

## Modelling of the kinetics adsorption of gold (I) cyanide complex ion by active carbons prepared from *Parinari macrophylla* shells

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### Abstract

Nowadays, one of the sectors to valorization of waste is their transformation in nobler materials rather than in energy. This study is about the valorization of agricultural waste (*Parinari Macrophylla* shells) for the development of active carbons, the characterization of porous materials gotten and the kinetic study for adsorption of gold (I) cyanide complex ion. The development is made by impregnation in KOH followed of a pyrolysis under flux of N<sub>2</sub> or CO<sub>2</sub>. The characteristics determined for adsorption are iodine index, methylene blue index, pH to point of zero charge (pH<sub>PZC</sub>) as well as the textures characteristics gotten by adsorption of nitrogen at 77 K. For adsorption of gold (I) cyanide complex ion, the kinetics model's pseudo-order 1, pseudo-order 2, the model of Elovich and those diffusions of Boyd and Weber-Morris are studied. The results of the characterization showed that samples are basic (pH<sub>PZC</sub> > 7), present the specific surfaces of 1008 m<sup>2</sup>/g and 1063 m<sup>2</sup>/g with percentages in microporous surface more than 78% and for microporous volume more than 71%. The kinetics of adsorption of gold (I) cyanide complex ion (Au(CN)<sub>2</sub>) obeys more to pseudo-order 2 model and a multi-linearity of the models of Elovich and diffusions during adsorption.

**Keywords:** Biomass; *Parinari macrophylla*; Active carbon; Gold; Adsorption; Kinetic

### 1. Introduction

The materials so-called porous cover a large range of applications because they step in several domains as for example catalysis [1-3], adsorption [4-6], electronics [7, 8] or medicine [9, 10]. They can be naturals or synthetics.

The technology of separation by adsorption constitutes today a technology of choice, in particular among those that are not based on liquid-gas equilibrium [11]. The separation by adsorption is based on a selective adsorption of different constituents gaseous or liquid by adsorbents favour to specifics interactions between surfaces of adsorbents and molecules adsorbed [11]. The knowledge the kinetics of adsorption presents a considerable convenient interest in the setting optimal work of an adsorbent during an industrial operation and in the knowledge of the factors to optimize for manufacture or improve an adsorbent driving to the possible fastest kinetics [12].

The active carbons appear among the adsorbents more used with a yearly production estimated to 1.1 million tons in 2014 [13]. They are used notably for the adsorption of gases and solute [14] because they present a large porosity and

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large specific surface, capable to go elsewhere 2,000 m<sup>2</sup>/g [15]. The porosity, the specific surface and the chemistry of surface can also be modulated by adapted treatments [16]. This material is essentially constituted of carbon and is gotten from all matter rich in carbon as peat, coal, bituminous coal, wood, or other plant matters [17]. It is why, many studies are led on development of activated carbons from agricultural wastes: *Balanites aegyptiaca* shells and *Hyphaene thébaïca* shells [4], pumpkin seed Shell [14], coffee grounds [18], coconut shell [19], waste of olive [20], shea and cotton shells [21]. Niger, like many other sub-Saharan countries, imports active carbon to use it in various domains like hydrometallurgy. In these factories, gold is extracted by the process of liquid-solid adsorption on the active carbon. However, the country has important quantities of type biomass waste, rich in organic matters [4]. Among these available biomasses, one finds the *Parinari macrophylla* shells. She is going to act as raw material used for the preparation of active carbon. These last will be characterized by their property's textures (specific surface, porous volume and mean pore diameters) as well as by the iodine index and methylene blue index. Then, these strong will be used to achieve the adsorption of gold (I) cyanide complex ion. The kinetics of this adsorption will be then modeled since to term, active carbons produced to the departure of these agricultural wastes would have to can be used for the recuperation of gold.

## 2. Material and methods

### 2.1. Development of the active carbons

Samples of active carbon (AC) are elaborated by impregnation to hydroxide of potassium followed of a pyrolysis under N<sub>2</sub> and/or CO<sub>2</sub> in a horizontal furnace (LENTON THERMAL DESIGNS, CSC model 12/600 HS), according to the detailed protocol below.

*Parinari macrophylla* (PM) shells are ground with the help of a grinder. Thanks to a sifting, the fraction of the diameter breaks understood between 2.5 mm and 5 mm separated to be impregnated in KOH 3:1:40 reports (mass of PM in g:masse of KOH in g:volume of water distilled in mL). The mixture is agitated during one hour and biomass impregnated separated of the excess of liquid then dried at the stove (T = 110 °C) during one night. Then, the pyrolysis is realised with three landings according to table 1 with a speed of fire-chamber of 5 °C/mins to reach these landings. Finally, samples are washed with water distilled for use Soxhlet until the value of pH water that was in contact with the active carbon is appreciably equal to 7.

**Table 1** Pyrolysis terms

	Temperature in °C	Duration of landing in minute	Nature of gas, with a debit 80 mL/min	
<b>Landing 1</b>	150	30	N <sub>2</sub>	N <sub>2</sub>
<b>Landing 2</b>	400	60	N <sub>2</sub>	CO <sub>2</sub>
<b>Landing 3</b>	800	120	N <sub>2</sub>	CO <sub>2</sub>
<b>Cooling until the ambient temperature</b>			N <sub>2</sub>	
<b>Name of sample</b>			PM-N <sub>2</sub>	PM-CO <sub>2</sub>

### 2.2. Characterization of active carbons elaborate

#### 2.2.1. Methylene blue index

One of industrial ways of characterization of the capacity of adsorption for active carbons is the determination of index. The methylene blue index is one of them.

A solution of methylene blue (stock solution) is prepared by dissolution of 1.5 g of powder of methylene blue (MB) (well stocked by MERCK) in 100 mL of acetic acid (50%) under agitation during 1 hour and in 60 °C. The mixture is cooled lets then under agitation during one night in order to be filtered thanks to a paper filters Whatman (CAT No. 10311814) and completed in 1 L with the distilled water.

Then, 100 mL of this solution is put in contact with 0.1 g of AC (dried at stove during one night) ground until a granulometry of 45 µm (for 75% in mass, at least) under agitation during 30 minutes, before being filtered on paper filters Whatman (CAT No. 1005-110).

Methylene blue index (IBM in g/100 g) is given by the equation (1) after reading the absorbances of stock solution and filtrate (dilute) to UV-Visible spectrophotometer at 620 nm. The stock solution is diluted 200 times (with distilled water) and the filtrate is also 200 times (with acetic acid 0.25%) before reading. The distilled water is used like white.

$$I_{BM} = \frac{(A_0 - A)}{A_0} * C * V * \frac{0.1}{m} * 1000 \dots \dots \dots (1)$$

Where;

$A_0$ : Absorbance of mother solution, diluted 200 times.

$A$ : Absorbance of sample after adsorption, diluted 200 times.

$C$ : Initial concentration of methylene blue, either 1.2 g/L (because the powder of MB used is to 82% of purity).

$V$ : Volume of methylene blue solution put in contact with sample, either 0.1 L.

$m$ : Mass of sample in g, either 0.1 g.

$\frac{0.1}{m} * 1000$  : Factor of conversion for express the quantity adsorbed for 100 g of solid.

### 2.2.2. Iodine index

The capacity of adsorption to smaller molecules by the active carbon can be appreciated industrially by the determination of iodine index. The determination of this index is done while being based on the ASTM D4607 - 94 norm [22]. This last rests on the adsorption of iodine in a solution in 0.1 N of  $I_2$  during  $30 \pm 1$  seconds after elimination of possible elements (sulfur compounds) capable to interfere with the adsorption of  $I_2$  by 10 mL of hydrochloric acid (5%). The elimination of sulfur compounds it makes itself while carrying to boiling point the suspension of active carbon in 10 mL of hydrochloric acid during  $30 \pm 2$  s. So, after adsorption the residual concentration in iodine is determined by titration to the sodium thiosulfate 0.1 N. While referring to the norm, this method permits to get iodine index some thanks to the necessary thiosulfate volume to title the residual iodine (no adsorbed) and to the mass of sample ( $AC$ ) committed.

### 2.2.3. Determination of pH of point to zero charge ( $pH_{PZC}$ )

Although it is gotten by pyrolysis of biomass to high temperature, the active carbon presents to his surface acids and/or basics functions. The  $pH_{PZC}$  is the pH for which the density of positive charges on the surface of active carbon is equal to the density of negative charges. The knowledge of  $pH_{PZC}$  is important for the adsorption because this last informs us on the net charge of the surface of active carbon when it is in solution, functional to the pH value of solution (superior or inferior to  $pH_{PZC}$  value). Indeed, for values of pH of solution inferior to  $pH_{PZC}$  value, the global charge of the active carbon is positive whereas it becomes negative when pH of solution is superior to  $pH_{PZC}$  [33,34]. It has been determined according to the method described by Regalbuto [23].

### 2.2.4. Textures properties (specific surface, porous volume and middle diameter of pores)

The specific surface and porous properties are very important parameters for a porous material, whatever is his use. That characteristics can be determined by the treatment of the curves of nitrogen adsorption to 77 K. These have been acquired by a device MICROMERITICS Gemini VII Surface Area & Porosity. The treatment by the computer software of the device permit to get the specific surface, the middle pore diameters and the total pore volumes (at  $P/P^\circ \approx 0.99$ ) by BET model, the surface microporous and volume microporous by the t-plot model and the surface mesoporous by the BJH model.

## 2.3. Adsorption of gold (I) cyanide complex ion by active carbon elaborate

The adsorption of  $Au(CN)_2^-$  on the two samples of active carbon elaborated has been achieved to departure by solution of potassium gold (I) cyanide ( $pH = 8$ ) to 7 mg/L of Au (about) and with a powder of active carbon which diameter of the speck is lower in 150  $\mu m$  (after grinding and sifting). Thus, 0.5 g of active carbon is put in contact, under agitation, with 200 mL of solution and sampling are done regularly to knew times between 1 min and 540 min (9 hours). The gold residual concentration is measured by spectrometry of atomic absorption of flame (Perkin Elmer, AAnalyst 400) to 242.80 nm. The *quantity of gold* adsorbed to every time  $t$  is given by the difference between the initial concentration and the residual concentration. The capacity of adsorption ( $q_t$  in mg/g) for active carbon is given by equation (2).

$$q_t = \frac{(c_i - c_t) * V}{m} \dots \dots \dots (2)$$

$C_i$  and  $C_t$  are the concentrations initial and final at a time  $t$  (mg/L),  $V$  the volume of solution (L) and  $m$  the mass of adsorbent (g).

### 2.4. Kinetics models

The kinetic study aims to follow evolution of the concentration of solution according to the time and try to model his evolution. For adsorption, some kinetic models permit to follow and to explain this evolution within the pores of adsorbent but also to the level of the liquid phase. The equation (3) expresses this variation according to the order of reaction. This kinetic study has been started to understand the dynamics of the adsorption reactions in terms of constants of order and speed [24].

$$\frac{dq}{dt} = k_n(q_m - q_t)^n \dots \dots \dots (3)$$

Where ;

- $n$  is the order of adsorption kinetics ( $n = 1$  or  $2$ ),
- $k$  is the kinetic constant (in  $\text{min}^{-1}$  for  $n = 1$  and in  $\text{g.mg}^{-1}.\text{min}^{-1}$  for  $n = 2$ ),
- $q_m$  is the quantity of solution adsorbed at equilibrium (mg/g),
- $q_t$  is the quantity of solute absorbed to the instant  $t$  (mg/g) and  $t$  is the time (min).

#### 2.4.1. Kinetic pseudo-order 1 model

His model has proposed by Lagergren in 1989 [25, 26]. After having replaced  $n$  by 1 in the equation (3), then integrated, one gets the equation (4). So, the tracing of  $\ln(q_m - q_t) = f(t)$ , give the kinetic constant via the slope of linearisation and the theoretical value of maximal capacity of adsorption via the origin ordered.

$$\ln(q_m - q_t) = \ln q_m - k_1 t \dots \dots \dots (4)$$

#### 2.4.2. Kinetic pseudo-order 2 model

To the image of Lagergren model, the kinetics of adsorption can be of pseudo-order 2 type. With the same reasoning (for  $n = 2$ ), one gets equation (5) which the tracing of  $\frac{t}{q_t} = f(t)$  gives the theoretical value of maximal capacity of adsorption via the slope and the kinetic constant via the origin ordered and the value of maximal capacity of adsorption.

$$\frac{t}{q_t} = \frac{t}{q_m} + \frac{1}{k_2 q_m^2} \dots \dots \dots (5)$$

Also, the initial rate of adsorption,  $h$  in  $\text{mg.g}^{-1}.\text{min}^{-1}$  is given by:

$$h = k_2 q_m^2 \dots \dots \dots (6)$$

#### 2.4.3. Elovich model

The equation simplified of Elovich model (equation (7)) is used to express the rate of growing of the quantity of solute on adsorbent (because of the increase of the surface cover) during the process of adsorption with time. The next linear form of Elovich equation has been applied (as suggested by Chien and Clayton [27]) to determine the theoretical values of initial rate of sorption and the parameter associated to the degree of surface cover.

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \dots \dots \dots (7)$$

Where ;

- $q_t$  is the quantity of solution adsorbed (mg/g),
- $\alpha$  is the initial rate of sorption ( $\text{mg.g}^{-1}.\text{min}^{-1}$ ),
- $\beta$  is associated to the degree of surface cover and the energy of activation for chimisorption (g/mg),
- $t$  is the time (min) [28-30].

2.4.4. Diffusion models

The process of adsorption can also be governed by the diffusion of solute in solution and in the pores of the adsorbent. Thus, we are talking about extra-particle diffusion and intra-particle diffusion that has been studied by Boyd and Weber-Morris models [20, 26, 29-31] respectively.

Boyd model (extra-particle diffusion)

The equations linked Boyd model are the following (equations (8-10)), with as  $B_t$  parameter (mathematical function of Boyd) and  $F$  (fraction of solute adsorbed to time  $t$ ). The other sizes are the same that those mentioned previously.

$$F = \frac{q_t}{q_m} = \frac{C_i - C_t}{C_i - C_{\text{éq}}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-n^2 B_t} \dots \dots \dots (8)$$

The expression of  $B_t$  according to  $F$  depends on the values of  $F$  (equations (9, 10)) [30,31].

$$B_t = (\sqrt{\pi} - \sqrt{\pi - \pi^2 \frac{F}{3}})^2 \text{ pour } F \leq 0.85 \dots \dots \dots (9)$$

$$B_t = -0.498 - \ln(1 - F) \text{ pour } F > 0.85 \dots \dots \dots (10)$$

The study of Boyd model has been made by tracing of  $B_t = f(t)$ .

Weber-Morris model (intra-particle diffusion)

This model been studied by tracing of  $q_t = f(\sqrt{t})$ ; (equation (11)) where  $q_t$  is the quantity of solute adsorbed to instant  $t$  (mg/g),  $k_{id}$  is the constant of diffusion (mg.g<sup>-1</sup>.min<sup>-1/2</sup>),  $t$  is the time (min),  $I$  is the relative constant to the limit of the layer (mg/g). What allowed to determine  $k_{id}$  and  $I$  that are leading coefficient and origin ordered (of the right), respectively.

$$q_t = k_{id}\sqrt{t} + I \dots \dots \dots (11)$$

3. Results and discussion

3.1. Characteristics of active carbons elaborate

3.1.1. Capacity of adsorption in aqueous solution

The values of index, as well for iodine that for methylene blue, show that the active carbons elaborated with an activation under CO<sub>2</sub> have a bigger capacity of adsorption (Table 2). It means that the sample activated under N<sub>2</sub> developed less porosity as well micro than meso. However, her value of iodine index is not really low; she is also comparable to the one of good number of commercial active carbons, as for example those of CHEMVIRON CARBON (838 mg/g to 876 mg/g) [32] and those of other authors (435mg/g to 1153 mg/g, 230 mg/g to 680 mg/g, 159 mg/g to 876 mg/g) [20, 21, 32]. These authors qualified their active carbons as having a good porosity. Our two samples have a good capacity of adsorption also and one can pretend that they developed good number of zones micro- and meso-porous at the time of the process of activation.

3.1.2. pH of point to zero charge (pH<sub>PZC</sub>)

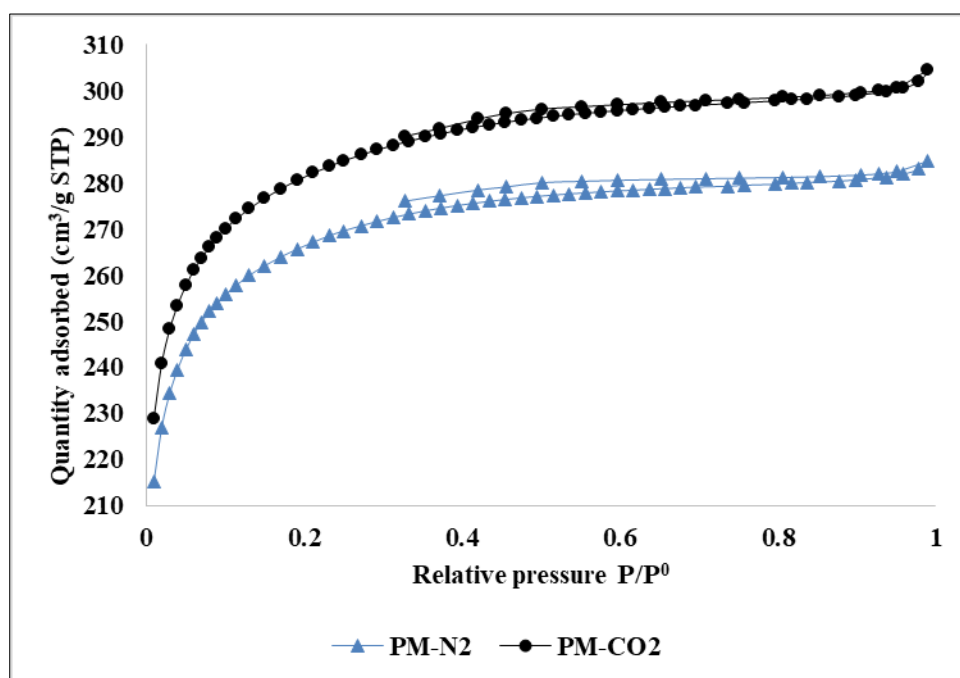
**Table 2** Iodine index, methylene blue index and pH<sub>PZC</sub> values

	Iodine index values (mg/g)	Methylene blue index values (g/100g)	pH <sub>PZC</sub> values
PM-N <sub>2</sub>	755	7	8.8
PM-CO <sub>2</sub>	1077	12	8.5

The  $\text{pH}_{\text{PZC}}$  values (Table 2) show that two samples are a basic nature. A priori, there are more basic functions (or stronger of basic functions) to the surface of these samples than of acidic functions. But one notices that PM-N<sub>2</sub> is slightly more basic than PM-CO<sub>2</sub>. It could be due to fact that this last has been gotten under flux of an acidic gas that could have contributed to the creation of acidic functions whereas the first under flux of a neutral gas, but more again by incorporation of nitrogen atoms in the carbon structure at the time of activation, knowing that these atoms confer generally a more basic character to the structure [35, 36].

### 3.1.3. Adsorption-desorption of nitrogen at 77 K

The textures characteristic (porosity, specific surfaces) of active carbons are determined by adsorption of nitrogen to 77 K. The isotherms of adsorption-desorption are presented by figure 1. Their pace is comparable of type I isotherm according to the classification of IUPAC with a very light buckle of hysteresis (flattened) of H4 type. It lets suppose that the active carbons elaborate are essentially microporous (elevated adsorption rate to weak relative pressures) with pores in the shape of crack [37]. It is a confirmation of that is often observed for active carbons.



**Figure 1** Isotherms of nitrogen adsorption-desorption at 77 K

For treatment of the data to figure 1, follow the results presented to table 3. The two samples do not present a big difference of specific surface values (1008 m<sup>2</sup>/g and 1063 m<sup>2</sup>/g for PM-N<sub>2</sub> and PM-CO<sub>2</sub> respectively) and of microporosity. This last is very raiser (more than 71% of the porous volume are microporous) with for consequence surface specific a lot of majorities microporous (79% of the present surface is micropores). Besides the midden diameter of the pores is lower to 20 Å, it confirms the microporous character of the two elaborate active carbons once moreover. However, even though the activation under CO<sub>2</sub> gives a slightly more important specific surface, the microporosity is also very important in the case of activation under N<sub>2</sub>. The values of specific surfaces, the porous volumes and the midden diameter of the pores are comparable to those of other works on the development of active carbons to departure of different biomasses [4, 13, 14, 18-20].

**Table 3** Results of nitrogen adsorption-desorption

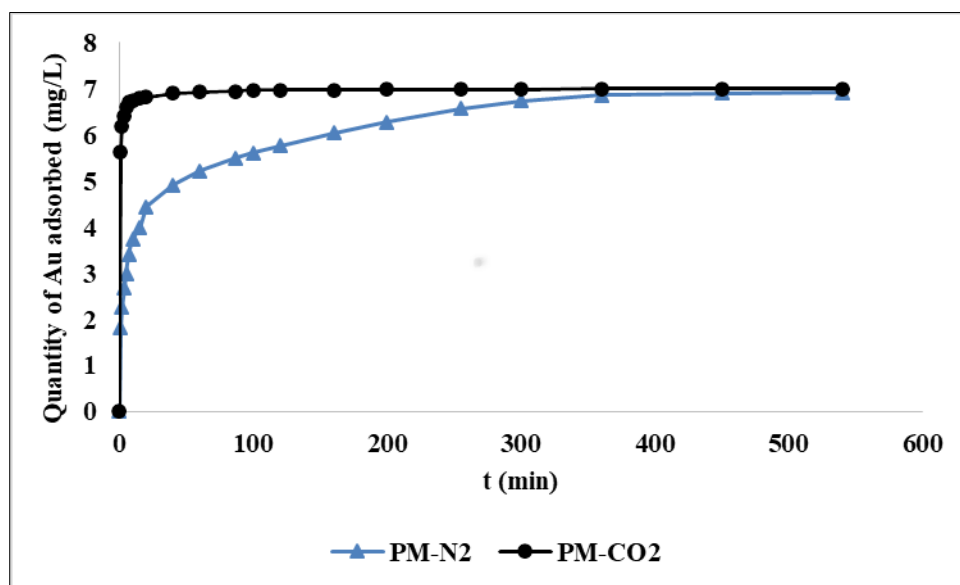
	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$S_{\text{micro}}$ (m <sup>2</sup> /g)	$S_{\text{micro}}/S_{\text{BET}}$	$V_{\text{total}}$ (cm <sup>3</sup> /g)	$V_{\text{micro}}$ (cm <sup>3</sup> /g)	$V_{\text{micro}}/V_{\text{total}}$	$d_{\text{midden}}$ (Å)
PM-N <sub>2</sub>	1008	800	0.794	0.440	0.320	0.726	17
PM-CO <sub>2</sub>	1063	839	0.790	0.471	0.336	0.713	18

### 3.2. Kinetic adsorption of $\text{Au}(\text{CN})_2^-$

Figure 2 represents the evolution of quantity of gold adsorbed, as  $\text{Au}(\text{CN})_2^-$ , according to time for the two samples of active carbon elaborated. In the first minutes, one notices an adsorption of gold complex is lot more louse by PM- $\text{N}_2$  than PM- $\text{CO}_2$ . For this last indeed, the landing is nearly reached in one hour, whereas for PM- $\text{N}_2$  adsorption progresses in a less fast way but to reach the same landing progressively after eight or nine hours. We will keep while PM- $\text{CO}_2$  has adsorbent power most elevated on a scale brief time (the order of one hour). It can be put in interrelationship with the results of methylene blue index and iodine index for the fast adsorption capacity, probably through a porosity a few larger (methylene blue) and by very similar values of specific surface for total capacity of adsorption (identical plateau after nine hours of setting in contact). Besides, PM- $\text{CO}_2$  is very slightly less microporous (table 3); the macropores as well as the mesopores probably constitute the ways passage of adsorbate at the while of adsorption process [11]. Otherwise, PM- $\text{CO}_2$  is also less basic (table 2). Therefore, he will present potentially more interactions (of attractive type) with the adsorbates who have negative charges, like  $\text{Au}(\text{CN})_2^-$ .

Thus, after 9 hours of contact time, the PM- $\text{N}_2$  has adsorbed equivalent of 13.82 kg of gold by ton of active carbon and PM- $\text{CO}_2$  13.98 kg of gold by ton of active carbon. These numbers are lower to what is returned in literature, because a ton of active carbon can adsorb until 70 kg of gold [38]. Furthermore, it is necessary to note that after one hour of contact time, the two samples have adsorbed equivalent of 10.46 kg gold by ton of active carbon (PM- $\text{N}_2$ ) and 13.86 kg gold for one ton of active carbon (PM- $\text{CO}_2$ ), that correspond respectively to percentages of extraction in Au of 74.46% and 98.70%.

In industrial environment, to have a good yield of extraction in Au, the active carbon passes in several containing tubs the lixivates of gold with very precise stay times. For our samples of active carbon, adsorbed the equivalents of 13.82 kg and 13.98 kg gold by ton of active carbon do not mean that they are saturated. These samples have adsorbed the maxima that they can adsorb in the conditions of experience with percentages of extraction in Au of 98.47% and 99.71%; respectively for PM- $\text{N}_2$  and PM- $\text{CO}_2$ . What means that if one makes them pass in several containing tubs solutions charged on Au, these samples can adsorber of the important quantities of gold by ton of active carbon, well beyond what is presented above.



**Figure 2** Evolution of quantity of Au adsorbed according to the time

#### 3.2.1. Kinetics pseudo-order 1 and 2 models

The application of equations (4) and (5) on data represented to figure 2 permit to get figures 3 and 4. The kinetic parameters descended of the rights regression of the two models (pseudo-order 1 and 2) are regrouped in table 4. Even though coefficients of determination ( $R^2$ ) and of interrelationship ( $r$ ) are relatively important for PM- $\text{N}_2$ , the value of  $q_{\text{exp}}$  is distinctly lower to  $q_{\text{cal}}$ . It indicates that this model is not adapted to adsorption of  $\text{Au}(\text{CN})_2^-$  on active carbons PM- $\text{N}_2$  and PM- $\text{CO}_2$ . On the other hand, for kinetic pseudo-order 2 model, the values for experimental and calculated capacities of adsorption are very near (less 2% of gap) and the coefficients of determination ( $R^2$ ) adjoin the unit. It

means that the adsorption of  $\text{Au}(\text{CN})_2^-$  on two samples of active carbon obeys to kinetic of pseudo-order 2 model. The constant of speed of pseudo-order 2 of PM-N<sub>2</sub> is about 30 times weaker than the one of PM-CO<sub>2</sub> (table 4), confirming that this last adsorbed the complex more quickly, as we had seen it in the figure 2. It is besides also factual by the initial adsorption rate (h) that gives the same order of report. These results are in agreements with several studies showed that adsorption on active carbon is pseudo-order 2 type [4,18,20,26]. However, R. Khosravi and al. [39] showed that the adsorption of  $\text{Au}(\text{CN})_2^-$  obeys to pseudo-order 1 model more. It could be due to fact that these authors used solutions of lixiviation of gold mineral, containing cyanicides of iron ( $\text{Fe}(\text{CN})_6^{4-}$ ), of copper ( $\text{Cu}(\text{CN})_3^{2-}$ ) (Fe and Cu are the constituents of the mineral as oxides and form some cyanide complex at the time of the lixiviation to cyanide) or of other elements; what can influence the adsorption of  $\text{Au}(\text{CN})_2^-$  on the active carbon.

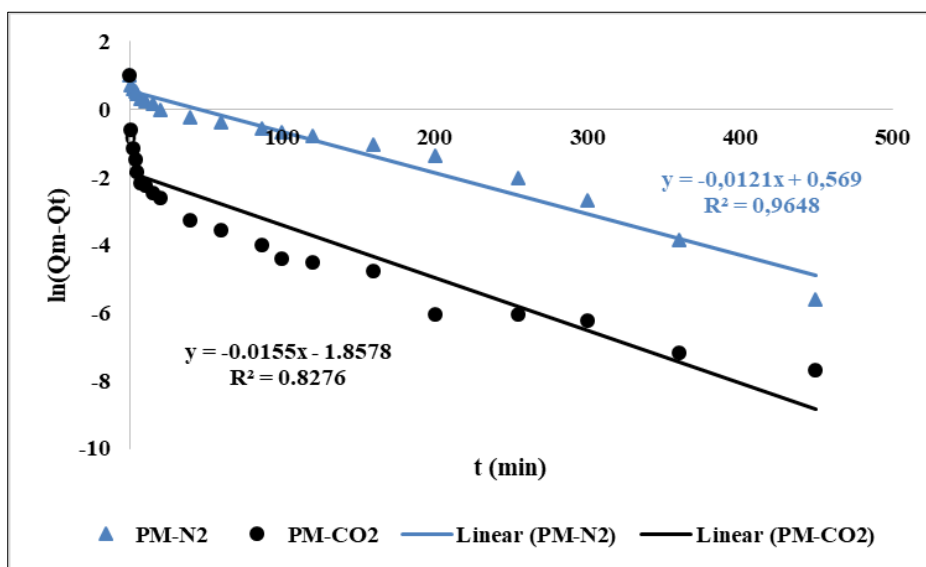


Figure 3 Kinetic pseudo-order 1

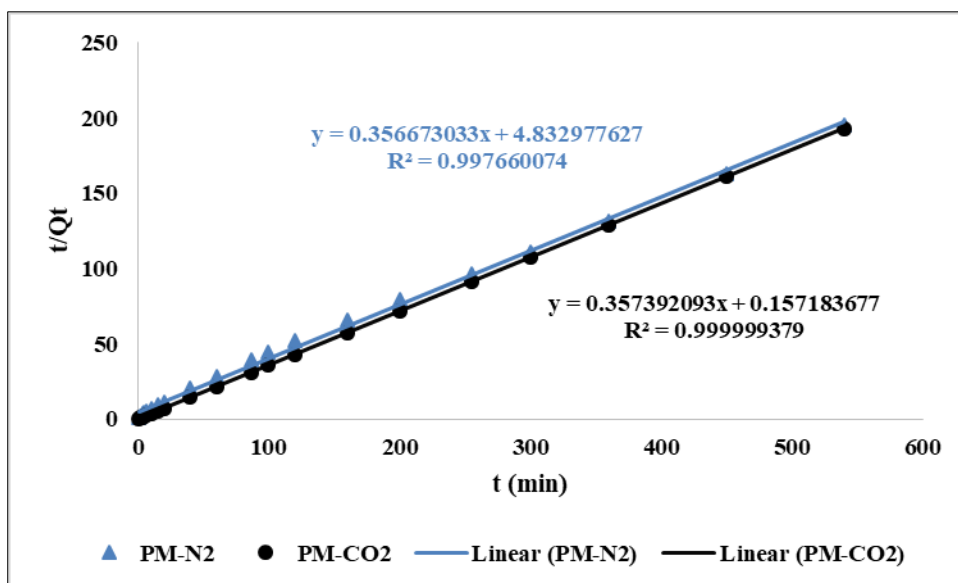


Figure 4 Kinetic pseudo-order 2



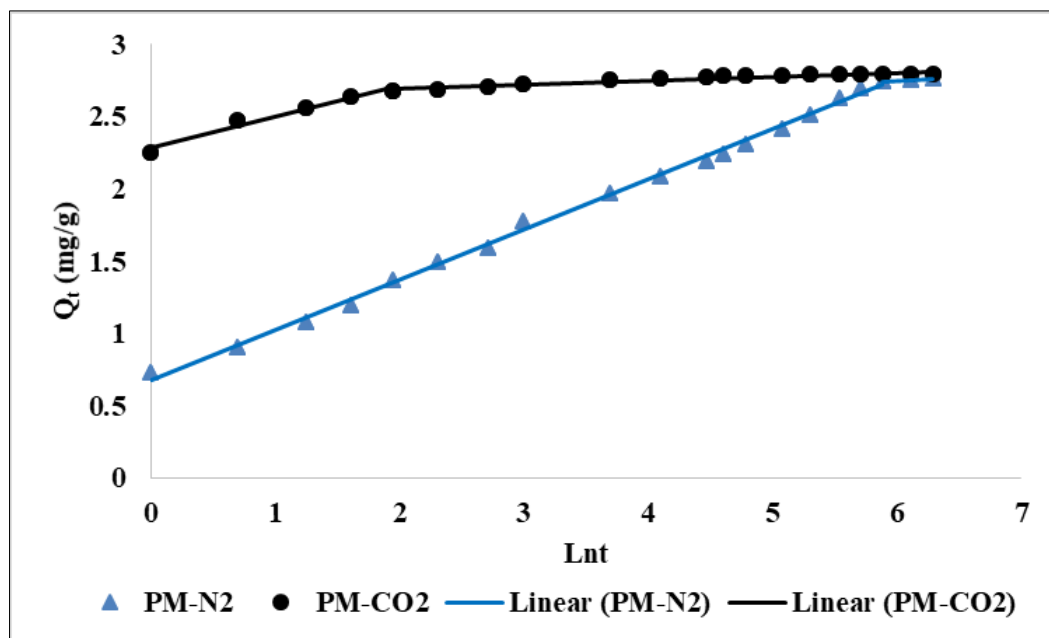
**Table 4** Kinetics pseudo-order 1 et 2 parameters

	Kinetic pseudo ordre 1				Kinetic pseudo ordre 2			
	$q_m(\text{exp})$ in mg/g	$q_m(\text{cal})$ in mg/g	$k_1$ in $\text{min}^{-1}$	$R^2$	$q_m(\text{cal})$ in mg/g	$k_2$ in $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$	$R^2$	$h$ in $\text{mg}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$
PM-N <sub>2</sub>	2.764	1.766	0.012	0.9648	2.803	0.026	0.9977	0.207
PM-CO <sub>2</sub>	2.796	0.156	0.016	0.8276	2.798	0.813	0.9999	6.362

3.2.2. Elovich model

The model of Elovich is used to describe the relation between adsorbate and adsorbent to the surface of this last. According to figure 5, the regression of this model presents in two zones. The first corresponds to phase where the molecules of adsorbate are in direct contact with the surface of adsorbent, but also one on the other with a weak thickness and the second corresponds to the equilibrium, when their interaction with the surface of the solid is weak or saturated, or even that there is not any more solute in solution. With coefficients of determination varying from 0.9111 to 0.9975, even though they are not as near of the unit that for pseudo-order 2 model, the model of Elovich also agrees to explain the interaction between  $\text{Au}(\text{CN})_2^-$  and the two samples of active carbon during process of adsorption.

In any case, the initial coefficient of sorption ( $\alpha$ ) is distinctly superior to the factor associated to the energy of activation for chimisorption ( $\beta$ ) (table 5), what is observed by some authors [25,29,40,41]. It is why, one can affirm that the process of adsorption of this complex on the active carbon is governed by physisorption.



**Figure 5** Elovich model

**Table 5** Parameters of drawn Elovich model application

	1 <sup>st</sup> zone			2 <sup>nd</sup> e zone		
	$\alpha_1$ in $\text{mg}/\text{g}\cdot\text{min}$	$\beta_1$ in $\text{g}/\text{mg}$	$R^2$	$\alpha_2$ in $\text{mg}/\text{g}\cdot\text{min}$	$\beta_2$ in $\text{g}/\text{mg}$	$R^2$
PM-N <sub>2</sub>	2.458	2.884	0.9975	$3.740\cdot 10^{18}$	18.797	0.9127
PM-CO <sub>2</sub>	8425.498	4.627	0.9715	$1.006\cdot 10^{40}$	36.232	0.9111

### 3.2.3. Models of diffusion

The figures 6 and 7 are results for application of diffusion models of Boyd and Weber-Morris (equations 8-11) to the results of adsorption of  $\text{Au}(\text{CN})_2^-$  on the two elaborate active carbons (data of figure 2). These figures show that the diffusions extra- and intra-particle makes themselves in three stages because of the multi-linearity (three zones) of the regression rights (figures 6,7). The parameters drawn from these linearisation are retaken by table 6.

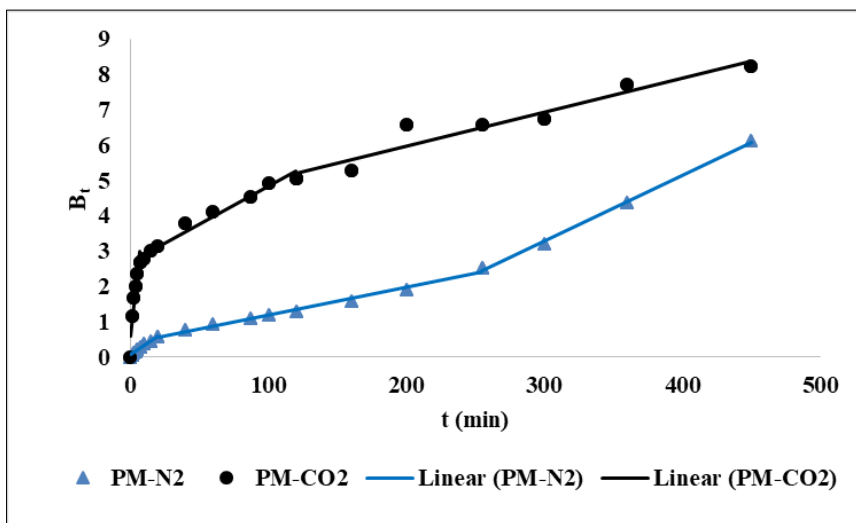


Figure 6 Boyd diffusion

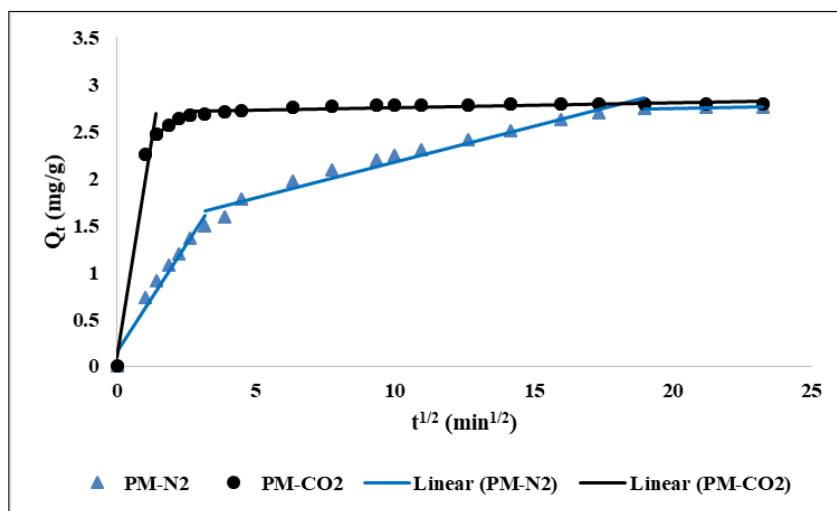


Figure 7 Weber-Morris diffusion

The values of the coefficients of determination for different zones for the two samples of active carbon studied indicate that the model of diffusion extra-particle (Boyd model) is better adapted during adsorption on PM-N<sub>2</sub> than on PM-CO<sub>2</sub> (for all phases) although it depends on the phases for the model of diffusion intra-particle. Nevertheless,  $k_{id}$  values shows that the diffusion of gold (I) cyanide complex in the pores is faster for PM-CO<sub>2</sub> than for PM-N<sub>2</sub>. It had already been underlined previously and has already been joined to the values of iodine index and methylene blue index.

However, if data present multilinear tracings, then two or several stages influence the process of sorption. It is supposed that the external resistance to the transfer of mass surrounding the particles is only meaningful to the beginning of the adsorption stage: it is represented by the first zone [26]. Indeed, the first zone can be explained by the diffusion of the complex of gold ( $\text{Au}(\text{CN})_2^-$ ) through the solution toward external surface of adsorbent, or the diffusion of the layer limits to solute. As for the second zone, it explains the progressive sorption stage, limited by the diffusion intra-particle of the solution. The presence of a third zones can be assigned to the final stage of equilibrium for which intra-particle diffusion began to slow down because of very weak concentration left in the solution [42], as returned by R. Khosravi

and al., [39]. But in the case of the adsorption on PM-CO<sub>2</sub>, the first zone (diffusion of solution toward external surface of adsorbent) is so fast than one can associate it at the second zone (limitation of adsorption by external and internal diffusion), and the last two zones can be associated to the phase of equilibrium (figures 2 and 7).

**Table 6** Parameters of Boyd and Weber-Morris diffusion

	1 <sup>st</sup> zone			2 <sup>nd</sup> zone			3 <sup>rd</sup> zone		
	<b>Boyd model</b>								
	<b>R<sup>2</sup></b>								
<b>PM-N<sub>2</sub></b>	0.9661			0.9877			0.9982		
<b>PM-CO<sub>2</sub></b>	0.8539			0.9738			0.9289		
	<b>Weber-Morris model</b>								
	<b>K<sub>id</sub> (mg/g.min<sup>½</sup>)</b>	<b>I (mg/g)</b>	<b>R<sup>2</sup></b>	<b>K<sub>id</sub> (mg/g.min<sup>½</sup>)</b>	<b>I (mg/g)</b>	<b>R<sup>2</sup></b>	<b>K<sub>id</sub> (mg/g.min<sup>½</sup>)</b>	<b>I (mg/g)</b>	<b>R<sup>2</sup></b>
<b>PM-N<sub>2</sub></b>	0.460	0.158	0.9572	0.076	1.414	0.9591	0.005	2.650	0.8956
<b>PM-CO<sub>2</sub></b>	1.843	0.093	0.9572	0.170	2.242	0.9818	0.005	2.707	0.6972

#### 4. Conclusion

The activation under flux of gas (N<sub>2</sub> and CO<sub>2</sub>) after impregnation in KOH of *Parinari macrophylla* shells permitted to produce active carbons of sufficiently elevated, propertied specific surface a porous volume interesting and microporous to more of 70% with a good faculty to adsorption in aqueous phase.

The sample activated under CO<sub>2</sub> present iodine index and methylene blue index more elevated than carbon activated under nitrogen, although the fact that the two samples have more or less the same specific surface. The total capacity of adsorption of gold (I) cyanide complex (Au(CN)<sub>2</sub><sup>-</sup>) is also identical for the two active carbons studied, but a lot faster when carbon is activated under CO<sub>2</sub>, sign of a diffusion difference in the beginning of the process.

The modelling of kinetics adsorption shows that adsorption of Au(CN)<sub>2</sub><sup>-</sup> obeys to pseudo-order 2 regime. A multilinearity is observed for the treatment according to Elovich model and the values more raised of the parameter  $\alpha$  in relation to  $\beta$  is the sign of a physisorption.

Boyd and Weber-Morris models diffusion permit to put separately in evidence the diffusion of the solution toward the surface of adsorbent, the diffusion in the pores (as well as the adsorption to its surface) and the phase of equilibrium. It is to note that the adsorption of Au(CN)<sub>2</sub><sup>-</sup> on the sample activated under CO<sub>2</sub> is so fast that the first two phases are nearly confounded.

Thus, samples of the active carbon gotten by valorization of the agricultural waste present very good characteristics of adsorption and are capable to adsorb gold (I) cyanide complex ion, complex formed by attack of the gold mineral by a solution of sodium cyanide (or potassium) in the middle industry of gold hydrometallurgy.

#### Compliance with ethical standards

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##### Disclosure of conflict of interest

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

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