Influence of the Surface Properties of the Bois Carré Seeds Activated Carbon for the Removal of Lead From Aqueous Ssolutions

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Abstract

An activated carbon from Bois carré (*Citharexylum Fruticosum L.*) seeds was prepared by chemical activation with phosphoric acid. The activated carbon obtained has a surface area of 594 m^2/g and a high content of acid groups of 3.44 $mmol.g^{-1}$. This carbon was studied for the removal of lead from water. Sorption studies were performed at 30 °C at different pH and adsorbent doses, in batch mode. Maximum adsorption occurred at pH 7 for an adsorbent dose of 1g/L. Kinetic studies, at the initial concentration of 150 mg/L of lead, pH 5 and an adsorbent dose of 1 g/L, yielded an equilibrium time of 30 h for this activated carbon. The kinetic data were modelled with the pseudo first order, the pseudo second order and the Bangham models. The pseudo second order model fitted the data well. The sorption rate constant (2.10^{-3} $mol^{-1}.Kg.s^{-1}$) and the maximum amount of lead adsorbed are quite good (0.18 $mol.kg^{-1}$) compared to the data found in literature. Sorption equilibrium studies were conducted in a concentration range of lead from 0 to 150 mg/L, at pH 5, adsorbent dose 1 g/L. In an aqueous lead solution with an initial concentration of 30 mg/L, activated Bois carré seed carbon removed (at equilibrium) 48 % of the heavy metal. The equilibrium data were modelled with the Langmuir and Freundlich equations, of which the latter gave the best fit. The Freundlich constants n (3.76 $L.mol^{-1}$) and Kf (1.06 $mol.kg^{-1}$) are in good agreement with literature. The Bois carré seed activated carbon is a very efficient carbon in terms of the metal amount adsorbed per unit of surface area (0. 06 m^2/g). This good result is due to the presence of many active acid sites on the surface of this activated carbon.

Introduction

The presence of metals in the environment can be natural or linked to human activities like mining, electroplating industries and fossils combustion. Metals are present in the atmosphere as well as in the water. Untreated effluents may have an adverse impact on the environment [1, 2]. Heavy metals including cadmium, lead and zinc are toxic to aquatic flora and fauna even in relatively low concentrations. Moreover, some of them can be assimilated, stored and concentrated by organisms [3, 4]. Heavy metals are the priority pollutants observed in many municipalities and specific and in the water by acid mine drainage or batteries industries [5, 6]. Lead is emitted in the atmosphere by the combustion of leaded gasoline [7, 8, 9, 10]. The maximum allowable lead recommended in drinking water is 0.05 mg/L according to the world health organization WHO guideline [11].

Various technologies such as precipitation, ion exchange, membrane filtration, reverse osmosis are used for the water treatment [12, 13, 14]. The use of adsorbents to remove heavy metal ions from wastewater is a well established process. The economics of this process depend mainly on the cost of the adsorbent material. As such, low cost adsorbents including biosorbents, clays and activated carbons are becoming the focus of many investigations [15, 16, 17]. Activated carbons can be produced from many raw materials such as agricultural and industrial wastes like palm shells or bagasse fly ash [18, 19]. The Bois carré

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(*Citharexylum Fruticosum L.*) seed is an agricultural by-product since only the leaves of the tree have a medicinal use. The preparation of activated carbon from bois carré seeds is by chemical activation with phosphoric acid at low temperature in order to economize energy and favour the formation of acidic oxygenated sites which are thought to be the active sites for the sorption of heavy metals [20]. The adsorption capacity of Bois carré seed activated carbon to remove lead from water is studied in this work. The basic objectives of the present investigation are to demonstrate the efficiency of this activated carbon for the removal of lead, to determine the optimum conditions for its use, to highlight the effect of the surface groups on the adsorption and to establish the adsorption mechanism.

Experimental methods

Reagents

The 85 % phosphoric acid solution used to prepare the activated carbon, the 69.4 % nitric acid solution and the NaOH used to fix the pH, the $Pb(NO_3)_2$ which is the lead ions source, the $NaNO_3$ used to fix the ionic force of the solution are all obtained from Prolabo. All solutions were prepared with deionised water.

The activated carbon

Preparation

The activated carbon from Bois carré seeds is prepared by soaking 10 g of seeds (size: 0.4-1 mm) with 30 g of 30 wt% phosphoric acid solution during 68h resulting in a solvent impregnation ratio of 0.9. Then the solid mixture is heated at 450 °C (heating rate: 10°C/min) for 2 h in a nitrogen atmosphere (60 mL/min). After cooling down to room temperature, the sample is rinsed with hot distilled water in a soxhlet extractor until the pH remains constant. Then, the activated carbon sample is dried at 105 °C for 2 days.

Characterization

Texture

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

The BET surface area, the DR-micropore volume, the mesopore volume, the median pore diameter and the DFT pore size distribution 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 [21] to the isotherm in the relative pressure (P/P°) range 0.05 and 0.3 and taking account the average area occupied by a molecule of N_2 to be equal to 16.2 $Å^2$.

The micropore volume (Vmi) is estimated from the N_2 adsorption isotherm by applying the Dubinin-Radushkevich equation [22] in the relative pressure (P/P°) range between 0.05 and 0.15 and the mesopore volume (Vme) as the volume of N_2 adsorbed at P/P° = 0.99 minus the micropore volume. The DFT pore size distribution is calculated by assuming a slit like geometry for the micropores [23].

Surface properties

The surface properties of the activated carbon are characterized via the well-known Boehm method [24]. Using this method, it is assumed that HCl neutralizes all of the basic groups; 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 [25]. 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 %.

In addition, a scanning electron microscope (SEM) Hitachi S-2500 is used to determine the surface textural characteristics of the activated carbon. The carbon is firstly mounted on an aluminium stub, then, the microscope is operated at an accelerating voltage of 200 kV and a working distance of 35 mm.

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 fixed pH. The flask is put in a stirrer water bath maintained at a constant temperature of 30 °C. The dose adsorbent D is calculated by the ratio W/V. The initial concentration of lead is 150 mg/L for the kinetic study or between 30 and 150 mg/L for the equilibrium study. Note that the initial concentrations of lead used in this study are similar to lead concentrations found in industrial effluents. The pH 3 and 5 are obtained by mixing predetermined volumes of 0.01 M HNO_3 to the lead solution; pH 7, 9 and 11 are obtained by adding predetermined volumes of 0.01 M NaOH.

At regular intervals for the kinetic study, and at the equilibrium time for the equilibrium study, 5 mL of solution is removed from the flask, filtered through a Whatmann 32 filter paper and the concentration of the remaining lead in solution is measured. Note that the stirring is stopped before each removing and 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 concentrations of lead are measured with an atomic absorption spectrometer AA240FS from Varian; the pH of the solutions are measured with a Mettler Toledo FG2 pHmeter. All glassware is presoaked in a 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

$$(C_t \text{ or } C_{eq}):\ Q\ (\mathrm{mg/g}) = (C_0 - C)/D \quad (1).$$

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

Characterization of the activated carbon

A picture of the Bois carré seeds and SEM migrographs of the Bois carré seeds and the activated carbon from Bois carré seeds can be seen in Fig.1 and 2.

Fig. 1. Picture of the Bois carré seeds.

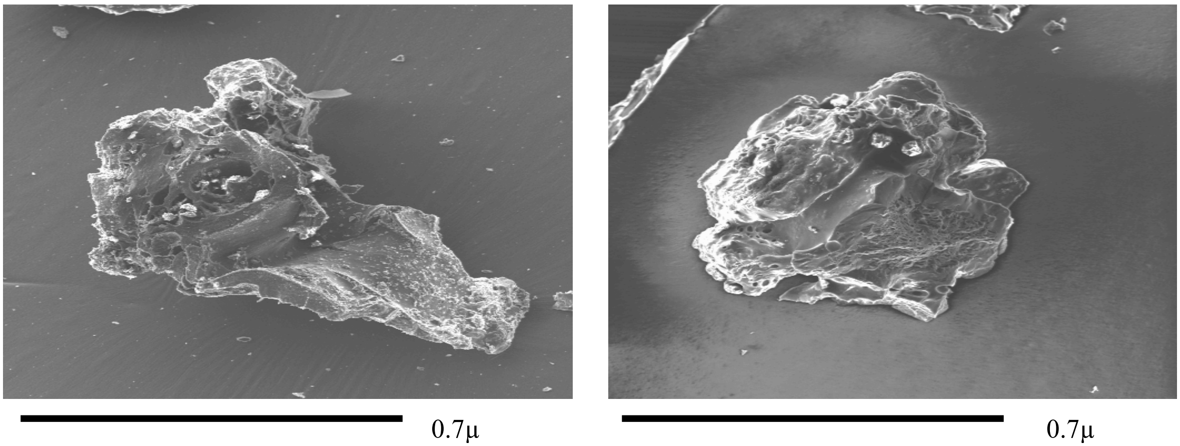

Fig. 2. a- SEM micrograph of the Bois carre seeds; b- SEM micrograph of the activated Bois carre seeds carbon.

In this study, the low temperature of activation of the carbon has been selected in order to economize energy and favour the development of oxygenated acid sites which are thought to be responsible of the chemisorption of lead [20]. Nevertheless, the textural properties of the activated carbon have also been studied.

The nitrogen adsorption/desorption isotherm for the activated Bois carré seed carbon is shown in Figure 3. The isotherm is of type IV according to the BDDT classification, with a distinct first (type I) part [26]. This kind of isotherm is characteristic for micro-mesoporous materials. The knee of the isotherm opens up revealing a widening of microporosity, the plateau is not horizontal due to the development of mesoporosity. Existence of mesopores is confirmed by the presence of a hysteresis loop. The hysteresis is of type B, implying a slit like pore geometry [26].

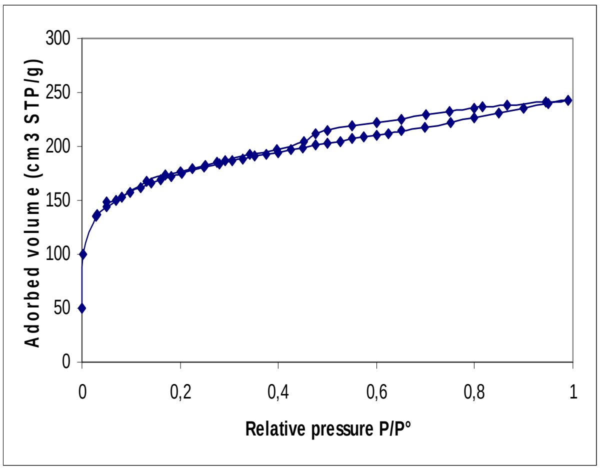

Fig. 3. Adsorption isotherm of N_2 at 77 K on the activated Bois carré seeds carbon.

The values of S_{BET}, Vmi, Vme obtained from the isotherm are listed in Table 1. The micropore volume is rather low as expected from the low temperature of activation. However, the presence of many mesopores (as expected from a chemical activation with phosphoric acid) can facilitate the access of the pollutant to the microporosity. The micropore size distribution of the activated carbon is studied according to the DFT model, one of the most adequate models for microporous materials. In figure 4, it is shown that there are many micropores of size 10-15 Å which is in relation to the size of lead atom (R_{Pb} = 1.5 Å).

The surface properties of the activated carbon are listed in Table 1. They are high as expected from the low temperature of activation. The total number of acid groups on the surface of the activated carbon is 3.44 mmol/g. It is a rather high content compared to other activated carbons which are generally in the range of 1 to 5 mmol/g [19]. The activated Bois carré seed carbon is an acid activated carbon. His pH PZC is inferior to 7 and it presents only acidic groups on its surface. The distribution of the acidity is large because alcohol, lactone and carboxylic groups are all present, with a predominance of alcohol groups.

Table 1

Surface properties of the activated carbon from Bois carré seeds

	Activated carbon from Bois carré seeds
S_{BET} (m^2/g)	594
V_{mi} (cm^3/g)	0.24
V_{me} (cm^3/g)	0.12
Median pore diameter (nm)	0.74
Total of acid oxygenated surface groups (mmol/g) :	3.44
- Carboxyl groups	0.58
- Hydroxyl groups	2.25
- Lactone groups	0.61
Total of basic oxygenated surface groups (mmol/g)	0.0
pH PZC	6.3

Sorption studies

Kinetic studies

The data

The uptake rate of lead by the activated carbon from Bois carré is studied at pH ~ 5 for an initial lead concentration of 150 mg/L, an adsorbent dose of 1g/L at 30 °C (Fig. 5). The sorption is quite rapid: 19 % of the lead is removed within the first two hours followed by a slow approach to equilibrium. This can be explained by the fact that, as the metal concentration increases on the surface with the reaction, the higher energy surface sites saturate and the adsorption shifts to the lower energy surface sites, resulting in a decrease of the sorption rate. Equilibrium is reached after 30 h.

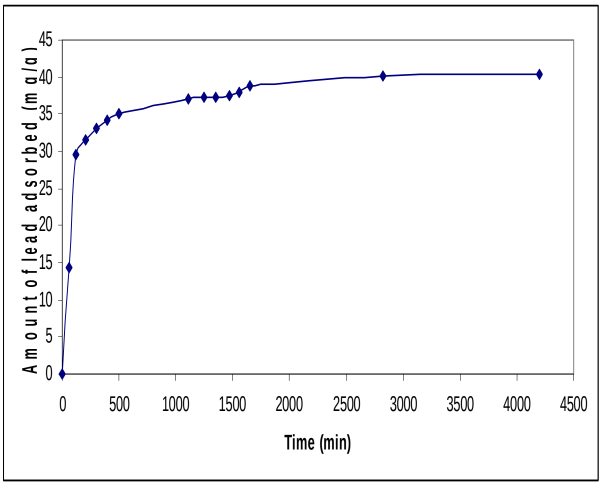

Fig. 5. Effect of time upon the adsorption of lead by the activated carbon from Bois carré seeds at 30 °C (initial conditions : pH ~ 5, D = 1 g/L, $C_{Pb2+, 0}$ = 150 mg/L)

Modelling the data

The kinetic results are fitted according to the linear form of the pseudo first order, the pseudo second order and the Bangham models:

- Bangham model: $Ln(Q_t) = f\{Ln(t)\}$;
- $Ln(Q_t) = \nu.Ln(t) + Ln(k)$ (2)
-
- Pseudo first order model [27, 28]:
- $Ln(Q_{max}–Q_t) = f\{t\}$;
- $Ln(Q_{max}–Q_t) = -k_1t + Ln(Q_{max})$ (3)
-
- Pseudo second order model [29]:
- $t/Q_t = f(t)$; $t/Q_t = t/Q_{max} + 1/[k_2(Q_{max})^2]$ (4)

Q_t (mol/kg) is the amount of lead adsorbed at a time t(s) and Q_{max} (mol/kg) is the maximum amount of lead adsorbed.

There are three steps in an adsorption process. First, the external diffusion of the adsorbate from the bulk solution to the adsorbent followed by the internal diffusion of the adsorbate to the sorption sites then the sorption itself. The two latter models are based on the fact that the sorption is the rate limiting step in the adsorption process including one or two adjacent sorption sites and the first one supposes that the diffusion is the rate limiting step. So, the fitting to the models will permit to elucidate the adsorption mechanism.

The values of the correlation coefficients R^2 are presented in Table 2. From this, a pseudo second order model can be put forward for the activated Bois carré seeds carbon. This means the rate limiting step in the process is the chemical sorption between the lead and the active sites of the carbon. This result is in agreement with the literature data [30, 31, 32, 33].

Table 2

Correlation coefficients obtained from the modeling of the kinetic data of the activated Bois carré seeds carbon obtained at 30°C in the initial conditions pH ~ 5, D = 1 g/L, $C_{Pb2+, 0}$ = 150 mg/L

	Time range (s)	R^2
Bangham	0-18000	0.801
Pseudo first order	0-12600	0.904
Pseudo second order	0-72600	0.993

The rate constant k_2 and the maximum amount of lead adsorbed $Q_{max,\ calc}$ are calculated from the curve fitting. $Q_{max,\ calc}$ is equal to 1/slope and k_2 is equal to slope^2/intercept. The value of k_2 (2.10^{-3} $mol^{-1}.Kg.s^{-1}$) is a good value according to the literature (moreover, it is well known that a high initial concentration of lead decreases the reaction rate). It can be related to the oxygenated acid groups present on the carbon surface. However, the different acid groups do not react in the same way. The COOH groups must be more favourable adsorption sites towards lead sorption than OH groups because of their lower pka and the lactone groups can be considered as non active sites because they cannot exchange hydrogen.

The value of the maximum amount of lead adsorbed obtained from the experiment or the fitting (40.2 or 38.5 mg/g) is also a good value compared to literature data (see Table 3), in spite of the low surface area of the activated carbon. Such a good value can be explained by the presence of many surface groups on the activated carbon enhancing the chemisorption of lead. Considering the amount of lead adsorbed per unit surface area (0.06 m^2/g) versus those of other activated carbons, the Bois carré seed activated carbon is very efficient.

Table 3

Rate constants (k_2) and maximum amounts of lead obtained ($Q_{max,\ calc}$) by fitting the pseudo second order equation to the activated carbons sorption results in this study and from references.

	This study	[30]	[31]	[32]	[33]
Activated carbon	Home made Granular	Home made Powdered	Commercial	Home made Powdered	Home made Powdered
Raw material	Bois carré seeds	Eucalyptus bark	Husks, pods of Moringa oleifera	Bamboo	Polygonum orientale linn
Activation treatment	Chemical H_3PO_4 at 450°C	Chemical H_3PO_4 at 500°C	n.a + Additional impregnation with H_3PO_4	Physical with air + impregnation with H_3PO_4 + washing with HCl	Chemical H_3PO_4 at 450°C
S_{BET} (m^2/g)	594	1239	725		1398
Sorption tests at : - T (°C) - D (g/L) - pH - initial concentration (mg/L)	 - 30 - 1 - 5 - 150	 - 25 - 4 - 5-6 - 100	 - 30 - 2 - 5.8 - 30	 - 29 - 1-5 - 5 - 50-90	 - 25 - 0.6 - 5 - 80
$Q_{max,\ exp}$ (mg/g)	40.2	93.2		50.5	102.0
$Q_{max,\ calc}$ (mg/g)	38.5	18.6	29.1	51.3	102.0
$Q_{max,\ calc}$ (mg/m^2)	0.06	0.01	0.04		0.07
k_2 (mg^{-1}.g.min^{-1})	$5.8.10^{-4}$	$1.6.10^{-4}$	$6.2.10^{-3}$	$4.3.10^{-3}$	$3.0.10^{-2}$

Equilibrium studies

The lead adsorption isotherm

The lead adsorption isotherm of activated Bois carré seed carbon at 30 °C is positive, regular and concave to the concentration axis. The isotherm is of type L (Fig. 6) according to Giles classification [34]. Pb(II) uptake at equilibrium is 48 % with a 30 mg/L initial lead concentration for the activated carbon from Bois carré seeds and decreases at higher concentrations. It can be explained by the fact that, as soon as there are available sites, chemisorption 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 cations. The final upsweep of the isotherm must be due to the competition between water and lead. The water, previously adsorbed, leaves the active sites of the carbon when the cation concentration increases. As a consequence, fresh lead is adsorbed and contributes to the upsweep in the isotherm at high lead concentration. It can be seen from figure 4 that the maximum amount of lead adsorbed at equilibrium ($Q_{max\ eq,\ exp}$) for the activated carbon from Bois carré seeds is 37.9 mg/g, which is in good agreement with the maximum amount of lead calculated (38.5 mg/g).

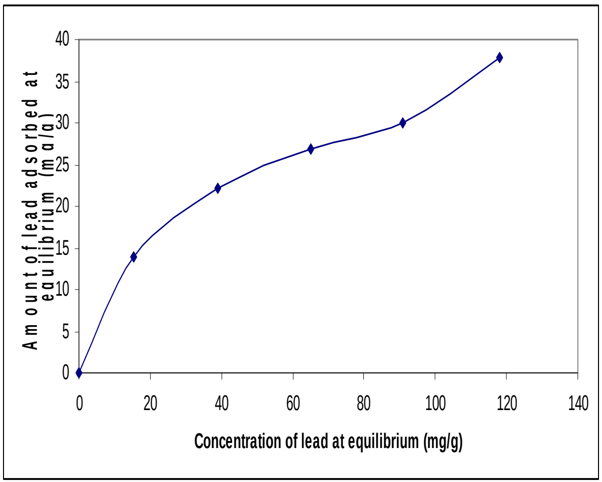

Fig. 6. Sorption isotherm of lead for the activated carbon from Bois carré seeds at 30 °C (initial conditions: pH ~ 5, D = 1 g/L, $C_{Pb2+,\ 0}$ = 0 - 150 mg/L)

Modelling the data

The equilibrium results are fitted according to the Langmuir and the Freundlich models [35, 36]. These models are the most used for a chemisorption process where a real chemical bond establishes between the adsorbent and the adsorbate. 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:

$$\text{Langmuir: } C_{eq}/Q_{eq} = f\{C_{eq}\};\ C_{eq}/Q_{eq} = C_{eq}/Q_m + 1/(KQ_m) \qquad (5)$$

$$\text{Freundlich: } Ln(Q_{eq}) = f\{Ln(C_{eq})\};\ Ln(Q_{eq}) = (1/n)\ Ln(C_{eq}) + Ln(Kf) \qquad (6)$$

Q_{eq} is the amount of lead adsorbed at equilibrium, Q_m is the monolayer amount of lead adsorbed (mol/kg); C_{eq} is the equilibrium concentration (mol/L). The fitting to the models will reflect the equilibrium process behaviour.

The values obtained for the squared correlation coefficient R^2 are respectively 0.911 for the Langmuir model and 0.973 for the Freundlich one, then, the Freundlich isotherm fits the data better. Consequently, the surface of the activated Bois carré seed carbon is inhomogeneous towards the lead adsorption. This result is in agreement with the different acid sites found on this activated carbon implying different ways of sorption for the lead. Moreover, this result fits with some of the literature data [37, 38, 39]. The Freundlich constants n, relative to the couple adsorbent-adsorbate, and Kf, the relative adsorption capacity, can be determined and compared to those found in literature (see table 4). Kf is calculated by taking the exponential of the intercept and n is equal to 1/slope. The values obtained (n = 3.76 L.mol^{-1} ; Kf = 1.06 mol.kg^{-1}) are good values according to literature: the sorption can be considered as good when n is comprised between 1 and 10 and it is the case for the activated Bois carré seeds carbon.

Table 4

Maximum amount of lead obtained at equilibrium ($Q_{max,\ eq}$) and Freundlich parameters (n, Kf) obtained in this study and from other works.

	This study	[37]	[38]	[38]	[39]
Activated carbon	Home made Granular	Commercial Granular	Commercial ACC CS1501	Commercial ACC RS1301	Commercial AC5
Raw material	Bois carré seeds				Cococonut shell
Activation treatment	Chemical H_3PO_4 at 450°C	Additional treatment with H_2S			Additional treatment with HCl and HNO_3
Activated carbon properties: - S_{BET} (m^2/g) - pH PZC - Total acid groups (mmol/g)	 - 594 - 6.3 - 3.44	 - 900 - 4.5 - 0.17	 -1680 - 7.5 - 1.10	 -1460 - 9.5 - 0.80	 -1070 -3.2 -1.96
Sorption tests at : - T (°C) - D (g/L) - pH - initial concentration range (mg/L)	 - 30 - 1 - 5 - 0-150	 - 20 - 2 - 5 - 0-70	 - 20 - 2 - 5 - 0-70	 - 20 - 2 - 5 - 0-70	 - - 2 - 4 - 0-260
$Q_{max\ eq,\ exp}$ (mg/g)	37.9	29.4	33.1	24.9	35.0
$Q_{max\ eq,\ exp}$ (mg/m^2)	0.06	0.03	0.02	0.02	0.03
n (L.mmol^{-1})	2.14		1.79	3.02	
n (L.g^{-1})	2.14	2.68			3.77
Kf (mmol.g^{-1})	0.23		0.12	0.17	
Kf (mg.g^{-1})	3.88	12.44			9.95

Sorption mechanism

To further understand the sorption mechanism of Pb(II), the final pH values at adsorption equilibrium are measured for an initial pH of ~ 5 for the isotherm at 30 °C. The final pH is lower than the initial pH at all initial metal ion concentrations. Furthermore, the final pH decreases when the initial metal concentration increases (Fig. 7). The drop in pH with a rise in the initial metal concentration is due to the release of H^+ from the carbon. Similar results for Cu(II), Pb(II), and Ni(II) adsorption on activated carbon cloth are reported by Kadirvelu et al [40]. The activated carbon contains carboxyl and hydroxyl groups which are active sites for the lead sorption. Carboxyl and hydroxyl groups can take part in the chemisorption process in the following manner:

$$2\ C\text{–}COOH + Pb^{2+} = C\text{–}COOPbOOC\text{–}C + 2\ H^+ \quad (7)$$

$$2\ C\text{–}OH + Pb^{2+} = C\text{–}OPbO\text{–}C + 2\ H^+ \quad (8)$$

Formation of hydroxylated species may be also considered:

$$C\text{–}COOH + Pb^{2+} + H_2O = C\text{–}COOPbOH + 2\ H^+ \quad (9)$$

$$C\text{–}COOH + Pb(OH)^+ = C\text{–}COOPbOH + H^+ \quad (10)$$

Note that all these reactions lead to an acidification of the solution during adsorption. This mechanism is somewhat different from those suggested in the literature since it uses one or two sorption sites where lead is linked to and respect the electro neutrality of the carbon surface [20].

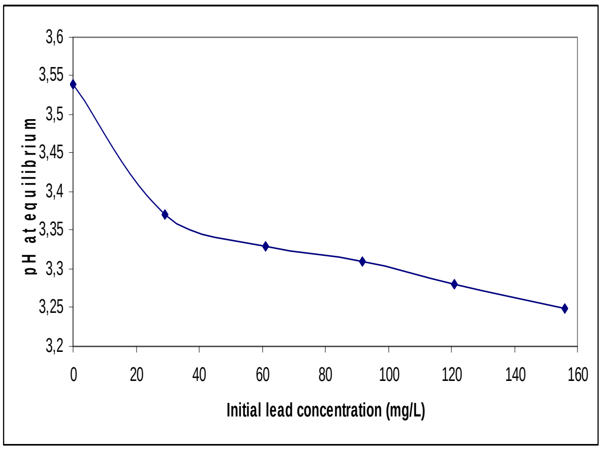

Fig. 7. Effect of the initial lead concentration upon the pH at equilibrium for the activated carbon from Bois carré seeds at 30 °C, D = 1 g/L, initial pH ~ 5.

Optimum conditions for the sorption

The adsorption of Pb by activated Bois carré seed is pH dependent. Experiments at equilibrium are conducted to determine the optimum pH. Figure 8 shows that the optimum pH is 7. This result can be explained by the following reasons taking account both the solution pH and the adsorbent pH.

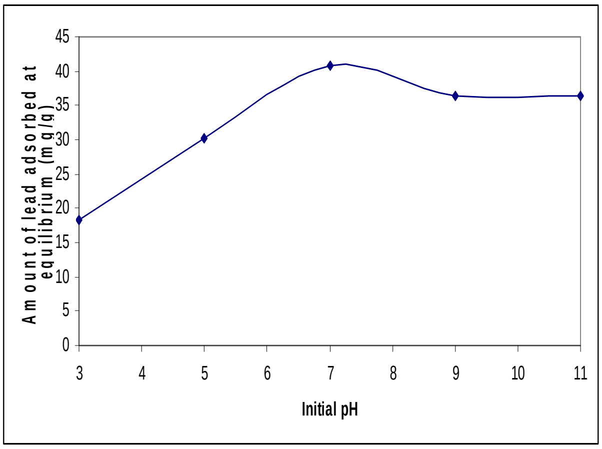

Fig. 8. Effect of the initial pH on the adsorption equilibrium of Pb(II) on the activated carbon from Bois carré seeds at 30 °C, D = 1 g/L, initial concentration of lead 150 mg/L.

The hydrolysis pH of Pb is thought to be 6.0 and the precipitation pH is 7.7 [41, 42, 43, 44]. Consequently, the predominant form of Pb(II) is Pb^{2+} at pH inferior to 6.0, $Pb(OH)^+$ between pH 6.0-7.7 and $Pb(OH)_2$ at pH superior to 7.7.

At pH inferior to pH PZC, the surface groups of the activated carbon are positively charged, consequently, the sorption of Pb^{2+} is not favoured because of the repulsive interactions between the carbon and the lead. Moreover, the Pb^{2+} competes more with the H^+ for the sorption on the active sites at low pH; at pH superior to pH PZC, the surface groups are negatively charged, consequently the sorption of Pb^{2+} and $Pb(OH)^+$ are favoured. On the opposite, at pH superior to 7.7, the sorption of $Pb(OH)_2$ is more difficult because the species is not charged. Hence the theoretical optimum pH lies between 6.0 and 7.7 as shown on Fig. 6.

The rate of Pb(II) uptake at equilibrium is studied versus adsorbent dose between 1 and 8 g/L. Figure 9 shows the dependence of this carbon dose. The uptake decreases when the dosage increases. When the quantity of activated carbon increases in the solution, the activated carbon grains end up clustering. The consequence is a decrease in the accessible surface, resulting in a decrease in the amount of lead adsorbed. In the case of activated carbon from Bois carré seeds, the maximum adsorption takes place at the adsorbent dose equal to 1g/L.

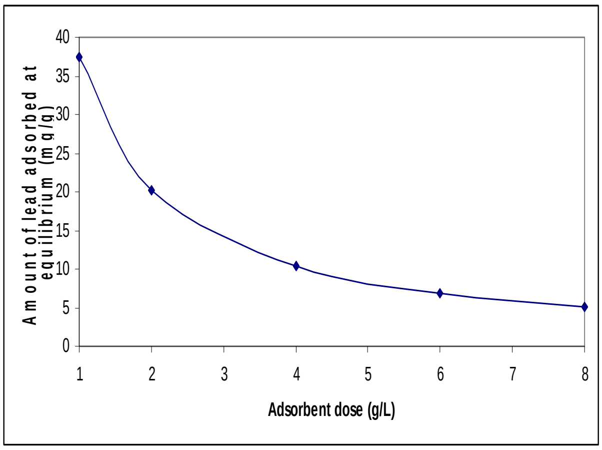

Fig. 9. Effect of the adsorbent dose on the adsorption equilibrium of Pb(II) on the activated carbon from Bois carré seeds at 30 °C, initial conditions : pH ~ 5, $C_{Pb2+, 0}$ = 150 mg/L.

Taking into account all parameters, the optimum conditions of use of the activated Bois carré seeds carbon at 30°C are at pH 7 for an adsorbent dose 1 g/L.

Conclusion

An activated carbon from Bois carré seeds is prepared by chemical activation with phosphoric acid at a relatively low activation temperature of 450°C to economize energy and favour the formation of acidic surface groups. The activated carbon is characterized and used for the remediation of Pb(II) in aqueous solutions. The sorption of Pb(II) is investigated at 30°C with varying initial lead concentrations, with varying initial pH and adsorbent doses. The study shows that, at 30 °C, the optimum initial conditions are a lead concentration of 30 mg/L, a pH of 7 and an adsorbent dose of 1g/L. The rate of adsorption of Pb(II) is well fitted by the pseudo second order kinetic model suggesting that the rate limiting step in the process is the sorption of the adsorbate by the adsorbent. The good rate of adsorption on the activated carbon (2.10^{-3} $mol^{-1}.Kg.s^{-1}$) is related to the high acidic surface properties of the activated carbon (3.44 mmol/g of total acid surface groups). The equilibrium of adsorption of Pb(II) is explained by the Freundlich model, assuming inhomogeneous sorption sites for the lead, the carboxylic sites being more reactive than the hydroxylic ones. A mechanism including the acid surface groups is suggested to explain the sorption of lead on this activated carbon. The surface area of the tested activated carbon is small compared to that of other activated carbons (594 m^2/g) as can be expected from the low activation temperature. Therefore, the surface area could be further increased by a physical activation, which will be shown in another paper. However, the activated Bois carré seeds carbon's ability to remove Pb(II) is remarkable (38.5 mg/g) and even more remarkable when considered in terms of the amount of lead adsorbed by unit of surface area (0.06 mg/m^2) versus that of other carbons. This is due to the presence of many acidic active sites on the surface of the activated carbon rendering it more effective in spite of a small surface area. In conclusion, it appears that production of chemically activated carbons from Bois carré seeds at low activation temperature might be used successfully to produce inexpensive sorbents for water lead treatment.

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