Kinetics and Thermodynamics of the Adsorption of Lead (II) on a Activated Carbon from Coconut Shells

L. Largitte[1]* and P. Lodewyckx[2]

[1]EA COVACHIMM 3592, Université des Antilles de la Guyane, Campus de Fouillole,
97110 Pointe-à-Pitre, France
[2]Royal Military Academy, Department of Chemistry, Renaissancelaan 30,
1000 Brussels, Belgium

Abstract

The effect of temperature on the adsorption of lead by an activated carbon from coconut shells is investigated. The pseudo second order equation is applied to the kinetic data obtained at different temperatures in order to determine the adsorption rate constants at these temperatures. Then, the Arrhenius equation is applied to the rate constants to determine the activation energy of the sorption reaction and the pre-exponential factor. By applying the Eyring equation to the rate constants, the standard thermodynamic activation parameters of the sorption reaction can also be calculated. In addition, the isotherms of lead adsorption on the activated carbon from coconut shells, at different temperatures, are determined and fitted by the Langmuir equation. The Van't Hoff equation is applied to the Langmuir equilibrium constants in order to determine the standard enthalpy of the sorption reaction. The other standard thermodynamic parameters (Gibbs standard enthalpy and standard entropy) are deduced. The isosteric standard sorption enthalpy is also determined by using both the classical approach and an adapted Clausius Clapeyron equation. The results are identical. The value obtained is higher, but more correct than that of Langmuir. On the basis of these thermokinetic parameters, the activated carbon from Coconut shells can be considered as a very efficient carbon for the sorption of lead and its sorption efficiency (rate and quantity) increase with the temperature.

Introduction

Heavy metals are ubiquitous in the environment. They are found in various industrial activities like manufacturing of alloys, electrical goods, chemical catalysis, metal surface finishing and batteries. During metallurgical processes, some amounts of metals are released into water bodies. The release of large quantities of heavy metals into the natural environment e.g. by irrigation of agricultural fields using sewage has resulted in a number of environmental problems [1]. Heavy metals can accumulate in the food chain due to their non biodegradability and persistence, and thus may pose significant dangers to human health [2]. According to the World Health Organization (WHO), the major toxic heavy metals contaminating drinking water are chromium, cobalt, copper, cadmium, lead and mercury. Amongst these, lead is one of the most toxic. It leads the list of environmental threats because, even at extremely low concentration, lead can cause brain damage in children [3]. The World Health Organization set a provisional limit of 0.05 mg/L for lead. Constant efforts are being made to develop improved and innovative methods of waste water treatment. While developing new methods, economic feasibility and user friendly concepts are given much importance. Various processes for the removal of metals are available but the most commonly used process is precipitation. By the addition of a suitable reagent in required quantity, the metal precipitated. But the sludge that is formed contains more amounts of heavy metals and the disposal of such sludge creates another problem.

So other treatment processes like ion exchange, reverse osmosis or adsorption processes are required after the precipitation process and before discharging into water bodies.

Consequently, the removal of metal requires two processes and the cost for this two stage treatment is high which is not suitable for most of the industries.

---

* Corresponding author. E-mail: lucie.largitte@univ-ag.fr

Keeping this in view, considerable attention has been given to develop low cost adsorbents for the removal of heavy metals. Activated carbon is the most widely used adsorbent because of its high surface area and versatility [4].

The aim of the present study is to investigate the effect of temperature on the adsorption of lead by an activated carbon from coconut shells in order to characterize the kinetic and thermodynamic parameters of the sorption reaction. The knowledge of these parameters will permit us to determine the optimal conditions for a maximum removal of lead. Different ways of obtaining the thermokinetic parameters are tested and compared. For the kinetic parameters, the Bangham, the pseudo first order, the second order models and the Arrhenius and Eyring equations are used. For the thermodynamic parameters, the Freundlich, the Langmuir, the Van't Hoff and an adapted Clausius Clapeyron equation are used. Moreover, the thermokinetic parameters of the activated coconut shells carbon will permit a better comparison with other activated carbons. However the literature data yield few results on this subject. Indeed, the usual comparisons for an adsorbent concern the rate constants or the maximum or equilibrium amounts adsorbed, which depend on the operating conditions. Using intrinsic parameters such as activation energy or reaction enthalpy, characterizing the sorption, independent of the operating conditions, is more effective in quantifying the efficiency of an activated carbon.

Nomenclature

Q_t: amount of lead adsorbed per unit mass of the adsorbent at time t, mg·g^{-1} or mol·kg^{-1}

Q_{eq}: amount of lead adsorbed at equilibrium per unit mass of the adsorbent, mg·g^{-1} or mol·kg^{-1}

C_t: lead concentration at time t, mg·L^{-1} or mol·L^{-1}

C_{eq}: lead concentration at equilibrium, mg·L^{-1} or mol·L^{-1}

R^2: linear regression coefficient

t: time, seconds

T: temperature, Kelvin

k_{ads}: adsorption rate constant for the pseudo-second-order model, mol^{-1}·kg·s^{-1}

K: adsorption equilibrium constant, L·mol^{-1} or L·kg^{-1}

E_a: activation energy, kJ·mol^{-1}

R: gas constant equal to 8.314 J·mol^{-1}·K^{-1}

A: Arrhenius factor, mol^{-1}·kg·s^{-1}

k_B: Boltzmann's constant equal to 1.38×10^{-23} m^2·kg·s^{-2}·K^{-1}

h_P: Planck's constant equal to 6.63×10^{-34} m^2·kg·s^{-1}

$\Delta G°$: standard free energy of the sorption reaction, kJ·mol^{-1}

$\Delta H°$: standard enthalpy of the sorption reaction, kJ·mol^{-1}

$\Delta S°$: standard entropy of sorption reaction, J·mol^{-1}·K^{-1}

$\Delta G°^{\#}$: standard free energy of activation, kJ·mol^{-1}

$\Delta H°^{\#}$: standard enthalpy of activation, kJ·mol^{-1}

$\Delta S°^{\#}$: standard entropy of activation, J·mol^{-1}·K^{-1}

Experimental Methods

Reagents

The 69.4% nitric acid solution used to fix the pH, the $Pb(NO_3)_2$ which is the lead ions source solution, the $NaNO_3$ used to fix the ionic force of the solution are from Prolabo. The solutions are prepared with deionised water.

Activated Carbon

The activated carbon used in this study is a commercial activated carbon from PICA named NC60. It goes through a physical activation with CO_2/H_2O at 900 °C. It is used as received.

Textural Properties

The texture of the activated carbon is characterized via adsorption of nitrogen at 77 K using a Micromeritics apparatus ASAP 2010. About 0.30 g of sample is out gassed at 250 °C for 48 h, prior to the adsorption measurements.

The BET surface area, the micropore volume and the mesopore volume of the activated carbon are determined from the N_2 adsorption isotherm.

The specific surface area (S_{BET}) is evaluated by applying the Brunauer et al equation [5] to the isotherm in the relative pressure (P/P°) range of 0.05 to 0.3, using the linear part and taking into account the average area occupied by a molecule of N_2 to be equal to 16.2 Å^2.

The micropore volume (V_{mi}) is estimated from the N_2 adsorption isotherm by applying the Dubinin–Radushkevich equation [6] and the mesopore volume (V_{me}) as the volume of N_2 adsorbed at P/P° = 0.99 minus the DR-micropore volume.

Surface Properties

The surface properties of the activated carbon are characterized via the Boehm method [7].

Using this method, it is assumed that NaOH is consumed by the whole of the acid groups (phenol, carboxylic and lactone groups); $NaHCO_3$ neutralizes the carboxylic groups; Na_2CO_3 reacts with both the carboxylic and the lactone groups. From the difference in Na_2CO_3 and $NaHCO_3$ consumed by the same sample, the concentration of lactone groups can be calculated. Similarly, the concentration of phenol groups can be determined from the difference in NaOH and Na_2CO_3 consumed by the same sample.

The pH PZC of the activated carbon is determined using the potentiometric titration method as described by [8]. 0.1 g carbon sample is mixed with

respectively 25 mL of 0.01 M NaNO$_3$ and 0.1 M NaNO$_3$ solution. The vials are shaken for 48 h at 150 rpm. Then, the solution from each vial is filtered through a 0.45 μm membrane filter. 10 mL of filtrate is titrated with a 0.05 M NaOH solution, in a glove box, under a nitrogen atmosphere while stirring. The intersection of the curves at 0.1 M and 0.01 M gives the pH PZC.

All the titrations for Boehm and pH PZC are performed on a 809 SM Titrino automatic titrator (Metrohm) and the maximum titrant dosing rate selected is 0.25 mL/min. Duplicates are performed for each sample and the relative standard error is equal or less than 3%.

Sorption Studies

In a typical adsorption run, a weight (W) of activated carbon is put in contact with a volume (V) of lead ion solution at a given initial concentration and at pH 5. The flask is put in a stirrer water bath maintained at a constant temperature. The dose adsorbent D is calculated by the ratio W/V.

The temperature varies from 20 to 40 °C, the dose adsorbent is 1 g/L for both the kinetic and the equilibrium studies. Acid pH 5 is obtained by mixing predetermined volumes of 0.01 M HNO$_3$ to the lead solution. The initial concentration of lead is 150 mg/L for the kinetic study and varies between 30 and 150 mg/L for the equilibrium study. Note that the initial concentrations of lead used in this study are in accordance with the lead concentrations found in industrial effluents.

At regular intervals for the kinetic study or only at the equilibrium time for the equilibrium study, 5 mL of solution is removed from the flask, filtered through a 0.45 μm filter and the concentration of lead remaining in the solution is measured. Note that the stirring is stopped before each removing, that the total volume removed does not exceed 10% of the initial volume of lead ion solution. So the volume can be considered constant during the sorption test. The concentration of lead present in the initial solution (C$_0$) and in the filtrated solutions (C) are measured with an atomic absorption spectrometer AA240FS from Varian; the pH of the solutions is measured with a Mettler Toledo FG2 pHmeter. All glassware is presoaked in a 0.5% HNO$_3$ solution, rinsed with deionised water and oven dried. All batch sorption tests and absorption measurements are duplicated.

The amount of lead adsorbed Q$_t$ for the kinetic study (or Q$_{eq}$ for the equilibrium study) is calculated by the difference between the initial (C$_0$) and the instantaneous (or equilibrium) lead concentration (C$_t$ or C$_{eq}$):

$$Q \ (mg/g) = (C_0 - C)/D \qquad (1)$$

The sorption data are fitted to the linear form of the models. So, linear regression analysis is applied to each set of adsorption data. The square correlation coefficient (R^2) representing the fit of the model to the data is calculated using Excel plot 2003.

Results and Discussion

Kinetic studies

The data

The uptake rate of lead on the activated carbon from coconut shells is studied at pH ~ 5 for an initial lead concentration of 150 mg/L, an adsorbent dose of 1 g/L at 23, 30 and 40 °C (Fig. 1). The amount of lead adsorbed increases in function of time whatever the temperature. The general sorption behaviour is the same for all the temperatures. The sorption is quite rapid within the first ten hours followed by a slow approach to equilibrium. It can be explained by the fact that, as the metal concentration increases on the surface with the reaction, the higher energy surface sites are saturated; then, the adsorption begins on the lower energy surface sites, resulting in a decrease of the sorption rate. The equilibrium is reached around 50 h for the activated Coconut shells carbon.
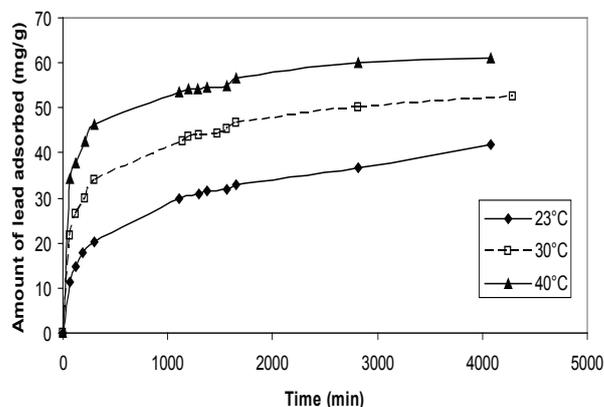

Fig. 1. Effect of time upon the adsorption of lead by the activated carbon from Coconut shells at 23, 30 and 40 °C (initial conditions: pH ~ 5, D = 1 g/L, C$_{Pb2+, 0}$ = 150 mg/L).

Modelling the Data

The Kinetic Models

The experimental data related to the adsorption of lead (II) on the activated carbon from coconut shells, at different temperatures, are fitted with the:

- Bangham equation:
$$Ln(Q_t) = vLn(t) + ln(k) \qquad (2)$$
- Pseudo first order equation [9]:
$$Ln(Q_{max}-Q_t) = -k_1t + ln(Q_{max}) \qquad (3)$$
- Second order equation [10]:
$$t/Q_t = t/Q_{max} + 1/[k_{ads}(Q_{max})^2] \qquad (4)$$

Q_t is the amount of lead adsorbed at a moment and Q_{max} is the maximum amount of lead adsorbed, both are expressed in mol/kg; t is the time, expressed in seconds.

The values of the square correlation coefficients R^2 are given in Table 1 for the three models. According to Table 1, the second order equation fits better to the data indicating that the sorption is the rate limiting step in the process. Figure 2 presents the curve fit of the pseudo second order model to the kinetic data at the three temperatures. Then, the rate constant k_{ads} can be determined for the sorption at 296, 303 and 313 K by the slope²/Intercept of the curve fitting. As it can be seen from the k_{ads} constants in Table 2, lead (II) is adsorbed faster at higher temperature. So, the sorption process with the activated Coconut shells carbon follows the Arrhenius law. The increase of k_{ads} with the temperature is explained by the fact that

more efficient collisions between the reactives activated carbon and lead occur at higher temperatures.

Table 1

Correlation coefficients obtained from the modelling of the kinetic data of the activated Coconut shells carbon obtained at different temperatures in the initial conditions pH ~ 5, D = 1 g/L, $C_{Pb2+, 0}$ = 150 mg/L

R^2	296 K	303 K	313 K
Bangham	0.992		
Pseudo first order	0.869		
Pseudo second order	0.995	0.991	0.999

Table 2

Rate constant k_2 obtained from the pseudo second order modelling of the kinetic data of the activated Coconut shells carbon obtained at different temperatures in the initial conditions pH ~ 5, D = 1 g/L, $C_{Pb2+, 0}$ = 150 mg/L

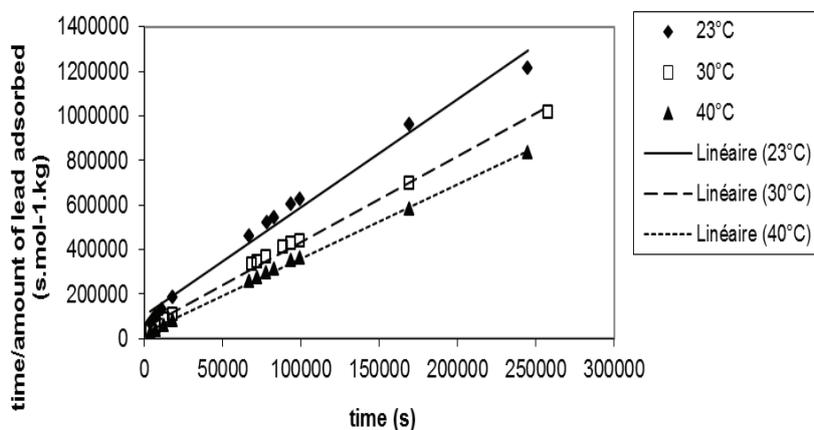|	296 K	303 K	313 K
k_{ads} (mol^{-1}·Kg.s^{-1})	6.10^{-4}	7.10^{-4}	10^{-3}

Fig. 2. Pseudo second order modelling of the kinetic data of the activated Coconut shells carbon obtained at 23, 30 and 40 °C in the initial conditions pH ~ 5, D = 1 g/L, C_{Pb2+0} equal to 150 mg/L.

The Arrhenius Equation

The k_{ads} constants related to the adsorption of lead at different temperatures on the activated coconut shells carbon are applied to the Arrhenius equation [11]: $Ln(k_{ads}) = Ln(A) - E_a/RT$ (5). The temperature T is expressed in Kelvin and k_{ads} in mol^{-1}·Kg·s^{-1}. Figure 3 shows the dependence of $Ln(k_{ads})$ on the inverse of the temperature. The activation energy (E_a) of the sorption reaction is determined by the slope of the curve fit mul-

tiplied by -R, R being the perfect gas constant. The Arrhenius factor (A) is calculated by taking the exponential of the intercept of the curve fit. E_a and A are respectively equal to 22.6 kJ·mol^{-1} and 5.9 mol^{-1}·Kg·s^{-1}. These results are compared to those of the literature data available concerning the kinetics of lead adsorption (see Table 3). The activation energy obtained is between those found by Sekar [12] and Gerçel [13] for the sorption of lead onto other activated carbons, idem for the Arrhenius factor.

Table 3
Kinetic parameters obtained for the sorption of lead
by the activated carbon from this study and from
other works

	This study	Sekar et al. [12]	Gerçel et al. [13]
E_a (kJ·mol^{-1})	22.6	35.5	12.1
A	5.9 mol^{-1}·kg·s^{-1}	261·6 s^{-1}	0.2 mol^{-1}·kg·s^{-1}
$\Delta H°^{\neq}$ (kJ·mol^{-1})	20.0		
$\Delta S°^{\neq}$ (J·mol^{-1}·K^{-1})	238.6		

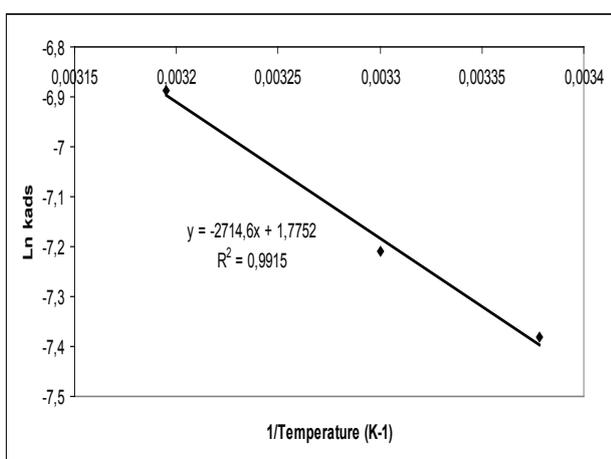
Fig. 3. Arrhenius plot for the kinetic data obtained at 23, 30 and 40 °C in the initial conditions pH ~ 5, D = 1 g/L, C_{Pb2+0} equal to 150 mg/L.

The Eyring Equation

The k_{ads} constants related to the adsorption of lead at different temperatures on the activated coconut shells carbon are also applied to the Eyring equation [11]: $Ln(k_{ads}/T) = Ln(k_B/h_P) + \Delta S°^{\neq}/R - \Delta H°^{\neq}/RT$ (6) where k_B is the Boltzmann constant and h_P is the Planck constant. The plot of $Ln(k_{ads}/T)$ versus the inverse of the temperature is shown in Fig. 4. The temperature T is expressed in Kelvin and k_{ads} in mol^{-1}·Kg·s^{-1}. The standard enthalpy of activation is calculated by the slope of the curve fit multiplied by -R. The standard entropy of activation by R.[Intercept − Ln(k_B/h_P)] (7). The standard Gibbs enthalpy of activation can be deduced from the expression (8): $\Delta G°^{\neq} = \Delta H°^{\neq} - T\Delta S°^{\neq}$. This gives values of $\Delta H°^{\neq} = 20.0$ kJ·mol^{-1} and $\Delta S°^{\neq} = 238.6$ J·mol^{-1}·K^{-1}. No results from literature were found in order to compare the activation parameters for the kinetic of lead sorption.
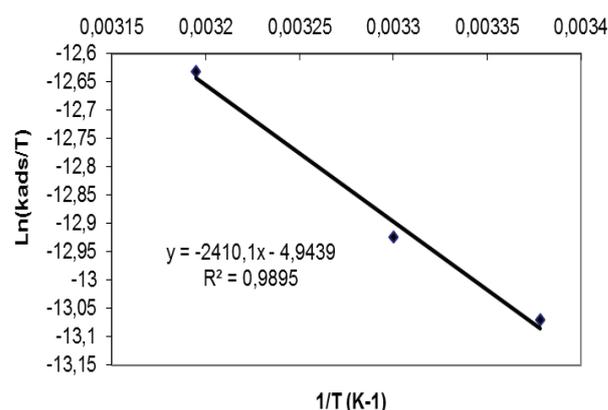

Fig. 4. Eyring plot for the kinetic data obtained at 23, 30 and 40 °C in the initial conditions pH ~ 5, D = 1 g/L, C_{Pb2+0} equal to 150 mg/L.

Equilibrium Studies

The Data

The lead (II) adsorption isotherms of activated coconut shells carbon are presented in Fig. 5. They are positive, regular and concave to the concentration axis whatever the temperature. The isotherms are of type L according to the Giles classification [14]. Pb(II) uptake at equilibrium is 100% with a 30 mg/L initial lead concentration for the activated carbon from coconut shells and decreases at higher concentrations whatever the temperature. It can be explained by the fact that, as long as there are available sites, the sorption increases with the lead concentration but as soon as all of the sites are occupied, a further increase in the lead concentration does not increase the amount of adsorbed lead cations. However, it can be seen from Fig. 5 that more lead is adsorbed at equilibrium at higher temperatures. So, the sorption equilibrium is favoured by a higher temperature.
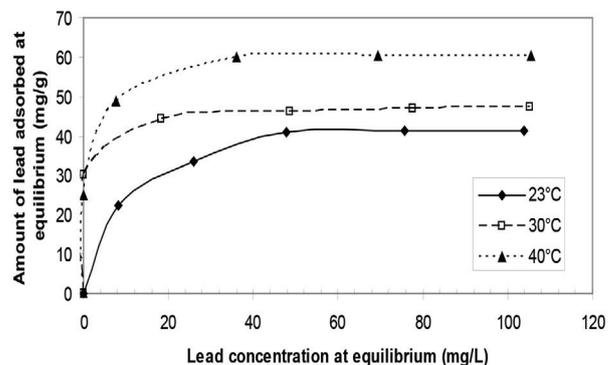

Fig. 5. Lead sorption isotherm for the activated carbon from Coconut shells at 23, 30 and 40 °C (initial conditions: pH ~ 5, D = 1 g/L, $C_{Pb2+, 0}$ = 0-150 mg/L).

Modelling the Data

The Isotherm Models

The equilibrium results are fitted according to the Langmuir and Freundlich models [15, 16]. The Freundlich model takes into account a variation in the adsorption energy of the sites during the adsorption process while Langmuir does not. The linear form of the both isotherm models is used:

- Langmuir:
$$C_{eq}/Q_{eq} = f(C_{eq}); \quad C_{eq}/Q_{eq} = C_{eq}/Q_m + 1/(K_L Q_m) \quad (9)$$
- Freundlich:
$$Ln(Q_{eq}) = f[Ln(C_{eq})]; \quad Ln(Q_{eq}) = (1/n)\, Ln(C_{eq}) + Ln(K_f) \quad (10)$$

Q_{eq} is the amount of lead adsorbed at equilibrium, Q_m is the monolayer amount of lead adsorbed, both are expressed in mol/kg; C_{eq} is the equilibrium concentration, it is expressed in mol/L. Figure 6 presents the Langmuir plots $C_{eq}/Q_{eq} = f(C_{eq})$.
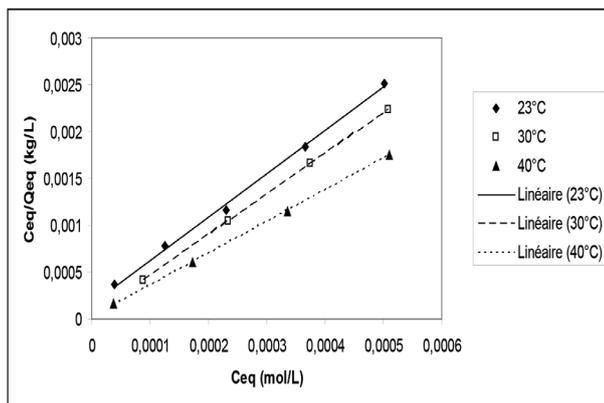

Fig. 6. Langmuir modelling of the equilibrium data of the activated Coconut shells carbon obtained at 23, 30 and 40°C in the initial conditions pH ~ 5, D = 1 g/L, C_{Pb2+0} varying from 0 to 150 mg/L.

The value of the squared correlation coefficient R^2 for the two models is given in Table 4. Analyses of the regression coefficients show that the Langmuir isotherm fits the data better. Consequently, K_L can be determined by the ratio slope/intercept.

Table 4
Correlation coefficients obtained from the modelling of the equilibrium data of the activated Coconut shells carbon obtained at different temperatures in the initial conditions pH ~ 5, $C_{Pb2+, 0}$ = 0-150 mg/L

R^2	296 K	303 K	313 K
Langmuir	0.995	0.999	0.999
Freundlich	0.989	0.170	0.036

The Thermodynamic Parameters

Using the Langmuir Model and the Vant'Hoff Equation

Equilibrium Constant

Table 5 gives the values of K_L obtained at each temperature. The values are high and increase with the temperature showing that the sorption is favoured by high temperatures.

Table 5
Equilibrium constants K_L obtained at different temperatures from the Langmuir modelling of the equilibrium data and equilibrium constant K_C obtained at different temperatures from the equilibrium data. Initial conditions: pH ~ 5, D = 1 g/L, $C_{Pb2+, 0}$ = 0-150 mg/L

	296 K	303 K	313 K
K_L	$4.8 \cdot 10^4$	$4.9 \cdot 10^5$	$3.8 \cdot 10^5$
K_C	$9.5 \cdot 10^2$	$4.4 \cdot 10^3$	$1.3 \cdot 10^4$

Free Standard Lead Sorption Enthalpy

The free standard lead sorption is calculated using the equation $\Delta G_L^\circ = -RTLn(K_L)$ (11). K_L is expressed in L.mol^{-1} and T, the temperature in Kelvin. The results are given in Table 6. The ΔG_L° values are negative and around - 30 kJ·mol^{-1}. Note that a negative sign of ΔG is an indication of a spontaneous reaction, but a negative sign of ΔG° is already promising for a process taking account that both terms are linked by equation (12): $\Delta G_L = \Delta G_L^\circ + RTLn(Q_R)$, Q_R being equal to Q_t/C_t (13).

Table 6
Thermodynamic parameters obtained either by fitting the Langmuir model to the data (with ΔH_L° = 79.8 kJ·mol^{-1} or using the classical method (with ΔH_C° = 117.7 kJ·mol^{-1}). Initial conditions: D = 1g/L; pH = 5; initial concentration range = 0-150 mg/L

	296 K	303 K	313 K
$\Delta G_L^\circ = - RTLnK_L$ (kJ·mol^{-1})	-26.5	-33.0	-33.4
$\Delta S_L^\circ = (\Delta H_L^\circ - \Delta G_L^\circ)/T$ (J·mol^{-1}·K^{-1})	359.1	327.3	361.7
$\Delta G_C^\circ = - RTLnK_C$ (kJ·mol^{-1})	-16.9	-21.2	-24.7
$\Delta S_C^\circ = (\Delta H_C^\circ - \Delta G_C^\circ)/T$ (J·mol^{-1}·K^{-1})	454.7	458.8	454.9

Standard Lead Sorption Enthalpy

The K_L constant at every temperature is applied to the Van't Hoff equation [17] (14): $Ln(K_L) = \Delta S_L^\circ/R$

- $\Delta H°_L/RT$ where $\Delta S°_L$ and $\Delta H°_L$ are respectively the standard entropy and enthalpy change for the adsorption. K_L is expressed in L·mol^{-1} and T, the temperature, in Kelvin. It is supposed that $\Delta H°_L$ is constant in the temperature range considered. Plotting the line Ln(K) in function of 1/T (Fig. 7) permits to obtain $\Delta H°_L$. Indeed, it is calculated by multiplying –R with the slope of the curve. $\Delta H°_L$ is positive indicating an endothermic process, indicating that the process is favoured at high temperature. $\Delta H_L°$ is equal to 79.8 kJ·mol^{-1}. This result is compared to those of the literature (see Table 7, [13, 18]). It can be seen that the sorption of lead onto the activated carbon from this study is the most energetic showing a more important impact of the temperature on the sorption at equilibrium for this activated carbon.
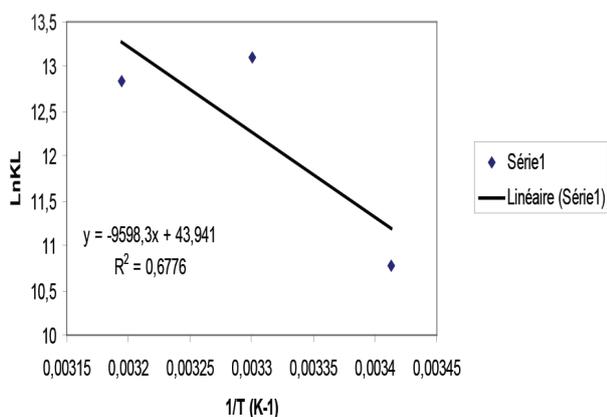

Fig. 7. Van't Hoff plot for the equilibrium data obtained at 23, 30 and 40 °C and fitted to the Langmuir model. Initial conditions pH ~ 5, D = 1 g/L, C_{Pb2+0} varying from 0 to 150 mg/L.

Table 7
Thermodynamic parameters obtained for the sorption of lead by the activated carbon from this study and from other works

	This study	Gerçel et al [13]	Patnukao et al. [14]	Sekar et al. [12]	Acharya et al. [19]
$\Delta H_L°$ (kJ·mol^{-1})	79.8	37.4	58.8		
$\Delta S_L°$ (J·mol^{-1}·K^{-1})	365.3	220.1	187.8		
$\Delta H_C°$ (kJ·mol^{-1})	117.7			93.4	44.0
$\Delta S_C°$ (J·mol^{-1}·K^{-1})	456.0			312.3	180

Standard Lead Sorption Entropy

The standard sorption entropy is calculated via the expression $\Delta S_L° = (\Delta H_L° - \Delta G°_L)/T$ (15). It is comprised between 360-370 J·mol^{-1}·K^{-1} as shown in Table 6. The positive value of $\Delta S_L°$ shows that the sorption process provides more randomness in the system. This result is compared to those of the literature in Table 7.

Using the Classical Approach and the Van't Hoff Equation

Equilibrium Constant

The equilibrium concentration (C_{eq}) for the same amount of lead adsorbed at equilibrium (Q_{eq} is taken equal to 40 mg/g) is determined at each temperature. KC is calculated with the following usual expression (16): $K_C = Q_{eq}/C_{eq}$. K_C is expressed in L·kg^{-1}. The values are given in Table 5. These K_C equilibrium constants are lower than the Langmuir ones. However, they show the same behaviour, increasing with temperature.

Note that some authors prefer to use the expression (17): $K_C' = (Q_{eq} \times D)/C_{eq}$ with Q_{eq} in mg/g, D in g/L and C_{eq} in mg/L or to recalculate C_{eq} with the isotherm model that better fits the equilibrium data. First, D = 1 g/L in this study, then, the results will not change. Secondly, the results are not upgraded in this study when C_{eq} is recalculated from the Langmuir equation.

Free Standard Lead Sorption Enthalpy

The free standard lead sorption is calculated via the equation $\Delta G_C° = -RT Ln(K_C)$ (11). The results are given in Table 6. They increase from 17 to 25 kJ·mol^{-1} with the temperature. The more negative $\Delta G_C°$, the more promising the sorption. It can be deduced that the sorption is favoured with the temperature. The results obtained with the classical method are lower than those obtained with the Langmuir one as expected from the lower equilibrium constants.

Standard Lead Sorption Enthalpy

The K_C constant at every temperature is applied to the Van't Hoff equation (14): $Ln(K_C) = \Delta S°_C/R - \Delta H°_C/RT$. Plotting the line Ln($K_C$) in function of 1/T permits to obtain $\Delta H°_C$ (see Fig. 8). $\Delta H°_C$ is positive, as obtained from the Langmuir results, indicating an endothermic process. $\Delta H°_C$ is equal to 117.7 kJ·mol^{-1}, a higher value than that obtained with the Langmuir modelling. This value is also more precise taking account the higher regression coefficient ob-

tained for the linearization of Ln(K) in function of the inverse of the temperature (0.97 against 0.68). This result is compared to those of the literature [12, 19]. As seen in Table 7, the result obtained is close to that of Sekar on another activated carbon from coconut shells [12].
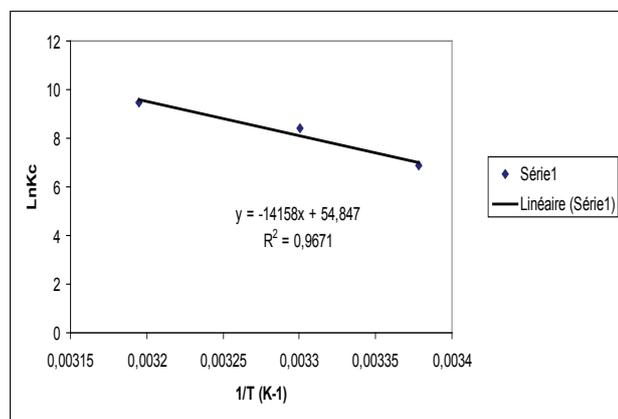

Fig. 8. Van't Hoff plot for the equilibrium data obtained at 23, 30 and 40 °C in the initial conditions pH ~ 5, D = 1 g/L, C_{Pb2+0} varying from 0 to 150 mg/L.

Standard Lead Sorption Entropy

The standard sorption entropy is calculated via the expression $\Delta S_C° = (\Delta H_C° - \Delta G_C°)/T$ (15). It is quasi constant and equal to 455 J·mol^{-1}·K^{-1} (see Table 7). It is not surprising that the standard entropy value is constant because as the $\Delta S_C°$ and the $\Delta H_C°$ are generally considered constant in the temperature range considered in thermodynamic studies. The positive value of $\Delta S_C°$ shows that the sorption process provides more disorder in the system as obtained from the Langmuir modelling. This result is compared to those from the literature as seen in Table 7, the value obtained is the highest one.

Using the Clausius-Clapeyron Equation Adapted to the Sorption Equilibrium Pb (II)$_{aq}$ ⇆ Pb (II)$_{ads}$

Standard Lead Sorption Enthalpy

The equilibrium concentrations (C_{eq}) for the same amount of lead adsorbed at equilibrium (Q_{eq} is chosen equal to 40 mg/g) at each temperature are determined.

Then, the C_{eq} values obtained are applied to the adapted Clausius–Clapeyron equation (17): Ln(C_{eq}) = B + $\Delta H°/RT$ where B is a constant and $\Delta H°$ is the enthalpy change for the adsorption of lead by the activated coconut shells carbon. C_{eq} is expressed in mol·L^{-1} and T in Kelvin. At our knowledge, it is

the first time this equation is used. The $\Delta H°$ value is calculated from the slope of the linear fit shown in Fig. 9. It is equal to 117.7 kJ·mol^{-1}, the same value that is obtained from the classical method. However, the Clausius-Clapeyron method is easier to use and can be recommended for the calculation of the standard enthalpy. Note that some authors have demonstrated an evolution of $\Delta H°$ in function of the evolution of the sorption reaction, calculating different $\Delta H°$ corresponding with different Q_{eq}. In this study, whatever the chosen Q_{eq}, the same $\Delta H°$ is found and this result is coherent with the Langmuir model fitting to the equilibrium data.
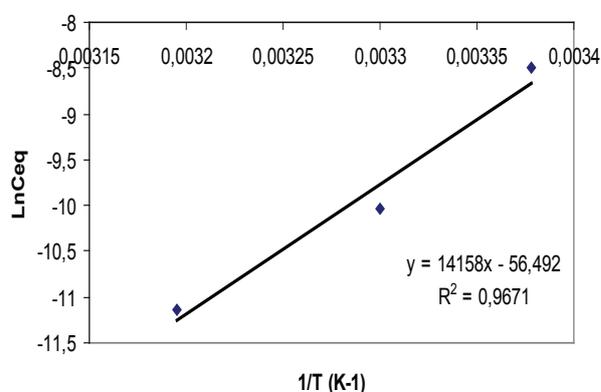

Fig. 9. Clausius Clapeyron plot for the equilibrium data obtained at 23, 30 and 40 °C in the initial conditions pH ~ 5, D = 1 g/L, C_{Pb2+0} varying from 0 to 150 mg/L.

Thermokinetic Understanding

High temperature favours the sorption from a kinetic point of view as well as from a thermodynamic one, taking into account that both rate and equilibrium constants increase with temperature. So, more Pb(II) can be adsorbed more rapidly with increasing temperature. This result is different from that of Li [20] who found that more lead is adsorbed at equilibrium with decreasing temperature.

First, considering the kinetics, the low value of the activation energy (22.6 kJ·mol^{-1}) shows that the sorption process is easy. This is confirmed from the results of the sorption activation thermodynamic parameters. $\Delta H°^{\neq}$ is equal to 20.0 kJ·mol^{-1} which is a low value and $\Delta S°^{\neq}$ is positive and equal to 238.6 J·mol^{-1}·K^{-1} which is indicative of a dissociative sorption process.

Then, considering the thermodynamics, whatever the way of calculating the parameters (Langmuir or classical method), the values obtained for the equilibrium constants are quite high. Consequently, the sorption of lead on the activated carbon is very

favourable. The activated carbon has a good affinity for Pb (II) as confirmed by the concavity of the adsorption isotherm.

$\Delta H°$ is equal to 79.8 kJ·mol^{-1} using the Langmuir model or 117.7 kJ·mol^{-1} using the classical or the Clausius Clappeyron method. However, the positive value of the standard enthalpy shows that the sorption process is endothermic and consequently favoured at high temperature. Moreover, the positive value of $\Delta H°$ shows that the sorption process is essentially a chemical process even if the value obtained for $\Delta H°$ is between the values of a physical ($\sim$ 30 kJ·mol^{-1}) and a chemical sorption process (> 200 kJ·mol^{-1}).

$\Delta S_C°$ is equal to 365.3 or 456.0 J·mol^{-1}·K^{-1} considering the Langmuir model or the classical method and shows that the lead sorption provides more randomness in the activated carbon.

According to these remarks and to the surface properties of the activated carbon given in Table 8, the sorption process seems to be, first, a chemical bond with the lead and the OH group of the carbon, then when all the sites are occupied a static interaction of the cation Pb (II) with the π electrons of the carbon present in the graphene layer.

Strangely enough, very few literature data can be found on thermokinetics of lead sorption [12]. Values such as activation energy and standard enthalpy change are useful parameters to predict the sorption results whatever the operating conditions. Indeed, the knowledge of A and E permits to calculate the rate constant at any temperature, both being linked by equation (5). The knowledge of $\Delta H°$ and $\Delta S°$ permits to determine K under any conditions in order to predict the direction and the final state of the sorption reaction (see equations (11), (12) and (15)).

Table 8
Surface properties of the activated carbon from
Coconut shells

	Activated carbon from Coconut shells
S $_{BET}$ (m^2/g)	1058
V$_{mi}$ (cm^3/g)	0.49
V$_{me}$ (cm^3/g)	0.00
Total of acid oxygenated surface groups (mmol/g): - Carboxyl groups - Hydroxyl groups - Lactone groups	0.3 0 0.3 0
Total of basic oxygenated surface groups (mmol/g):	0.9
pH PZC	9.2

Conclusions

The aim of this study is to investigate the effect of the temperature on the adsorption of lead by an activated carbon from coconut shells. The kinetic data fit the pseudo second order model and the rate constants are determined. Increasing the temperature increases the rate constants. The equilibrium fits the Langmuir model and the equilibrium constants are determined. Increasing the temperature increases also the equilibrium constants. Consequently, both kinetics and thermodynamics of the sorption of Pb(II) on this activated carbon are favoured by high temperature. However, the rate and the equilibrium constants depend on the operating conditions and intrinsic parameters (independent of the operating conditions) such as activation energy and sorption enthalpy, are better and more general parameters to characterize the sorption and comparing adsorptives. Using the Arrhenius equation permits to determine the activation energy of the sorption reaction. It is equal to 22.6 kJ·mol^{-1}. Such a low activation energy shows that the sorption process is very easy. Using the adapted Clausius Clapeyron equation, which, at our knowledge, is done for the first time in this work, one can calculate the standard enthalpy of the sorption reaction. It is equal to 117.7 kJ·mol^{-1}, typical for an essentially chemical endothermic sorption process. On the basis of the thermokinetic results obtained, the activated coconut shells carbon must be used around 30 °C for the sorption of lead. More generally speaking, this activated carbon can be used efficiently for the treatment of water polluted by heavy metals. In addition, the knowledge of the thermokinetic parameters will permit to predict sorption results under any operating conditions without having to refer to supplementary experiments.

Acknowledgements

References

1. G.S. Murugesan, M. Sathishkumar, K. Bioresour. Technol. 97 (2006) 483-487.
2. M. Kobya, E. Demirbas, E. Senturk, M. Bioresour. Technol. 96 (2005) 1518-1521.
3. M. Ahmedna, W.E. Marshall, A.A. Husseiny, R.M. Rao, I. Goktepe, Water Res. 38 (2004) 1062-1068.
4. S.A. Wasay, S. Barrington, S. Tokunaga, Water, Air Soil Pollut. 116 (1999) 449-460.
5. S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc. 60 (1938) 309-319.

6. M.M. Dubinin, G.M. Plavnik, Carbon. 6 (1968) 183-192.

7. H.P. Boehm, Carbon. 32 (1994) 759-769.

8. J.S. Noh and J.A. Schwarz, Carbon. 28 (1990) 675-682.

9. Lagergren, S., Zur theorie der sogenannten adsorption ̈geloster stoffe. K. Sven. Vetenskapsakad. Handlingar. 24 (4) (1898), 1-39.

10. Y.S. Ho, G.McKay, Pseudo second order model for sorption processes, Process Biochem. 34 (1999). P. 451-465.

11. P. Morlaes, J.C. Morlaes, Cinétique chimique, Vuibert. 1981. 310 p.

12. M. Sekar, V. Sakthi, S. Rengaraj, Journal of colloid and Interface science. 279 (2004) 307-313.

13. O. Gerçel, H.F. Gerçel, Chemical engineering journal. 132 (2007) 289-297.

14. C.H. Giles, T.H. MacEwan, S.H. Nakhwa, D. Smith, J. Chem. Soc. 111 (1960) 3973-3993.

15. I. Langmuir, J. Am. Chem. Soc. 40 (1918) 1361-1403.

16. H. Freundlich, W.J. Helle, J. Am. Chem. Soc. 61 (1939) 2-28.

17. R. Perrin, et J.E. Scharff, Chimie Industrielle 2ᵉ édition, ed. Dunod, (2002).

18. P. Patnukao, A. Kongsuwan, P. Pavasant, Journal of Environmental Sciences. 20 (9) (2008) 1028-1034.

19. J. Acharya, J.N. Sahu, C.R. Mohanty, B.C. Meikap, Chemical Engineering Journal. 149 (1-3) (2009) 249-262.

20. K. Li, X. Wang, Bioresource Technology. 100 (11) (2009) 2810-2815.

Received 18 July 2013