

Activated Carbon Based on Acacia Wood (*Auriculeaformis*, Côte d'Ivoire) and Application to the Environment through the Elimination of Pb²⁺ Ions in Industrial Effluents

Drissa Ouattara Kra¹, Grah Patrick Atheba^{1,2*}, N'da Arsène Kouadio³, Patrick Drogui², Albert Trokourey¹

¹Laboratoire de Chimie Physique, Université Félix Houphouët Boigny de Cocody-Abidjan, Abidjan, Côte d'Ivoire

²Institut National de la Recherche Scientifique (INRS-ETE), Université du Québec, Quebec City, Canada

³Laboratoire de Bioénergie, Centre National de Recherche Agronomique (CNRA), Abidjan, Côte d'Ivoire

Email: *grahpatrick.atheba@gmail.com

How to cite this paper: Kra, D.O., Atheba, G.P., Kouadio, N.A., Drogui, P. and Trokourey, A. (2021) Activated Carbon Based on Acacia Wood (*Auriculeaformis*, Côte d'Ivoire) and Application to the Environment through the Elimination of Pb²⁺ Ions in Industrial Effluents. *Journal of Encapsulation and Adsorption Sciences*, 11, 18-43. <https://doi.org/10.4236/jeas.2021.111002>

Received: November 15, 2020

Accepted: March 28, 2021

Published: March 31, 2021

Copyright © 2021 by author(s) and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

The objective of this study is to develop carbon, that of *Acacia auriculeaformis* through its activation in order to eliminate lead in an aqueous medium. A series of activated carbon has been prepared by chemical activation with phosphoric acid, sodium hydroxide and sodium chloride. The determination of the physico-chemical properties of the prepared carbon guided the choice of phosphoric acid activated carbon as the best adsorbent for the elimination of lead(II) in an aqueous solution. Pb²⁺ adsorption tests in batch mode have shown that the adsorption capacity is influenced by various parameters such as mass, pH, concentration of Pb²⁺ ions and contact time linked to the medium and the adsorbent. Adsorption isotherms, kinetic models and thermodynamics have been used to describe the adsorption process. The equilibrium data for activated charcoal correspond well to the model of Freundlich, Langmuir, Temkin and Kiselev. The kinetic adsorption data proved to be better described by the pseudo-second order model with external and intraparticle diffusion which are two decisive steps in the adsorption process of Pb²⁺ ions. Thermodynamics and adsorption isotherms predict a spontaneous exothermic surface reaction, of the chemisorption type, with ion retention in orderly monolayers on the heterogeneous surface of the adsorbent. Tests carried out with this adsorbent material have contributed to the elimination of the Pb²⁺ ions contained in an industrial effluent with a reduction rate reaching 42.52% against 85.90% in a synthetic solution.

Keywords

Acacia auriculaeformis, Activated Carbon, Lead(II) Ion, Adsorption Isotherms, Kinetics

1. Introduction

Most developing countries today face enormous environmental problems. Indeed, the increase in industrial and human activities such as mining, painting, welding, refineries, the use of pesticides, herbicide, and fertilizers, the manufacture of electronic products and accumulator batteries liberate each year a large number of metallic elements in the aquatic ecosystem, causing contamination of water and soil [1]. The heavy metals most often called metallic trace elements (MTE), are widely distributed in our environment and are of ecological importance given their high toxicity for living organisms. Even at low concentrations, these metals can be toxic to organisms including humans [2] [3]. Some heavy metals are non-biodegradable pollutants that are stored for several decades in water reservoirs and soil environments [4]. Among these is lead. Lead, heavy metal, very persistent and largely favorable for the environment is a toxic substance which accumulates in the organism and disturbs it, the nervous system, the blood, the gastrointestinal tract, the cardio-vascular and kidney. Lead is a possible human carcinogen. Exposure to lead can cause sterility in adults, mortality, postnatal morbidity and disruption of the endocrine system [5].

Several methods have been used to remove metallic trace elements and in particular lead, present in wastewater and contaminated soil. These are the processes of chemical precipitation [6], ion exchange [7], coagulation-flocculation [8], complexation [9], membrane filtration [10], electrochemical process [11], etc. However, these techniques are often either ineffective, expensive or produce secondary waste that is difficult to treat [12] [13]. Furthermore, adsorption is a widely used method for water treatment, due to its advantages, notably its low cost, its high efficiency at low cation concentration, and an easy operation without side effects on the environment [14] [15].

In this study, we focused on the adsorption process using activated carbon. Activated charcoal is a material consisting essentially of carbonaceous material with a porous structure obtained from the carbonization of carbonaceous materials, such as biomass, which is easily accessible in Côte d'Ivoire. Among these carbonaceous materials, coconut hulls [16] [17] [18], peanut and soy hulls [19], *Pterygota macrocarpa* wood [20] have proven to be good precursors for the removal of organic compounds and inorganic. In the search for natural resources for the local production of cheaper activated carbon, we were interested in carbon from the wood of *Acacia auriculaeformis* whose abundance is reported and whose use is limited to fuel. Previous work by Kra *et al.* [21] has already shown the adsorbent properties of activated carbon from this species of wood.

The objective of this research is to assess the efficiency of elimination of lead by activated carbon from *Acacia auriculaeformis* by adsorption in aqueous media. Otherwise, it is a question of valorizing the carbon based on this species of *Acacia*. A characterization of the prepared adsorbents was carried out in order to provide a relationship between structure and adsorption capacity of lead(II) ions. In addition, the effects of contact time, initial concentration of lead(II) ions, pH, and dose of adsorbent were examined. The adsorption kinetics, isotherm models and thermodynamic parameters of lead(II) on the synthesized adsorbent were briefly discussed.

2. Methodology

2.1. Preparation of Activated Carbon

The raw material is carbon from *Acacia auriculaeformis* prepared in an experimental butane gas retort at the technological research station (TRS) of the National Center for Agronomic Research in Cocody (Abidjan, Ivory Coast). Activation is done by impregnation for 24 hours of pieces of *Acacia auriculaeformis* carbon coarsely crushed in the form of dice in three oxidizing agents H_3PO_4 , NaOH, and NaCl. The samples obtained after impregnation are dried and ground. The ground material whose diameter is between 125 μm and 2 mm is recovered using an Afnor sieve and placed in a muffle furnace (Nabertherm brand 30°C - 3000°C) at 800°C for 6 hours [21]. The carbonization conditions are presented in Table 1. After the heat treatment, the carbon obtained are cooled and then washed several times with distilled water until the pH of the washing solution is between 6.5 equal to 7.

2.2. Characterization of Carbon

2.2.1. Characterization of the Porous Texture

The textural properties of all the samples were determined by nitrogen adsorption experiments at the temperature of liquid nitrogen (77 K) with a Quantachrom Autosorb1. The samples were all first degassed at 150°C for 6 h under vacuum before the N₂ adsorption/desorption tests. The surfaces were calculated by applying the BET equation (Brunauer-Emmet-Teller) to the first part of the isotherms. The total pore volume in each sample was evaluated from the amount of nitrogen adsorbed at the highest relative pressure examined. The results of the

Table 1. Preparation conditions of activated carbon.

Oxidizing agents	Carbonization temperature (°C)	Oven residence time (Hour)	Abbreviation of the carbon obtained
Activated with H_3PO_4 commercial diluted to 10%	800	6	CAA
Activated with NaOH 1N	800	6	CAB
Activated with NaCl 36.5 g/L	800	6	CAS

texture study are given in **Table 2**. Surface micrographs of the samples before and after adsorption were taken using a JSM-840 model scanning electron microscope (SEM) for surface micro-analysis.

2.2.2. Chemical Characterization

The method of Boehm [22] was used to determine the composition of active carbon in an acid or basic surface group. Concentration solutions of 0.1 N of strong bases of NaHCO₃, Na₂CO₃ and NaOH as well as strong acid of HCl were prepared. The number of sites of the various acid functions is calculated by considering that NaHCO₃ neutralizes the carboxylic groups, Na₂CO₃ neutralizes the carboxylic groups and the lactone groups and NaOH neutralizes the carboxylic, lactone and phenolic groups. The number of basic sites is calculated from the amount of HCl which has reacted with carbon.

The pH_{ZPC} was determined by the pH derivative method according to [23], using 100 mg of activated carbon and 50 mL of 0.01 M NaCl solutions with a pH varying from 2 to 12, pH adjusted by adding a 0.01 M HCl or NaOH solution. The suspensions are kept under constant stirring, at room temperature, for 48 h, in order to determine the final pH. The pH_{ZPC} is the point where the pH_{final} = f(pH_{initial}) curve intercepts the first bisector pH_{final} = f(pH_{initial}).

2.2.3. Yield, Ash Rate and Iodine Value

➤ The values of the yields from the production of active carbon are estimated by application of formula (1):

Table 2. Adsorption isotherm models.

Isotherm model	Equation	Linear form	Curve
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{1}{q_e} = \frac{1}{q_m K_L} \cdot \frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e} = f\left(\frac{1}{C_e}\right)$
Freundlich	$q_e = K_F C_e^{\frac{1}{n_F}}$	$\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e$	$\ln q_e = f(\ln C_e)$
Temkin	$\frac{q_e}{q_m} = \theta = \frac{RT}{\Delta Q} \ln(A_T C_e)$	$q_e = B \cdot \ln A_T + B \cdot \ln C_e$	$q_e = f(\ln C_e)$
Dubinin-Radushkevich	$\frac{q_e}{q_{mDR}} = \exp(-\beta \varepsilon^2)$	$\ln q_e = \ln q_{mDR} - \beta \varepsilon^2$	$\ln q_e = f(\varepsilon^2)$
Kiselev	$K_1 C_e = \frac{\theta}{(1-\theta)(1+K_n \theta)}$	$\frac{q_m}{(q_m - q_e) C_e} = \frac{K_1 q_m}{q_e} + K_1 K_n$	$\frac{q_m}{(q_m - q_e) C_e} = f\left(\frac{q_m}{q_e}\right)$
Fowler-Guggenheim	$K_{FG} C_e = \frac{\theta}{1-\theta} \exp\left(\frac{2\theta W}{RT}\right)$	$\ln\left[\frac{C_e (q_m - q_e)}{q_e}\right] = -\ln K_{FG} + \frac{2W}{RT} \frac{q_e}{q_m}$	$\ln\left[\frac{C_e (q_m - q_e)}{q_e}\right] = f\left(\frac{q_e}{q_m}\right)$

with: q_e and q_m : the adsorption capacities respectively at equilibrium and maximum (mg/g); C_e : residual concentration at equilibrium (mg/L); K_L , K_F , K_{FG} , K_1 ; Langmuir, adsorption-adsorbent constants, respectively Freundlich, Fowler-Guggenheim and Kiselev; K_n : Constant of complex formation between adsorbed molecules of Kiselev; W : Interaction energy between adsorbed molecules (kJ·mol⁻¹) from Fowler-Guggenheim. ΔQ : Variation of the Temkin adsorption energy (kJ/mol). A_T : Temkin equilibrium constant (L·mg⁻¹); $B = \frac{RTq_m}{\Delta Q}$ (J·mol⁻¹): Constant linked to the heat of adsorption; $R = 8.314$ kJ·K⁻¹·mol⁻¹:

Constant of ideal gases; $T(K)$: Absolute temperature; q_{mDR} : Maximum adsorption capacity in micropores (mg/g) of Dubinin-Radushkevich; ε : Polanyi potential; β : Constant linked to the energy of adsorption (mol²·kJ⁻²) according to D-R. $\theta = q_e/q_m$: Degree of overlap.

$$R(\%) = \frac{\text{mass of activated carbon}}{\text{mass of the precursor}} \times 100 \quad (1)$$

- The ash content of the carbon is determined according to the ASTM method (American Standards Technology Method) [24]. The carbon samples are calcined at 650°C in a muffle furnace for 7 hours. The ash rate is given by the following relation (2):

$$C(\%) = \frac{m_2 - m_0}{m_1 - m_0} \times 100 \quad (2)$$

m_0 : mass of the dry and empty crucible;

m_1 : mass of the assembly (crucible and activated carbon);

m_2 : crucible mass after cooling containing the ash.

- To determine the iodine value, we used a method which is an adaptation of the CEFIC 1989 method and the AWWA B600-76 standard applied by Ousmaila *et al.* [25]. Thus, a mass $m = 0.2$ g of activated carbon is placed in a 100 ml beaker. 20 mL of a 0.02 N solution of I_2 are added to the pipette, and then stirred for 4 to 5 min. After filtering the mixture on filter paper, 10 mL of the filtrate are removed and dosed with a 0.1 N sodium thiosulfate solution in the presence of two drops of starch paste until the solution is completely discoloured and iodine index (Q_{I_2}) is determined from the following Formula (3):

$$Q_{I_2} = \frac{\left[C_0 - \frac{C_n \cdot V_n}{2V_{I_2}} \right] * M_{I_2} * V_{abs}}{m_{AC}} \quad (3)$$

V_n : volume of sodium thiosulfate poured at the equivalence (mL);

C_n : concentration of sodium thiosulfate (mol/L);

C_0 : initial concentration of I_2 ;

V_{I_2} : Volume of I_2 dosed;

M_{I_2} : Molar mass of iodine (253.81 g/mol);

V_{abs} : adsorption volume (20 mL);

M_{AC} : mass of activated carbon (g).

2.3. Adsorption Experiences

2.3.1. Adsorbent Used

Activated carbon with the best physicochemical properties has been used for the removal of metal ions (Pb^{2+}) in aqueous solution.

2.3.2. Preparation of the Mother Solution of the Adsorbate

Lead nitrate II $Pb(NO_3)_2$ with a molar mass of 331.2 g/mol produced in the form of a white powder used in this study is characterized by a purity of 99.5% (Merck product). It was bought with a chemical sales company in Abidjan. All the series of lead(II) solution of well-defined concentration (10 mg/L - 500 mg/L) are obtained by dilution with distilled water of the mother solution of 1000 mg/L in lead element (*i.e.* 4.036 g $Pb(NO_3)_2$ in 1000 mL of distilled water). The nitrate ions are chosen for their low capacity complexing with respect to many cations.

The solutions of the metal cation of various experiments carried out are prepared with 65% nitric acid in order to allow good solubility.

2.3.3. Metering Method and Apparatus

All the adsorption tests were carried out in batch mode by putting 50 mL of lead(II) solution in 250 mL Erlenmeyer flasks. These suspensions are placed under constant stirring of 350 rpm at room temperature of the room (27°C). After the time considered, the suspensions are filtered on whatman 44 filter paper. The residual concentration of lead(II) element in the filtered solution is determined using a Varian SpectrAA 110 brand Atomic Absorption Spectrometer at length. 261.42 nm wave.

The effects of the contact time, the dose of activated carbon, the pH of the solution, the concentration of Pb²⁺ ion and the temperature (27°C - 75°C) were studied by adsorption of Pb²⁺; then:

- to study the effect of the mass of carbon, the lead(II) solution at 100 mg/L is brought into contact for 120 min, with different masses of carbon (0.1; 0.25; 0.5; 1 and 2 g);
- with regard to the adsorption kinetics and the effect of the initial concentration of the solution, the kinetic tests were carried out for 5 min to 180 min, by mixing volumes of 50 mL of lead(II) solution with different concentrations (50, 100, 300 and 500 mg/L) with 0.5 g of activated carbon;
- in order to examine the influence of the pH of the solution on the adsorption capacity, 0.5 g of carbon is stirred with 50 mL of lead(II) solution at 300 mg/L. The pH of the solutions was adjusted to the following values (2, 4, 5, 6, 7, 9 and 11) at the start of the experiment with solutions of sulfuric acid or sodium hydroxide (0.1N). The evolution of the adsorption being controlled as a function of the equilibrium time;
- To study the effect of temperature on the adsorption of lead(II) ions, the experiments were carried out by adding the mass of 0.5 g of carbon to 50 mL of the metallic solution of lead(II) at different concentrations. Initials, at temperatures varying between 27°C and 75°C;
- For the adsorption isotherm, 0.5 g of carbon is added to various lead(II) solutions at different concentrations (20, 40, 60, 80, 100, 200 and 300 mg/L) and stirred for the time of balance.

In all cases, the adsorption capacity q_t (mg/g) or q_e and the elimination rate TA (%) of the lead element (II) are calculated respectively by the relations (4) and (5):

$$q_t = \frac{(C_0 - C_r) \cdot V}{m} \quad (4)$$

$$TA(\%) = \frac{C_0 - C_r}{C_0} \cdot 100 \quad (5)$$

with:

V = volume of lead solution (L);

C_0 = initial concentration of the solution (mg/L);
 C_r = residual concentration of the solution (mg/L);
 m = mass of activated carbon used (g).

2.3.4. Adsorption Isotherms and Kinetic Models

The application of adsorption isotherms is very useful for describing the interaction between the adsorbent and the adsorbent. There are several models for analyzing experimental adsorption equilibrium data. In this study, six two-parameter models (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich (D-R), Kiselev and Fowler-Guggenheim models) were applied. Kinetic models such as pseudo-first order, pseudo-second order, intraparticle, Boyd and Elovich diffusion models [26] [27] were used to understand the kinetics of adsorption. **Table 2** and **Table 3** present the equations and parameters of these adsorption isotherms and these kinetic models. The experimental results were evaluated by simple plots of the linear forms of the two-parameter equations, with which it is possible to calculate the values of the adsorption parameters. For our study, the correlation coefficient R^2 was used to assess the validity of the theoretical isotherms. Indeed, the correlation coefficient of the straight line of a model close to unity reflects the applicability of this model to the adsorption of the adsorbate on the adsorbent.

2.3.5. Thermodynamic Study

The thermodynamics of lead(II) adsorption on CAA carbon is studied through the calculation of thermodynamic parameters such as standard free enthalpy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) of the experiment using the following Equations (6) and (7):

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (6)$$

$$\Delta G^\circ = -RT \ln K_L \quad (7)$$

By replacing ΔG° of relation (6) in (7) we obtain Equation (8):

Table 3. Kinetic adsorption models.

Kinetics model	Equation	Linear form	Curve
Pseudo-first order	$dq_t/dt = k_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln(q_e - q_t) = f(t)$
Pseudo-second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$t/q_t = f(t)$
intraparticle diffusion	-	$q_t = k_{dt} t^{0.5} + C$	$q_t = f(t^{0.5})$
Model of Boyd	$F = 1 - \left[\frac{6}{\pi^2} \right] \exp(-B_1 t)$	$B_1 = -0.4977 - \ln(1 - F)$	$B_1 = f(t)$
Model of Elovich	-	$q_t = \frac{1}{\beta} \ln(\alpha \cdot \beta) + \frac{1}{\beta} \ln t$	$q_t = f(\ln t)$

with: q_e and q_t : The adsorption capacities respectively at equilibrium and at time t ; k_1 and k_2 : respectively the speed constants of the pseudo-first order and the pseudo-second order; α : the initial adsorption rate; β : Constant linked to the extent of surface coverage; k_{dt} : The intraparticle diffusion rate; C : Constant indicating the thickness of the boundary layer; $F = q_t/q_e$ fraction of the solute adsorbed at time t .

$$\ln K_L = \left(\frac{\Delta S^\circ}{R} \right) - \left(\frac{\Delta H^\circ}{R} \right) \cdot \frac{1}{T} \quad (8)$$

The plotting of the $\ln K_L$ curve as a function of $\frac{1}{T}$ allows the estimation of the thermodynamic parameters.

2.3.6. Treatment of Industrial Effluent on Activated Carbon

Adsorption tests on activated carbon of the lead element contained in the industrial effluent are carried out. Among the experimental conditions retained: the quantities of activated carbon used are: 0.5 g; 1 g; 1.5 g and 2 g for 50 mL of polluted water solution. The contact times are 120 min and 1440 min (24 h). The samples are adjusted to the pH level to have the optimum adsorption pH of the metallic element. The tests are carried out in batch mode on the effluent in the presence of activated carbon and the concentrations before and after treatment are measured by an atomic absorption spectrometer in order to determine the residual concentration and the rate of reduction.

3. Results and Discussion

3.1. Characterization of Activated Carbon

The different characteristics of the carbon studied are summarized in **Table 4**. These characteristics make it possible to assess the adsorbing power of the carbon. Indeed, a material will be even more adsorbent that it has a low ash rate, high surface functions and a large specific surface [20]. The results show that

Table 4. Characteristics of different activated carbon.

Parameters	Values		
	CAA	CAB	CAS
Yield (%)	41.81	26.25	48.87
Ash rate	5	14.9	6.6
Iodine index	304.57	190.35	380.71
pH _{pzc}	4.8	8.4	6.8
Textural properties			
S_{BET} (m ² /g)	561.60	265.00	395.40
Cumulative pore volume (cm ³ /g)	0.26	0.13	0.20
Pore width (Å)	11.26	11.76	11.78
Surface functions			
Acid groups (mégq·g ⁻¹)	1.85	0.35	0.80
Carboxylic	0.75	-	-
Phenol	0.40	0.35	-
lactone	0.70	-	0.80
Basic groups (mégq·g ⁻¹)	0.18	1.18	0.69

these characteristics vary from sample to sample. However, CAA has the lowest center rate, the largest pore volume and therefore the largest specific surface, the highest amount of acid group and therefore favourable for the adsorption of cations. In fact, the results of the Boehm titration show that most of the acid functional groups are carboxylic, followed by the laconic and phenolic groups on this carbon. The total number of basic surface sites is less than the total number of acidic surface sites. This agrees with pH_{PZC} , which is also acidic. These results show that the characteristics of the carbon prepared depend on the nature of the oxidizing chemical agent. CAA carbon with good physicochemical characteristics was chosen to carry out the adsorption tests in order to assess its real adsorption capacity. The metallic solutions used are on the one hand synthetic solutions containing lead(II), and on the other hand a real solution containing several metallic trace elements including lead.

3.2. Adsorption of Metal Ions on Activated Carbon

3.2.1. Effect of Carbon Mass

As shown in **Figure 1**, the increase in CAA significantly affects the removal of the Pb^{2+} cation. In other words, the amount of Pb^{2+} adsorbed increases with the amount of CAA. With the increase in the dose of adsorbent from 0.1 to 2 g (*i.e.* 2 to 40 g/L), the percentage of removal of Pb^{2+} increased from 70% to 80%. Furthermore, the maximum retention is already obtained for a mass of 0.5 g of activated carbon (10 g/L). Beyond this mass, there is stability in the rate of reduction which could be explained by the saturation of the carbon. This quantity of mass necessary to fix the maximum of metal ions Pb^{2+} , which will be retained for the rest of our work as optimal mass. This improvement in the retention rate of metal ions in the mass of activated carbon increases is mainly due to an increase in the number of active adsorption sites within the CAA. In fact, if the mass of activated carbon in the solution is large, the number of sites will also be. Consequently, the probability of interaction (solute-site) also increases. This same trend has been reported by Bendaho *et al.* [28].

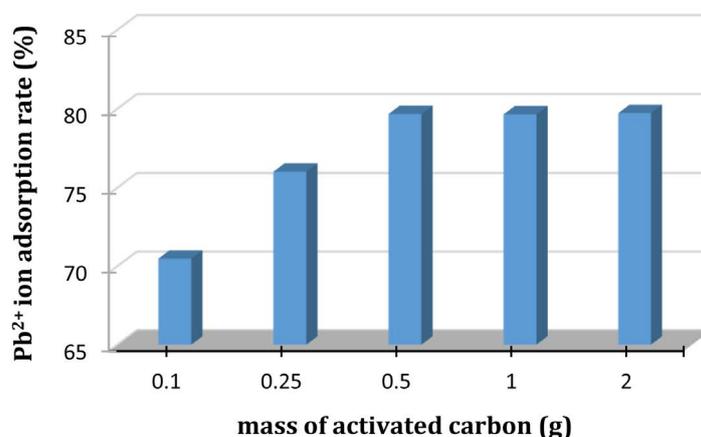


Figure 1. Influence curve of the mass of CAA on the adsorption of the Pb^{2+} ion.

3.2.2. Effect of Contact Time and Initial Concentration of the Solution

The effect of the contact time on the adsorption of Pb^{2+} on the CAA was carried out at 27°C at different initial concentrations of Pb^{2+} (Figure 2). Adsorption is shown to increase rapidly and is followed by a step without significant variation in adsorption. The rapid adsorption at the initial stage may be due to the occupation of active centers of CAA, thus providing many active sites easily accessible to Pb^{2+} ions. By increasing the time and the concentration, the availability of the remaining active sites decreases, thus leading to a long time to reach equilibrium [29]. This is explained by the fact that most of the vacant sites will be quickly occupied by Pb^{2+} cations, but the few remaining sites will be gradually occupied due to the high concentration of Pb^{2+} and the overflow of available sites. In solution, at low concentration of Pb^{2+} 50 - 100 mg/L, equilibrium is obtained after 30 min, while at high concentration (300 - 500 mg/L), a longer equilibrium time of 90 min. In addition, the overall retention is comparable for the four concentrations with a yield which increases when the concentration increases with orders of magnitude of 48%, 61%, 81% respectively for the concentrations of 50, 100, and 300 mg/L excepted when the initial concentration is 500 mg/L corresponding to a yield of 64%. Furthermore, the increase in the initial concentration of Pb^{2+} leads to an increase in the adsorption capacity, which suggests that the increase in the concentration of lead(II) ions promotes mass transfer from the aqueous phase to the phase solid. Similar observations were made by Murat *et al.* [30]. Thus, the adsorption at equilibrium increased from 2.4 to $32\text{ mg}\cdot\text{g}^{-1}$ with an increase in the initial concentration from 50 to 500 mg/L. For our study, 81% is the maximum retention rate, corresponding to an equilibrium time of 90 min and an initial concentration of 300 mg/L. This 90 min duration could have been used as equilibrium time, but 120 min duration was used to allow maximum adsorption of the carbon for the study of the adsorption isotherms.

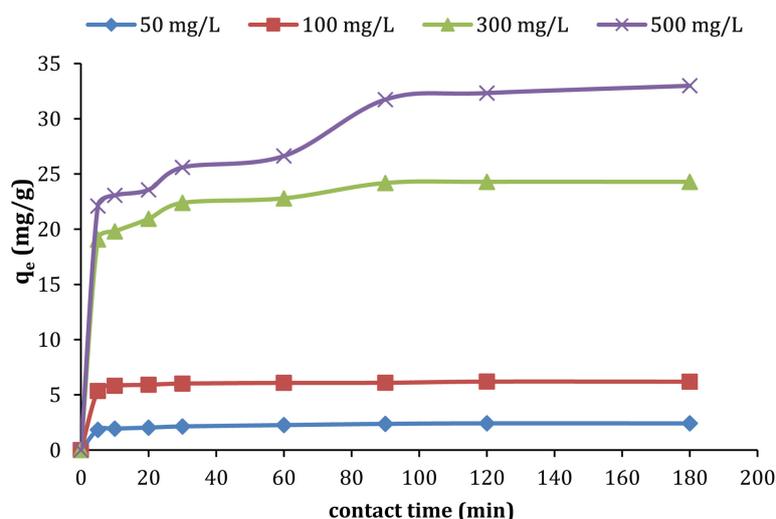


Figure 2. Equilibrium time and influence of the initial concentration of Pb (II) ions.

3.2.3. Effect of the pH of the Initial Solution

The initial pH of the aqueous solution remains one of the most important factors in determining the adsorption properties of the adsorbent. The removal of metal ions by adsorption depends greatly on the pH of the solution [31] [32]. Thus, the effect of the pH of the starting solution on the adsorption of Pb^{2+} was studied between 2 and 11 at room temperature (27°C), a contact time of 120 minutes and a Pb^{2+} concentration of $300\text{ mg}\cdot\text{L}^{-1}$. **Figure 3** shows the initial effect of the pH of the adsorption of Pb^{2+} by the CAA. It shows that the initial concentration of Pb^{2+} increases to 146.06 mg/L ($\text{pH} = 2$) to 43.19 mg/L ($\text{pH} = 5$) and then rises to 130.60 mg/L ($\text{pH} = 11$). Thus, the percentage of adsorption increases (43.19% to 85.90%) with the increase in pH from 2 to 5 and decreases (85.90% to 56.46%) when the pH drops from 5 to 11. In Indeed, according to **Table 2**, the pH_{PZC} value of CAA is approximately 4.8. This indicates that when the pH of the solution is above 4.8; the surface of CAA will have a net negative charge therefore will tend to attract more Pb^{2+} ions., while at a pH lower than 4.8, the surface of CAA will have a positive charge therefore will tend to repel Pb^{2+} ions [33].

The low abatement rates observed between $2 \leq \text{pH} < 4.8$ could also be explained by the competitive effect between the H^+ and Pb^{2+} cations which compete for the negative adsorption sites existing on the carbon surface. The surface of the adsorbent being positively charged due to the H^+ already adsorbed will tend to repel Pb^{2+} ions. On the other hand, a remarkable capacity for eliminating Pb^{2+} was observed when the pH was increased from 5 to 11. This decrease in adsorption in the basic medium could be explained by a change of phase of the ion lead(II) by the formation of lead complexes such as $\text{Pb}(\text{OH})_2$ and insoluble forms since the pH of the addition of NaOH controlled the medium, thus increasing the concentration of OH^- in the medium [34]. The decrease in the adsorption of Pb^{2+} at alkaline pH could be due to the neutralization of the acid sites present in the activated carbon by hydroxyl ions OH^- . A similar trend has been reported by Madhava *et al.* [35] when removing Pb and Zn on activated carbon. In total, the removal of lead(II) could therefore be done either by electrostatic interactions,

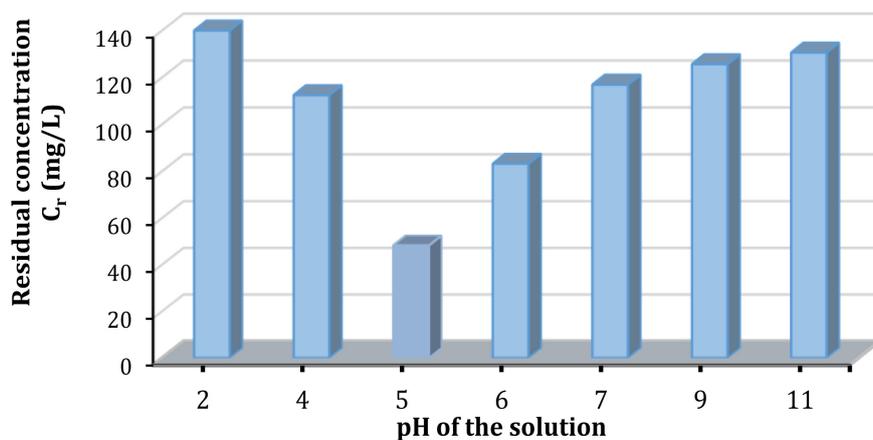


Figure 3. Residual concentration of lead(II) as a function of the initial pH of the solution for an initial concentration of 300 mg/L .

by complexation or by ion exchange. Since the alkaline conditions accelerate the formation of hydroxyl complexes resulting in poor adsorption of Pb^{2+} by CAA, the $\text{pH} = 5$ seems to be the best for the adsorption of Pb^{2+} by CAA in the context of our study.

3.2.4. Adsorption Isotherms

The adsorption isotherm indicates that the adsorbate molecules are shared between the adsorbent and the liquid phase at equilibrium as a function of the adsorbate concentration. In this study, the equilibrium data obtained for the adsorption of lead(II) ions on the CAA were analyzed by considering the isothermal model of Langmuir, Freundlich, Temkin, Dubinin-Radushkevich, Fowler-Guggenheim and Kiselev. The linear forms of the different isotherms are described by the equations in **Table 2**.

- Langmuir isotherm

The linear form of the Langmuir isotherm equation is given in **Table 2**. The two parameters K_L and q_m are determined from a graph $\frac{1}{q_e}$ as a function of

$\frac{1}{C_e}$ (**Figure 4(a)**). The Langmuir isotherm is frequently evaluated by a separation factor, R_L , which is defined by:

$$R_L = \frac{1}{1 + K_L C_0}$$

where C_0 is the initial solute

concentration. Depending on the R_L value, the adsorption is said to be: favorable if $0 < R_L < 1$; unfavorable if $R_L > 1$; linear if $R_L = 1$ and irreversible if $R_L = 0$. [36]. According to the data calculated and presented in **Table 5**, R_L is greater than 0 but less than 1, which indicates that the Langmuir isotherm is favorable. Based on this research, the maximum single-layer coverage capacity (Q_m) of the Langmuir model was established at 74.07 mg/g, K_L at 0.0356 L/mg, R_L (separation factor) at 0.412, which indicates that the sorption equilibrium is favorable and the value of R^2 is equal to 0.96, which proves that the sorption data correspond well to the Langmuir model.

In addition, the value of the adsorption capacity from this acacia wood obtained in the context of our study is high compared to other adsorbent raw materials found in the literature (**Table 6**), thus showing that our CAA carbon is effective in removing Lead(II) ions from water.

According to Langmuir's model, adsorption is carried out on a homogeneous energy surface by the formation of monolayer without any interaction between the adsorbed species. However it gives no information on the heterogeneity of the adsorbent. Let's check through Freundlich model if adsorption also occurs on heterogeneous surfaces.

- Freundlich isotherm

This isotherm is commonly used to describe the adsorption characteristics of the heterogeneous surface [50]. These data often correspond to the empirical equation proposed by Freundlich in **Table 2** with n_p , an indicator of adsorption intensity. The Freundlich isotherm is obtained by plotting the linearized equation

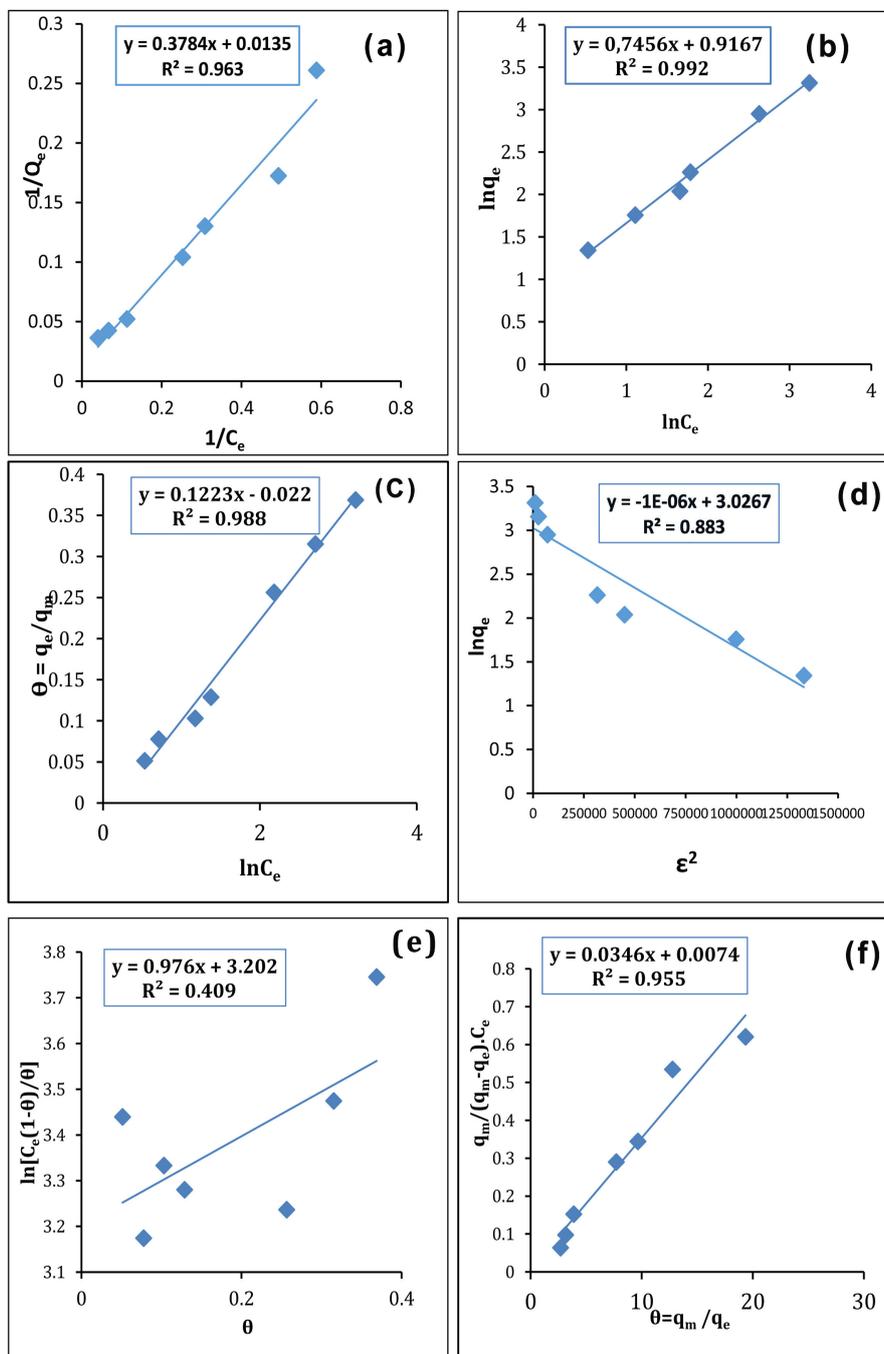


Figure 4. Isothermal models of Langmuir (a), Freundlich (b), Temkin (c), Dubinin-Radushkevich (d), Fowler-Guggenheim (e) and Kiselev (f) for the elimination of Pb²⁺ using CAA carbon.

$\ln(q_e) = f(\ln C_e)$ (Figure 4(b)). The linearly transformed equation was applied to correlate the sorption data where $1/n$ is a heterogeneity parameter, the smaller $1/n$, the greater the expected heterogeneity. This expression is reduced to a linear adsorption isotherm when $1/n = 1$. If n is between one and ten, this indicates a favourable sorption process [51]. According to the data in Table 5, this value of $1/n = 0.7456$ while $n = 1.33$ indicates that the sorption of Pb²⁺ on CAA is

Table 5. Pb²⁺ adsorption parameters on CAA according to Langmuir models, Freundlich, Temkin, Dubinin-Radushkevich, Fowler-Guggenheim and Kiselev.

Equilibrium model	Parameters	Values
Isotherm of Langmuir	q_m (mg/g)	74.07
	K_L (L/mg)	0.0356
	R_L	0.085 - 0.412
	R^2	0.963
Isotherm of Freundlich	K_F (L/g)	2.501
	n	1.33
	R^2	0.992
Isotherm of Temkin	A_T (L/mg)	0.835
	B	0.1223
	ΔQ (kJ/mol)	20.394
	R^2	0.988
Isotherm of Dubinin-Radushkevich	q_s (mg/g)	20.54
	β (mol ² ·kJ ⁻²)	10 ⁻⁶
	E (kJ·mol ⁻¹)	0.707
	R^2	0.883
Isotherm of Fowler-Guggenheim	K_{FG} (L/mg)	0.040
	W (kJ·mol ⁻¹)	1.217
	R^2	0.409
Isotherm of Kiselev	K_1	0.0346
	K_n	0.213
	R^2	0.955

favourable and that the value of R^2 is 0.99. The Langmuir and Freundlich isotherms do not consider the energy aspect during adsorption, the Temkin model is used to obtain information on the variation of the adsorption energy.

- Temkin isotherm

The Temkin isotherm considers the fact that the heat of adsorption of all the molecules of the cover layer decreases linearly with the cover due to the decrease in adsorbent-adsorbate interactions. Adsorption is characterized by a uniform distribution of the binding energies at the surface. The linear form of the Temkin isothermal model is given by the equation of **Table 2**. The plot of $q_e = f(\ln C_e)$ (**Figure 4(c)**) allows to determine $B_T = \frac{q_m RT}{\Delta Q}$, then by introducing a value of q_m (for example from the Langmuir application) calculates the variation in adsorption energy ΔQ . In **Table 5**, the correlation coefficient (R^2) obtained is close

Table 6. Comparative results of the adsorption capacity of various adsorbents of lead(II) ions.

Origin of activated carbon	Adsorption conditions			Adsorption capacity (mg/g)	Réf
	pH	<i>t</i> (°C)	Adsorbent dosage (g/L)		
Peanut shell	6.0	20	0.6	113.96	[37]
Coconut shell	5.6	25	2.0	76.66	[38]
<i>Acacia auriculaeformis</i>	5.0	27	10.0	74.07	<i>Our study</i>
Bamboo carbon	5.0	29	1.0	53.76	[39]
Polypyrrole	5.5	23	5.0	50.00	[40]
Sugar beet pulp	5.3	25	8.0	43.50	[41]
Moringa oleifera	6	25	-	38.52	[42]
Soy hull	5.0	23	10.0	39.37	[43]
Coconut shell Norit 1240	4.0	25	5.0	39.06	[44]
Date core	5.2	25	4.0	30.70	[45]
Juniperus Procera	4.6	25	8.0	30.30	[46]
Pine cone	6.7	25	2.0	27.53	[2]
Apricot stone	6.5	25	10.0	22.85	[47]
Apricot stone	6.0	20	1.0	21.38	[48]
Hazelnut shell	5.7	18	12.0	13.05	[49]

to 1; thus, showing that the Temkin model is applicable. The variation of the adsorption energy ΔQ resulting from the linearization of the Temkin model is positive (20.394 kJ/mol) which implies that the adsorption reaction is exothermic. Similar values of the adsorption energy have been reported by Oualid *et al.* [52] during the copper (II) adsorption study. The Temkin isotherm does not determine the nature of the adsorption, so the Dubinin and Radushkevich isotherm is used.

- Isotherm of Dubinin-Radushkevich

The Dubinin-Radushkevich isotherm (D-R) is applied to determine the nature of the adsorption mechanism based on the theory of potential assuming that the surface of the adsorbent is heterogeneous. The isotherm of D-R is given by the equation of **Table 2** with: the Polanyi potential given by the relation $\varepsilon = \ln\left(1 + \frac{1}{C_e}\right)$.

The linear form makes it possible to trace the curve $\ln q_e = f(\varepsilon^2)$ (**Figure 4(d)**) and to determine β then calculate the average energy of adsorption E (kJ·mol⁻¹) by using the equation:

$$E = \frac{1}{\sqrt{2\beta}}$$

$E < 8 \text{ kJ}\cdot\text{mol}^{-1}$: physisorption dominates the sorption mechanism;

$8 < E < 16 \text{ kJ}\cdot\text{mol}^{-1}$: ion exchange is the dominant factor;

$E > 16 \text{ kJ}\cdot\text{mol}^{-1}$: sorption is dominated by intra-particle scattering.

In **Table 5** the value found of the free energy E to estimate the type of Pb^{2+} adsorption process is $0.707 \text{ kJ}\cdot\text{mol}^{-1}$. This value belongs to the energy interval when physisorption dominates ($E < 8 \text{ kJ}\cdot\text{mol}^{-1}$). However, the regression coefficient is far from unity (0.883) so this model is not applicable. In order to assess the interaction energies between adsorbed molecules, the Fowler-Guggenheim isotherm was applied.

- Fowler-Guggenheim isotherm

The Fowler-Guggenheim model is based on statistical thermodynamics and takes into account the interactions between adsorbed molecules. The molecules adsorbed on the nearest neighboring sites have an interaction energy equal to $2W/Z$ with Z the number of lateral coordinates, that is to say the number of nearest neighbours.

If $W > 0$, the adsorbed molecules repel each other.

If $W < 0$, the adsorbed molecules attract each other.

By representing the curve $\ln \left[\frac{C_e (q_m - q_e)}{q_e} \right] = f \left(\frac{q_e}{q_m} \right)$, the slope leads to

$2W/RT$ and the intercept at $-\ln K_{FG}$. The experimental results of the Pb^{2+} adsorption isotherms modelled by the Fowler-Guggenheim equation are represented by **Figure 4(e)** and the parameters recorded in **Table 5**. The interaction energy value $W = 1.217 \text{ kJ}\cdot\text{mol}^{-1} > 0$ stipulates that the adsorbed Pb^{2+} cations repel each other. However, this result cannot be taken into account because the regression coefficient is low: 0.409. This model is limited to the interactions taking place between the adsorbed molecules but does not provide information on the formation of a possible complex between the adsorbed molecules. Let's check if there is complex formation through the Kiselev model.

- Kiselev isotherm

The Kiselev model leads to the determination of a complex formation constant which supposes adsorption in a monomolecular layer according to the equation in **Table 2**. The graphic representation of the linear form

$\frac{q_m}{(q_m - q_e)C_e} = f \left(\frac{q_m}{q_e} \right)$, allows to deduce K and K_r . The experimental results of

the isothermal adsorption equilibria of the Pb^{2+} cation on the CAA modelled by the Kiselev equation are grouped in **Figure 4(f)** and in **Table 5**. This model applies fairly well to the adsorption of the Pb^{2+} cation about correlation coefficients equal 0.955. This implies that there is formation of complexes between the cations adsorbed on the surface of the activated carbon. These results confirm once again the high rate of metal cation abatement in alkaline media when studying the effect of pH on adsorption. By way of illustration, the formation of Pb complex is moreover observable on the surface of the CAA charcoal through the SEM pictures of **Figure 5**.

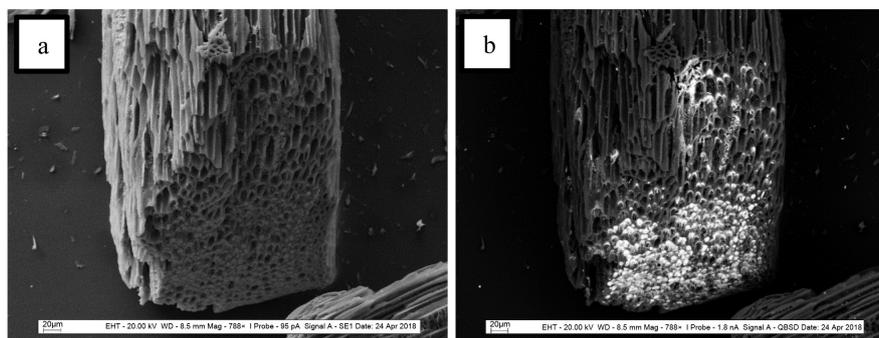


Figure 5. Morphology of CAA carbon before and after adsorption of Pb(II). (a) Before adsorption of Pb(II); (b) After adsorption of Pb(II).

3.2.5. Effect of Temperature and Determination of Thermodynamic Quantities

The effect of temperature on the adsorption of Pb^{2+} was carried out at temperatures ranging from 27°C to 75°C in 50 mL of Pb^{2+} solutions of different concentrations from 40 to $300\text{ mg}\cdot\text{L}^{-1}$. The equilibrium contact time for adsorption is fixed at 120 minutes. It is observed that the amount of Pb^{2+} adsorbed decreases by increasing the temperature from 27°C to 75°C (Figure 6), indicating that the reaction is exothermic. The thermodynamic parameters ΔG° , ΔH° and ΔS° are determined from Equations (5), (6) and (7) and the plot of $\ln K_L$ as a function of $1/T$ (Figure 7) Where, K_L is the constant of Langmuir equilibrium ($\text{L}\cdot\text{mg}^{-1}$) at each temperature multiplied by the density of water ($10^6\text{ mg}\cdot\text{L}^{-1}$) according to Dos Santos *et al.* [53] and T the absolute temperature. The values of the parameters ΔG° ($\text{kJ}\cdot\text{mol}^{-1}$), ΔS° ($\text{kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and ΔH° ($\text{kJ}\cdot\text{mol}^{-1}$) are summarized in Table 7. The negative value of ΔG° , suggests that the process of adsorption of Pb^{2+} by CAA is spontaneous. The negative value of ΔH° indicates the exothermic nature of the adsorption process according to Chouchane *et al.* [54] and Emna *et al.* [55] and shows that the transfer of Pb^{2+} ions from the aqueous phase to the solid phase releases energy. Retention is ordered at the solid/liquid interface during adsorption due to the negative value of ΔS° . Furthermore, the standard enthalpy value (of the order of $-51\text{ kJ}\cdot\text{mol}^{-1}$ less than $-40\text{ kJ}\cdot\text{mol}^{-1}$) during the adsorption of the Pb^{2+} ion indicates that chemisorption is involved in this adsorption process according to Kumar *et al.* [23].

3.2.6. Kinetic Adsorption

The kinetic study of the experimental data allows a description of the fixing mechanisms and provides information relating to the mode of transfer of solutes from the liquid phase to the solid phase. Like the adsorption equilibria, the adsorption kinetics of a material can also be modelled. For this purpose, the literature reports a certain number of models which are quite used, among which appear the models of pseudo-first order and pseudo-second order, the model of Elovich, the model of intraparticle diffusion and the model of Boyd [56]. In order to understand the nature of the Pb^{2+} adsorption phenomenon on CAA in the framework of our study, the mathematical equations describing the kinetic

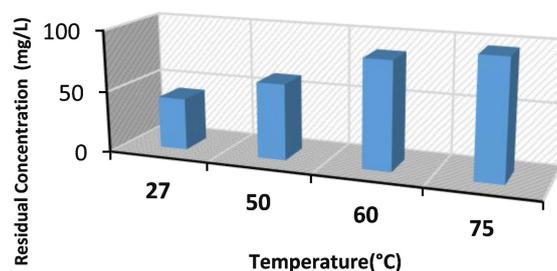


Figure 6. Effect of temperature on the elimination of Pb^{2+} for initial concentration $C_0 = 300 \text{ mg/L}$.

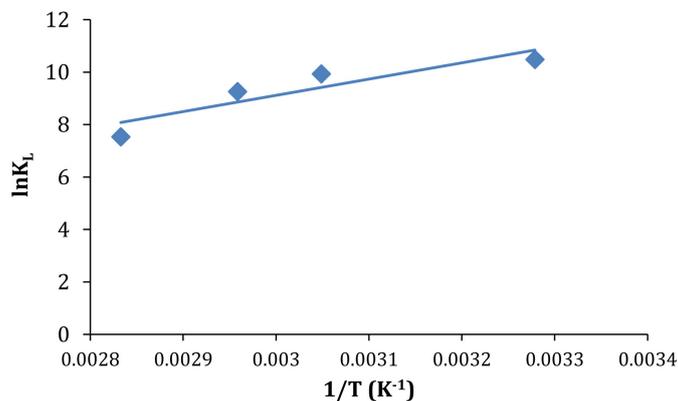


Figure 7. Plot of $\ln K_L$ curves as a function of $1/T$ for the estimation of thermodynamic parameters.

Table 7. Thermodynamic parameters of Pb^{2+} adsorption on CAA.

T (K)	$\ln K_L$	ΔS° (kJ·mol ⁻¹ ·K ⁻¹)	ΔH° (kJ·mol ⁻¹)	ΔG° (kJ·mol ⁻¹)
300	10.4822484			-27.884
303	9.92739524	-0.078	-51.502	-26.073
333	9.25491058			-25.286
348	7.5315351			-24.105

models (Table 3) were used to adjust the experimental data. Figure 8 presents the linear plot of the intraparticle diffusion and pseudo-first order, pseudo-second order, Elovich and Boyd equations. The calculated kinetic constants of all the applied models are indicated in Table 8. On the one hand, about the values of the correlation coefficient, it is clear that the adsorption of Pb^{2+} on the CAA follows the pseudo-second-order model. This adsorption reaction therefore depends on the concentrations of the adsorbent and the adsorbate. On the other hand, the study reveals that the intraparticle diffusion model is involved in the adsorption process. However it does not correspond alone to the limiting stage of the reaction of adsorption of $\text{Pb}(\text{II})$ by CAA. It is also limited by extra-particulate transport because the straight lines obtained during the plot of B_t as a function of time for different initial concentrations of lead(II) illustrated in Figure 8(e) do not pass through the origin.

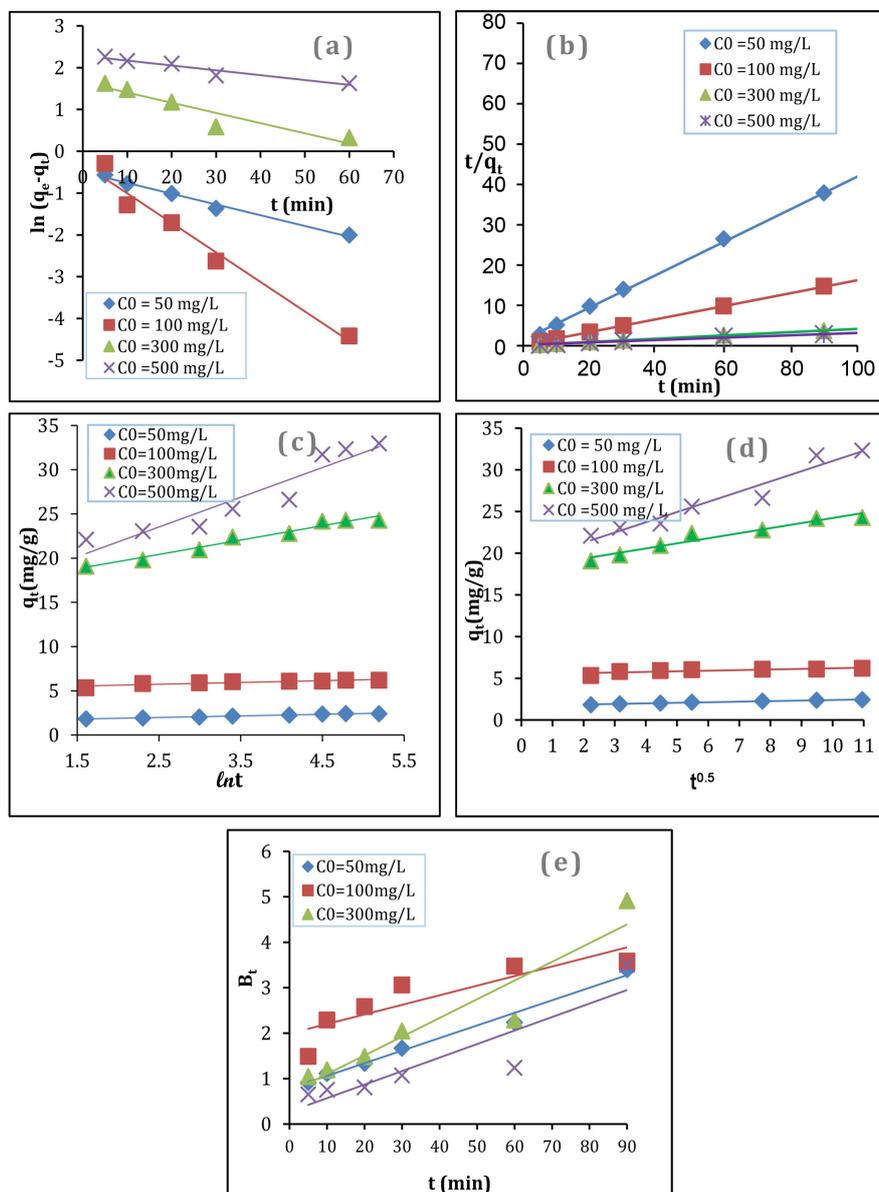


Figure 8. Kinetic models of pseudo-first order (a), pseudo-second order (b), Elovich (c), intraparticle diffusion (d) and Boyd (e) applied to the adsorption of Pb^{2+} on CAA.

3.2.7. Application to the Elimination of Pb^{2+} Ions in Real Wastewater

The tests are aimed at determining the mass of activated carbon and the contact time required to remove a maximum amount of Pb^{2+} ions in real wastewater. The results are shown in **Figure 9**. The residual concentration of Pb^{2+} ions decreases with increasing mass of activated carbon regardless of the contact time. For a contact time of 120 min, the residual concentration decreases from 4.40 to 2.61 mg/L, *i.e.* a maximum reduction rate of 40.52%. As for the contact time of 1440 min (24 h), the residual concentration fluctuates when the mass of coal increases and the maximum reduction rate recorded is 29.20%. These results show that the amount of lead eliminated, although it depends on the amount of AC involved, also depends on the contact time. The more the mass of AC increases

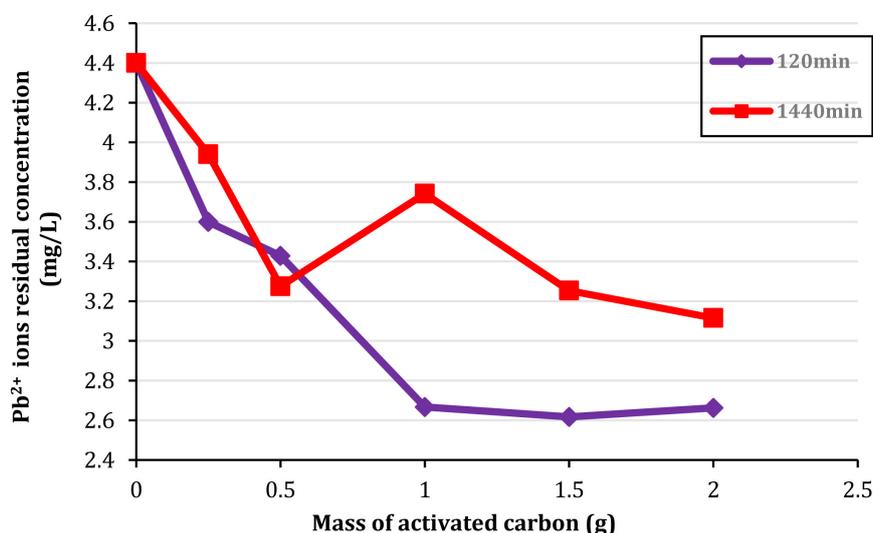


Figure 9. Residual concentration of the lead element in wastewater as a function of the mass of AC for a contact time of 120 min and 1440 min.

Table 8. Kinetic parameters for the adsorption of Pb²⁺ on CAA.

pseudo-first order model						pseudo-second order model				
C ₀ (mg/L)	q _e (exp)	k ₁ (min ⁻¹)	q _e (cal) (mg/g)	Δq	R ²	k ₂ (g·mg ⁻¹ ·min ⁻¹)	q _e (cal) (mg/g)	Δq	R ²	
50	2.37	0.0258	0.59	1.78	0.9884	0.1167	2.46	0.09	0.9996	
100	6.09	0.0706	0.77	5.3	0.9728	0.0223	6.22	0.13	0.9999	
300	24.18	0.0244	5.2	18.98	0.8854	0.0143	24.69	0.51	0.9997	
500	31.73	0.0116	9.4	23.33	0.9265	0.0037	34.12	2.39	0.9952	

Intraparticle diffusion model					Model of Elovich		
C ₀ (mg/L)	q _e (exp)	k _{id} (g·mg ⁻¹ ·min ⁻¹)	C (mg·g ⁻¹)	R ²	α (mg·g ⁻¹ ·min ⁻¹)	β (g·mg ⁻¹)	R ²
50	2.37	0.0671	1.7272	0.9776	4964.2183	5.6517	0.9852
100	6.09	0.0727	5.4751	0.7022	1.2686E+11	4.8947	0.8441
300	24.18	0.6086	18.139	0.9434	23967.1062	0.6163	0.9660
500	31.73	1.2256	18.806	0.9464	89.7483	0.2976	0.8942

and the shorter the contact time, the more important the elimination of lead by AC becomes. The maximum value of the rate of elimination of the Pb²⁺ cation recorded in the industrial effluent (40.52%) is moderately significant to judge the efficiency of our coal about the reduction rate reaching around 86% in the case of synthetic solutions. This difference could be justified by a possible competition between several pollutants contained in real wastewater. Among these pollutants could be found several other metal cations, nitrites, nitrates, phosphates, sulphates, and certain organic materials. In addition, the difference in the maximum elimination rate observed between the case of the contact time of 120 min and that of 1440 min, could be explained by desorption when the contact time becomes too long.

4. Conclusion

In this study, three activated carbons were synthesized from *Acacia auriculaeformis* carbon produced in Côte d'Ivoire. The CAA, CAB and CAS coals were obtained by activation with three oxidizing agents respectively H_3PO_4 , NaOH and NaCl. The physical properties determined by adsorption/desorption of N_2 , SEM analysis and chemical properties such as the Boehm titration of activated carbons show that they have functionalized surfaces and have good microporosity. A comparative study of the characteristics of these different coals has shown that CAA carbon is suitable for the elimination of metal cations and in particular Pb^{2+} ion studied. Data from Pb^{2+} adsorption equilibrium study performed on the CAA showed that the simulated adsorption isotherms are correctly described by Langmuir, Freundlich, Temkin and Kiselev models. Thus, the ultimate adsorption capacity reached is 74.04 mg/g on the surface of the supposedly heterogeneous adsorbent. The adsorption reaction is exothermic with possible formation of a complex between the metal cations on the surface of the activated carbon. According to a kinetic study, it has been observed that adsorption corresponds well to the kinetic model of pseudo-second order reflecting a chemical adsorption dominated by the formation of a covalent bond between the adsorbate. As for the mechanism, intraparticle diffusion is not the only process limiting the adsorption reaction; extra-granular diffusion is involved. Thermodynamic data reveals that the adsorption reaction is spontaneous, exothermic, and retention is ordered at the solid/liquid interface. Furthermore, the value of the standard enthalpy (of the order of $-51 \text{ kJ}\cdot\text{mol}^{-1}$ less than $-40 \text{ kJ}\cdot\text{mol}^{-1}$) during the adsorption of the Pb^{2+} ion indicates that chemisorption is involved in this adsorption process. *Acacia auriculaeformis* carbon activated with phosphoric acid has been shown to be a carrier with a generally high adsorption affinity for the cation Pb^{2+} . Indeed, this adsorbent material has contributed to average retention of the ions contained in an industrial effluent with a reduction rate reaching 42.52% against 85.90% in synthetic solutions. The abundance of *Acacia auriculaeformis* wood generated by the forests of the CNRA (Centre National de Recherche Agronomique, Côte d'Ivoire), can offer a low-cost adsorption material that can possibly contribute to the treatment of metalliferous effluents.

Acknowledgements

The authors express their heartfelt thanks to Prof. Serge KALIAGUINE, Chemical Engineering Division, University Laval, Canada, for BET analysis facility, and to Doctor Lazare YAO, head of the Central Agrochemical and Ecotoxicology laboratory (LCAE) at LANADA in Abidjan, CÔTE d'Ivoire for analyzes with an atomic absorption spectrometer.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Chen, Y., Xu, J., Xie, R., Huang, L. and Jiang, J. (2018) Impacts of Biochar and Oyster Shells Waste on the Immobilization of Arsenic in Highly Contaminated Soils. *Journal of Environmental Management*, **217**, 646-653. <https://doi.org/10.1016/j.jenvman.2018.04.007>
- [2] Milan, M., Milovan, P., Aleksandar, B., Aleksandra, Z., Marjan, R. (2011) Removal of Lead(II) Ions from Aqueous Solutions by Adsorption Onto Pine Cone Activated Carbon. *Desalination*, **276**, 53-59. <https://doi.org/10.1016/j.desal.2011.03.013>
- [3] Mimanne, G., Benhabib, K. and Benghalem, A. (2014) Etude de l'Adsorption des Métaux Lourds (Pb et Cd) en Solution Aqueuse sur Charbon Actif et Montmorillonite Sodée de l'Ouest Algérien. *Journal of Materials and Environmental Science*, **5**, 1298-1307.
- [4] Han, Y., Boateng, A.A., Qi, P.X., Lima, I.M. and Chang, J. (2013) Heavy Metal and Phenol Adsorptive Properties of Biochars from Pyrolyzed Switch Grass and Woody Biomass in Correlation with Surface Properties. *Journal of Environmental Management*, **118**, 196-204. <https://doi.org/10.1016/j.jenvman.2013.01.001>
- [5] Gercel, O. and Gercel, H.F. (2007) Adsorption of Lead(II) Ions from Aqueous Solutions by Activated Carbon Prepared from Biomass Plant Material of *Euphorbia rigida*. *Chemical Engineering Journal*, **132**, 289-297. <https://doi.org/10.1016/j.cej.2007.01.010>
- [6] Ahn, C.K., Park, D., Woo, S.H. and Park, J.M. (2009) Removal of Cationic Heavy Metal from Aqueous Solution by Activated Carbon Impregnated with Anionic Surfactants. *Journal of Hazardous Materials*, **164**, 1130-1136. <https://doi.org/10.1016/j.jhazmat.2008.09.036>
- [7] Amuda, O.S., Giwa, A.A. and Bello, I.A. (2007) Removal of Heavy Metal from Industrial Wastewater Using Modified Activated Coconut Shell Carbon. *Biochemical Engineering Journal*, **36**, 174-181. <https://doi.org/10.1016/j.bej.2007.02.013>
- [8] Hecini, L. and Achour, S. (2014) Coagulation-floculation au sulfate d'aluminium de composés organiques phénoliques et effet de sels de calcium et de magnésium. *Revue des Sciences de l'Eau*, **27**, 271-280. <https://doi.org/10.7202/1027810ar>
- [9] Chikhi, M. (2008) Etude de la complexation des cations métalliques en vue de leur séparation par un procédé membranaire. Thèse de Doctorat d'État Université Mentouri Constantine, Algérie, département de chimie industrielle, 144 p.
- [10] Brahim, S., Patrick, D., Géraldo, B., Jean, F.B. and Marc, H. (2011) État actuel des connaissances des procédés de bioréacteur à membrane pour le traitement et la réutilisation des eaux usées industrielles et urbaines. *Revue des Sciences de l'eau*, **24**, 283-310. <https://doi.org/10.7202/1006478ar>
- [11] Liu, Y., Yan, J., Yuan, D., Li, Q. and Wu, X. (2013) The Study of Lead Removal from Aqueous Solution Using an Electrochemical Method with a Stainless Steel Net Electrode Coated with Single Wall Carbon Nanotubes. *Chemical Engineering Journal*, **218**, 81-88. <https://doi.org/10.1016/j.cej.2012.12.020>
- [12] Deng, L., Su, Y., Su, H., Wang, X. and Zhu, X. (2007) Sorption and Desorption of Lead(II) from Wastewater by Green Algae *Cladophora fascicularis*. *Journal of Hazardous Materials*, **143**, 220-225. <https://doi.org/10.1016/j.jhazmat.2006.09.009>
- [13] Mohandas, J., Kumar, T., Rajan, S.K., Velmurugan, S. and Narasimhan, S.V. (2008). Introduction of Bifunctionality into the Phosphinic Acid Ion-Exchange Resin for Enhancing Metal Ion Complexation. *Desalination*, **232**, 3-10. <https://doi.org/10.1016/j.desal.2008.01.005>

- [14] Ahmad, M., Rajapaksha, A.U., Lim, J.E., Zhang, M., Bolan, N., Mohan, D., Vithanage, M., Lee, S.S. and Ok, Y.S. (2014) Biochar as a Sorbent for Contaminant Management in Soil and Water: A Review. *Chemosphere*, **99**, 19-33. <https://doi.org/10.1016/j.chemosphere.2013.10.071>
- [15] Richards, S., Dawson, J. and Stutter, M. (2019) The Potential Use of Natural vs Commercial Biosorbent Material to Remediate Stream Waters by Removing Heavy Metal Contaminants. *Journal of Environmental Management*, **231**, 275-281. <https://doi.org/10.1016/j.jenvman.2018.10.019>
- [16] Bossombra, K.V., Tchirioua, E., Ekou, L. and Trong-On, D. (2018) Nitrogen Enrichment of Activated Carbon Made from Coconut Shell of Ivory Coast and Its Application in Cd²⁺ Ions Removal. *Australian Journal of Basic and Applied Sciences*, **12**, 38-44.
- [17] Gnonsoro, U.P., Yao, K.M., Yao, B.L., Kouassi, A.M., Dembélé, A., Kouakou, Y.U., Ouattara, K.P.H., Diabaté, D. and Trokourey, A. (2015) Adsorption du benzo(a)pyrène sur du charbon activé à base de coques de coco provenant de Côte d'Ivoire. *International Journal of Biological and Chemical Sciences*, **9**, 2701-2711. <https://doi.org/10.4314/ijbcs.v9i5.39>
- [18] Atheba, P., Allou, N.B., Drogui, P. and Trokourey, A. (2018) Adsorption Kinetics and Thermodynamics Study of Butylparaben on Activated Carbon Coconut Based. *Journal of Encapsulation and Adsorption Sciences*, **8**, 39-57. <https://doi.org/10.4236/jeas.2016.82003>
- [19] Ouattara, K.P.H. (2014) Etude de l'adsorption de l'aspirine sur des charbons activés préparés à partir de coques d'arachide (*Arachis hypogaea*) et de soja vert (*vigna radiata*). N° d'ordre 916/2014, Thèse de doctorat, Université Félix Houphouët Boigny d'Abidjan, Côte d'Ivoire, 131 p.
- [20] Yobouet, Y.A., Aboua, K.N., Adouby, K. and Yao, K.B. (2018) Élimination du plomb et du cuivre en solution aqueuse par des charbons à base de bois de *Pterygota macrocarpa*. *Afrique Science*, **14**, 38-47.
- [21] Kra, D.O., Kouadio, N.A., Atheba, G.P., Coulibaly, B., Allou, N.B., Gbassi, K.G. and Trokourey, A. (2015) Modélisation des propriétés adsorbantes de charbons activés issus de deux variétés d'*Acacia* (*auriculaformis* et *mangium*). *International Journal of Innovation and Scientific Research*, **13**, 542-553.
- [22] Boehm, H.P. (1994) Some Aspects of the Surface Chemistry of Carbon Blacks and Other Carbons. *Carbon*, **32**, 759-769. [https://doi.org/10.1016/0008-6223\(94\)90031-0](https://doi.org/10.1016/0008-6223(94)90031-0)
- [23] Kumar, D.B. and Smaïl, K. (2011) Étude cinétique et thermodynamique de l'adsorption d'un colorant basique sur la sciure de bois. *Revue des sciences de l'eau/ Journal of Water Science*, **24**, 131-144. <https://doi.org/10.7202/1006107ar>
- [24] Gueu, S., Yao, B., Adouby, K. and Ado, G. (2006) Heavy Metals Removal in Aqueous Solution by Activated Carbons Prepared from Coconut Shell and Seed Shell of Palm Tree. *Journal of Applied Sciences*, **13**, 2789-2793. <https://doi.org/10.3923/jas.2006.2789.2793>
- [25] Ousmaila, S.M., Adamou, Z. and Ibrahim, D. (2016) Préparation et caractérisation de charbons actifs à base de coques de noyaux de *Balanites Eagyptiaca* et de *Zizyphus Mauritiana*. *Journal de la Société Ouest-Africaine de Chimie*, **41**, 59-67.
- [26] Marwa, F.E., Mohamed, R.E.A. and Hassan, S.H. (2016) Adsorption Profile of Basic Dye onto Novel Fabricated Carboxylated Functionalized Co-Polymer Nanofibers. *Polymers*, **8**, Article No. 177. <https://doi.org/10.3390/polym8050177>
- [27] Nethaji, S., Sivasamy, A. and Mandal, A.B. (2013) Adsorption Isotherms, Kinetics and Mechanism for the Adsorption of Cationic and Anionic Dyes Onto Carbon-

- ceous Particles Prepared from *Juglans regia* Shell Biomass. *International Journal of Environmental Science and Technology*, **10**, 231-242. <https://doi.org/10.1007/s13762-012-0112-0>
- [28] Bendaho, D., Ainad, T.D. and Bassou, D. (2014) Adsorption du cuivre Cu(II) en solution par l'argile brute et activée de la région de Tiout-Naama sud-ouest Algérien. *Revue science des matériaux*, **2**, 23-34.
- [29] Song, H.L., Jiao, F.P., Jiang, X.Y., Yu, J.G., Chen, X.Q. and Du, S.L. (2013) Removal of Vanadate Anion by Calcined Mg/Al-CO₃ Layered Double Hydroxide in Aqueous Solution. *Transactions of Nonferrous Metals Society of China*, **23**, 3337-3345. [https://doi.org/10.1016/S1003-6326\(13\)62873-3](https://doi.org/10.1016/S1003-6326(13)62873-3)
- [30] Murat, E., Suat, U., Selhan, K. and Turgay, T. (2013) Removal of Lead(II) Ions from Aqueous Solutions onto Activated Carbon Derived from Waste Biomass. *The Scientific World Journal*, **2013**, Article ID: 146092. <https://doi.org/10.1155/2013/146092>
- [31] Lee, X.J., Lee, L.Y., Hiew, B.Y.Z., Gan, S. and Gopa, K. S. (2017) Multistage Optimizations of Slow Pyrolysis Synthesis of Biochar from Palm Oil Sludge for Adsorption of Lead. *Bioresource Technology*, **245**, 944-953. <https://doi.org/10.1016/j.biortech.2017.08.175>
- [32] Bardestani, R., Roy, C. and Kaliaguine, S. (2019) The Effect of Biochar Mild Air Oxidation on the Optimization of Lead(II) Adsorption from Wastewater. *Journal of Environmental Management*, **240**, 404-420. <https://doi.org/10.1016/j.jenvman.2019.03.110>
- [33] N'guadi, B.A., Jitu, S. and Rajib, L.G. (2018) Use of Calcined Mg-Al Layered Double Hydroxides to Regulate Endocrine Disruptor Methylparaben in Excess as Adsorbent and as Control Releasing Agent in Normal Situations. *Journal of Environmental Chemical Engineering*, **6**, 1189-1200. <https://doi.org/10.1016/j.jece.2017.12.015>
- [34] Abou-El-Sherbini, K.S., Kenawy, I.M., Hafez, M.A., Lotfy, H.R. and Abd Elbary, Z.M. (2015) Synthesis of Novel CO₃²⁻/Cl⁻-Bearing 3(Mg + Zn)/(Al + Fe) Layered Double Hydroxides for the Removal of Anionic Hazards. *Journal of Environmental Chemical Engineering*, **3**, 2707-2721. <https://doi.org/10.1016/j.jece.2015.09.015>
- [35] Madhava, R.A., Chandra, R.A., Seshaiyah, A.K., Choudary, B. and Wang, M.C. (2008) Activated Carbon from *Ceiba pentandra* Hulls, an Agricultural Waste, as an Adsorbent in the Removal of Lead and Zinc from Aqueous Solutions. *Waste Management*, **28**, 849-858. <https://doi.org/10.1016/j.wasman.2007.01.017>
- [36] Karagoz, S., Tay, T., Ucar, S. and Erdem, M. (2008) Activated Carbons from Waste Biomass by Sulfuric Acid Activation and Their Use on Methylene Blue Adsorption. *Bioresource Technology*, **99**, 6214-6222. <https://doi.org/10.1016/j.biortech.2007.12.019>
- [37] Ricordel, S., Taha, S., Cisse, I. and Dorange, G. (2001) Heavy Metals Removal by Adsorption onto Peanut Husks Carbon: Characterization, Kinetic Study and Modeling. *Separation and Purification Technology*, **24**, 389-401. [https://doi.org/10.1016/S1383-5866\(01\)00139-3](https://doi.org/10.1016/S1383-5866(01)00139-3)
- [38] Kikuchi, Y., Qian Q., Machida, M. and Tatsumoto, H. (2006) Effect of ZnO Loading to Activated Carbon on Pb(II) Adsorption from Aqueous Solution. *Carbon*, **44**, 195-202. <https://doi.org/10.1016/j.carbon.2005.07.040>
- [39] Lalhruaitluanga, H., Jayaram, K., Prasad, M.N.V. and Kumar, K.K. (2010) Lead(II) Adsorption from Aqueous Solutions by Raw and Activated Charcoals of *Melocanna baccifera* Roxburgh (Bamboo)—A Comparative Study. *Journal of Hazardous Materials*, **175**, 311-318. <https://doi.org/10.1016/j.jhazmat.2009.10.005>

- [40] Alghamdi, A.A., Al-Odayni, A.B., Saeed, W.S., Al-Kahtani, A., Alharthi, F.A. and Aouak, T. (2019) Efficient Adsorption of Lead(II) from Aqueous Phase Solutions Using Polypyrrole-Based Activated Carbon. *Materials*, **12**, Article No. 2020. <https://doi.org/10.3390/ma12122020>
- [41] Pehlivan, E., Yanik, B.H., Ahmetli, G. and Pehlivan, M. (2008) Equilibrium Isotherm Studies for the Uptake of Cadmium and Lead Ions onto Sugar Beet Pulp. *Bioresource Technology*, **99**, 3520-3527. <https://doi.org/10.1016/j.biortech.2007.07.052>
- [42] Oliveira, T.F., Moraes, P.L.A., César, M.V.J., Vieira, F.M., Bergamasco, R. and Vieira, A. (2019) Analysis of the Influence of Natural Adsorbent Functionalization (*Moringa oleifera*) for Pb(II) Removal from Contaminated Water. *Environmental Progress & Sustainable Energy*, **32**, e13318. <https://doi.org/10.1002/ep.13318>
- [43] Johns, M.M., Marshall, W.E. and Toles, C.A. (1998) Agricultural By-Products as Granular Activated Carbons for Adsorbing Dissolved Metals and Organics. *Journal of Chemical Technology & Biotechnology*, **71**, 131-140. [https://doi.org/10.1002/\(SICI\)1097-4660\(199802\)71:2%3C131::AID-JCTB821%3E3.0.CO;2-K](https://doi.org/10.1002/(SICI)1097-4660(199802)71:2%3C131::AID-JCTB821%3E3.0.CO;2-K)
- [44] Kouakou, Y.U., Ello, A.S., Yapó, A.J., Gouli-Bi, I.M. and Trokourey, A. (2014) Study of Lead Adsorption on Activated Carbons. *International Journal of Biological and Chemical Sciences*, **8**, 1254-1261. <https://doi.org/10.4314/ijbcs.v8i3.38>
- [45] Abdulkarim, M. and Al-Rub, F.A. (2004) Adsorption of Lead Ions from Aqueous Solution onto Activated Carbon and Chemically-Modified Activated Carbon Prepared from Date Pits. *Adsorption Science & Technology*, **22**, 119-134. <https://doi.org/10.1260/026361704323150908>
- [46] Ali, I.H., Al Mesfer, M.K., Khan, M.I., Danish, M. and Alghamdi, M.M. (2019) Exploring Adsorption Process of Lead(II) and Chromium(VI) Ions from Aqueous Solutions on Acid Activated Carbon Prepared from *Juniperus procera* Leaves. *Processes*, **7**, Article No. 217. <https://doi.org/10.3390/pr7040217>
- [47] Kobya, M., Demirbas, E., Senturk, E. and Ince, M. (2005) Adsorption of Heavy Metal Ions from Aqueous Solutions by Activated Carbon Prepared from Apricot Stone. *Bioresource Technology*, **96**, 1518-1521. <https://doi.org/10.1016/j.biortech.2004.12.005>
- [48] Mouni, L., Merabet, D., Bouzaza, A. and Belkhiri, L. (2011) Adsorption of Pb(II) from Aqueous Solutions Using Activated Carbon Developed from Apricot Stone. *Desalination*, **276**, 148-153. <https://doi.org/10.1016/j.desal.2011.03.038>
- [49] Imamoglu, M. and Tekir, O. (2008) Removal of Copper(II) and Lead(II) Ions from Aqueous Solutions by Adsorption on Activated Carbon from a New Precursor Hazelnut Husks. *Desalination*, **228**, 108-113. <https://doi.org/10.1016/j.desal.2007.08.011>
- [50] Dada, A.O., Olalekan, A.P., Olatunya, A.M. and Dada, O. (2012) Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Isotherms Studies of Equilibrium Sorption of Zn²⁺ Unto Phosphoric Acid Modified Rice Husk. *Journal of Applied Chemistry*, **3**, 38-45.
- [51] Dipu, B., Shigeo, S. and Shigeru, K. (2008) Surface Modified Carbon Black for As(V) Removal. *Journal of Colloid and Surface Science*, **319**, 53-62. <https://doi.org/10.1016/j.jcis.2007.11.019>
- [52] Oualid, H. and Emmanuel, N. (2005) Etude des équilibres et de la cinétique d'adsorption du cuivre Cu(II) sur des particules réactives dans un réacteur fermé, parfaitement agité et thermostaté. *Lebanese Science Journal*, **6**, 59-68.

-
- [53] Dos Santos, R.M., Gonçalves, R.G., Constantino, V.R., Santilli, C.V. and Borges, P.D. (2017) Adsorption of Acid Yellow 42 Dye on Calcined Layered Double Hydroxide: Effect of Time, Concentration, pH and Temperature. *Applied Clay Science*, **140**, 132-139. <https://doi.org/10.1016/j.clay.2017.02.005>
- [54] Chouchane, T., Chouchane, S., Boukari, A., Balaska, A. and Samar, M.H. (2011) Elimination du plomb en solution par la science du bois. *Revue des énergies renouvelables*, **14**, 613-626.
- [55] Emna, Z., Ferial, K., Mohamed, S.M. and Hermouch, Y. (2015) Étude cinétique et thermodynamique de l'adsorption d'un métal lourd (Fer(III)) sur un déchet de clou de girofle en milieu aqueux. *Matériaux et Techniques*, **103**, Article No. 705. <https://doi.org/10.1051/mattech/2016005>
- [56] Rather, L.J., Shahid, U.I., Khan, M.A. and Mohammad, F. (2016) Adsorption and Kinetic Studies of *Adhatoda vasica* Natural Dye onto Woolen Yarn with Evaluations of Colorimetric and Fluorescence Characteristics. *Journal of Environmental Chemical Engineering*, **4**, 1780-1796. <https://doi.org/10.1016/j.jece.2016.03.003>