



## Recovery of *borassus* palm tree and bamboo waste into activated carbon: application to the phenolic compound removal

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Received 22 Feb 2020,  
Revised 11 Sept 2020,  
Accepted 14 Sept 2020

### Keywords

- ✓ Hadamard design,
- ✓ Activated carbon,
- ✓ Adsorption,
- ✓ 2,4-dimethylphenol.

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### Abstract

Activated carbons from *borassus aethiopicum* and bamboo's fibers were prepared by chemical activation. The optimal conditions of preparation were studied according to an Hadamard experimental design. From the results, only the chemical product has an influence on the adsorption capacity of the activated carbons. Two activated carbons (bpAC and ACB) showed better characteristics with iodine number and methylene blue adsorption capacity of 655.5 - 627.7 mg.g<sup>-1</sup> and 329.5 - 474.7 mg.g<sup>-1</sup> respectively. These activated carbons also have a fairly high percentage of carbon (65.78% and 52.42%). Adsorption experiments were carried out on 2,4-dimethylphenol (2,4-DMP), a molecule chosen as a model pollutant, to evaluate the adsorbent properties of these two activated carbons. Kinetics data were well adapted to the pseudo-second order model with a correlation coefficient  $R^2 = 1$ . The adsorption isotherms showed high equilibrium adsorption capacities (227.3 and 169.5 mg.g<sup>-1</sup> respectively for bpAC and ACB). The Freundlich model describes with good accuracy ( $R^2 = 0.99$  with CAR and 0.98 with CAB) the increase in the adsorbate concentration at the surface of the adsorbent compared to the increase of the adsorbate concentration. in the aqueous solution.

### 1. Introduction

Phenolic derivatives are predominant in the various oil refinery effluents, including, 2,4-dimethylphenol (2,4-DMP). The chosen compound as model pollutant in this study is representative of the problematic molecules present in industrial wastewater refractory to conventional biological treatments [1]. This compound also known under the name of 2,4-xyleneol is a typical pollutant in petrochemical effluents. A large number of products utilize 2,4-DMP as a feedstock or constituent for the production of phenolic antioxidants, disinfectants, solvents, pharmaceuticals, insecticides, fungicides, plasticizers, rubber chemicals, polyphenylene oxide, dyestuffs, wetting agents, and as an additive or constituent of gasoline, lubricants, and cresylic acid [2]. 2,4-DMP is used in the manufacture of a wide range of commercial products for industry and agriculture [3]. It is indicated as a very toxic product (R24/25, R34, R51/53) according to the agency of American Environmental Protection [4]. Its presence in petroleum fractions and coal tars, together with its use as a chemical feedstock or constituent for the manufacture of numerous products, clearly indicates the potential source for water contamination. Hence, disposal of chemical and industrial process wastes and distribution from normal product applications represent feasible modes of entry of 2,4-DMP into the environment. Examples of the latter mode include pesticide applications, asphalt and roadway runoff, and the washing of dyed materials [5].

Several methods have been developed for the removal of this pollutant such as adsorption or degradation by oxidation. Advanced oxidation processes (AOPs) appeared to be an adequate means to remove this type of refractory compounds by producing highly oxidative species [6,7]. Studies have shown the positive effect of the use of ozone or the combination of ozone with zeolites to remove 2,4-DMP [1,7,8]. However, studies by Munter et al. [9] on the cost of AOPs for the removal of aromatic compounds from water have shown that these processes are generally more expensive than the adsorption. Adsorption is based on the property of materials (adsorbents) to fix substances (gases, metal ions, organic molecules, etc.) on their surface. In theory, all solids have adsorbent properties, but the most commonly solids used are the activated carbons, followed by zeolites, silica gels and activated [1,10]. The particularly high adsorption capacities of activated carbons are related to their highly developed porous structures, their large available surfaces and their very specific interactions with many organic and inorganic compounds [11]. In addition to their effectiveness in adsorbing multiple molecules, activated carbons can also be used in many applications as a catalyst or catalytic support for many reactions including hydrogenation, oxidation, halogenation, hydration, isomerization and polymerization [12–14]. However, the demand of activated carbon is expected to dramatically increase since the consumption is forecasted to triple by 2024 [15]. Raw materials commonly used for the production of activated carbon are wood, coal, petroleum residues, peat, lignite and polymers, which are very expensive and non-renewable [16–18]. Precursors conventionally used industrially could be replaced by new precursors cheap, accessible and available in abundant quantities. It is in this context that many authors try to valorize waste of all origins [15,19,20]. The growing global interest in preserving the environment of solid waste resulting from various activities and human transformations, has attracted the attention of industry to find techniques to reduce or otherwise enhance this waste. In developing countries, landfilling is the commonly used waste treatment method compared to incineration and composting [21,22]. However, this method does not seem to be the most rational approach, because of the by-products generated during the decomposition of this waste. The use of this waste as a precursor for the preparation of activated carbon not only produces an adsorbent useful for the purification of contaminated environments, but also helps to minimize solid waste [23]. Many studies showed comparable efficiency of activated carbon derived from waste to commercial adsorbents for wastewater treatment: removal of dyes, metal ions, pharmaceuticals products, organic pollutants or natural organic matter [15,19].

The aim of this study is to prepare and test efficiency of activated carbons based innovative low-cost precursors. In the context of research on the valorization of biomass, it seemed wise to integrate some abundant raw materials that are not use. Thus, *borassus* palm tree and bamboo's canes are used as precursors. 2,4-dimethylphenol (2,4-DMP) was selected as a model molecule as it is representative of toxic biorefractory molecules detected in industrial rejections (disinfectants, solvents, insecticides, pharmaceuticals...) [8]. The physical and chemical properties of activated carbons, as well as its adsorption properties for 2,4-DMP elimination were determined.

## 2. Material and Methods

### 2.1. Reagents

Ethanol (EtOH) and methanol (MeOH) used for High Performance Liquid Chromatography (HPLC) analyses are HPLC grade (Sigma Aldrich). 2,4-dimethylphenol  $C_8H_{10}O$  (2,4-DMP, 98% purity) was purchased from Sigma Aldrich. 2,4-DMP properties are as followed: a molar mass of  $122.17 \text{ g mol}^{-1}$ , a boiling temperature of  $212 \text{ }^\circ\text{C}$ , a pKa of 10.6 and a kinetic diameter of  $7.3 \text{ \AA}$ . Synthetic solutions of 2,4-

DMP were prepared with water purified by a Millipore Milli-Q UV. Ethanol (EtOH) and methanol (MeOH) used for High Performance Liquid Chromatography (HPLC) analyses are HPLC grade and were also purchased from Sigma Aldrich. Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) was purchased from Merck and the other reagents (HCl, NaOH, Na<sub>2</sub>SO<sub>4</sub>, methylene blue, iodine) used in this study were also supplied by Sigma Aldrich.

## 2.2. Production of activated carbon

In order to promote natural raw materials, the petioles of *borassus* palm and bamboo canes were used as precursors. These raw materials (RM) were collected in the locality of Yamoussoukro (Ivory Coast), then cut into small pieces, washed with distilled water and sun-dried for three days (Figure 1).



**Figure 1:** Petioles of *Borassus* palm (A) and bamboo canes (B)

Preparation of the activated carbons was done according to the usual method [24,25] and the influence of the parameters was studied, using the methodology of the experimental designs. For the synthesis of activated carbons, the Hadamard plan was used. This type of plan allows having a first evaluation of the factors' influences on the desired response from a reduced number of tests, even for an important number of factors. It is often used in first approach. The equation of the model is written in the following form:

$$y = b_0 + \sum_{i=1}^n b_i X_i \quad (1)$$

With,  $b_0$  the average coefficient,  $b_i$  the effect of factors  $X_i$  and  $y$  the result of the experiment.

Table 1 gives the experimental domain.

**Table 1:** Experimental domain.

Level	-1	+1
<b>X<sub>1</sub>: Raw materials</b>	Bamboo canes	Petioles of <i>Borassus</i>
<b>X<sub>2</sub>: Activating agent</b>	NaOH	H <sub>3</sub> PO <sub>4</sub>
<b>X<sub>3</sub>: Concentration of activating agent</b>	1 M	3 M
<b>X<sub>4</sub>: Impregnation time</b>	24 h	48 h
<b>X<sub>5</sub>: Carbonization temperature</b>	400 °C	600 °C
<b>X<sub>6</sub>: Carbonization time</b>	3 h	5 h

Table 2 gives the experimental design. Activation technique consisted to impregnate 200 g of raw material in 250 ml of solution at the appropriate concentration for a given time at room temperature (30 ± 2°C).

Table 2: Experimental design.

Tests	Raw materials	Activating agent	Concentration (mol.l <sup>-1</sup> )	Impregnation time (h)	Carbonization temperature (°C)	Carbonization time (h)
1	<i>Borassus</i>	H <sub>3</sub> PO <sub>4</sub>	3	24	600	3
2	Bamboo	H <sub>3</sub> PO <sub>4</sub>	3	48	400	5
3	Bamboo	NaOH	3	48	600	3
4	<i>Borassus</i>	NaOH	1	48	600	5
5	Bamboo	H <sub>3</sub> PO <sub>4</sub>	1	24	600	5
6	<i>Borassus</i>	NaOH	3	24	400	5
7	<i>Borassus</i>	H <sub>3</sub> PO <sub>4</sub>	1	48	400	3
8	Bamboo	NaOH	1	24	400	3

The substrate is recovered by filtration, dried at 105 °C for 24 h. The possible residues of carbonization were eliminated by an abundant washing with distilled water. Activated carbons obtained are then dried in an oven at 105°C for 24 h. After cooling to the desiccator, the dried carbons are crushed and then sieved with a 100 µm mesh screen. As factors of interest, the iodine number and the methylene blue adsorption capacity were used. Given the qualitative parameters, test 1 was triplicated.

### 2.3. Determination of iodine number

Iodine number determination is a simple and rapid test, giving an indication of the microporosity of activated carbons [26,27]. The procedure used is an adaptation of the CEFIC method [28] and the standard AWWA B 600-90 [29]. The method consists of treating 100 mL of a 0.1 N solution of iodine with 0.1 g of activated carbon in hot and acidic conditions for 30 seconds. The treated solution is then filtered and titrated with a 0.1 N solution of sodium thiosulfate with starch paste as an end of reaction indicator. The iodine number (in mg.g<sup>-1</sup>) is the capacity of iodine adsorbed by one gram of activated carbon for a residual concentration of 0.02 N. It is calculated from the following formula:

$$\text{Iodine number (mg.g}^{-1}\text{)} = \frac{12693N_{I_2} - 279,246N_{th}V_{th}}{m} \quad (2)$$

With, N<sub>I<sub>2</sub></sub> (N), the normality of iodine solution =0,1 N; N<sub>th</sub> (N) and V<sub>th</sub> (ml) the normality and the volume of the solution of sodium thiosulfate respectively; m (g), the mass of activated carbon.

### 2.4. Methylene blue (MB) adsorption capacity

Activated carbon to adsorb medium and large-sized molecules [25]. It can be measured to quantify mesopores and macropores. It reflects a strong adsorption capacity for large molecules. The methylene blue adsorption tests were carried out by mixing 0.3 g of AC with 100 ml of methylene blue solution at 1000 mg.l<sup>-1</sup>. After stirring for 24 h, the suspension was filtered and the residual MB concentration was measured at 664 nm using a UV/VIS spectrophotometer. The adsorption capacity of MB is given by the following equation:

$$MB(\text{mg.g}^{-1}) = \frac{(\mathcal{T}_i - \mathcal{T})}{m} \times V \quad (3)$$

Where  $\mathcal{T}_i$  is the initial concentration of MB solution (mg.l<sup>-1</sup>);  $\mathcal{T}$ , the residual concentration of MB solution (mg.l<sup>-1</sup>); m, the activated carbon mass (g) and V, the MB solution volume (l).

### 2.5. Elemental analysis (C,H,N)

The contents of C, H and N (%) of activated carbons were measured using elemental analysis (PERKIN ELMER 2400 Series II). The samples were finely ground (100 µm) before using for C, H, N analysis.

The method comprises burning a known mass sample at a high temperature (about 1000 °C) under an oxygen atmosphere. In the presence of excess oxygen and combustion reagents, the samples were completely burned and reduced to CO<sub>2</sub>, elemental gases, H<sub>2</sub>O and N<sub>2</sub>. The gases (CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>) produced were separated in a chromatographic column and detected by a thermal conductivity detector.

### 2.6. Nitrogen adsorption/desorption isotherm

The porous structure of the activated carbons was characterized by N<sub>2</sub> adsorption/desorption at -193 °C using an ASAP 2010M apparatus (Micromeritics, Norcross, Georgia).

### 2.7. Kinetic experiment

Kinetic experiment was carried out by agitating 500 mL of solution doped at 100 mg.l<sup>-1</sup>, and 0.05 g of activated carbon at 25°C. At regular intervals, an amount of the sample was taken, then filtered through a PTFE membrane of porosity equal to 0.45 µm (Fisherbrand) before being analysed.

The amount of adsorption at time t, q<sub>t</sub> (mg.g<sup>-1</sup>) was calculated by:

$$q_t = \frac{(C_0 - C_t) \times V}{m} \quad (4)$$

Where C<sub>0</sub> and C<sub>t</sub> (mg.g<sup>-1</sup>) are the liquid phase concentrations of the 2,4-DMP at initial and time t, respectively. V is the volume of solution (l) and m is the mass of the activated carbon (g).

### 2.8. Adsorption isotherms

The experiments were carried out in 125 mL flasks containing 100 mL of 2,4-DMP solution at different concentrations (0 to 1 g.l<sup>-1</sup>) and 0.1 g of activated carbon. These flasks were kept in a thermostat shaker bath (rotary agitator located inside a thermo bath controlled at 25 °C). After equilibrium, the bottles were withdrawn from the bath and the solutions were filtered using a PTFE membrane of porosity equal to 0.45 µm before being analysed. To investigate the adsorption capacity of the activated carbon, Langmuir [30] and Freundlich [31] isotherms were analysed. The Langmuir equation is given by the following formula:

$$q_e = q_m \frac{K_L C_e}{1 + K_L C_e} \quad (5)$$

Where, q<sub>e</sub> is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg.g<sup>-1</sup>), C<sub>e</sub> is the equilibrium concentration of the solute in the bulk solution (mg.l<sup>-1</sup>), q<sub>m</sub> is the maximum adsorption capacity (mg.g<sup>-1</sup>) giving the information about adsorption capacity for a complete monolayer (mg.g<sup>-1</sup>); and K<sub>L</sub>, the constant related to the adsorption energy (l.mg<sup>-1</sup>). A plot of 1/q<sub>e</sub> versus 1/C<sub>e</sub> gives the adsorption coefficients. The Freundlich isotherm is an empirical equation based on sorption on a heterogeneous surface. It is commonly presented as:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (6)$$

Where K<sub>F</sub> and n are the Freundlich constants. K<sub>F</sub> indicates the relative adsorption capacity of the adsorbent and 1/n the adsorption intensity, indicates the tendency of the adsorbate to be adsorbed [32,33]. This formula was exploited in its linear form.

### 2.9. Analytical technic

The concentration of 2,4-DMP in the solution was determined using HPLC. The column used was a C18 grafted silica (Zorbax Eclipse XDB-C18) having the following characteristics: 150 mm in length, 4.6 mm in diameter and 5 µm in average provided by the silica particles. Isocratic elution with a solvent

mixture containing 60% ethanol and 40% water was applied at a flow rate of 0.7 mL.min<sup>-1</sup>. The volume injected was 20 µL. The corresponding retention time of 2,4-DMP was 5 minutes under these conditions. The wavelength used in the UV detector was 280 nm.

### 3. Results and discussion

#### 3.1. Optimization of the conditions of the activated carbons preparation

The objective of this part is to screen the factors in order to identify those that have an effect on the process of activated carbons preparation. Table 3 gives the results obtained for each experiment carried out. The responses show that the chosen experimental domain is sensitive to the variations of the various factors selected. Indeed, standard deviations on the responses are quite high (128.3 and 214.9 respectively for the MB adsorption capacity and the iodine number). Table 4 gives the coefficients calculated using the linear regression of the Excel Solver.

Table 3: Experimental responses

Test	Raw materials	Activating agent	Concentration (mol.l <sup>-1</sup> )	Impregnation time (h)	Carbonization temperature (°C)	Carbonization time (h)	Responses	
							Iodine number (mg.g <sup>-1</sup> )	MB adsorption capacity (mg.g <sup>-1</sup> )
1	<i>Borassus</i>	H <sub>3</sub> PO <sub>4</sub>	3	24	600	3	655.5	329.5
2	Bamboo	H <sub>3</sub> PO <sub>4</sub>	3	48	400	5	627.7	474.7
3	Bamboo	NaOH	3	48	600	3	173.7	129.7
4	<i>Borassus</i>	NaOH	1	48	600	5	132.6	103.8
5	Bamboo	H <sub>3</sub> PO <sub>4</sub>	1	24	600	5	112.1	127.5
6	<i>Borassus</i>	NaOH	3	24	400	5	302.5	166.4
7	<i>Borassus</i>	H <sub>3</sub> PO <sub>4</sub>	1	48	400	3	425.8	269.1
8	Bamboo	NaOH	1	24	400	3	240.9	163.1

Table 4: Estimation and statistics of different coefficients

	b <sub>0</sub>	b <sub>1</sub>	b <sub>2</sub>	b <sub>3</sub>	b <sub>4</sub>	b <sub>5</sub>	b <sub>6</sub>	Experimental error (Se)
<b>Iodine number</b>	338.8	45.2	121.4	106.0	6.1	-65.3	-40.1	57.15
<b>MB adsorption capacity</b>	220.4	-3.2	79.6	54.5	23.7	-47.7	-2.4	34.6

It appears that the different coefficients obtained range from -65.3 to 121.4 and -47.7 to 79.6 respectively for the iodine number and the MB adsorption capacity. After repeating test 1, the respective experimental errors are 57.15 (iodine number) and 34.6 (MB adsorption capacity). A coefficient is significant if in absolute value, it is greater than twice the experimental error [34]. Thus, only the activating agent influences the responses. From the results, it is clear that activation with orthophosphoric acid gives values of iodine number and MB adsorption capacity higher than the activation with sodium hydroxide. This chemical agent is known as the best activating agent. It allows the production activated carbon with good qualities and developing important porous structures with large specific surface areas [35].

#### 3.2. Carbon (C), hydrogen (H) and nitrogen (N) contents of activated carbons

Activated carbons with the best properties are those obtained with the tests 1 and 2. These two activated carbons noted respectively bpAC and ACB were retained for this study. Table 5 gives the chemical composition (C, H, N) of bpAC and ACB.

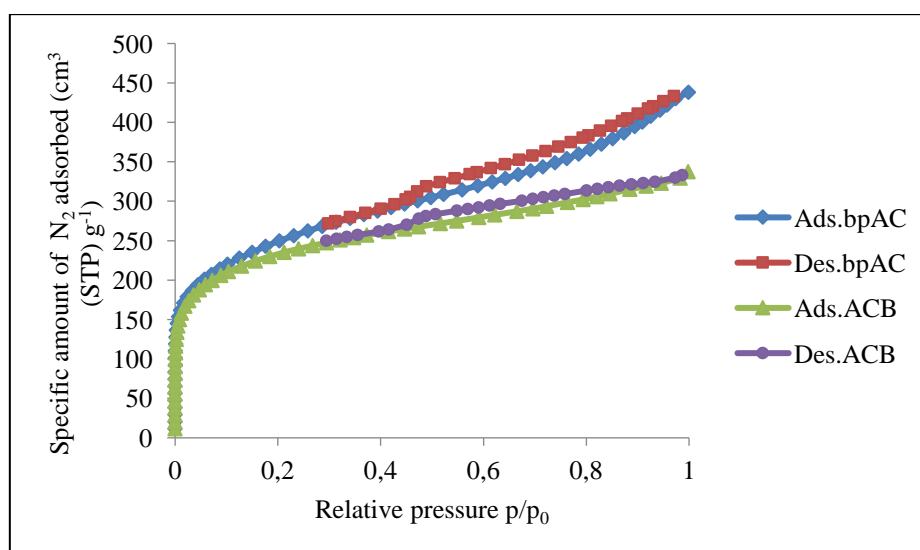
Table 5: Elemental composition of activated carbons.

	<b>C</b>	<b>H</b>	<b>N</b>
<b>bpAC</b>	65.78	1.04	0.44
<b>ACB</b>	52.42	1.36	0.56

The results show that the activated carbons prepared mainly contain carbon (52-65%) with small amounts of hydrogen (1-1.3%) and nitrogen (0.4-0.5%). The hydrogen content of the studied activated carbons is higher than the typical value of 0.5% [36]. This may be due to the presence of water in the precursor (7-9%). These values are in agreement with those found by some authors which vary from 42.2 to 72.4% for carbon; 1.6 to 7.1% for hydrogen and 0.1 to 1.4 for nitrogen [37–41].

### 3.2. Carbon (C), hydrogen (H) and nitrogen (N) contents of activated carbons

The nitrogen adsorption/desorption isotherm at -193 °C for the adsorbents prepared are shown in figure 2.



**Figure 2:** Nitrogen adsorption/desorption isotherm at -193 °C of bpAC and ACB

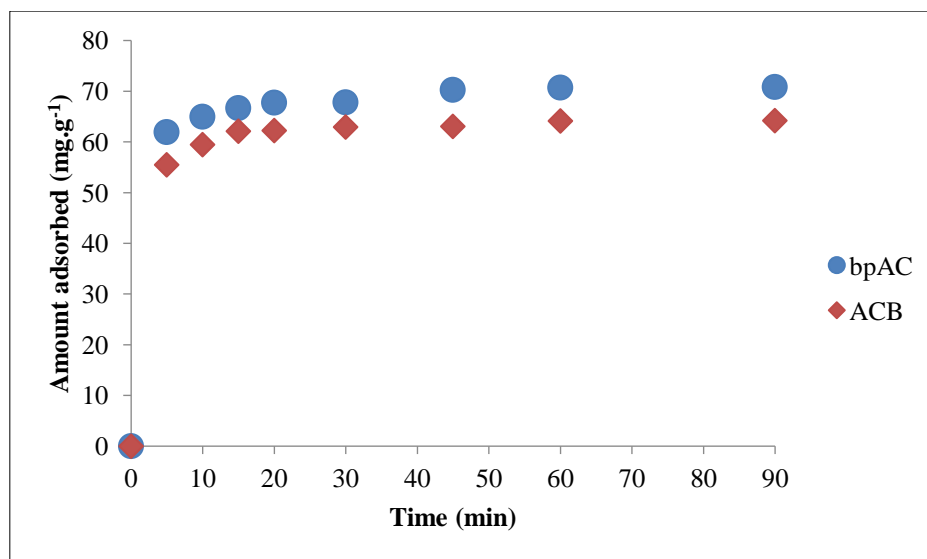
The plateau is not reached which indicates an enlargement of the pores [42]. Isotherms of those activated carbons are a mixture of type II and IV according to the classification of International Union of Pure and Applied Chemistry (IUPAC) [43]. A hysteresis loop occurs in adsorption and desorption processes, indicating a coexistence between micropores and mesopores. The loop being less marked on the level of ACB compared to bpAC showed that the mesoporous volume of this last is more significant.

### 3.4. Carbon (C), hydrogen (H) and nitrogen (N) contents of activated carbons

Study of the adsorption kinetics is important because the adsorption rate which is one of the adsorbent efficiency criteria and the adsorption mechanism can be obtained. This study was carried out with the synthetic solution. Figure 3 shows the evolution of the amount of 2,4-DMP adsorbed over time.

The figure shows a rapid adsorption during the first 15 minutes, then a slow evolution to reach equilibrium after 60 minutes of reaction. 75% and 68% of initial 2,4-DMP were removed by bpAC and ACB, respectively. This rapidity is due to the availability of the large number of vacant adsorption sites on the surface of activated carbons at the initial stage of adsorption and the particle size of the activated carbon ( $\leq 100 \mu\text{m}$ ) [37,44]. This first phase constitutes the essential of the adsorption phenomenon because the kinetics of fixation is limited by the low residual concentration. In the second step, the occupation of the deep adsorption sites requires a diffusion of the adsorbate within the micropores of the adsorbent [45]. According to some studies, the elimination of phenolic compounds with activated carbon

is about 60-80% in the first hour of reaction, followed by a very slow approach to reach a maximum value at equilibrium [46,47]. These data were modeled using the pseudo-first order and pseudo-second order equations. Correlation coefficients and kinetic constants are given in Table 6.



**Figure 3:** Evolution of the amount of 2,4-DMP adsorbed as a function of time:  $[2,4\text{-DMP}]_0 = 100 \text{ mg.l}^{-1}$ ;  $V = 500 \text{ ml}$ ;  $\text{pH}_i = 5.3$ ;  $T=25 \text{ }^\circ\text{C}$ ;  $m_{\text{CA}} = 0.5 \text{ g}$

**Table 6:** Kinetic constants of pseudo first and second order models.

		bpAC	ACB
Pseudo-first order	$R^2$	0.7229	0.6065
	$k_1 \text{ (min}^{-1}\text{)}$	0.0621	0.0533
	$q_{e,\text{exp}} \text{ (mg.g}^{-1}\text{)}$	70.6596	64.1105
	$q_{e,\text{cal}} \text{ (mg.g}^{-1}\text{)}$	16.3987	11.1942
	$\chi^2$	179.5423	250.1403
Pseudo-second order	$R^2$	0.9995	0.9998
	$k_2 \text{ (g.mg}^{-1}\text{.min}^{-1}\text{)}$	0.01824	0.02734
	$q_e \text{ exp (mg.g}^{-1}\text{)}$	70.6596	64.1105
	$q_{e,\text{cal}} \text{ (mg.g}^{-1}\text{)}$	70.9219	64.1025
	$\chi^2$	0.00097	$9.8872 \cdot 10^{-7}$

In the case of the pseudo-first order kinetics, equilibrium adsorption determined experimentally ( $q_{e,\text{exp}}$ ) is different from that calculated ( $q_{e,\text{cal}}$ ). On the other hand, the equilibrium adsorbed quantity determined experimentally is closer to the one calculated using the pseudo-second-order kinetic model, which confirms that the modeling of the pseudo-second-order kinetics for the 2,4-DMP adsorption is acceptable. In addition, the high values of the  $R^2$  coefficient of determination obtained by the pseudo-second-order model ( $R^2=1$ ) (Table 7) confirmed its applicability for the description of the experimental data. Comparative statistical analyzes were performed between the two models (Table 3). In fact, optimization practices require an error analysis to examine the compatibility of the proposed model with the experimental results. Thus, chi-square ( $\chi^2$ ) was used to illustrate the quality of the kinetic data adjustment, expressed in equation 6 [48,49].  $\chi^2$  measures the goodness of fit between the experimental and calculated equilibrium adsorption capacity.

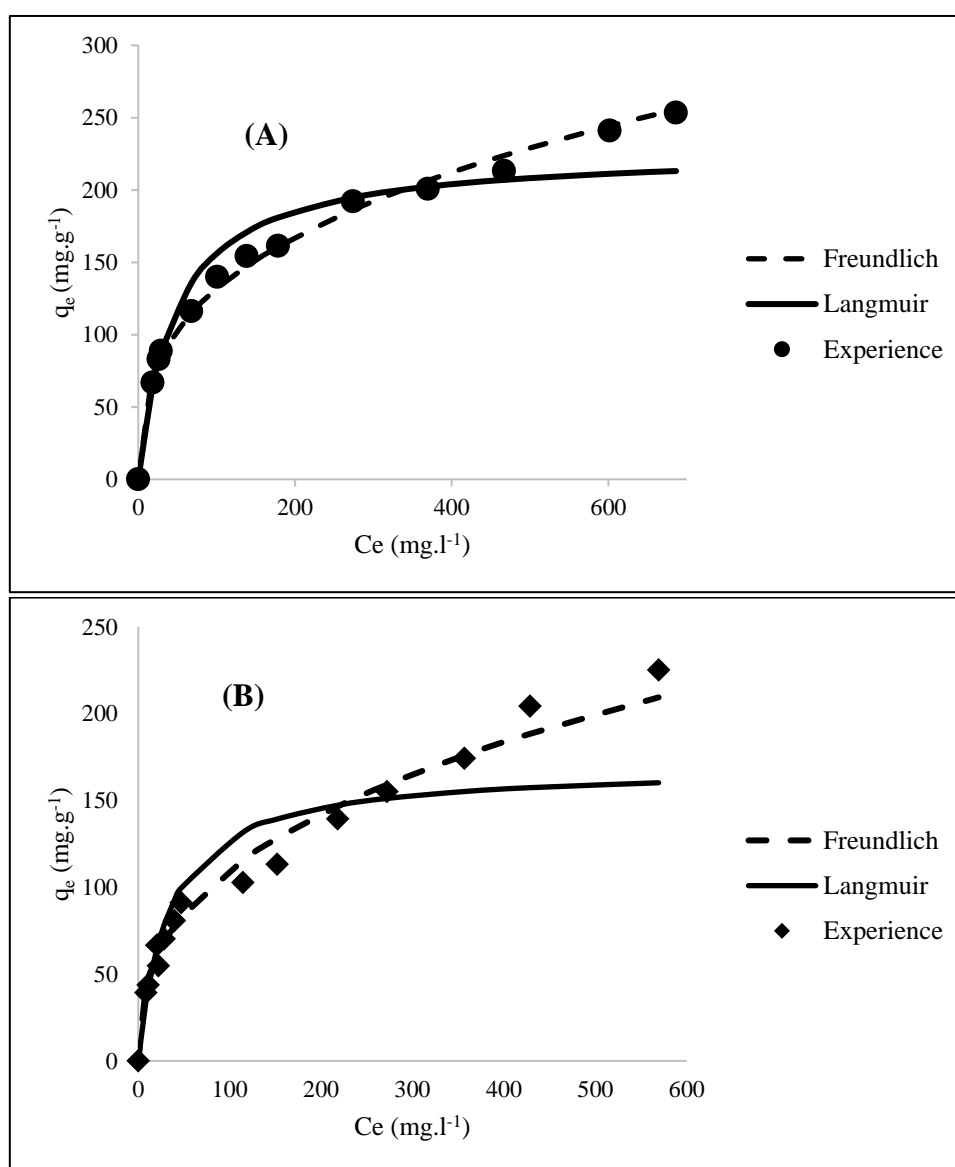


$$\chi^2 = \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \quad (7)$$

$\chi^2$  values of the pseudo-second-order model should be the lowest. This model is able to describe experimental data perfectly. Adsorption is therefore controlled by chemisorption [50,51]. Similar results have been obtained by other authors [51–53].

### 3.5. 2,4-DMP adsorption isotherm on bpAC and ACB

Langmuir and Freundlich isotherm models have been chosen to describe equilibrium data. The acceptability and adequacy of the isotherm equation to the equilibrium data were compared using the correlation coefficient  $R^2$ . Figure 4 presents experimental data and the representations of Langmuir and Freundlich models of bpAC (A) and ACB (B).



**Figure 4:** Experimental data and representations of Langmuir and Freundlich isotherms models of bpAC (A) and ACB (B) in synthetic solution:  $[2,4\text{-DMP}]_0 = (0 \text{ to } 1000 \text{ mg.l}^{-1})$ ;  $V = 100 \text{ ml}$ ;  $\text{pH}_i = 5.3$ ;  $T = 25 \text{ }^\circ\text{C}$ ;  $m_{CA} = 0.1 \text{ g}$

The amount of adsorbed pollutant increases with the equilibrium concentration. In fact, the increase in the concentration induces the elevation of the driving force of the concentration gradient, therefore the

increase of the diffusion of the 2,4-DMP molecules in solution through the surface of the activated carbons [45–47,50–53]. The adsorption isotherms of phenolic compounds do not show a plateau at a high equilibrium concentration [54]. According to the IUPAC classification [43], isotherms can be described, in the range of the concentrations studied, by a type II isotherm. This isotherm is characteristic of most activated carbons with a wide pore distribution, favoring multilayer adsorption. The study on the adsorption of 2,4-DMP on zeolites, conducted by Aboussaoud indicated adsorption in monolayer [1]. From the Langmuir and Freundlich linear transforms, maximum capacities values and adsorption constants were deduced (Table 7). bpAC and ACB show good adsorption capacity of 2,4-DMP comparable to other activated carbon results. The  $R^2$  values obtained show that the Freundlich model, typical of multilayer adsorptions, correctly represents the adsorption isotherm of 2,4-DMP at 25 °C, which can be explained by the micro-mesoporous properties of activated carbons: several layers of adsorbate can be superposed inside this type of pores. Concerning Freundlich constants, the high value of  $n$  ( $2 < n < 10$ ) indicates a stronger adsorption interactions between adsorbate and adsorbent [55,56].

**Table 7:** Constants of Langmuir and Freundlich adsorption isotherms of 2,4-DMP at 25 °C.

		Synthetic solution		Wastewater spiked with 2,4-DMP	
		CAR	CAB	CAR	CAB
Langmuir	$R^2$	0.96	0.93	0.91	0.98
	$K_L$ (l.mg <sup>-1</sup> )	0.02	0.03	0.08	0.02
	$q_m$ (mg.g <sup>-1</sup> )	227.3	169.5	192.3	238.1
Freundlich	$R^2$	0.99	0.98	0.98	0.97
	$K_F$ (mg.g <sup>-1</sup> (l.mg <sup>-1</sup> ) <sup>1/n</sup> )	26.8	19.7	32.3	17.9
	$n$	2.9	2.8	2.9	2.2

### 3.6. Application to a wastewater spiked with 2,4-DMP

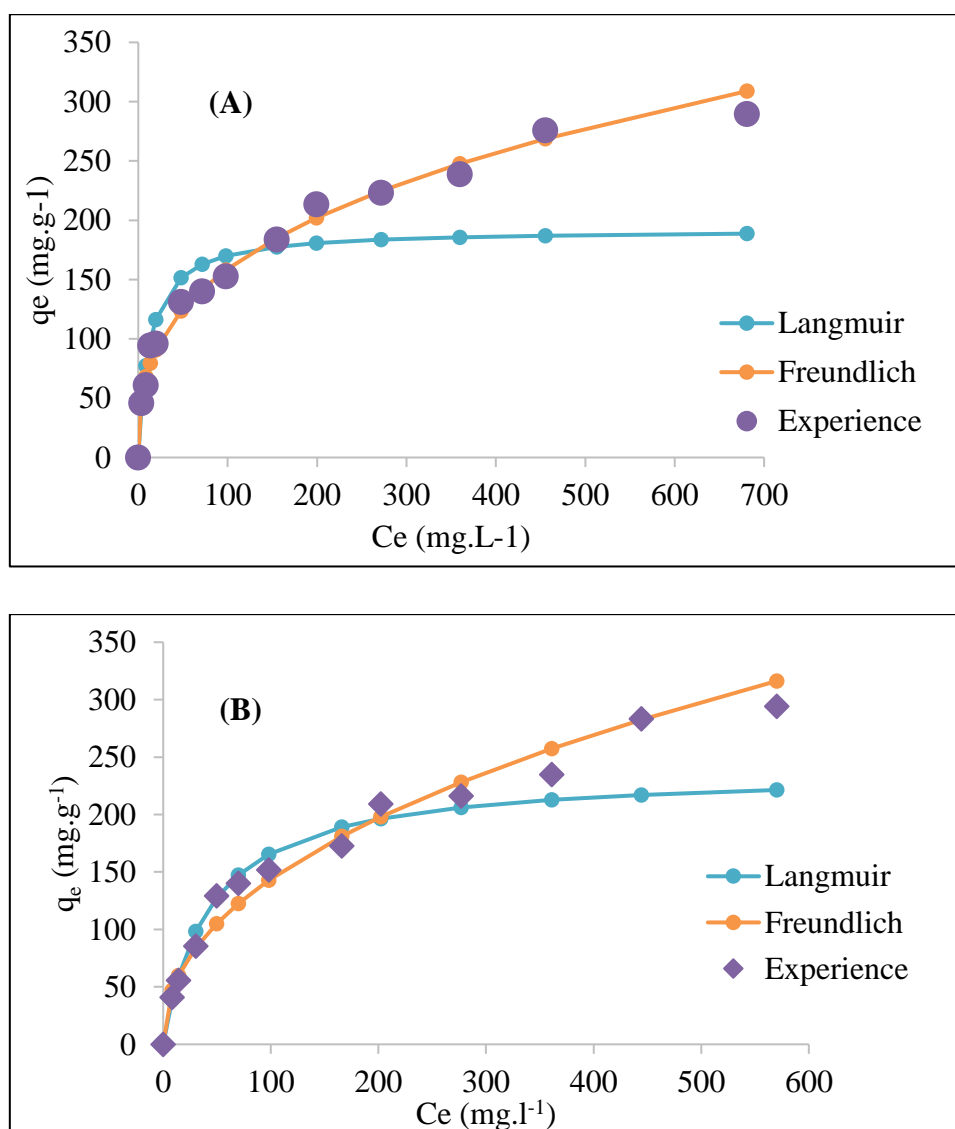
This study was carried out with a wastewater sampled from the domestic sewage treatment plant of Nailloux (Occitanie, France). This effluent was spiked with 2,4-DMP to evaluate bpAC and ACB efficiency in complex medium. The operating conditions were the same as those applied for the study of the synthetic water and its characteristics are detailed in table 8.

**Table 8:** Characteristics of the effluent sampled from the domestic sewage treatment plant of Nailloux [8].

<b>H</b>	8
<b>BOD<sup>a</sup></b> (mg <sub>O2</sub> .l <sup>-1</sup> )	2
<b>COD<sup>b</sup></b> (mg <sub>O2</sub> .l <sup>-1</sup> )	30
<b>Ammonium</b> (mg <sub>N</sub> .l <sup>-1</sup> )	0.9
<b>Nitrogen kjeldahl</b> (mg <sub>N</sub> .l <sup>-1</sup> )	2.1
<b>Nitrates</b> (mg.l <sup>-1</sup> )	1.5
<b>Nitrites</b> (mg.l <sup>-1</sup> )	0.5
<b>Total phosphorus</b> (mg.l <sup>-1</sup> )	0.3
<b>IC</b> (mg.l <sup>-1</sup> )	79

<sup>a</sup>Biochemical Oxygen Demand; <sup>b</sup>Chemical Oxygen Demand.

Compare to the adsorption in synthetic solution, 2,4-DMP adsorption capacity seems higher in real solution than in synthetic solution (Table 7). It is possible that this improvement in solute retention is due to reactions with organic material adsorbed on the activated carbon. Some authors have already noted similar phenomena [57]. Another explanation for this phenomenon could come from the fact that the wastewater used in this study contains nitrite ions (Table 8). Patnaik and Khoury have shown that the simple contact of nitrite ions with phenolic wastewater under ambient conditions, even at trace concentrations, can form nitrophenols [58]. However, it has been shown that the adsorption of phenolic compounds decreases in the following order: nitrophenol > chlorophenol > aminophenol > cresol > phenol [59]. In fact, the higher the electron-attracting group in the aromatic ring, the greater the adsorption capacity of the activated carbons. Electrostatic interactions and hydrogen bonding between the activated carbon surface and solute molecules explain these adsorption data [59,60]. More the withdrawing substituent electron is high in the aromatic ring, the greater the adsorption capacity of the phenolic compound is large [59]. Experimental data and the representations of Langmuir and Freundlich isotherms models are shown in Figure 5.



**Figure 5:** Experimental data and representations of Langmuir and Freundlich isotherms models of bpAC (A) and ACB (B) in wastewater spiked with 2,4-DMP:  $[2,4\text{-DMP}]_0 = (0 \text{ to } 1000 \text{ mg.l}^{-1})$ ;  $V = 100 \text{ ml}$ ;  $\text{pH}_i = 5.3$ ;  $T = 25 \text{ }^\circ\text{C}$ ;  $m_{CA} = 0.1 \text{ g}$

## Conclusion

This study focused on the preparation of activated carbons made from agricultural waste: *borassus* palm tree and bamboo stems. The technique for preparing these activated carbons has shown that only the activating agent has an effect on their adsorption capacities. The performances of the two activated carbons with the best iodine number and methylene blue adsorption (bpAC and ACB) were evaluated through kinetic studies and isotherm adsorption of 2,4-DMP, a molecule chosen as a model pollutant, both in synthetic solution and in wastewater spiked with 2,4-DMP. These activated carbons showed good adsorption performance of 2,4-DMP with maximum capacities ranging from 169 to 227 mg.g<sup>-1</sup> in a synthetic solution and from 192 to 238 mg.g<sup>-1</sup> in a wastewater spiked with 2,4-DMP. Kinetic data are well represented by a pseudo-second-order model. The Freundlich model has described with good precision.

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