



# Adsorption of $Pb^{2+}$ ions by Activated carbons obtained from Maize cobs by Chemical activation with $ZnCl_2$ : Role of Physical and Chemical properties

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## Abstract

*The evaluation of the effectiveness of adsorption of activated carbons obtained from maize cobs by chemical activation with zinc chloride in removing lead(II) ions commonly found in municipal water in Cameroon was investigated. Batch experiments were conducted to study the effect of the contact time and initial concentration of Pb(II) ions for five maize cobs activated carbons and for a commercial one. The properties of the studied materials are correlated to their adsorption capacities. The carbon obtained from the hard part of the cob is the one which adsorbs best  $Pb^{2+}$ . Its adsorption percentage at 60 ppm is 32.97% and its  $K_d$ -value about  $0.45 \text{ cm}^3/\text{mg}$ . The commercial sample with an adsorption percentage of about 99% and  $k_d$ -value of about  $97.73 \text{ cm}^3/\text{mg}$  is by far the best adsorbent. The intraparticle diffusion seems to be the rate-limiting step.*

**Keywords:** Adsorption, activated carbon, maize cobs, lead (II), batch experiments, intraparticle diffusion.

## Introduction

The contamination of waste and industrial water by heavy metals is a great environmental problem. The rivers and the torrents are generally used like dump of waste by industries. These industries do not make any provision to treat this waste before their rejection in the natural environments from where the pollution of environment, water, soil, food chain and ground water. Several methods have been used to treat heavy metals effluents such as reduction precipitation, ion exchange, electrochemical reduction, evaporation, ultrafiltration, reverse osmosis, adsorption and direct precipitation<sup>1</sup>. Most of the methods mentioned above are not feasible in small and medium sized industries and even in large industries, they are very expensive; hence the need to choose simple techniques which are economical, efficient and especially clean such as adsorption on microporous solid. Adsorption is highly recommended for elimination of organic and inorganic substances at low concentrations that pollute the environment and those that are present in effluents. The process is simple, inexpensive and easily achievable. It requires for its realization a microporous adsorbent, which can exchange ions and make chemical bonds and which are easy to regenerate.

There are varieties of adsorbent materials such as silica gel, zeolites, synthetic adsorbents (resins), clays, activated alumina and activated carbon. Activated carbon (AC), the water industry's standard adsorbent for the reclamation of municipal and industrial wastewater for potable<sup>2</sup> is the mostly used because of its physicochemical and textural properties<sup>3,4</sup>. ACs have been chosen not only because of its porous nature and adsorptive capacity but also because of the abundance of raw material for

its preparation making it less expensive<sup>5</sup>. Five activated carbons obtained from chemical activation of maize cobs with zinc chloride  $ZnCl_2$  and a commercial activated carbon are used in this work.

Although the contents of heavy metals (Pb, Co, Ni, Hg, Ag, Cu, Zn, etc) are very weak in water in Cameroon (between 50-1000 ppm), it is important to undertake studies aiming at reducing to the maximum these contents taking into account toxicity of these metals. Our choice was made on lead because among the heavy metals detected in Cameroon's water (particularly the Central lake and Melenlake in Yaounde), this metal is most dangerous by far. It is at all dangerous as it can be accumulated in the ground and organisms but also in the food chain. Moreover there does not exist a threshold judged without effect for this metal from where need for reducing to the maximum the presence of lead in the environment. In the Central lake of Yaounde, the lead content varies between 15.1  $\mu\text{g/L}$  and 18.2  $\mu\text{g/L}$  (either an average of 17.4  $\mu\text{g/L}$ )<sup>6</sup>. In the Melen lake, this content varies between 17.0  $\mu\text{g/L}$  and 23.0  $\mu\text{g/L}$  (either an average of 20.1  $\mu\text{g/L}$ )<sup>6</sup>.

Several authors studied the adsorption of the lead ions  $Pb^{2+}$  in aqueous solution on the activated carbon of agricultural waste origin. Some of them adsorbed the  $Pb^{2+}$  ions on the activated carbon of coffee residues<sup>2</sup>, the other on the activated carbon made by hazelnuts husk<sup>7</sup>, adsorbed  $Pb^{2+}$  ions, on AC obtained from pecan shell<sup>8</sup>, on activated obtained from coconut shell and seed shell of palm tree<sup>9</sup>, on activated carbon obtained from apricot and peach stone<sup>10</sup> and on activated carbon obtained from cashew nuts shell<sup>11</sup>. These authors obtained very interesting results and their studies showed the availability of activated

carbon obtained from lignocellulosic agricultural waste to remove lead (II) ions in aqueous solutions. But their work consisted essentially on playing with adsorption parameters such as initial concentrations, adsorption duration, quantities of adsorbents or the pHs of solutions without taking into consideration the roles that may play physicochemical properties of materials prepared during the adsorption.

The influence of physico-chemical and textural properties of activated carbons, initial concentration and contact time on the sorption capacity was investigated. Pseudo-first order, second order, Elovich and Weber and Morris intraparticle diffusion kinetic models were used to identify the possible mechanisms of such sorption process. The Langmuir and Freundlich models were used to analyze the sorption equilibrium.

## Material and Methods

Four activated carbons sample labelled M10-60-100, M10-24-10, MAPZC3 and MAPZC5 obtained by chemical activation with ZnCl<sub>2</sub> of maize cobs have been used in this study. For purposes of comparison, a commercial powdered activated carbon sample of animal origin labelled OA00 and produced from PROLABO, RHÔNE-POULENC, N° 22614 was used. The textural and physico-chemical properties of all the materials used in this study are summarized in table-1.

<sup>a</sup>GAC: Granular activated carbon; <sup>b</sup>PAC: Powder activated carbon; S.S.A: Specific Surface Area; B.E.T: Brunauer-Emmett-Teller; M10-60-100: Maize cobs activated carbon (light part) obtained with 10% ZnCl<sub>2</sub> solution and time residence=60 minutes; M10-24-100: Maize cobs (light part)

activated carbon obtained with 10% ZnCl<sub>2</sub> solution and time residence=24 hours; MAPZC3: Maize cobs (light part) activated carbon obtained with 2g of solid ZnCl<sub>2</sub>; MAPZC5: Maize cobs activated carbon (hard part) obtained with 1g of solid ZnCl<sub>2</sub>; OA00: Animal origin activated carbon produced by PROLABO, Rhône Poulenc.

The various lead solutions are obtained starting from lead nitrate Pb(NO<sub>3</sub>)<sub>2</sub>. A lead nitrate was obtained from Sigma-Aldrich Corporation (St Louis, MO). Solutions of lead of concentrations ranging between 60 and 150 ppm were prepared.

In each of 6 Flask's (for each activated carbon sample) of 100 mL, 0.05 g of activated carbon was placed and 50 mL of aqueous solution of Pb<sup>2+</sup> added. The solution concentrations were respectively 60, 70, 90, 110, 130, 150 ppm. All the mixtures thus obtained are agitated 15 at the same time on a magnetic stirrer of type Variomag (Electronic rührer Multipoint HP15) at a temperature of 25°C and a speed of 500 rpm during one night to reach equilibrium. At equilibrium each sample is filtered and the residual concentration is determined by ICP/OES.

The device is same as that previously described but the kinetic study is made only on the concentration of 60 ppm and in this case the aliquots were drawn every five minutes into a pipette Pasteur and filtered in order to remove any carbon particles and their concentrations measured by ICP/OES. It is realized that at the end of 40 minutes for all the samples the concentration does not change any more, thus the equilibrium adsorbed concentration is reached.

**Table-1**  
**Characteristics of different activated carbons samples**<sup>12,13</sup>

Adsorbent	Physical aspect	pH	S.S.A by B.E.T (m <sup>2</sup> /g)	Pores volume (cm <sup>3</sup> /g)	Cristallinity given by X-rays studies
M10-60-100	<sup>a</sup> GAC	5.60	0.4312	0.000279	amorphous
M10-24-100	GAC	5.50	5.2605	0.002713	amorphous
MAPZC3	GAC	5.96	7.1314	0.002196	amorphous
MAPZC5	GAC	4.40	701.6853	0.393830	amorphous
OA00	<sup>b</sup> PAC	9.34	81.8638	0.176634	Cristallizes: hydroxyl-apatite, quartz, feldspar
Adsorbent	SEM results:surface aspect		EXD results		FTIR results : surface functional groups
M10-60-100	Heterogeneous with macropores		C(80%);O(7%);Si(2%);Cl(6%); K(1%);Zn(2%)		-OH,-CH <sub>2</sub> ,-CH <sub>3</sub> ,-CO, CHO, -C <sub>6</sub> H <sub>5</sub> ,-CH-
M10-24-100	Heterogeneous with macropores		C(80%);O(9%);Si(2%);Cl(6%); K(1%);Zn(2%)		OH,-CH <sub>2</sub> ,-CH <sub>3</sub> ,-CO, CHO, -C <sub>6</sub> H <sub>5</sub> ,-CH-
MAPZC3	Heterogeneous with macropores and mesopores		C(80%);O(11%);Cl(3%);Zn(2%)		-OH,-CH <sub>2</sub> ,-CH <sub>3</sub> ,-CO, CHO, -C <sub>6</sub> H <sub>5</sub> ,-CH-
MAPZC5	Homogeneous and compact with few micropores		C(80%);O(16%);Si(1%);Al(1%); Fe(1%);S(2%)		-OH,-CH <sub>2</sub> ,-CH <sub>3</sub> ,-CO, CHO, -C <sub>6</sub> H <sub>5</sub> ,-CH-
OA00	Homogeneous with some micropores		C(10%);O(40%);Ca(29%);P(15%) Na(1%);Mg(1%)		-OH,-CH <sub>2</sub> ,-CH <sub>3</sub> ,-NH -C≡C-, -CO,-CH-

After adsorption on the various studied adsorbents, the different filtrates were diluted by a nitric acid solution HNO<sub>3</sub> 1M. The analysis of the lead samples was carried out by using a Thermo iCAP 6500 inductively coupled plasma-Optical Spectrometry Emission (ICP/OES).

0.05g of activated carbon was mixed in 50 mL of distilled water under a temperature of 25°C to determine the pH of the solution containing the activated carbon before and after adsorption of lead (II). After agitation, the pH of each sample was measured with a pH-meter of the type METTLER TOLEDO MP220.

## Results and Discussion

Taking into account the low content of Pb<sup>2+</sup> ions in the waters of Cameroon, a particular accent is carried to concentration 60 ppm (which was retained besides to make the kinetic studies in the continuation) for which the percentages of adsorption and the K<sub>d</sub>-values are presented in table-2.

The K<sub>d</sub>-value is a factor related to the concentration of a contaminant (in this study lead) between the solid (activated carbon) and the aqueous solution. It's the ratio of the quantity of the sorbate adsorbed per mass of adsorbent to the amount of sorbate remaining in solution (see equation below).

$$K_d = \frac{\text{Mass of adsorbates sorbed}}{\text{Mass of adsorbates in solution}}$$

The adsorption percentage is the relationship between the quantity of adsorbed species and the initial quantity.

°Adsorption percentage: values obtained using initial amount before and after adsorption ; <sup>d</sup>K<sub>d</sub>-values : values obtained using the equation above; M10-60-100: Maize cobs activated carbon (light part) obtained with 10% ZnCl<sub>2</sub> solution and time residence=60 minutes; M10-24-100: Maize cobs (light part) activated carbon obtained with 10% ZnCl<sub>2</sub> solution and time residence=24 hours; MAPZC3: Maize cobs (light part) activated carbon obtained with 2g of solid ZnCl<sub>2</sub>; MAPZC5: Maize cobs activated carbon (hard part) obtained with 1g of solid ZnCl<sub>2</sub>; OA00: Animal origin activated carbon produced by PROLABO, Rhône Poulenc.

K<sub>d</sub>-values and the percentages of adsorption permit to deduce that the activated carbon of maize cobs obtained are good

adsorbents. Knowing that certain activated carbon of maize cobs such as MAPZC3 and MAPZC5 with respective percentages of adsorption of 35.55% and 32.97% to 60 ppm adsorb lead considerably. But commercial sample OA00 with a value of k<sub>d</sub>=97.73 cm<sup>3</sup>/g and a percentage of adsorption of about 98.99% to 60 ppm is by far the best adsorbent of lead at this concentration. Knowing that k<sub>d</sub>-value is a measure of how readily one specie is sorbed on the surface of solid, the commercial activated carbon is by far the sample in which lead is the most readily sorbed on the surface and the sample M10-60-100 with k<sub>d</sub>-value of about 0.026 cm<sup>3</sup>/g is the less one (table-2).

Some authors<sup>14</sup> recommend a lead k<sub>d</sub>-value of 10cm<sup>3</sup>/mg for agricultural and surface soils for use in Handford site Farm (USA). These values are higher than those of maize cobs activated (0.026-0.545 cm<sup>3</sup>/mg). This is due to the fact that in soil lead is more readily sorbed than in activated carbon particularly in agricultural waste activated carbons. Other authors<sup>15</sup> showed that in soil containing minerals like monmorillonite, illite and kaolinite, lead would preferentially exchange with calcium. The absence of minerals in maize cobs activated carbons explained the low values of k<sub>d</sub>-values obtained for these materials. Past studies<sup>16</sup> showed that lead is preferentially adsorbed by exchange on material readily replacing calcium. This is the case of the material OA00 which contains a large amount of calcium (29%) (see EDX results on Table-1). On the other hand, it is showed that materials containing apatite and its derivatives like hydroxyl-apatite adsorb very strongly lead<sup>17</sup>. These observations explained the large value obtained for lead k<sub>d</sub>-value on material OA00.

With regard to the activated carbon of maize cobs the modes of obtaining the various samples and the various physicochemical properties (Table-1) explain the disparities observed on the level of the percentages of adsorption and K<sub>d</sub>-values. The mineralogical compositions of commercial sample OA00 as seen previously explain the strong affinity of this material to adsorb lead.

As observed in Table-2, there exists a correlation between the percentage of adsorption and k<sub>d</sub>-values. Indeed more the percentages of adsorption are high more the k<sub>d</sub>-value are large that's more the activated carbon adsorbs lead (II) more this one is more readily sorbed on the surface of the activated carbon.

**Table-2**  
**K<sub>d</sub>-values measurements and adsorption percentage of lead Pb (II) on activated carbon at 60ppm**

Adsorbent	M10-60-100	M10-24-100	MAPZC3	MAPZC4	MAPZC5	OA00
Initial concentration	60ppm					
Adsorption percentage <sup>c</sup>	2.68%	12.49%	35.55%	1.11%	32.97%	98.99%
K <sub>d</sub> -value (cm <sup>3</sup> /mg) <sup>d</sup>	0.02632	0.13414	0.54501	0.01076	0.44815	97.72660

The table-3 below represents the capacities or the percentages of adsorption of the activated carbon obtained starting from lignocellulosic materials in particular of agricultural wastes with respect to the Pb<sup>2+</sup> ions. Although higher work presented shows than a commercial activated carbon OA00 which is animal origin adsorbs much more lead than all the activated carbon of maize cobs, it appears that these maize cobs activated carbons (see Table-3 below) adsorb Pb<sup>2+</sup> ions as much as all the other activated carbon of agricultural waste or vegetal origin indexed in the literature<sup>2</sup>.

The analysis and design of sorption separation process require the relevant equilibrium sorption, which is the most important piece of information in understanding the sorption process<sup>2</sup>. Figure-1 represents the isotherms of adsorption of lead Pb (II) on the activated carbon of maize cobs and on the commercial activated carbon sample of animal origin OA00. For all the samples, the amount of lead adsorbed increased exponentially with the increased of initial concentration of lead (II) that's more the concentration of activated carbon are great more the activated sites on the surface of activated carbon are available. But at higher equilibrium concentrations, the saturation of the

adsorption sites is observed, thus because of the fact that most Pb<sup>2+</sup> ions contact with binding sites, the equilibrium concentration of the adsorption becomes independent of Pb<sup>2+</sup> concentration. Same results are obtained by several authors on activated carbon of agricultural wastes. It was shown that the amount of Pb<sup>2+</sup> ions removed in aqueous solution by activated carbon developed from coffee residue activated with zinc chloride increased when initial concentration increased<sup>2</sup>. Similar observations were made with activated carbon obtained from coconut shell and seed shell of palm tree<sup>9</sup>, with activated carbon from pecan-shell<sup>8</sup>, with apricot and peach stone activated carbon<sup>10</sup> and with cashew nuts shell activated carbon<sup>11</sup>.

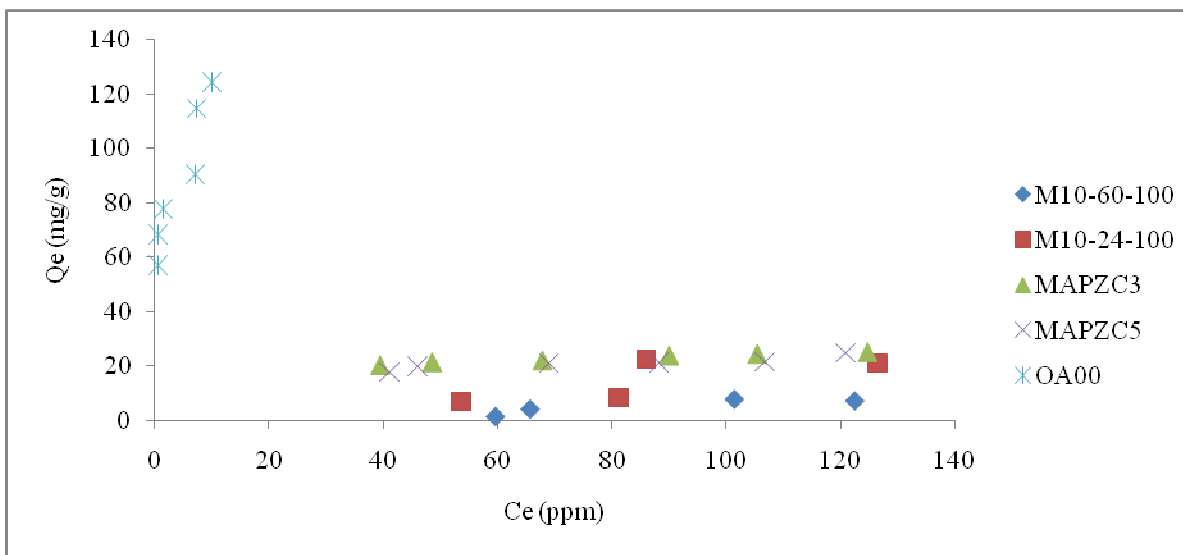
In order to determine the adsorption parameters of lead II on studied activated carbons, Freundlich and Langmuir isotherms have been studied. The various constants characteristic of adsorption for each model and each sample were obtained by using MS Excel of Windows. All the constants are found in Table-4. The different parameters of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinity of sorbent<sup>2</sup>.

**Table-3**  
**Adsorption capacities of lead II ions on lignocellulosic activated carbon in the literature**

Adsorbent	Pb <sup>2+</sup> ions concentrations	Adsorption percentage (%) or adsorption capacities (mg/g)	Authors
Pecan shell-base AC	0.5mM(0.2g of AC/100 mL of solution)	50%	Bansode et al. (2003) <sup>8</sup>
Coconut shell activated carbon	300ppm	58.75%	Gueu et al. (2006) <sup>9</sup>
Seed shell of palm tree activated carbon	300ppm	50.67%	Gueu et al. (2006) <sup>9</sup>
Apricot stone	25ppm (1g of Ac/100 mL of solution)	86%	Nageeb (2009) <sup>10</sup>
Peach stone	25ppm (1g of Ac/100 mL of solution)	73.7%	Nageeb (2009) <sup>10</sup>
Coconut shell activated carbon	50mg/L	26.5mg/g	Machida et al. (2005) <sup>18</sup>
Cashew nuts shell activated carbon	40mg/L	28.90mg/g	Tangjuank et al. (2009) <sup>11</sup>
Maize cobs activated carbon	60ppm	2.68-35.55%/27.7mg/g	This study
Coffee residue AC	10-9mg/L	9.65-62.57mg/g	Boudrahem et al. (2009) <sup>2</sup>

**Table-4**  
**Adsorption constants of Pb (II) on the activated carbon**

Adsorbent	Freundlich <sup>e</sup>				Langmuir <sup>f</sup>			
	b <sub>F</sub>	n	a <sub>F</sub> ((mg/g). (mg/L) <sup>-1/n</sup> )	R <sup>2</sup>	K <sub>L</sub> (L/g)	A <sub>L</sub> (L/mg)	Q <sub>L</sub> (mg/g)	R <sup>2</sup>
M10-60-100	1.8719	0.534	0.0011	0.744	0.0212	0.0065	-3.2478	0.660
M10-24-100	1.3832	0.723	0.0229	0.625	0.1054	0.0023	-32.0513	0.698
MAPZC3	0.1822	5.448	10.4395	0.984	1.8918	0.0683	27.7008	0.966
MAPZC5	0.2199	4.544	8.1076	0.809	1.4043	0.0527	26.6700	0.830
OA00	0.2194	4.558	69.3246	0.881	21.7391	0.1935	112.3596	0.856



$C_e$  and  $Q_e$  are respectively concentration in liquid phase and adsorbed amount of lead (II) at equilibrium; M10-60-100: Maize cobs activated carbon (light part) obtained with 10%  $ZnCl_2$  solution and time residence=60minutes; M10-24-100: Maize cobs (light part) activated carbon obtained with 10%  $ZnCl_2$  solution and time residence=24 hours; MAPZC3: Maize cobs (light part) activated carbon obtained with 2g of solid  $ZnCl_2$ ; MAPZC5: Maize cobs activated carbon (hard part) obtained with 1g of solid  $ZnCl_2$ ; OA00: Animal origin activated carbon produced by PROLABO, Rhône Poulenc

Figure-1

**Adsorption isotherm of lead II on activated carbon of maize cobs and on commercial activated carbon**

$b_F$ ,  $n$  and  $a_F$  were obtained from the linear form of the Freundlich isotherm equation using data from Fig. 1;  $K_L$ ,  $A_L$ ,  $Q_L$  were obtained from the linear form of the Langmuir isotherm equation using data from Fig. 1;  $r^2$  values are the correlation coefficients of the two linear relationships; M10-60-100: Maize cobs activated carbon (light part) obtained with 10%  $ZnCl_2$  solution and time residence=60minutes; M10-24-100: Maize cobs (light part) activated carbon obtained with 10%  $ZnCl_2$  solution and time residence=24 hours; MAPZC3: Maize cobs (light part) activated carbon obtained with 2g of solid  $ZnCl_2$ ; MAPZC5: Maize cobs activated carbon (hard part) obtained with 1g of solid  $ZnCl_2$ ; OA00: Animal origin activated carbon produced by PROLABO, Rhône Poulenc.

As a whole one realizes that the two studied isotherms explain with difficulty the adsorption of the  $Pb^{2+}$  ions on various coals taking into account the values of the determination coefficients of  $R^2$  which all are very weak and lower than 0.96 except for the sample MAPZC3 with values of  $R^2$  equal to 0.984 and 0.966 for the isotherms Freundlich and Langmuir respectively. The applicability of Langmuir isotherm to the adsorption process is due to the fact that after the formation of monoionic layer of metal ions on the surface of adsorbent at lower concentrations, any further formation of layer metal ions is highly hindered at higher concentration due to the interaction between the metal ions on the surface of the adsorbent and in the bulk of solution<sup>19</sup>.

But beyond all these consideration it is important to confirm the strong affinity of the  $Pb^{2+}$  ions to being adsorbed by commercial activated carbon OA00 as observed with higher  $K_d$ -value and adsorption percentage. Indeed more the constant of Langmuir  $K_L$  is large; more the affinity is strong between lead and the activated carbon. Thus sample OA00 with a value of  $K_L=1.4043$  L/g is the material which with greatest affinity for the  $Pb^{2+}$  ions followed by samples MAPZC3 and MAPZC5 which with values of  $K_L$  respectively of  $K_L$  equal to 1.8918 L/g and 1.4043 L/g have also a strong affinity to adsorb the  $Pb^{2+}$  ions. It is not the case for the samples M10-60-100 and M10-24-100 where the values of  $K_L$  are very low (0.0212L/g and 0.1054L/g respectively). This same order is followed by the  $K_d$ -values and the capacities of adsorption at 60 ppm (see Table 2). The values of  $K_L$  obtained during the adsorption of  $Pb^{2+}$  ions on coffee residue activated carbon<sup>2</sup> vary in the range 0.1624-0.3966 L/g. These values are smaller than those obtained in this work (0.0212-1.8918 L/g) which means that  $Pb^{2+}$  ions have more affinity on maize cobs activated carbon than those obtained with coffee residue activated carbon<sup>2</sup>.

In addition the exponents of the Freundlich isotherm  $n=1/b_F$  for the samples M10-60-100 and M10-24-100 have as respective values 0.534 and 0.723 what explains well adsorbent properties of these materials which in the final analysis are not good adsorbents with respect to  $Pb^{2+}$  ions. This is not the case of materials MAPZC3, MAPZC5 and OA00 which have all of the values of  $n$  ranging between 1 and 10 (see Table-4) confirming

the fact that the adsorption of the  $Pb^{2+}$  ions is favorable for these materials. Indeed adsorption according to the isotherm of Freundlich is favorable if the values of  $n$  lie between 1 and  $10^{2.20}$ . There is a relation between the values of  $a_F$  the Freundlich partition constant (Table-4) and the adsorption capacities (Table-2). More values of  $a_F$  are large more the adsorption capacities are high and therefore more the strength connecting the  $Pb^{2+}$  ions on the surface of activated carbons is high. Thus the commercial activated carbon sample OA00 with a value of  $a_F$  around  $69.32 (mg/g).(mg/L)^{-1/n}$  is that on which  $Pb^{2+}$  ions are strongly linked while the sample M10-60-100 with a value of  $a_F$  around  $0.001(mg/g).(mg/L)^{-1/n}$  is the one with the least ability to adsorb  $Pb^{2+}$  ions. This result is similar to that observed in the Langmuir isotherm. Some authors obtained similar results and showed in the study of the adsorption of geosmin onto activated carbon from pecan shell<sup>21</sup> that higher  $a_F$  value are characteristic of greater binding forces of geosmin in these activated carbons.

The pH of the various solutions containing materials studied before adsorption and after adsorption of the  $Pb^{2+}$  ions are consigned in Table-5.

**Table-5**  
**pH of the activated carbon and clays studied**

Adsorbents	Concentration (ppm)	pH measured <sup>g</sup>
M10-10-100	0	5.60
	70	4.28
	90	4.30
	110	4.73
	130	4.96
M10-24-100	0	5.50
	70	4.36
	90	4.57
	110	4.41
	130	4.50
MAPZC3	0	5.96
	70	4.80
	90	5.44
	110	4.97
	130	4.80
MAPZC5	0	4.40
	70	3.65
	90	3.65
	110	3.57
	130	3.55
OA000	0	9.34
	70	6.99
	90	7.13
	110	7.09
	130	6.88

<sup>g</sup>pH obtained before adsorption (0 ppm) and after adsorption ; M10-60-100: Maize cobs activated carbon (light part) obtained

with 10% ZnCl<sub>2</sub> solution and time residence=60minutes; M10-24-100: Maize cobs (light part) activated carbon obtained with 10% ZnCl<sub>2</sub> solution and time residence=24 hours; MAPZC3: Maize cobs (light part) activated carbon obtained with 2g of solid ZnCl<sub>2</sub>; MAPZC5: Maize cobs activated carbon (hard part) obtained with 1g of solid ZnCl<sub>2</sub>; OA00: Animal origin activated carbon produced by PROLABO, Rhône Poulenc.

In general way, the pH does not vary much when the concentration increases for the same sample. This result is not the same as that obtained in the study of the solubility of lead, zinc and copper added to mineral soils<sup>22</sup> where it is observed that the pH in the aqueous phase decreases when the concentration increases. This could be explained by the fact that the various studied concentrations are very close and in addition the study mentioned above<sup>22</sup> has been made in the ground, the aqueous phase contains several metals what is not the case for materials studied in this work where lead is the only metal in the medium.

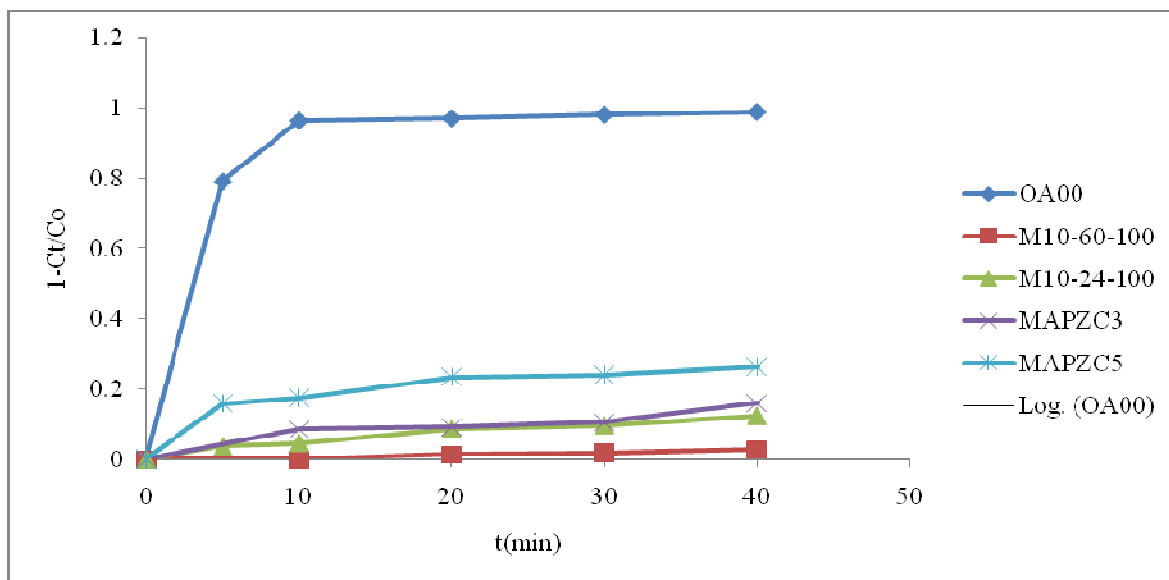
In addition, the study of lead adsorption onto apricot stone and peach stone<sup>10</sup> showed that the lead (II) amount adsorbed increased as pH increase from 6-6.5 and the maximum adsorption of this metal is observed at pH<7. After pH7 the adsorption of this metal decreased. The same result was obtained in the adsorption of lead on montmorillonite clay<sup>23</sup>. Moreover, some authors showed that the adsorption of heavy metal (Pb, Cu, Cd, Zn, Ni) on the biomass of phormidium sp<sup>24</sup> was suitable at pH 5. Particularly for lead the maximum adsorption was 13.600 mg/kg. In the same way, other authors showed that the optimum pH for removal of Cd, Cu and Mo using carbonaceous material developed from the waste slurry generated from fertilizer plant<sup>25</sup> was about pH6, for Cr and Hg was at pH2 while for Pb it was almost in the range 6-7.

All these examples show that the activated carbon of maize cobs with pHs≤7 (Table-5), create in aqueous medium an environment very favorable to the adsorption of the  $Pb^{2+}$  ions.

The pH is an important factor but not sufficient for a maximum adsorption of lead (II). In effect the texture of materials (porosity and surface appearance), the physical and chemical properties as described above also have a great influence on the adsorption. The adsorption parameters such as initial concentrations as explained above and especially the contact time also play an important role.

To establish an appropriate contact time effect between activated carbon and the  $Pb(II)$  ions solution, sorption capacities of metal ions are measured as a function of time at 60 ppm. The removal of lead II was shown to increase with time and attained a maximum value at 40 minutes for many samples and thereafter it remained constant. For samples MAPZC3 and MAPZC5 equilibrium is reached well after 40 minutes. Figure-2 represents the effect of contact time in the adsorption of  $Pb(II)$  on the activated carbon samples.





$C_0$  and  $C_t$  are respectively initial and time  $t$  (in minutes) concentration of lead (II); M10-60-100: Maize cobs activated carbon (light part) obtained with 10%  $ZnCl_2$  solution and time residence=60minutes; M10-24-100: Maize cobs (light part) activated carbon obtained with 10%  $ZnCl_2$  solution and time residence=24 hours; MAPZC3: Maize cobs (light part) activated carbon obtained with 2g of solid  $ZnCl_2$ ; MAPZC5: Maize cobs activated carbon (hard part) obtained with 1g of solid  $ZnCl_2$ ; OA00: Animal origin activated carbon produced by PROLABO, Rhône Poulenc.

Figure-2

Time variation of Pb(II) adsorption on activated carbon. (Conditions:  $C_0=60ppm$ , rate=500rpm and  $T=25^\circ C$ )

Contact time required for the maximum removal of lead (II) by activated carbon sample (Figure-2). There is step increase in the adsorption in the initial stages of the reaction as seen in the curves (Figure- 2). The time variation curve is smooth and continuous for all the samples and this indicates the formation of monolayer coverage on the outer interface of the adsorbent.

These results reveal that the uptake of sorbate species is fast at the initial stage of the contact period for all adsorbents and thereafter it becomes slower near equilibrium (Figure-2). Between these two stages of the uptake, the rate of sorption is found to be nearly constant. This is obvious by the fact that a large number of vacant sites are available for sorption during the initial stage, and after a lapse of time the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute ions on the solid and the bulk phase. Similar results were obtained with lead on the activated carbon of agricultural wastes<sup>2</sup> with times relatively shorter (equilibrium time of 15 minutes) and on commercial activated carbon<sup>26</sup> (equilibrium time of 60 minutes). In the adsorption of lead (II) on cashew nut shells activated carbon<sup>11</sup>, it was found that equilibrium times being in the range 20-150 minutes. The equilibrium times even longer (more than 1 hour) have been obtained in the removal of Pb(II) from aqueous solution using carbon derived from agricultural wastes<sup>27</sup>.

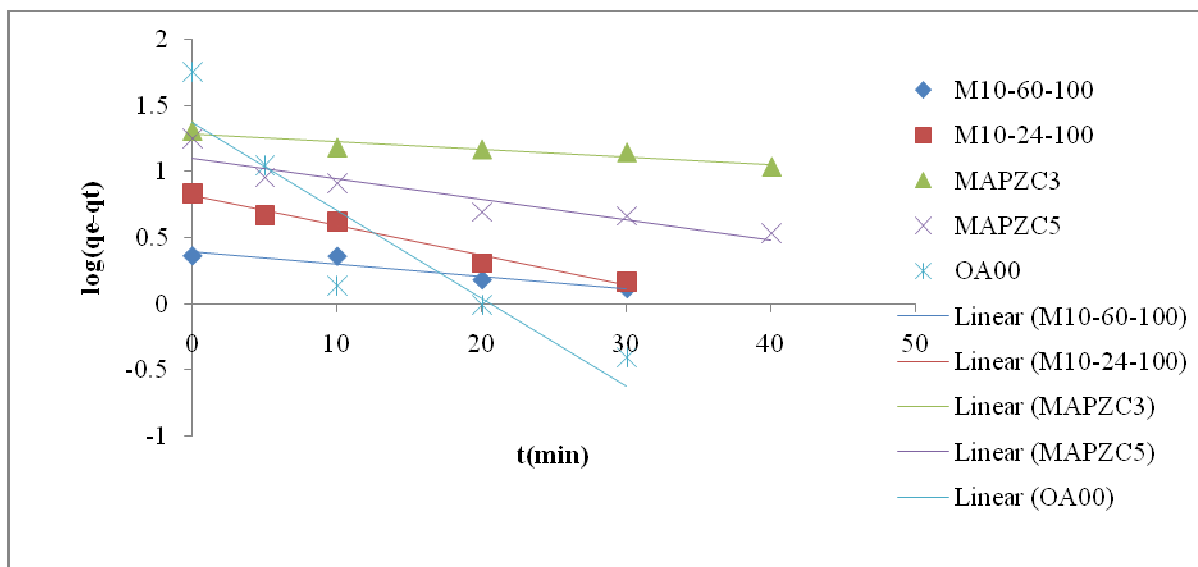
On figure-2, the adsorption of the  $Pb^{2+}$  ions on the M10-60-100 sample is practically constant and the adsorbed quantities are very weak. This is explained by the adsorbent properties observed during the characterization of this material (absence of

minerals, composed not very porous, weak specific surface and very small quantities of surface functions) (see Table-1). Samples MAPZC3 and MAPZC5 because of the small porosity observed, rather important surface functions observed by FTIR results (Table-1) adsorb best the  $Pb^{2+}$  ions than the first two samples.

Commercial material OA00 is by far the best adsorbing observed (see the curve above on Figure-2). The textural and physicochemical properties of this material explain this strong affinity with respect to the  $Pb^{2+}$  ions. Indeed the microporosity detected on this sample, the presence of minerals such as the hydroxyapatite. Indeed two main mechanisms can be observed between hydroxylapatite in sample OA00 and  $Pb^{2+}$  ions: ion exchange between  $Pb^{2+}$  and  $Ca^{2+}$  at the hydroxyapatite lattice<sup>28</sup>, and hydroxyapatite dissolution followed by lead phosphate precipitation<sup>1,17,30,31</sup>.

The study of the effect of the contact time between activated carbon and Pb(II) solution as a function of time above confirms the results obtained by the  $K_d$ -values and the adsorption percentage.

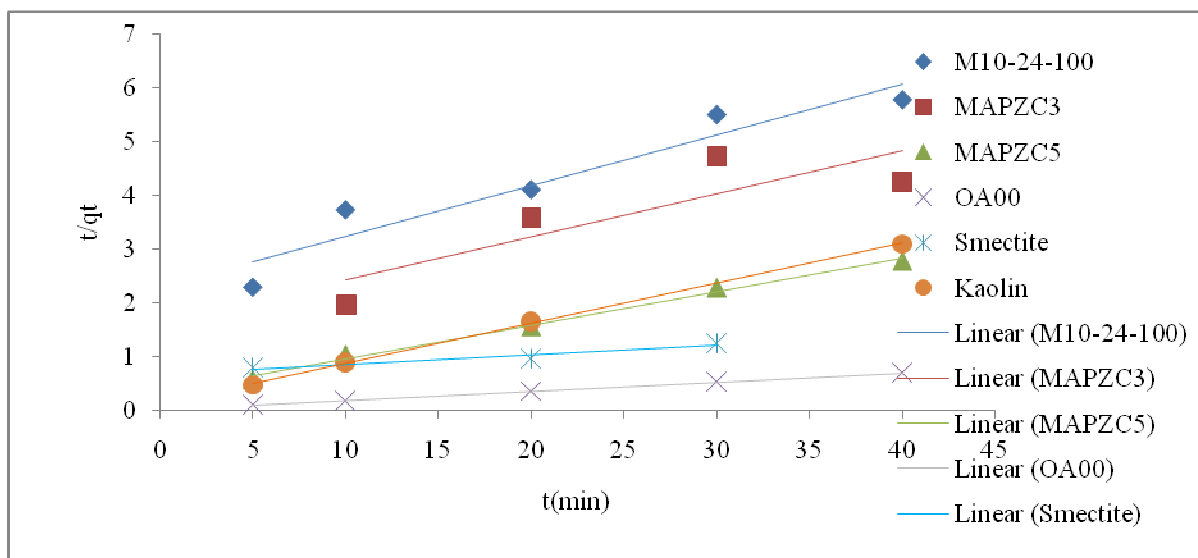
In order to study the kinetic model of lead II adsorption at 60 ppm by maize cobs activated carbon, pseudo-first order or Lagergren model, pseudo-second order model, Elovich model and Weber and Morris intra-particle diffusion model were tested. The obtained statistics parameters based on linear regression (figures-3 to 6 for each kinetic model) for all the four models are given in table-6.



$q_e$  and  $q_t$  are respectively amount of lead adsorbed at equilibrium and at time  $t$ (in minutes). ; M10-60-100: Maize cobs activated carbon (light part) obtained with 10%  $ZnCl_2$  solution and time residence=60minutes; M10-24-100: Maize cobs (light part) activated carbon obtained with 10%  $ZnCl_2$  solution and time residence=24 hours; MAPZC3: Maize cobs (light part) activated carbon obtained with 2g of solid  $ZnCl_2$ ; MAPZC5: Maize cobs activated carbon (hard part) obtained with 1g of solid  $ZnCl_2$ ; OA00: Animal origin activated carbon produced by PROLABO, Rhône Poulenc.

Figure-3

Lagergren plots from the removal of  $Pb^{2+}$  ions by adsorption on activated carbon from maize cobs and on commercial sample

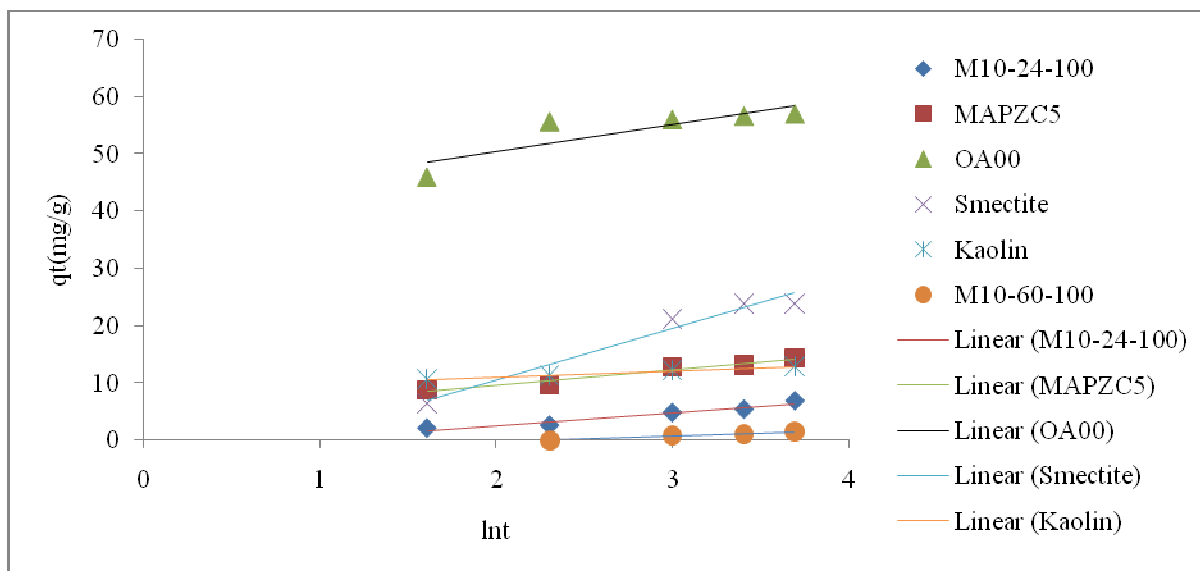


$q_t$  is amount of lead (II) adsorbed at time  $t$  (in minutes); ; M10-60-100: Maize cobs activated carbon (light part) obtained with 10%  $ZnCl_2$  solution and time residence=60minutes; M10-24-100: Maize cobs (light part) activated carbon obtained with 10%  $ZnCl_2$  solution and time residence=24 hours; MAPZC3: Maize cobs (light part) activated carbon obtained with 2g of solid  $ZnCl_2$ ; MAPZC5: Maize cobs activated carbon (hard part) obtained with 1g of solid  $ZnCl_2$ ; OA00: Animal origin activated carbon produced by PROLABO, Rhône Poulenc

Figure-4

Pseudo-second order plots from the removal of  $Pb^{2+}$  ions by adsorption on maize cobs activated carbon and on commercial activated carbon OA00

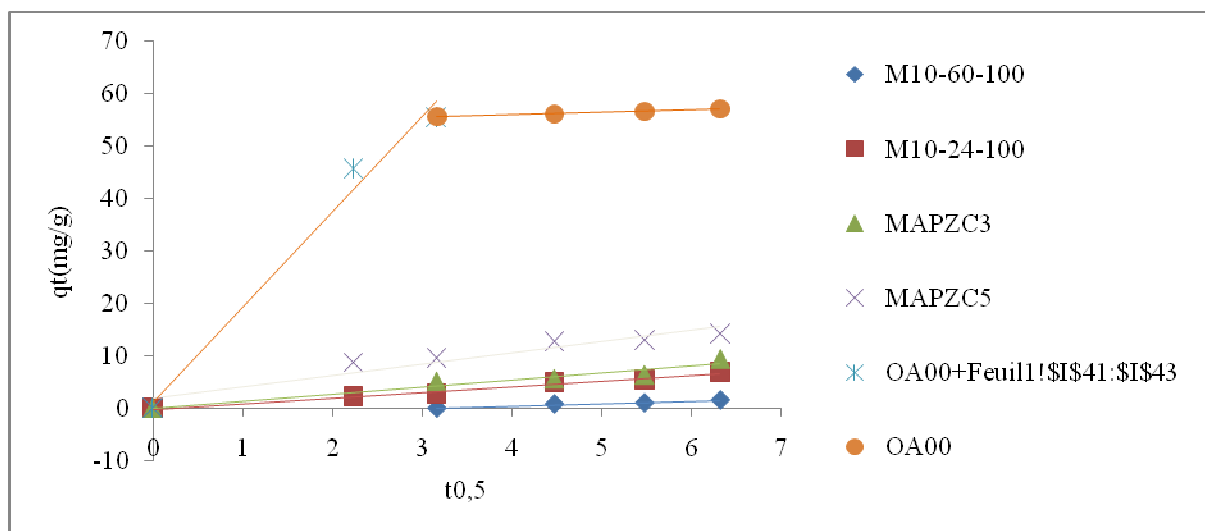




$q_t$  is amount of lead (II) adsorbed at time  $t$  (in minutes); ; M10-60-100: Maize cobs activated carbon (light part) obtained with 10% ZnCl<sub>2</sub> solution and time residence=60 minutes; M10-24-100: Maize cobs (light part) activated carbon obtained with 10% ZnCl<sub>2</sub> solution and time residence=24 hours; MAPZC3: Maize cobs (light part) activated carbon obtained with 2g of solid ZnCl<sub>2</sub>; MAPZC5: Maize cobs activated carbon (hard part) obtained with 1g of solid ZnCl<sub>2</sub>; OA00: Animal origin activated carbon produced by PROLABO, Rhône Poulenc.

Figure-5

Elovich plots from the removal of the removal of Pb<sup>2+</sup> ions on maize cobs activated carbon and on commercial activated carbon OA00



$q_t$  is amount of lead (II) adsorbed at time  $t$  (in minutes); ; M10-60-100: Maize cobs activated carbon (light part) obtained with 10% ZnCl<sub>2</sub> solution and time residence=60 minutes; M10-24-100: Maize cobs (light part) activated carbon obtained with 10% ZnCl<sub>2</sub> solution and time residence=24 hours; MAPZC3: Maize cobs (light part) activated carbon obtained with 2g of solid ZnCl<sub>2</sub>; MAPZC5: Maize cobs activated carbon (hard part) obtained with 1g of solid ZnCl<sub>2</sub>; OA00: Animal origin activated carbon produced by PROLABO, Rhône Poulenc

Figure-6

Weber and Morris intra-particle diffusion plots from the removal of Pb<sup>2+</sup> ions on maize cobs activated carbon and on a commercial activated carbon OA00

**Table-6**  
**Adsorption kinetic model rate constants for the activated carbon from maize cobs and for the commercial activated carbon OA00**

Adsorbent	Kinetic Models								
	Pseudo-first order <sup>h</sup>				Pseudo-second order <sup>i</sup>				
	q <sub>e,exp</sub> (mg/g)	q <sub>e,calc</sub> (mg/g)	K <sub>1</sub> (min <sup>-1</sup> )	R <sup>2</sup>	q <sub>e,exp</sub> (mg/g)	q <sub>e,calc</sub> (mg/g)	K <sub>2</sub> (g/mg.min)	h(mg/g.min)	R <sup>2</sup>
<b>M10-60-100</b>	1,5685	2,4940	0,0216	0,862	/	/	/	/	/
<b>M10-24-100</b>	6,9185	6,5978	0,0523	0,979	6,9185	10,5485	0,0039	0,4367	0,913
<b>MAPZC3</b>	20,3184	19,2132	0,0134	0,893	20,3184	12,4378	0,0040	0,6182	0,734
<b>MAPZC5</b>	17,7328	12,7556	0,0362	0,874	17,7328	15,8983	0,0121	3,0525	0,994
<b>OA00</b>	57,0865	23,4855	0,0665	0,831	57,0865	58,4795	0,0178	60,9756	0,999
Adsorbent	Kinetic Models								
	Elovichmodel <sup>k</sup>			Weber and Morris intra-particlediffusion <sup>l</sup>					
	α(mg/g.min)	β(g/mg)	R <sup>2</sup>	K <sub>id1</sub> (mg.g <sup>-1</sup> .min <sup>-0,5</sup> )	K <sub>id2</sub> (mg.g <sup>-1</sup> .min <sup>-0,5</sup> )	C <sub>1</sub>	C <sub>2</sub>	R <sup>2</sup>	
<b>M10-60-100</b>	0,1072	0,9469	0,973	/	0,4663	/	- 1,4108	0,972	
<b>M10-24-100</b>	5,2400	0,4428	0,940	/	1,0816	/	- 0,2218	0,983	
<b>MAPZC3</b>	/	/	/	/	1,3330	/	0,1112	0,940	
<b>MAPZC5</b>	11,8764	0,3659	0,955	/	2,1690	/	1,9582	0,912	
<b>OA00</b>	7363,2637	0,2104	0,722	18,5500	0,4432	54,2430	1,1997	0,985/0,979	

<sup>h,i</sup>q<sub>e,exp</sub> and q<sub>e,calc</sub> are respectively experimental and calculated amount of lead adsorbed at equilibrium, values of q<sub>e,calc</sub> are obtained from the linear form of the Lagergren and pseudo-second order equation using data from fig. 3 and 4; <sup>h,i</sup>K<sub>1</sub> and K<sub>2</sub> are respectively pseudo-first and pseudo second order constant obtained from the linear form of the Lagergren and pseudo-second order equation using data from fig. 3 and 4; <sup>k</sup>α and β are respectively Elovich speed constant and Elovich desorption constant obtained using linear form of the elovich equation using data from fig. 5; <sup>l</sup>K<sub>id1</sub> and k<sub>id2</sub> are intraparticle diffusion constants obtained from the Weber and Morris equation by using data from fig. 6; <sup>l</sup>C<sub>1</sub> and C<sub>2</sub> are Weber and Morris constants obtained from the Weber and Morris equation by using data from fig. 6 ; R<sup>2</sup> are correlation coefficients from the linear relationships.

The linearity of the plots is not evident for all the samples and for all the models. The pseudo-second order kinetic model cannot be applied to the adsorption of the Pb<sup>2+</sup> ions in the field of the concentrations considered to the sample M10-60-100. For the same sample the determination coefficient R<sup>2</sup> for Lagergren model is very low (R<sup>2</sup>=0.862), this value implies that this model also is not adequate to describe the adsorption of Pb<sup>2+</sup> ions on the sample M10-60-100. The insufficiency of the first-order model to fit the kinetic data could possibly be due to a boundary layer controlling the beginning of the sorption process<sup>32</sup>. On the other hand the Elovich and the Weber and Morris intra-particle diffusion models with respective determination coefficients of 0.973 and 0.972 describe this adsorption well. The Lagergren

kinetic model and the Weber and Morris intra-particle diffusion model with respective determination coefficients of 0.979 and 0.983 are those which describe best the adsorption of the Pb<sup>2+</sup> ions on the material M10-24-100 whereas the pseudo second order (R<sup>2</sup>=0,994) and the Elovich model (R<sup>2</sup>=0,955) are those which describe best the adsorption of the same ions on sample MAPZC5. The applicability of the pseudo-first order in the material M10-24-100 is confirmed by the fact that the calculated value of adsorbed quantities 6.9185 mg/g agrees well with the experimental one 6.5978 mg/g. As for sample MAPZC3, the Weber and Morris intra-particle diffusion model only described rather well the adsorption of the Pb<sup>2+</sup> ions on this material (R<sup>2</sup>=0.940). The adsorption of the Pb<sup>2+</sup> ions is suitably described by the kinetic model of pseudo-second order in commercial sample OA00 where the correlation coefficient is close to 1 (R<sup>2</sup>=0.999) but also by the Weber and Morris intra-particle diffusion model for whom two correlation coefficients corresponding at the two stages of the adsorption on this material (R<sup>2</sup>=0,985 and R<sup>2</sup>=0,979) are observed. In addition the very close values to the experimental and theoretical quantities adsorbed in the pseudo-second order kinetic model confirms the applicability of this model in the adsorption of the Pb<sup>2+</sup> ions on commercial sample OA00. Two kinetics equations models (Lagergren and pseudo-second order) were used to describe Pb(II) sorption onto activated carbon from pecan-shell<sup>2</sup> and it was appeared that the sorption data followed the pseudo-second order model.

The adsorption mechanism of a sorbate onto activated carbon

follows three steps: film diffusion, pore diffusion and intra-particle diffusion. The slowest of three steps controls the overall rate of the process. In a batch reactor pore diffusion and intra-particle diffusion are often the rate limiting step<sup>33</sup>.

The intra-particle diffusion seems to be the limiting stage in the adsorption of lead (II) on the activated carbon of maize cobs. Indeed the study of the Weber and Morris intra-particle diffusion model of the adsorption of the Pb<sup>2+</sup> ions on the activated carbon of maize cobs shows that in all the cases the first two stages (film diffusion and pore diffusion) are very fast to observe (Figure-6). This is explained by the very great number of macropores present in these samples. The intra-particle diffusion with relatively low speeds ( $K_{id}$  values vary between 0.4663mg/g.min<sup>0.5</sup> for the M10-60-100 sample and 2.1690mg/g.min<sup>0.5</sup> for the sample MAPZC5) seems to be the limiting stage which controls the process of adsorption. The adsorption of the ions pb<sup>2+</sup> in commercial sample OA00 is carried out in two stages (see Figure-6). Contrary to the activated carbon of maize cobs, one could represent the first stage characteristic of the transfer of mass in the adsorbent taking place with boundary layer diffusion with a relatively high speed about 18.155mg/g.min<sup>0.5</sup>. But as in the maize cobs activated carbons it is the intraparticle diffusion (second part of the curve) which controls adsorption with a speed about 0.4432mg/min<sup>0.5</sup>. The values of  $K_{id1}$  and  $K_{id2}$  show that the intra-particle diffusion resistance is due to micropores observed in the material OA00.

The values of intercept C (Table-6) give an idea about the boundary layer thickness. The larger is the intercept, the greater is the boundary layer effect<sup>34</sup>. The intercept is maximum for the sample OA00 (54.243) and minimum for the sample M10-60-100 (-2.1887) indicating that the boundary layer is maximum in the material OA00 and minimum in the material M10-60-100. It's also important to note that this effect is relatively important in the sample MAPZC5 (1.9582). These results are in conformity with the adsorbed capacities and once more the physicochemical and textural properties of different activated carbons explained these observations.

For the samples MAPZC5 and OA00 who appear to be the best adsorbents, the determination coefficients  $R^2$  for the intra-particle diffusion model present values of 0.912 and 0.985/0.979 which are lower than that of the pseudo-second order model and that of the Elovich model for the sample MAPZC5 (0.994 and 0.955 respectively) and that of the pseudo-second order for the sample OA00 (0.999). These values do not refute the fact that the adsorption of the Pb<sup>2+</sup> ions on these materials followed the intra-particle diffusion model, but these values state simply that this model is not the only controlling step. Other mechanisms such as complexation or ion exchange play an important role in the process<sup>35</sup>. Similar results were obtained in the studies of the adsorption of methylene blue onto risk<sup>36</sup> and of the V adsorption of red congo by perlite<sup>37</sup>.

Weber and Morris intra-particle diffusion model presents the large enough correlation coefficients for the majority of the activated carbon studied (see Table-6) what leads to conclude that in batch system adsorption, the intra-particle diffusion seems to be the limiting phenomenon in the mechanism of adsorption. The microporosity observed on the surface of the most materials although few explain why the diffusion is expected at the surface<sup>19</sup>.

The applicability of both models showed that adsorption of lead II process is complex and involves more than one mechanism.

## Conclusion

The adsorption of Pb<sup>2+</sup> ions carried out the applicability of the maize cobs activated carbons at being used in the purification of waters. Some of these carbons adsorb Pb<sup>2+</sup> as well as the commercial one. The carbon's properties and environmental parameters played a significant role in this process.

These carbons can mainly be used in the purification of the water in Cameroon where water sources are abundant but needing treatment. The experimental results obtained by this process can be useful in designing the batch experimental set up for removal of lead (II) from water using maize cobs activated carbons.

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