Removal of lead from aqueous solutions by adsorption with surface precipitation

L. Largitte · S. Gervelas · T. Tant ·
P. Couespel Dumesnil · A. Hightower ·
R. Yasami · Y. Bercion · P. Lodewyckx

Abstract An activated carbon from Coconut (*Cocos nucifera*) shells was prepared by physical activation with carbon dioxide and water vapor. The activated carbon obtained has a surface area of 1058 m^2 g^{-1} and such a high micropore volume of 0.49 cm^3 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. Lead precipitation was observed on the surface of the activated carbon. Maximum adsorption occurred at pH 9 for an adsorbent dose of 2 g L^{-1}. Kinetic studies, at the initial concentration of 150 mg L^{-1} of lead, pH 5 and an adsorbent dose of 1 g L^{-1}, yielded an equilibrium time of 50 h for this activated carbon. The kinetic data were modeled 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 (7×10^{-4} mol^{-1} Kg s^{-1}) and the maximum amount of lead adsorbed (0.23 mol kg^{-1}) are quite good compared to the data found in literature. Sorption equilibrium studies were conducted in a concentration range of lead from 0 to 150 mg L^{-1}. In an aqueous lead solution with an initial concentration of 30 mg L^{-1}, at pH 5, adsorbent dose 1 g L^{-1}, activated Coconut shell carbon removed at equilibrium 100 % of the heavy metal. The equilibrium data were modeled with the Langmuir and Freundlich equations, of which the former gave the best fit. The Langmuir constants $Q_{max\ eq}$ (0.23 mol kg^{-1}) and K_L (487667 L mol^{-1}) are in good agreement with literature. XPS studies identified adsorbed species as lead carbonates and/or lead oxalates and precipitates as lead oxide and/or lead hydroxide on the activated carbon surface. The Coconut shell activated carbon is a very efficient carbon due to its high surface area, to the presence of many micropores on its surface and to the presence surface groups like hydroxyls promoting adsorption in the porous system and lead crystal precipitation on the activated carbon surface.

L. Largitte (✉) · S. Gervelas
COVACHIM M2E, Université des Antilles de la Guyane, Campus de Fouillole, BP 250, 97157 Pointe-à-Pitre Cedex, France
e-mail: lucie.largitte@univ-ag.fr

T. Tant · P. C. Dumesnil
Laboratoire Hygiène et environnement, Institut Pasteur, Morne Jolivière, 97139 Abymes, France

A. Hightower · R. Yasami
Engineering Department, Harvey Mudd College, Claremont, CA, USA

Y. Bercion
GTSI, Université des Antilles de la Guyane, Campus de Fouillole, BP 250, 97157 Pointe-à-Pitre Cedex, France

P. Lodewyckx
Department of Chemistry, Royal Military Academy, Renaissancelaan 30, 1000 Brussels, Belgium

1 Introduction

The presence of heavy metals like aluminium, chromium, manganese, iron, cobalt, nickel, copper, zinc, cadmium, mercury and lead in the environment is ubiquitous. During the metallurgical processes of manufacturing of alloys, electrical goods, chemical catalysis, metal surface finishing and batteries, some amounts of metals are released into

bodies of water. The release of large quantities of heavy metals into the natural environment e.g. irrigation of agricultural fields by polluted water results in a number of environmental problems (Murugesan et al. 2006). Due to their non-biodegradability and persistence, the heavy metals can accumulate in the soil, in the water, in the food chain, and thus may pose a significant danger to human health (Kobya et al. 2005). This phenomenon is amplified in French Guyana and in the West Indies. In French Guyana, the wild gold washing releases in the rivers high quantity of heavy metals, in the West Indies, each heavy metal problem of pollution is concentrated due to the narrowness of the islands.

Among heavy metals, lead leads the list of environmental threats because, even at extremely low concentration, lead has been shown to cause brain damage in children (Ahmedna et al. 2004). Lead is mostly found in the inorganic form especially in +1, +2 oxidation states. The guidelines of World Health Organization (WHO) recommend a provisional limit of 0.05 mg L^{-1} for lead.

Constant efforts are made to develop improved and innovative methods of 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 suitable reagent of required quantity, under proper reaction condition, the metal precipitates. 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 subsequently after the precipitation process. The cost for such a two stage treatment is high. Keeping this in view, considerable attention has been given to develop low cost adsorbents for removal of the different heavy metals. In nature, there are many materials which possess the properties of ion exchange and adsorption: zeolite, apatite, bentonite, etc. Similarly many waste materials like fly ash (Apac et al. 1998), red mud and blast furnace slag (Dimitrova 1996) are also used to remove the heavy metals from polluted water. Agricultural and forestry products such as saw dust, rice husk, used tea, straw, seeds are used too (Ajmal and Hussain Khan 1998; Ulmanu et al. 1996; Ulmanu et al. 1995; Orhan and Buyukgungor 1993; Maranon and Sastre 1991; Said et al. 1992; Gharaibeh et al. 1998). However, activated carbon is the most widely used adsorbent due to its high surface area (Bansal et al. 1988). The present study is undertaken to investigate the adsorption of lead using an activated carbon from coconut shells (*Cocos nucifera*) keeping in view that the coconut trees are abundant in Guyana and in the West indies and their wastes can be useful to purify the water.

2 Experimental methods

2.1 Reagents

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 strength of the solution are all obtained from Prolabo. All solutions are prepared with deionised water.

2.2 The activated carbon

The activated Coconut shell carbon is a commercial activated from PICA named NC60. It is prepared by physical activation with carbon dioxide and water vapor. The activated carbon sample, as received, is dried at 105 °C for 2 days and used for the sorption experiments.

2.2.1 Characterization

2.2.1.1 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 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 (Brunauer et al. 1938) to the linear part of the BET plot 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 (Dubinin 1960) in the linear part of the DR plot 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 (Olivier 1995).

2.2.1.2 Surface properties The surface properties of the activated carbon are characterized via the well-known Boehm method (Boehm 1994). The pH PZC of the activated carbon is determined using the potentiometric titration method as described by (Noh and Schwarz 1990). 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^{-1}. Duplicates are performed for each sample and the relative standard error is equal or <3 %.

The surface properties of the activated carbon are also measured by XPS (X-Ray Photoelectron Spectroscopy). XPS measurements are performed in an ultrahigh vacuum chamber of an M-probe surface spectrometer. Samples are irradiated with monochromatic Al KR X-rays (1486.6 eV) incident at 35° from the surface. ESCA-2000 software is used to collect and analyze the data. As the samples are conducting materials, no charge correction is applied to the spectra.

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

2.3 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 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^{-1} for the kinetic study or between 30 and 150 mg L^{-1} 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

$$\left(C_t \text{ or } C_{eq}\right) : Q \left(mg \ g^{-1}\right) = (C_0 - C)/D. \tag{1}$$
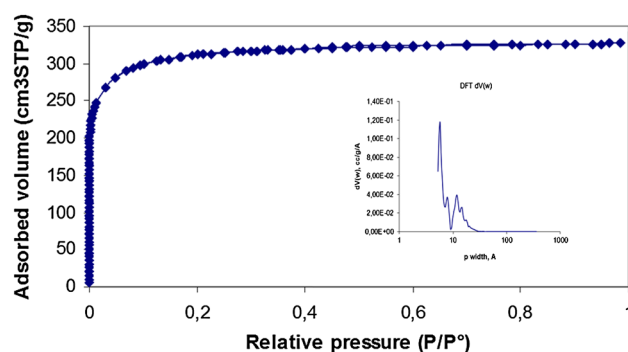
Fig. 1 Adsorption isotherm of N_2 at 77 K on the activated Coconut shells carbon. Pore size distribution of the activated carbon from Coconut shells by applying the DFT method to the nitrogen adsorption isotherm at 77 K

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.

3 Results and discussion

3.1 Characterization of the activated carbon

The textural properties of the activated carbon have been studied.

The nitrogen adsorption/desorption isotherm for the activated Coconut shells carbon is shown in Fig. 1. The isotherm is of type I according to the BDDT classification, characteristic for microporous materials (Gregg and Sing 1982).

The values of S_{BET}, Vmi, Vme obtained from the isotherm are listed in Table 1. The micropore volume is high in agreement with such a high surface area. The micropore size distribution of the activated carbon is studied according to the DFT model, one of the most adequate models for microporous materials, as shown in Fig. 1. The DFT plot shows that there are many micropores of size 6 Å which is in relation to the size of hydrated lead ($R_{Pbaq} = 4.01$ Å according to Nightingale 1959 or 5.2 Å according to Marcus 1991).

Note that Vme listed in Table 1 is equal to zero, however, the pore size distribution shows that the value of the mesopore volume is rather small but not negligible. It can be due to an overestimate value of the micropore volume calculated by the DR model.

The surface properties of the activated carbon are also listed in Table 1. The total number of acid groups on the surface of the activated carbon is weak (0.3 mmol g^{-1})

**Table 1** Surface properties of the activated carbon from Coconut shells

	Activated carbon from Coconut shells
S_{BET} (m^2 g^{-1})	1058
Vmi (cm^3 g^{-1})	0.49
Vme (cm^3 g^{-1})	0.00
Total of acid oxygenated surface groups (mmol g^{-1})	0.3
Carboxyl groups	0
Hydroxyl groups	0.3
Lactone groups	0
Total of basic oxygenated surface groups (mmol g^{-1})	0.9
pH PZC	9.2

Table 2 Assigned peaks, atomic percentage (AT) and atomic area ratio (AR) for XPS spectra of lead loaded and unloaded activated carbons

Peak (eV)	NC60		Pb-NC60	
	AT (%)	AR (%)	AT (%)	AR (%)
C1s	89.1		67.8	
285.0 (C–C, C–H)		78.2		44.1
286.5 (C–O)		15.9		25.6
287.6 (C=O)		5.9		4.6
288.9 (O=C–O, PbCO$_3$, PbC$_2$O$_4$)				25.7
O1s	10.9		24.1	
530.7 (PbO)				24.6
531.8 (C=O, CO$_3$)		41.6		51.3
533.4 (C–O)		58.4		24.1
Pb4f			8.1	
138.7 (PbO, Pb(OH)$_2$)				58.3
140.0 (PbCO$_3$, PbC$_2$O$_4$)				41.7

compared to the total number of basic groups in presence (0.9 mmol g^{-1}). The distribution of the acidity is narrow because only alcohol groups are present. The activated coconut shells carbon is a basic activated carbon and his pH PZC is superior to 7.

XPS analysis is used for evaluations of the changes in the chemical bonding states and concentrations of the surface functional groups formed by chemical surface modification (Stavropoulos and Zabaniotou 2005). Table 2 summarizes the XPS peak assignments and distributions associated with fits to XPS. XPS results confirms the
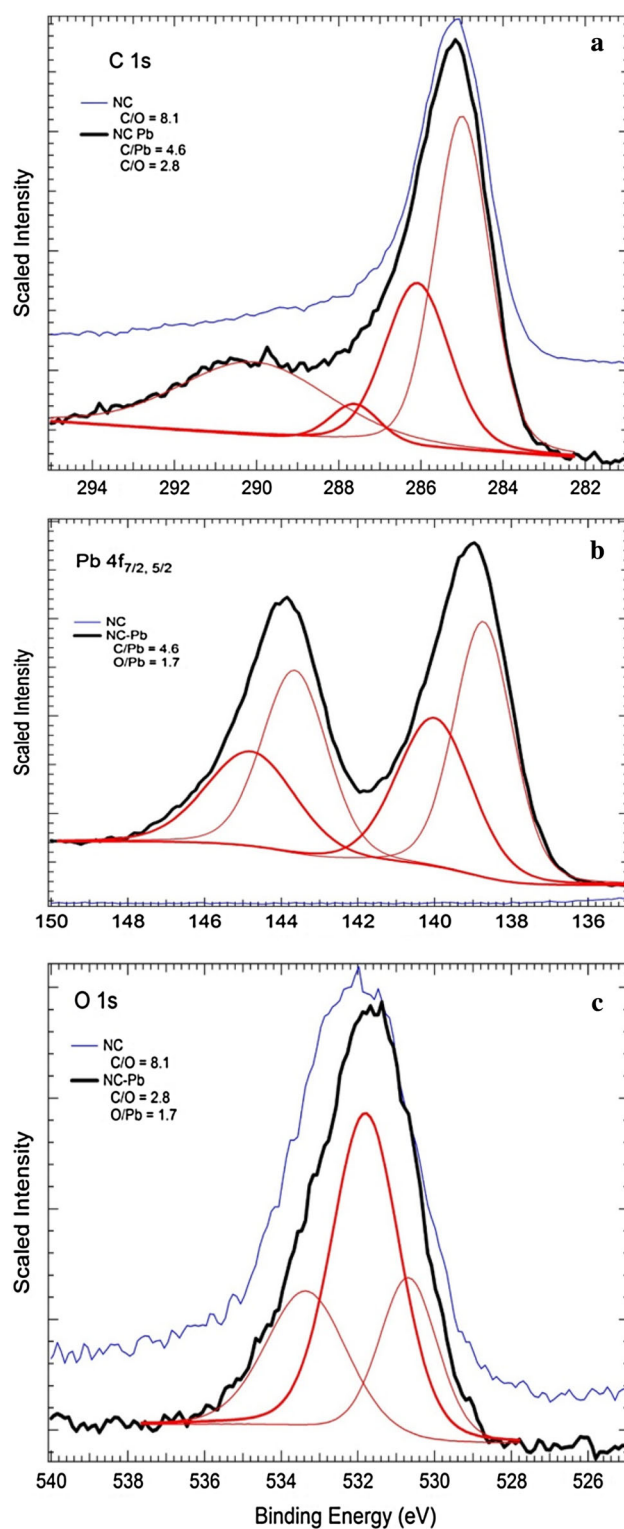
Fig. 2 XPS spectrum on C1s, Pb4f and O1s activated carbons from Coconut shells before and after sorption experiments respectively noted NC, NC-Pb

Fig. 3 SEM micrograph of activated carbon from Coconut shells before (**a**) and after (**b**) sorption experiments; Lead crystal precipitation on the surface of the activated carbon from coconut shells (**c**)
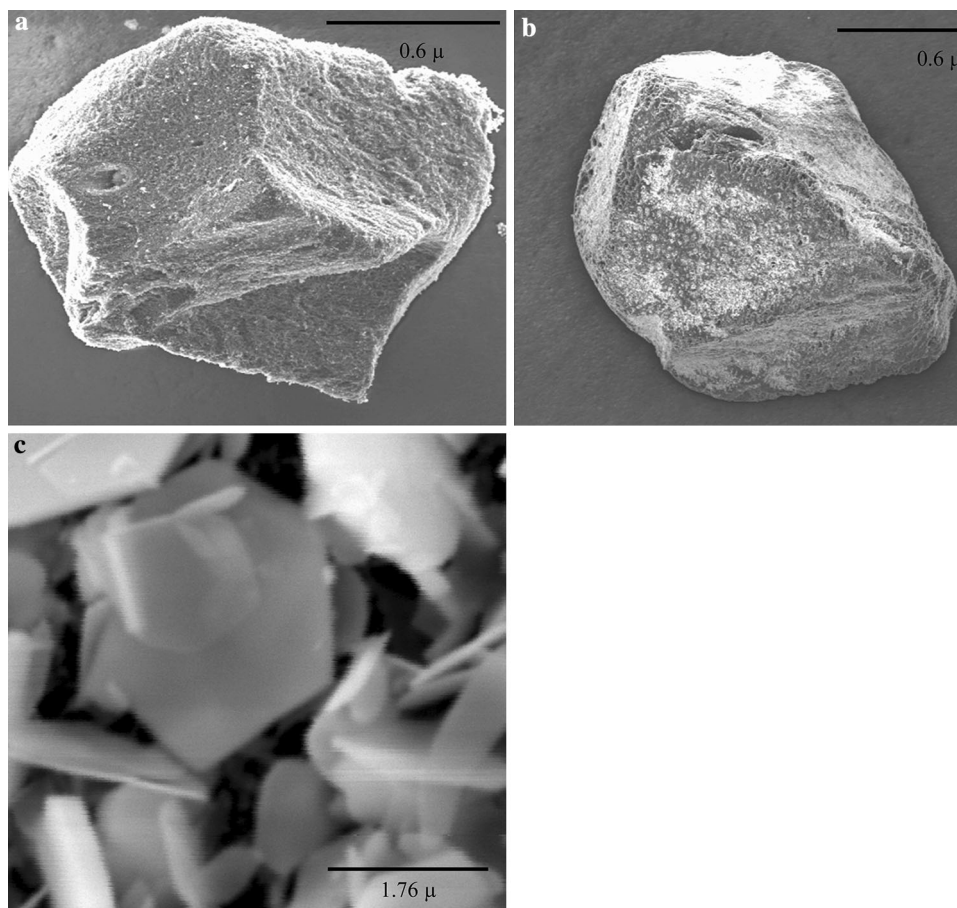
presence of oxygenated groups on the surface of the activated carbon. The C1s spectrum (Fig. 2a) is deconvoluted into three components. Peaks have been assigned to C–C and C–H (285.0 eV), C–O (286.5 eV) and C=O (287.6 eV).

3.2 Adsorption inner and outer the porous system

SEM micrographs of the activated carbon before and after lead sorption at 30 °C, initial pH 5, initial lead concentration 150 mg L^{-1} and adsorbent dose 1 g L^{-1} are shown in Fig. 3. By magnification of the micrograph from the activated carbon in contact with lead, it can be clearly seen a crystal precipitation on the surface of the activated carbon.

XPS analysis permits to clearly identify the precipitate as oxygenated lead complexes. Pb4f7/2,5/2 peaks (Fig. 2b) are deconvoluted into two pairs of peaks with the Pb4f7/2 peaks assigned to PbO/Pb(OH)$_2$ (138.7 eV) and PbCO$_3$/PbC$_2$O$_4$ (140.0 eV). These assignments correspond to lead oxide/lead hydroxide precipitates and lead carbonate/lead oxalate adsorbates. This is supported by the O1s spectrum (Fig. 2c) which shows a growth in the peaks assigned to PbO/Pb(OH)$_2$ (530.7 eV) in the lead loaded activated carbon and

subsequent redistribution of C=O/CO$_3$ (531.8 eV) and C–O (533.4 eV) peaks. In the C1s spectrum, a peak corresponding to O=C–O, PbCO$_3$, PbC$_2$O$_4$ (288.9 eV) appears for the lead loaded activated carbon. The area of the peaks associated with 288.9 eV C1s relative to the area associated with the 140.0 eV Pb4f suggests that associated O=C–O bonds are associated with the formation of carboxyl–metal complexes (Vázquez et al. 2009).

The presence of Pb(OH)$_2$ can be explained by the presence of complexation reactions between the lead and the surface groups of the activated carbon during the sorption process. Pb(OH)$_2$ crystals grow on the surface of the activated carbon after Pb forms a complex with the oxygenated groups of the carbon surface. A mechanism in agreement with those results will be further suggested in Sect. 3.5.

It can be suggested that the surface precipitation exists also in the porous system when Pb^{2+} diffuse into the micropores where it is adsorbed. First, the adsorption with precipitation takes place in the internal porous system. However, due to the narrowness of the pore and the continuous growth of the crystal, the phenomenon keeps on evaluate outer the porous system and then can be observed on the SEM micrographs.

Fig. 4 Effect of time upon the adsorption of lead by the activated carbon from Coconut shells at 30 °C (initial conditions: pH ∼5, D = 1 g L^{-1}, C$_{Pb2+, 0}$ = 150 mg L^{-1})
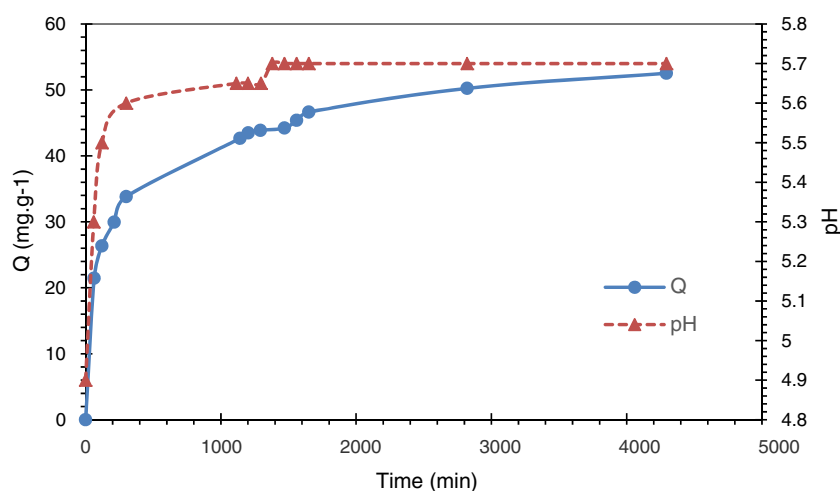
This phenomenon has already been observed in only one paper at my knowledge, for the adsorption of copper by a polyacrylo amidino diethyleneamine activated carbon fiber (Ko and Choi 2007). In this paper, the precipitation begins at pH 5, 20 °C. The precipitates are in the shape of plaques while they are hexagonal in our study. The only common point between the both activated carbons seems to be their alkalinity, indeed, the both are basic. So maybe, this precipitation capability can be correlated with the nature of the carbon.

3.3 Sorption studies

3.3.1 Kinetic studies

3.3.1.1 The data The uptake rate of lead by the activated carbon from Coconut shell is studied at pH ∼5 for an initial lead concentration of 150 mg L^{-1}, an adsorbent dose of 1 g L^{-1} at 30 °C (Fig. 4). The sorption is quite rapid: 16 % of the lead is removed within the first 2 h 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 lower energy surface sites saturate and the adsorption shifts to the higher energy surface sites, resulting in a decrease of the sorption rate. Equilibrium is reached after 50 h.

3.3.1.2 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 models:

$$Ln(Q_t) = f\{Ln(t)\}; Ln(Q_t) = v\,Ln(t) + Ln(k) \quad (2)$$

Pseudo first order model (Lagergren 1898; Ho et al. 1996):

$$Ln(Q_{max}-Q_t) = f(t); Ln(Q_{max}-Q_t) = -k_1t + Ln(Q_{max}) \quad (3)$$

Pseudo second order model (Ho and McKay 1999):

$$t/Q_t = f(t); t/Q_t = t/Q_{max} + 1/\left[k_2(Q_{max})^2\right] \quad (4)$$

Q_t (mol kg^{-1}) is the amount of lead adsorbed at a time t(s) and Q_{max} (mol kg^{-1}) 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 3. From this, a pseudo second order model can be put forward for the activated Coconut shells carbon. This means the rate limiting step in the process is the chemical sorption between the lead and the active sites of the carbon and that the sorption process takes place on two sites. This result is in agreement with the literature data found for the sorption of lead by physically activated carbons (Sreejalekshmi et al. 2000; Mohan et al. 2007; Madhava Rao et al. 2008).

The rate constant k$_2$ and the maximum amount of lead adsorbed Q$_{max, calc}$ are calculated from the curve fitting. The value of k$_2$ (7 × 10^{-4} mol^{-1} Kg s^{-1}) is a low value according to the literature available for the activated carbons from lignocellulosic precursors having followed a physical activation.
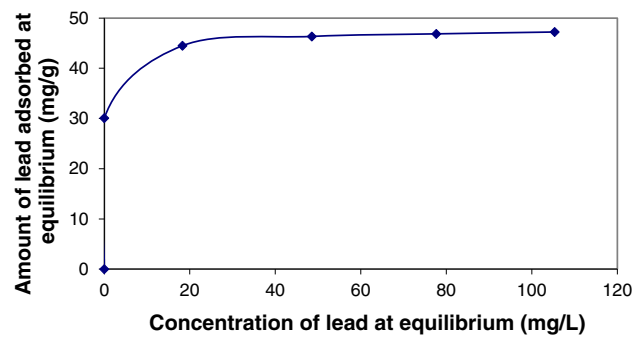
Table 3 Correlation coefficients obtained from the modelling of the kinetic and equilibrium data of the activated Coconut shells carbon obtained in the initial conditions, Temperature 30 °C, pH ~ 5, $D = 1$ g L^{-1}, $C_{Pb2+, \, 0} = 150$ mg L^{-1} for the kinetic study and varying from 0 to 150 mg L^{-1} for the equilibrium study

	Time range (s)	R^2
Kinetic		
Bangham	0–18000	0.992
Pseudo first order	0–18000	0.869
Pseudo second order	0–78000	0.996
Equilibrium		
Langmuir	∞	0.999
Freundlich	∞	0.170

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

The slow lead crystal growth on the activated carbon maybe can explain such a low value. However, the value of the maximum amount of lead adsorbed obtained from the experiment or the fitting (50.2 or 46.9 mg g^{-1}) is really a good value compared to literature data (see Table 4). This result is in agreement with the high surface area of the activated carbon, the high micropore volume, the presence of alcohol groups on its surface and the crystal growth observed which all enhance the sorption yield.

3.3.2 Equilibrium studies

3.3.2.1 The lead adsorption isotherm

The lead adsorption isotherm of activated Coconut shells carbon at 30 °C is positive, regular and concave to the concentration axis. The isotherm is of type L (Fig. 5) according to Giles classification, characteristic of strong adsorbate adsorbent interactions (Giles et al. 1960). Pb(II) uptake at equilibrium is 100 % with a 30 mg L^{-1} initial lead concentration for the activated carbon from Coconut shells 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. It can be seen from Fig. 5 that the maximum amount of lead adsorbed at equilibrium ($Q_{max \, eq, \, exp}$) for the activated carbon from Coconut shells is 47.2 mg g^{-1} and it is coherent with the previous results.

Table 4 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	Sreejalekshmi et al. (2000)	Mohan et al. (2007)	Madhava Rao et al. (2008)
Activated carbon	Commercial Granular	Home made	Commercial F400	Home made
Raw material	Coconut shells	Sawdust	na	Ceiba pentendra hulls
Activation treatment	Physical $CO_2 + H_2O$	Physical H_2O	na	Physical H_2O
Activated carbon properties				
S_{BET} (m^2 g^{-1})	1058	na	984	na
Total acid groups (mmol g^{-1})	0.3	4.02	na	na
Microporous volume (cm^3 g^{-1})	0.49	na	0.47	na
Sorption tests at				
T (°C)	30	30	25	na
D (g L^{-1})	1	2	10	6
Initial pH	5	5	5	6
Initial concentration (mg L^{-1})	150	104	113	50
$Q_{max, \, exp}$ (mg g^{-1})	50.2	na	11.2	8.3
$Q_{max, \, calc}$ (mg g^{-1})	46.9	40.61	11.3	8.3
k_2 (mg^{-1} g min^{-1})	2.1×10^{-4}	2.2×10^{-3}	1.2×10^{-3}	2.71×10^{-2}

Na not available

Table 5 Maximum amount of lead obtained at equilibrium ($Q_{max, eq}$) and Langmuir constant (K_L) obtained in this study and from other works

	This study	Sreejalekshmi et al. (2000)	Mishra and Patel(2009)	Issabayeva et al. (2006)	Machida et al. (2005)
Activated carbon	Commercial Granular	Homemade carbon	na	Commercial Granular	Commercial Granular
Raw material	Coconut shells	Sawdust	na	Palm shell	Coconut shells
Activation treatment	Physical $CO_2 + H_2O$	Physical H_2O	na	na	na
Activated carbon S_{BET} (m^2 g^{-1})	1058	na	655	957	1000
Sorption tests at					
T (°C)	30	30	25	27	20
D (g L^{-1})	1	2	20	5	2
Initial pH	5	5	6	5	na
Initial concentration range (mg L^{-1})	0–150	0–414	0–100	0–145	0–62
$Q_{max\ eq,\ calc}$ (mg g^{-1})	47.2	93.4	6.68	95.2	10.8
K_L (L mol^{-1})	487667	2790	10360	1.1	21000

Na not available

3.3.2.2 Modelling the data The equilibrium results are fitted according to the Langmuir and the Freundlich models (Langmuir 1918; Freundlich and Helle 1939). These models are the most used for a chemisorption process where a real chemical bond establishes between the adsorbent and the adsorbate. Langmuir theory is based on the assumption that all adsorption sites are equally active, the surface is energetically homogeneous and that a monolayer surface coverage is formed with no interactions between molecules adsorbed. On the other hand, the Freundlich model is an empirical equation that was originally developed to overcome some limitations of the Langmuir's theory by taking into account the surface heterogeneity and that there might exist intermolecular interactions between the adsorbate molecules. The linear form of the both isotherm models is used:

Langmuir:

$$C_{eq}/Q_{eq} = f\{C_{eq}\};$$
$$C_{eq}/Q_{eq} = C_{eq}/Q_{maxeq} + 1/(K_L Q_{maxeq}) \quad (5)$$

Freundlich:

$$Ln(Q_{eq}) = f\{Ln(C_{eq})\};$$
$$Ln(Q_{eq}) = (1/n) Ln(C_{eq}) + Ln(Kf) \quad (6)$$

Q_{eq} is the amount of lead adsorbed at equilibrium, $Q_{max\ eq}$ is the monolayer amount of lead adsorbed (mol kg^{-1}); C_{eq} is the equilibrium concentration (mol L^{-1}). The fitting to the models will reflect the equilibrium process behaviour.

The values obtained for the squared correlation coefficient R^2 are respectively 0.999 for the Langmuir model and 0.170 for the Freundlich one, then, the Langmuir isotherm fits the data better. Consequently, the surface of the activated Coconut shells carbon is homogeneous towards the lead adsorption. This result is in agreement with the single type of acid sites found on this activated carbon. Moreover, this result fits with some of the literature data (Sreejalekshmi et al. 2000; Mishra and Patel 2009; Issabayeva et al. 2006; Machida et al. 2005). The Langmuir constants $Q_{max\ eq}$, and K_L can be determined and compared to those found in literature for activated carbons from lignocellulosic precursors (see Table 5). The values obtained ($Q_{max\ eq,\ calc}$ = 47.2 mg g^{-1}; K_L = 487667 L mol^{-1}) are good values according to literature.

Such a high K_L can be explained by the lead surface precipitation inner and outer the porous system. This is confirmed by the calculation of the maximum surface covered by the lead using the expression (7) which exceeds that of the external surface area:

$$S_{Pb}(m^2 g^{-1}) = Q_{max,eq}(mol\ g^{-1}) \times 6.02 \times 10^{23}(mol^{-1}) \times 4 \times \Pi \times R_{Pb(aq)}^2(m^2)$$
$$(7)$$

leading to a S_{Pb} equal to 279.8 m^2 g^{-1} taking account $R_{Pb(aq)}$ equal to 4.01×10^{-10} m (Ferro-Garcia et al. 1990). Then, the ratio S_{Pb}/S_{BET} can be calculated, it is equal to 0.26. Moreover, the sorption can be considered as favorable when
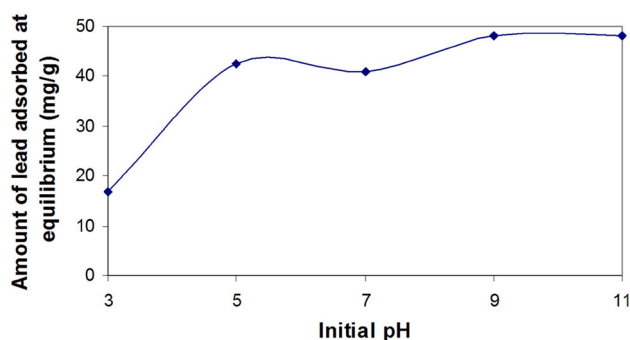
$$R_L = 1 - (Q_{eq}/Q_{max,eq}) \quad (8)$$

is comprised between 0 and 1 (Mohan et al. 2007) and it is always the case for the activated Coconut shells carbon studied here as it can be seen in Table 6. For example, for

Table 6 R_L values at T = 30 °C, pHi = 5, D = 1 g L^{-1}

Initial lead concentration C_0 (mg L^{-1})	Q_{eq} (mg g^{-1})	$R_L = 1 - (Q_{eq}/Q_{max\ eq})$
30	30	0.364
60	44.5	0.057
90	46.3	0.019
120	46.9	0.006
150	47.2	0

Fig. 7 Effect of the adsorbent dose on the adsorption equilibrium of Pb(II) on the activated carbon from Coconut shells at 30 °C, initial conditions: pH ∼5, $C_{Pb2+,\ 0}$ = 150 mg L^{-1}
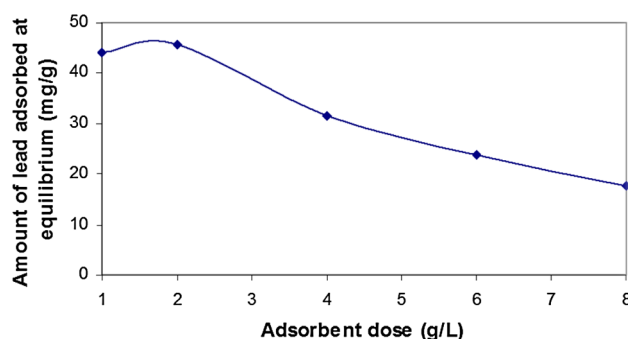

Fig. 6 Effect of the initial pH on the adsorption equilibrium of Pb(II) on the activated carbon from Coconut shells at 30 °C, D = 1 g L^{-1}, initial concentration of lead 150 mg L^{-1}

an initial concentration of 120 mg L^{-1}, R_L is equal to 0.008 and lower is R_L, most favorable the adsorption is. Moreover, it can be noted that the amount of lead adsorbed in the sorption process increases with the initial lead concentration, as observed for the surface precipitation increasing with lead initial concentration using SEM analysis.

3.4 Optimum conditions for the sorption

Experiments at equilibrium are conducted to determine the optimum pH. It can be seen from Fig. 6 that the adsorption of Pb by activated Coconut shells carbon is pH dependent, the adsorption at equilibrium globally increases with the pH and stays constant from pH 9. Consequently, the optimum pH is 9. These results are coherent with those observed by SEM which show a crystal precipitation increase with the pH which goes both with the formation of Pb(OH)$_2$ at high pH in the solution. The influence of pH on the sorption results can be explained by both the solution pH and the pH PZC of 9.2 of the adsorbent.

At pH inferior to pH PZC, the surface groups of the activated carbon are positively charged, consequently, the sorption of Pb(II) is not favored because of the repulsive interactions between the carbon and the lead. Moreover, the Pb^{2+} more competes with the H$^+$ for the sorption on the active sites when the pH is lower. At pH superior to pH

PZC, the surface groups are negatively charged, consequently the sorption of Pb II is favored.

The rate of Pb(II) uptake at equilibrium is studied versus adsorbent dose between 1 and 8 g L^{-1}. Figure 7 shows the dependence of this carbon dose. The uptake passes through a maximum when the dosage increases. Indeed, increasing the adsorbent dose provides more adsorption sites resulting in an increase in the amount of lead adsorbed. However, when the quantity of activated carbon in the solution is too big, 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 Coconut shells, the maximum adsorption takes place at the adsorbent dose equal to 2 g L^{-1}.

Taking into account all parameters, the optimum conditions of use of the activated Coconut shells carbon at 30 °C are at pH 9 for an adsorbent dose 2 g L^{-1}.

3.5 Sorption mechanism

To further understand the sorption mechanism of Pb(II), the pH in function of time (Fig. 4) and the final pH values at equilibrium versus initial concentration are measured at 30 °C (Fig. 8).

Figure 4 shows that the pH increases with adsorption then stabilizes. Figure 8 shows that the final pH at equilibrium is higher than the initial pH for all the initial metal ion concentrations. It is explained by considering an ion exchange mechanism with competitive sorption between H$^+$ and Pb^{2+}. H$^+$ is preferentially adsorbed on the basic activated carbon, then, the concentration of H$^+$ in the solution decreases and the solution pH increases from 5 to 6–7. Note that this result is different from (Largitte et al. 2012).

Moreover, it can be seen from Fig. 8 that more important is the initial lead concentration, lower is the final pH. So, the competition between H$^+$ and Pb^{2+} is accentuated with the
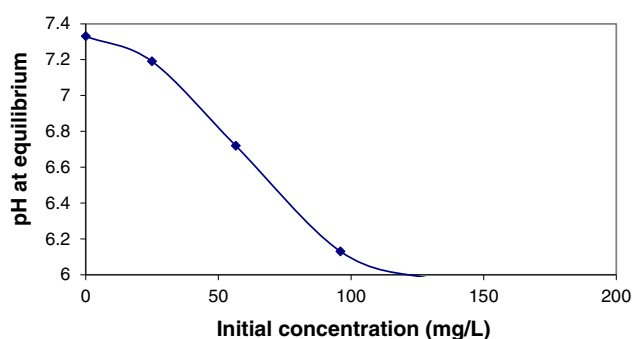
Fig. 8 Effect of the initial lead concentration upon the pH at equilibrium for the activated carbon from Coconut shells at 30 °C, D = 1 g L^{-1}, initial pH ∼5

increase in the initial lead concentration. Similar results for Cu(II), Pb(II), and Ni(II) adsorption on activated carbon cloth are reported by Kadirvelu et al. (2000). However, this result is surprising since the amount of lead adsorbed increases with the initial lead concentration for this activated carbon. Then, it can be put forward that the fraction of lead removed by external surface precipitation increases with both the initial concentration and the pH to the detriment to that removed by adsorption in the porous system.

In the sorption mechanism, either the form of surface groups or the form of Pb(II) must be taken in account. The hydrolysis pH of Pb is thought to be 6.0 and the precipitation pH is 7.7 (Lee and Davis 2001; Netzer and Hughes 1984; Burgess 1978; Gomez-Serrana et al. 1998). Consequently, the predominant form of Pb(II) is Pb^{2+} at pH inferior to 6.0, Pb(OH)$^+$ between pH 6.0–7.7 (pH range obtained at equilibrium in these experiments) and Pb(OH)$_2$ at pH superior to 7.7. The other lead complexes containing more than one lead ion are not considered in reason of their low ration in the aqueous system, in the working conditions. Moreover, usually in chemistry, the factor that dictates the lower coordination number governs the formation of the complex lead/surface groups of the carbon.

Concerning the surface of the activated carbon, it is basic, so, the hydroxyl groups of the activated carbon, in their basic form must be considered for the sorption mechanism.
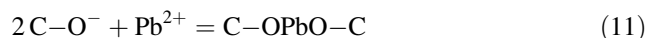
By the way, the chemisorption process in the aqueous solution can be described in the following manner: To explain the increasing pH:
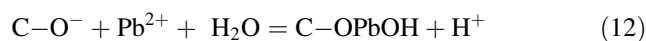
$$C-O^- + H_2O = C-OH + HO^- \tag{9}$$

To explain the sorption competition between H$^+$ and Pb^{2+} to the detriment of Pb^{2+}:

$$C-OH + H_2O = C-OH_2^+ + HO^- \tag{10}$$
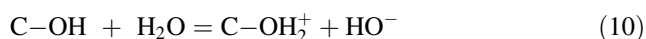
To explain the two sites sorption according to the kinetic results:

$$2\,C-O^- + Pb^{2+} = C-OPbO-C \tag{11}$$

To explain the sorption at pH < 6:

$$C-O^- + Pb^{2+} + H_2O = C-OPbOH + H^+ \tag{12}$$

To explain the sorption at 6 < pH < 7.7:

$$C-O^- + Pb(OH)^+ = C-OPbOH \tag{13}$$

To explain the sorption by surface precipitation inner and outer of the porous system at pH < 6:

$$C-O^- + Pb^{2+} + 2H_2O = C-OPb(OH)_2 + 2\,H^+ \tag{14}$$
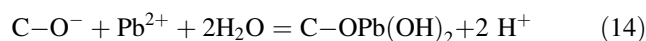
To explain the sorption by surface precipitation in and out of the porous system at 6 < pH < 7.7:

$$C-O^- + Pb(OH)^+ + H_2O = C-OPb(OH)_2 + H^+ \tag{15}$$
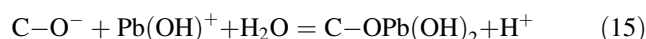
4 Conclusion

An activated carbon from Coconut shells is prepared by physical activation with carbon dioxide and water vapor. The activated carbon is characterized and used for the remediation of Pb(II) in aqueous solutions. The activated carbon has a BET surface of 1058 m^2 g^{-1} and it is basic in spite of the presence of many alcohol groups on its surface.

The sorption of Pb(II) on this activated carbon is investigated at 30 °C with varying initial lead concentrations, with varying initial pH and adsorbent doses. At 30 °C, the optimum initial conditions are a pH of 9 and an adsorbent dose of 2 g L^{-1}. The study shows that there is a crystal growth on the activated carbon surface, inner and outer the porous system, during the sorption process which depends on pH and initial concentration.

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 on two sites of the adsorbent. The rate constant of adsorption is equal to 7 × 10^{-4} mol^{-1} Kg s^{-1}.

The equilibrium of adsorption of Pb(II) is explained by the Langmuir model, assuming homogeneous sorption sites for the lead in agreement with the single alcohol groups found on the surface of the activated carbon. The Langmuir constants Q$_{max\ eq}$ and K$_L$ are respectively 0.23 mol kg^{-1} and 487667 L mol^{-1}. Such a high K$_L$ is linked to the lead precipitation on the surface of the activated carbon. XPS studies identified adsorbed species as lead carbonates and/ or lead oxalates and precipitates as lead oxide and/or lead hydroxide on the activated carbon after the lead sorption.

A mechanism including the alcohol groups present at the surface of the activated carbon in their basic form is suggested to explain the sorption of lead on this activated carbon.

However, the activated Coconut shells carbon's ability to remove Pb(II) is remarkable (50.2 mg g^{-1}) versus that of other carbons. In conclusion, it appears that production of physically activated carbons from Coconut shells might be used successfully to produce inexpensive sorbents for water lead treatment. The next paper will deal to a more deeply study on the surface precipitation for this carbon.

References

Ahmedna, M., Marshall, W.E., Husseiny, A.A., Rao, R.M., Goktepe, I.: The use of nutshell carbons in drinking water filters for removal of trace metals. Water Res. **38**, 1062–1068 (2004)

Ajmal, M., Hussain Khan, A.: Role of sandwust in the removal of copper (II) from industrial wastes. Water Res. **32**(10), 3085–3091 (1998)

Apac, R., Tutem, E., Hugul, M., Hizal, J.: Heavy metal cation retention by unconventional sorbents (red mud and fly ashes). Water Res. **32**(2), 430–440 (1998)

Bansal, R.C., Donnet, J.B., Stoeckli, H.F.: Active Carbon. Marcel Dekker, New York (1988)

Boehm, H.P.: Some aspects of the surface chemistry of carbon blacks and other carbons. Carbon **32**, 759–769 (1994)

Brunauer, S., Emmett, P.H., Teller, E.: Adsorption of gases in multimolecular layers. J. Am. Chem. Soc. **60**, 309–319 (1938)

Burgess, J.: Metal Ions in Solution. Ellis Horwood, New York (1978)

Dimitrova, S.V.: Metal sorption on blast furnace slag. Water Res. **30**(1), 228–232 (1996)

Dubinin, M.M.: The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces. Chem. Rev. **60**(2), 235–241 (1960)

Ferro-Garcia, M., Rivera-Utrilla, A., Bautista-Toledo, J.: Removal of lead from water by activated carbons. Carbon **28**, 545–552 (1990)

Freundlich, H., Helle, W.J.: Ubber die adsorption in lusungen. J. Am. Chem. Soc. **61**, 2–28 (1939)

Gharaibeh, S.H., Abu-El-Sha'r, W.Y., Al-Kofahi, M.M.: Removal of selected heavy metals from aqueous solutions using processed solid residue of olive mill products. Water Res. **32**(2), 498–502 (1998)

Giles, C.H., MacEwan, T.H., Nakhwa, S.H., Smith, D.: Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. J. Chem. Soc. **10**, 3973–3993 (1960)

Gomez-Serrana, V., Macias-Garcia, A., Espinosa-Mansilla, A., Valenzuela-Calahorro, C.: Adsorptionof mercury, cadmium and lead from aqueous solution on heat-treated and sulphurized activated carbon. Water Res. **32**, 1–4 (1998)

Gregg, S.J., Sing, K.S.W.: Adsorption, Surface Area and Porosity. Academic Press, London (1982)

Ho, Y.S., McKay, G.: Pseudo second order model for sorption process. Process. Biochem. **34**, 451–465 (1999)

Ho, Y.S., Wase, D.A.J., Foster, C.F.: Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat. Environ. Technol. **17**, 71–77 (1996)

Issabayeva, G., Aroua, M.K., Sulaiman, N.M.N.: Removal of lead from aqueous solutions on palm shell activated carbon. Bioresour. Technol. **97**, 2350–2355 (2006)

Kadirvelu, K., Faur-Brasquet, C., Le Cloirec, P.: Removal of Cu(II), Pb(II) and Ni(II) by adsorption onto activated carbon cloths. Langmuir **16**, 8404–8409 (2000)

Ko, Y.G., Choi, U.S.: Observation of metal ions adsorption on novel polymeric chelating fiber and activated carbon fiber. Sep. Purif. Technol. **57**, 338–347 (2007)

Kobya, M., Demirbas, E., Senturk, E., Ince, M.: Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. Bioresour. Technol. **96**, 1518–1521 (2005)

Lagergren, S.: Zur theorieDer Sogenannten adsorption geloster stoffe Kungliga Svenska Vetenskapsakademiens. Handlingar **24**, 1–39 (1898)

Langmuir, I.: Adsorption of gases on glass, mica and platinum. J. Am. Chem. Soc. **40**, 1361–1403 (1918)

Largitte, L., Gervelas, S., Tant, T., Dumesnil, P.C., Lodewyckx, P.: Influence of the surface properties of the Bois carré seeds activated carbon for the removal of lead from aqueous solutions. Eurasian Chem. Technol. J. **14**(3), 201–210 (2012)

Lee, S.M., Davis, A.P.: Removal of cu(II) and cd(II) from aqueous solution by seafood processing waste sludge. Water Res. **35**, 534–540 (2001)

Machida, M., Aikawa, M., Tatsumoto, H.: Prediction of simultaneous adsorption of Cu(II) and Pb(II) onto activated carbon by conventional Langmuir type equation. J. Hazard. Mater. **120**, 271–275 (2005)

Madhava Rao, M., Chandra Rao, G.P., Seshaiah, K., Choudary, N.V., Wang, M.C.: Activated carbon from *Ceiba pentandra* hulls, an agricultural waste, as an adsorbent in the removal of lead and zinc from aqueous solutions. Waste Manag. **28**, 849–858 (2008)

Maranon, E., Sastre, H.: Ion exchange equilibria of heavy metals onto chemically modified apple residues. Solv. Extr. Ion Exch. **9**(3), 515–531 (1991)

Marcus, Y.: Thermodynamics of solvation of ions. Part 5—gibbs free energy of hydration at 298.15 K. J. Chem. Soc. Faraday Trans. **87**(18), 2995–2999 (1991)

Mishra, P.C., Patel, R.K.: Removal of lead and zinc ions from water by low cost adsorbents. J. Hazard. Mater. **168**, 319–325 (2009)

Mohan, D., Pittman Jr, C.U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P.H., Alexandre-Franco, M.F., Gomez Serrano, V., Gong, H.: Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. J. Colloid Interface Sci. **310**, 57–73 (2007)

Murugesan, G.S., Sathishkumar, M., Swaminathan, K.: Arsenic removal from groundwater by pretreated waste tea fungal biomass. Bioresour. Technol. **97**, 483–487 (2006)

Netzer, A., Hughes, D.E.: Adsorption of copper, lead and cobalt by activated carbon. Water Res. **18**, 927–933 (1984)

Nightingale, E.R.: Phenomenological theory of ion solution. Effective radii of hydrated cations. J. Phys. Chem. **63**, 1381–1387 (1959)

Noh, J.S., Schwarz, J.A.: Effect of HNO$_3$ treatment on the surface acidity of activated carbons. Carbon **28**, 675–682 (1990)

Olivier, J.P.: Modeling physical adsorption on porous and nonporous solids using density functional theory. J. Porous Mater. **2**, 9–17 (1995)

Orhan, Y., Buyukgungor, H.: The removal of heavy metals by using agricultural waste. Water Sci. Tech. **28**(2), 247–255 (1993)

Said, O.M., Shalmor, M.B., Egila, J.N.: A note on the binding of nickel and copper ions by cellulose materials. Bioresour. Technol. **43**, 63–65 (1992)

Sreejalekshmi, K.G., Anoop Krishnan, K., Anirudhan, T.S.: Adsorption of Pb(II) and Pb(II)-citric acid on sawdust activated carbon: Kinetic and equilibrium isotherm studies. J. Hazard. Mater. **161**, 1506–1513 (2000)

Stavropoulos, G.G., Zabaniotou, A.A.: Production and characterization of activated carbons from olive-seed waste residue. Microporous Microporous Mater. **82**, 79–85 (2005)

Ulmanu, M., Teodorescu, R., Anger, I., Neagu, E.: Contribution to the study of advanced removal of cadmium onto the diluted solution using adsorbent materials: optimum contact time determination.

In: Proceedings of Chemistry and Chemical Engineering Conference, vol. I, Part 2, Bucharest, pp. 296–303 (1995)

Ulmanu, M., Segarceanu, T., Vasiliu, C., Anger, I.: Removal of copper from dilute aqueous solutions by adsorbent and ion exchange materials: ion exchange developments and applications. In: SCI Conference IEX_96, UK, pp. 51–159 (1996)

Vázquez, G., Calvo, M., Freire, M.S., González-Alvarez, J., Antorrena, G.: Chestnut shell as heavy metal adsorbent: optimization study of lead, copper and zinc cations removal. J. Hazard. Mater. **172**, 1402–1414 (2009)