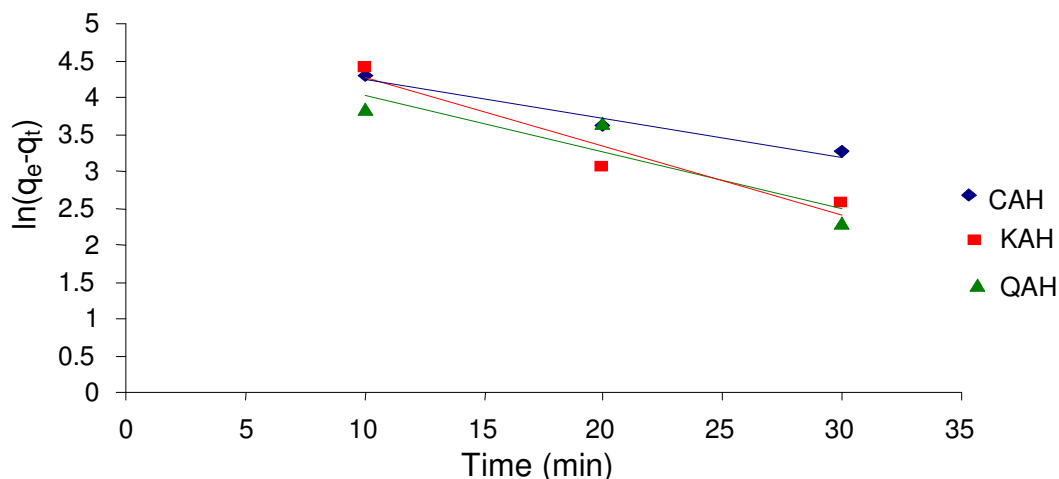


Figure 5. Pseudo-first-order plots for Pb (II) ions on acid activated carbons (pH 5, 308K, initial Pb (II) ions concentration 2000 mg/L).

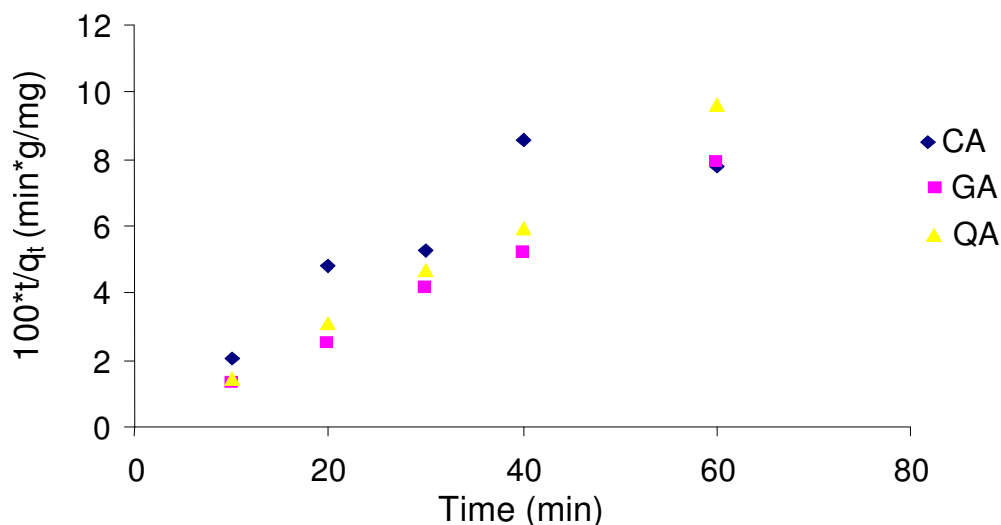


Figure 6. Pseudo second order plots for Pb (II) ions on acid activated carbons (pH 5, 308K, initial Pb (II) ions concentration 2000 mg/L).

Table 3. Pseudo-first-order and pseudo-second-order kinetics parameters for adsorption of Pb (II) ions on acid activated carbons at 308K and at pH 5.

| Activated carbon | Pseudo first order | | | Pseudo second order | | | q_{ex} (mg/g) |
|------------------|--------------------|-----------------------------|-------|---------------------|------------------|--------|-----------------|
| | q_e (mg/g) | k_1 (min^{-1}) | R^2 | q_e (mg/g) | k_2 (g/mg*min) | R^2 | |
| CAH | 117.2 | 0.052 | 0.96 | 851 | 0.065 | 0.7537 | 719 |
| GAH | 178.03 | 0.092 | 0.92 | 756 | 0.84 | 0.9930 | 682 |
| QAH | 122.7 | 0.077 | 0.85 | 625 | 0.1458 | 0.9971 | 634 |

the Table 3.

The Lagergren adsorption rate constant, k_1 (min^{-1}) for GAH (0.092) is higher than for QAH (0.077) and CAH (0.052). This parameter has been obtained with correlation coefficient of 0.96 (CAH), 0.92 (GAH) and

0.85 (QAH) respectively. The amounts of Pb (II) ions adsorbed at the equilibrium attained after 40 min evaluated by the use of Lagergren's model are very weak in comparison to experimental values.

The pseudo-first-order kinetics parameters in similar

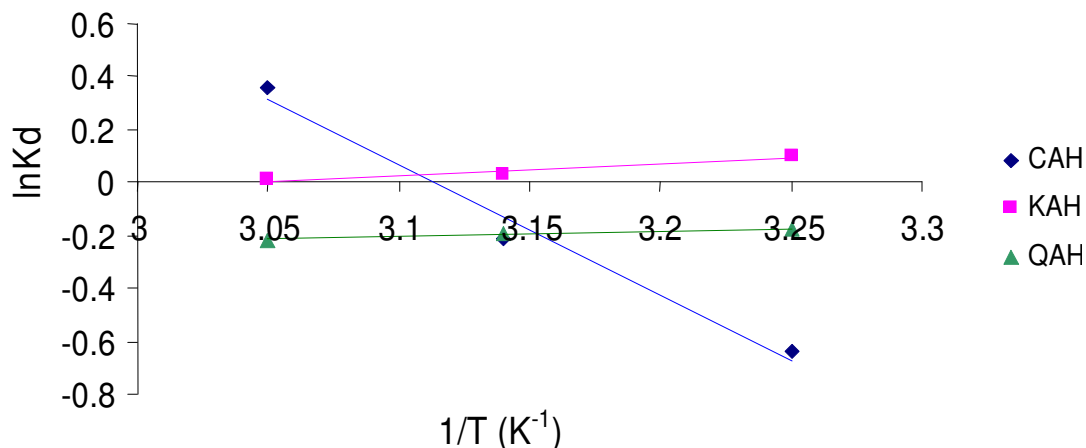


Figure 7. Plots of $\text{Ln}K_D$ as function of $1/T$ (K) (pH 5 and initial concentration of Pb (II) ions 2000 mg/L).

Table 4. Thermodynamic parameters for the adsorption of Pb (II) on activated carbons at different temperatures ($C_0 = 1000$ mg/L pH 6)

| | ΔH° (kJ/mol) | ΔS° (kJ/mol/K) | ΔG° (kJ/mol) | R^2 |
|-----|---------------------------|-----------------------------|---------------------------|-------|
| CAH | 0.05 | 0.159 | (308K) -48.92 | 0.99 |
| | | | (313K) -49.72 | |
| | | | (318K) -50.51 | |
| GAH | -0.006 | 0.0157 | (308K) -4.86 | 0.811 |
| | | | (313K) -4.92 | |
| | | | (318K) -4.99 | |
| QAH | -0.004 | 0.00711 | (308K) -2.19 | 0.85 |
| | | | (313K) -2.23 | |
| | | | (318K) -2.26 | |

values of the adsorption of Pb (II) have been reported in the literature (Gupta and Bhattacharyya, 2005; Gueu et al., 2007).

The second order rate constant K_2 , varies (Table 3) from 0.0655 g/(mg*min) for CAH, to 0.14855 g/(mg*min) for QAH and to 0.84 g/(mg*min) for GAH respectively. Computed and experimental values of the amount of Pb (II) ions adsorbed on acid activated carbons surface are comparable.

Values of pseudo-second-order rate constant for Pb (II) adsorption of comparable level have been obtained by Qiaohui Fan et al. (2009) for the adsorption of Pb (II) on palygorskite.

Thermodynamics studies

In order to determine the thermodynamic feasibility and the thermal effects accompanying the adsorption process, the amounts of Pb (II) ions adsorbed on each activated carbon (q_e) and the equilibrium concentration

C_e (mg/L) of Pb (II) in aqueous solution were measured at 308, 313 and 318K.

The plots $\text{Ln}K_D$ versus $\frac{1}{T}$ (Figure 7) give effectively a linear relationship with correlation coefficients of 0.99 for CAH, 0.85 for QAH and 0.81 for GAH. Calculated thermodynamic parameters such as ΔS° , ΔH° and ΔG° are given in Table 4.

The adsorption process is accompanied by a positive value of the entropy, positive (CAH) and negative (GAH and QAH) values of the enthalpy. Gibbs free energy is found with negative values. Comparable behavior has been shown in the literature for Pb (II) adsorption (Shu-Guang, 2007).

DISCUSSION

Results concerning the effect of pH on adsorption capacity are generally interpreted if it is considered sides of weak pH and of high pH. In the low pH side (pH < 3),

there is an excess of H_3O^+ ions which are in repulsive competition with Pb (II) ions in the aqueous solution for the attainment of available adsorption sites on the surface of adsorbents. In these conditions, the level of the amount of Pb (II) ions adsorbed is low. In the side with $pH > 3$, the concentration of H_3O^+ is negligible, the interaction adsorbent-adsorbate concerns preponderantly adsorption sites on the surface of activated carbon and Pb (II) ions, and the amount of Pb (II) ions adsorbed is high. Similar results have been reported by Ayari et al. (2007).

The effect of concentration of Pb (II) solution on adsorption capacity can be explained as the following manner. At a relative low Pb (II) ions concentration, the available adsorption sites on activated carbon are relatively higher than the number of Pb (II) cations given by the adsorbate solution; the amount of Pb (II) ions adsorbed in this case is weak. In the opposite, when concentration of lead solution is progressively high, the adsorption becomes also more and more efficient. The amount of Pb (II) ions adsorbed on clay increases with the increase in concentration of lead solution. Similar results have been reported by other workers e.g., Pb (II), Ni (II) and Cd (II) on kaolinite and montmorillonite (Gupta and Bhattacharyya, 2008, Jain and Ram, 1997).

The values of Freundlich adsorption parameters, K_F and n , have been obtained with very great correlation through the adsorption of Pb (II) on each of acid activated carbon. The differences on numerical values observed could be attributed to nature of wood served to prepare activated carbons. The result $n > 1$, indicates that the process is realized according to favorable adsorption conditions (Goel et al., 2005). The Freundlich constant n is also considered as a measure of deviation from the unity: $n = 1$ for linear adsorption, $n > 1$ corresponds to the case of physical adsorption and $n < 1$ indicates that the adsorption is a chemical process (Ijagbemi et al., 2009). The n values obtained in this work indicate that the adsorption of Pb (II) ions on activated carbons CAH, GAH and QAH is controlled by a physical process. The Freundlich isotherm does not predict any saturation of the adsorbent by adsorbate; thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface (Erdem et al., 2004).

The Langmuir isotherm parameters have been obtained with all correlation coefficients $0.77 < R^2 < 0.94$. The values of Langmuir monolayer capacity, q_m , are very high. This is an indication of great affinity of each of these acid activated carbons for Pb (II).

The R_L values for this work ranged between 0.416 and 0.81 (QAH), 0.178 and 0.565 (GAH) and between 0.13 and 0.48 (CAH) support favorable adsorption of Pb (II) ions on the activated carbon adsorbents. The high values of Langmuir equilibrium constant, b (L/g) > 1 , for CAH, correspond to strong bonding, as in chemical adsorption process. In opposite, the weak values of Langmuir equilibrium constant, b (L/g) < 1 , for QAH and GAH, are an indication of physical interaction.

The selective adsorption of Pb (II) on acid activated carbons originates to wood from which were prepared activated carbons.

These results have demonstrated that, the description of the adsorption process by the means of Langmuir isotherm model is valid.

The values of the adsorption parameters indicate the potential use of the acid activated carbons for metal removal. Similar ranges of values have been reported for adsorption of Pb (II) ions on granular activated carbon (Goel et al., 2005), bentonite (Zhu et al., 2008), chemically modified rice husk and sawdust (Saravanne et al., 2002).

The parameters of the pseudo-first-order and pseudo-second-order kinetic models have been obtained with very high values of correlation coefficients. In spite of the curves of pseudo-first-order kinetics been linear, large differences were found between experimental and modeled values of q_e . The pseudo-first-order kinetic model does not fit well the experimental data. The pseudo-second-order plots yield weak differences in computed and experimental values of q_e .

The reason of these small differences might be the uncertainty inherent in obtaining the experimental q_e values. Similar results have been reported by Ho and McKay (1999).

The negative values of Gibbs free energy indicate that the process is spontaneously feasible as reported by Gupta et al. (2008). The exothermic interaction between Pb (II) and GAH and QAH is also reported. It corresponds to related negative values of the enthalpy change. The enthalpy change of activated carbon CAH has a positive value, an indication of an endothermic process.

The considerably low values of ΔH^0 show weak interactions, corresponding to a physically controlled process, between Pb (II) ions and the activated carbons. In the other hand, the values of ΔS^0 are positive, indicating that Pb (II) ions in aqueous solution are in a much more ordered state compared to the chaotic distribution when adsorbed. Similar results are reported by Gueu et al. (2007) from the removal of Pb (II) on coconut shell and seed hull palm tree carbons.

Conclusion

The results show that CAH, GAH and QAH acid (H_3PO_4) activated carbons prepared from cola edulis shell, pentaclethra macrophylla husk and aucoumea kleaneana sawdust (Raponda et al., 2003) show a high adsorption capacity to be used as adsorbents for the removal of Pb (II) ions from aqueous solutions. The amounts of Pb (II) ions adsorbed on coals increase with pH and initial concentration of Pb (II) solutions. The adsorption experimental data are fitted both by the Freundlich isotherm and Langmuir isotherm models. The pseudo-second-order kinetics model has given a best fit of kinetic experimental data than the pseudo-first-order kinetic

model. The adsorption phenomenon is spontaneous. It is accompanied by endothermic (CAH) and exothermic (GAH) and (QAH) thermal exchanges.

The selective adsorption of Pb (II) on acid activated carbons has been obtained according to the sequence CAH>GAH>QAH.

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