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# Adsorption of Methyl Orange and Chromium (VI) onto Activated Carbon Obtained from Eucalyptus Sawdust by Chemical Activation with Zinc Chloride (ZnCl<sub>2</sub>)



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# ABSTRACT

The objective of this work is to prepare an Activated Carbon (AC) from eucalyptus sawdust, having an important pore structure and the best chemical properties for the removal of Methyl Orange (MO) and chromium (Cr-VI) in an aqueous medium. The materials were activated with zinc chloride (ZnCl<sub>2</sub>). The latter were characterized by thermogravimetric analysis, differential thermal and differential scanning calorimetry (TG-DTG-DSC), Fourier transforms infrared (FT-IR), pH at zero charge point (pH<sub>PZC</sub>), iodine number (I12), and methylene blue number (IMB). The evaluation of adsorption capacity consisted of discussing the effects of contact time, solution pH, and the effect of temperature using a batch adsorption technique. In addition, different kinetic models (first-order, second-order, and Intra-particle diffusion) and adsorption isotherms (Langmuir, Freundlich) were applied. Analysis of the TG curve illustrates the presence of hemicellulose, cellulose, and lignin, thus confirming the lignocellulosic structure of Eucalyptus Sawdust. Samples AC1/1, AC1/2, and AC1/3 prove to be the best absorbents. The measurement of their iodine numbers gave, respectively  $I_{12}$  (1269.000, 1395.900, and 1395.900 mg/g) indicating a better microporosity and the specific surface area by iodine adsorption (S<sub>12</sub>, 1282.900, 1411. 200, and 1411.200 m<sup>2</sup>/g) justifies the development of porosity. The pseudo-second-order kinetic model better describes the adsorption of MO and chromium (VI) on AC with  $R^2 = 1$  for MO and  $R^2 \ge 0.9996$  for chromium (VI). The thermodynamic study gave negative values of free energy which justify the feasibility and spontaneity of the adsorption process of MO and chromium (VI) on AC, the positive values of free enthalpy and entropy reflect that the process is endothermic and reflect the good affinity of chromium (VI) on AC due to pore swelling, whereas, negative values indicate that the process is exothermic and indicate an increase in order at the solid/liquid interface. The heat of adsorption value ( $\Delta H^{\circ}$ > 42 kJ mol<sup>-1</sup>) indicates that the chromium (VI) adsorption process on AC is chemical. On the other hand, the adsorption of MO on AC ( $\Delta H^{\circ} < 42 \text{ kJ mol}^{-1}$ ) is of the physical type.

# **INTRODUCTION**

In recent decades, many chemical molecules have been detected and quantified in natural waters and advances in toxicology and epidemiology allow their effects on health to be assessed. Most of these new substances come from the increased production and use of derived natural compounds (fertilizers, metals), as well as new synthetic molecules (pesticides, pharmaceuticals, cosmetics) [1]. Organic pollutants, whether of natural or anthropogenic origin, are dispersed in various compartments of the environment and are likely to seriously affect natural ecosystems and ultimately human health [2].

Adsorption remains one of the most widely used pollutant removal techniques due to its efficiency, ease of implementation, and affordable investment cost. This method requires the choice of an adsorbent having good properties such as zeolites or polymer resins, silica gels, activated aluminas, and Activated Carbon (AC) [3].

AC is cited preferentially among the many materials considered to be the most promising for the elimination of organic and mineral micropollutants [4]. Various studies have been devoted to the production of activated charcoals from lignocellulosic biomass: grape seeds[4], almond shell [5], coconut shell [6], date pits [7], peach stones [8], woods [9], pods of *Flamboyant delonixregia* [10].

AC is obtained either by chemical activation or by physical activation. The physical activation takes place in two stages and at high temperatures between 400-900°C, unlike the chemical activation which takes place at the same time as the carbonization under an inert atmosphere between 400 and 600°C, after impregnation of the precursor by an activating agent such as phosphoric acid [11], zinc chloride [12], alkaline carbonates [13], potassium hydroxide [14], and more recently sodium hydroxide [15]. The chemical activation is followed by the heat treatment step, and finally by a washing step to remove chemical agents and the products of inorganic reactions [16].

The main objective is to prepare activated carbon from eucalyptus sawdust, having an important pore structure and the best chemical properties for the reduction of Methyl Orange (MO) and Chromium (Cr-VI) in an aqueous medium. As a specific objective, we will prepare activated carbons from eucalyptus sawdust by chemical activation with Zinc Chloride (ZnCl<sub>2</sub>),

characterize them, and test the performance of activated carbons prepared for the removal of MO and Cr-VI in an aqueous medium. The adsorption study consisted of discussing the effects of contact time and the pH of the solution using a batch adsorption method. The effect of temperature made it possible to carry out a thermodynamic study to define the nature of the absorption phenomenon. In addition, different kinetics models (first-order, second-order, and Intra-particle diffusion) and adsorption isotherms (Langmuir and Freundlich) were used for the evaluation of adsorption capacity.

#### METHODOLOGY

# **Preparation of Activated Carbon (AC)**

The precursor used in this study for the preparation of AC is eucalyptus sawdust from the Baboaté locality located 6 km from the city of Bafang in the Haut Nkam department of the Cameroon western region the geographic coordinates of the harvesting site are 5°9 '25 N Latitude and 10 ° 10 '37 E Longitude.

The eucalyptus sawdust was first washed to remove impurities and then sun-dried for 5 days to remove all traces of water. After that, it was crushed using a hammer mill type grinder to obtain a powder. A particle size analysis (sieving) was carried out to retain the characterized fine particles with a diameter of 100 µm. The powder obtained was impregnated with zinc chloride using the experimental protocol of Mbaye thesis (2014) [17]. In three beakers of 250 mL each, 10 g of the sieved powder was introduced, followed by 10, 20 and 30 g of zinc chloride previously dissolved in 160 mL of distilled water, the products were obtained by varying the mass ratio (mass of precursor/mass of ZnCl<sub>2</sub>) are called AC1/1, AC1/2 and AC1/3 respectively. The resulting mixture was stirred for 2 h on the magnetic stirrer at room temperature and then dried in an oven at110°C for 48 hours. The impregnated precursor was placed in a ceramic crucible and introduced into a NABERTHERM brand oven and then calcined at a maximum temperature of 450°C with a rise rate of 5°C/min for an hour of residence. At the end of the calcination, the activated carbon obtained was cooled and washed thoroughly with distilled water while controlling the pH until neutralization of the rinsing water pH = 7. The activated carbon obtained was dried in an oven at 110°C for 24 hours, cooled to room temperature then recovered and stored in flasks.

#### Characterization of the powder and prepared activated carbon

Thermogravimetric, Differential Thermal and Differential Scanning Calorimetry (ATG-DTG-DSC) analysis were performed to determine the lignocellulosic constituents (hemicellulose, cellulose and lignin) and the maximum carbonization temperature of the sieved eucalyptus sawdust powder.

The chemical functions present on the surface of the precursor material and the prepared activated carbon are determined by Fourier to transform infrared (FT-IR). The method consists of obtaining pellets by compressing the samples with potassium bromide (KBr). Samples were taken, scanning for wavenumbers from 4000 to 400 cm<sup>-1</sup>, using an FTIR spectrometer.

#### pH at zero charge point

The zero charge point pH (pH<sub>ZCP</sub>) is defined as the pH of the aqueous solution in which the solid exists under neutral electrical potential. It is determined for all activated carbons using the method of Lopez (1999) [18]. For this purpose, 0.1 M NaCl solutions with a pH between 2 and 10 (adjusted by adding an aqueous solution of NaOH or HCl) of 0.1 M were first prepared. The Hanna-type pH meter was used for pH measurement. A volume of 30 mL of a 0.1 M sodium chloride (NaCl) solution was contacted with a mass of 0.05 g of activated carbon and stirred for 8 hours on the magnetic stirrer at room temperature. The mixture was filtered through filter paper (Whatman) and a new pH measurement was taken. The zero point charge pH is determined from the intersection of the curve of  $\Delta$ pH versus the initial pH of the solution.

#### **Iodine number**

The technique used is that of the Duchet Study Center, which is an adaptation of the CEFIC 1989 method and the AWWA B 600 - 78 standard. The samples studied were characterized by measuring the iodine number (mg/g) using a 0.02 N iodine solution. A volume of 50 mL of the iodine solution was treated with a mass of 0.05 g of activated carbon for 4 min. After equilibrium, 10 mL of the iodine filtrate in the presence of a starch solution was titrated with 0.1 N sodium thiosulfate. The iodine number  $Q_{I2}$  (mg/g) can be calculated by the following formula:

$$Q_{12} = \frac{\left(C_{0} - \frac{C_{n}V_{n}}{2V_{I_{2}}}\right) \times M_{I_{2}}V_{abs}}{m_{CA}}$$
(1)

With:  $V_n$ : the volume of sodium thiosulfate (mL),  $C_n$ : the concentration of sodium thiosulfate (0.1 mol/L),  $C_0$ : the concentration of the initial iodine solution (0.02 mol/L),  $V_{I2}$ : the volume of iodine assayed (10 mL), MI<sub>2</sub>: the molar mass of iodine (253.81 g/mol),  $V_{abs}$ : the adsorption volume (20 mL) and  $m_{AC}$ : mass of the activated carbon (g).

Knowing the amount of iodine adsorbed at equilibrium per gram of activated carbon ( $Q_e$ ) leads to the determination of the specific surface area ( $S_{12}$ ) by applying the relationship:

$$S_{I2} = Q_{e.} \sigma N_A / MI_2 (m^2.g^{-1}) = 1, 28.105 Q_e / MI_2 (m^2.g^{-1}).$$
(2)

The area occupied by an iodine molecule is equal to  $\sigma = 21.3 \text{ Å}^2$  and  $N_A = 6,023.10^{23} \text{ mol}^{-1}$  is the Avogadro number and the molar mass of iodine (MI<sub>2</sub>) is 126.9 g/mol.

#### Methylene blue number

The procedure used is that of the CEFIC method with some slight modifications. A mass of 0.05 g of activated carbons was dried in an oven at 110 °C for 24 hours and then mixed with a volume of 50 mL of a methylene blue solution of concentration 30 mg/L. The mixture was stirred magnetically at room temperature for 2 hours. The filtrate was assayed with "SCHOTT Instrument" a brand UV-Visible spectrophotometer at a maximum wavelength of 660 nm. The elimination rate (Rd, %) and the adsorbed amount (Qe, mg/g) of methylene blue were determined by the following formulae:

Rd (%) = 
$$\frac{c_0 - c_g}{c_0} \times 100$$
 (3)

$$Q_e = \frac{c_0 - c_e}{m} \ge V \tag{4}$$

Where:  $C_o$  is the Initial Concentration of BM (mg/L),  $C_e$  is the Concentration of MB in the equilibrium mixture (mg/L), m is the mass of the adsorbent (g) and V is the Volume of the solution containing the MB (mL).

The  $S_{MB}$  specific surface area was estimated by the methylene blue adsorption method from the following equation:

 $S_{BM} = Q_e. A_m. N_A/M_{MB}$  (5) Where:  $S_{MB}$  is the specific surface area determined using MB as adsorbate (m<sup>2</sup>/g); (A<sub>m</sub>) is the air occupied by a molecular number of MB (175 Å<sup>2</sup>), Q<sub>e</sub> is the adsorption capacity of MB (mg/g), N<sub>A</sub> is the Avogadro number (6,023.1023 mol<sup>-1</sup>) and M<sub>MB</sub> is the molar mass of MB of (319.85 g.mol<sup>-1</sup>) [19].

# Ash content

An initial mass of 0.5 g of activated carbon was calcined in an oven at a maximum temperature of 650°C at a heating rate of 5°C/min and a residence time of 3 hours.

The ash content is determined from the following formula:

$$C(\%) = \frac{m_2 - m_0}{m_1 - m_0} \times 100$$
(6)

With:  $m_0$ : mass of the empty crucible,  $m_1$ : mass of crucible + sample before calcination, and  $m_2$ : mass of crucible + sample after calcination.

# Removal of Methyl Orange (MO) and Chromium (VI) on prepared activated carbon

The adsorption of MO and Cr-VI on activated carbon was carried out as follows: a mass of 0.05 g of the AC was brought into contact with a volume of 30 mL of the polluted solution of known concentration. The mixture was stirred magnetically at room temperature for a well-defined time t, then the filtrate was assayed with a UV-Visible spectrophotometer at a maximum wavelength of 350 nm for Cr-VI and 465 nm for OM.

# Kinetic studies of Chromium (VI) and Methyl Orange (MO) adsorption on Activated Carbon

The following three mathematical models were tested to model the adsorption kinetics of methyl orange and Cr-VI on prepared activated carbon.

#### Pseudo-first order kinetic model

The linear form of the pseudo-first-order model is given by the following relation [20]:

$$\operatorname{Ln}\left(\mathbf{Q}_{\mathrm{e}}-\mathbf{Q}_{\mathrm{t}}\right)=\operatorname{Ln}\mathbf{Q}_{\mathrm{e}}-\mathbf{K}_{1}\,\mathrm{t}\tag{7}$$

With:  $k_1$  the rate constant for pseudo-first-order kinetics (min<sup>-1</sup>)  $Q_t$  and  $Q_e$  the adsorption capacities at time t (mg of adsorbate/g of adsorbent] and at equilibrium (mg of adsorbate/g of adsorbent), respectively. The constants of the model are determined graphically by plotting Ln ( $Q_e$ - $Q_t$ ) as a function of t. In addition, the half-adsorption time at equilibrium ( $t_{1/2}$ , min) and the difference between the adsorption capacities at equilibrium ( $\Delta q$ ) are determined by the following equations:

$$t_{1/2} = \frac{Ln2}{K_1} = \frac{0,693}{K_1}$$
(8)

$$\Delta q = \left| \mathbf{Q}_{\text{emax}} (\exp) - \mathbf{Q}_{\text{e}} (\operatorname{th}) \right| \tag{9}$$

Where:  $Q_{emax}$  (exp) is the adsorption capacity obtained experimentally and  $Q_e$  (th) is the theoretical adsorption capacity deduced from the kinetic relationships.

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# Pseudo-second order kinetic model

#### The linear form of the pseudo-second-order model is described by the following equation [21]:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_g^2} + \frac{1}{Q_g} t \tag{10}$$

Where:  $k_2$  is the rate constant for second-order kinetics  $(g.mg^{-1}.min^{-1})$ ,  $Q_t$  and  $Q_e$ : The adsorption capacities at time t (mg of adsorbate/g of adsorbent) and at equilibrium (mg of adsorbate/g of adsorbent), respectively. The adsorption kinetic rate constant  $K_2$ , as well as the amount of solute adsorbed at equilibrium Qe, are determined experimentally from the plot of t/Qe = f(t). Thus, the half-adsorption time  $(t_{1/2})$  in (min<sup>-1</sup>), the difference ( $\Delta q$ ) (equation 9) and the initial adsorption rate (h) in (mg. $g^{-1}min^{-1}$ ) are obtained from the following relations:

$$t_{1/2} = \frac{1}{K_2 Q_{\theta}(th)} \tag{11}$$

$$\mathbf{h} = \mathbf{K}_2 \cdot \mathbf{Q} \mathbf{e}^2 \ (\mathbf{t}\mathbf{h}) \tag{12}$$

#### Kinetic model of intra-particle diffusion

The linear model of intra-particle diffusion is given by the following equation [22]:

$$Q_{t} = K_{d} \times t^{1/2} + I \tag{13}$$

Where:  $K_d$  is the intra-particle diffusion rate constant (mg. $g^{-1}$ . $min^{-1/2}$ ) and I is the constant related to the thickness of the boundary layer (mg/g).

The representation of  $Q_t$  as a function of  $(t^{1/2})$  makes it possible to calculate  $K_d$ , I and to highlight the different stages of the adsorption process.

### Chromium (VI) and methyl orange adsorption isotherms on activated carbon

# Langmuir model

The linear form of the Langmuir isotherm is described by the following equation [23]:

$$\frac{1}{Q_{\varepsilon}} = \frac{1}{\kappa_L Q_{max} c_{\varepsilon}} + \frac{1}{Q_{max}}$$
(14)

 $I = I \land A \land A$ 

Where:  $C_e$  is the concentration of the solute at equilibrium (mg/L),  $Q_e$  is the amount of solute adsorbed per unit mass of adsorbent (mg/g),  $Q_{emax}$  is the maximum theoretical adsorption capacity (mg/g) and  $K_L$  is the Langmuir constant of the adsorption equilibrium (L/mg).

The lines are obtained from the plot of  $\frac{1}{Q_{\varepsilon}} = f(\frac{1}{C_{\varepsilon}})$ .

# Freundlich model.

The linear form of the Freundlich isotherm is given by the following expression [24]:

$$\log(\mathbf{Q}_{e}) = \log\left(\mathbf{K}_{F}\right) + \frac{1}{n_{f}}\log\left(\mathbf{C}_{e}\right)$$
(15)

Where:  $n_F$  is the constant indicative of the adsorption intensity, Ce is the Concentration of the equilibrium solute (mg/L) and  $K_F$  is the constant relating to the adsorption capacity of the adsorbent (Freundlich constant ) ( $mg^{1-(\frac{1}{n})} L^{1/n} g^{-1}$ ). The parameters  $K_F$  and  $n_F$  are determined from the graphical representation of log ( $Q_e$ ) = f (log ( $C_e$ )).

# Thermodynamic aspects of adsorption of chromium (VI) and methyl orange on activated carbon

The thermodynamic parameters such as variation of free energy ( $\Delta G^{\circ}$ ), free enthalpy ( $\Delta H^{\circ}$ ), and entropy ( $\Delta S^{\circ}$ ) were determined from the following equations:

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{16}$$

$$Ln K_{d} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$
(17)

$$K_{d} = \frac{Q_{e}}{C_{e}}$$
(18)

Where:  $\Delta G^{\circ}$  is the change in free energy (kJ. mol<sup>-1</sup>),  $\Delta H^{\circ}$  is the change in free enthalpy (kJ. mol<sup>-1</sup>),  $\Delta S^{\circ}$  is the change in entropy (k<sup>-1</sup>. J. mol<sup>-1</sup>.), R is the ideal gas constant (8.314 J. mol<sup>-1</sup>. K<sup>-1</sup>), T is the absolute temperature (°K), It is the concentration of the adsorbate at equilibrium (mg.L<sup>-1</sup>) and Q<sub>e</sub> is the adsorption capacity of the adsorbate at equilibrium (mg. g<sup>-1</sup>).

The values of  $\Delta H^{\circ}$  and  $\Delta S^{\circ}$  were determined from the plot of Ln K<sub>d</sub> = f (1/T).

#### **RESULTS AND DISCUSSION**

#### Characterization of the powder of eucalyptus sawdust and prepared activated carbon

#### Thermogravimetric analysis

Figure 1 shows the thermogram coupled to TG/DTG/DSC of eucalyptus sawdust powder.



Figure 1: Thermogram analysis of eucalyptus sawdust powder coupled with TG/DTG/DSC

It follows from the coupled TG/DTG/DSC analysis of the eucalyptus sawdust powder that the thermogram is subdivided into four stages: the first mass loss at 9.51 % marked by endothermic peaks around 66 to 169°C could be due to the dehydration reaction. This is explained by the departure of the moisture contained in the biomass, as well as the water molecules said to be linked by physical van Der Waals bonds, which leave at a temperature slightly above 100°C. The second mass loss at 58.93 % marked by an exothermic peak around 310°C could be attributed to the degradation of the hemicelluloses. This high temperature is explained by its low hemicellulose content. Then, the third mass loss at 20.87 % marked by an exothermic peak around 401°C could be that of the thermal decomposition of cellulose. Finally, the fourth mass loss at 4.40% manifested by an exothermic peak around 448°C could be the thermal decomposition of hemicellulose is in contradiction with the results of Tang and Bacon (1964) who showed that the thermal decomposition of cellulose is between 240 and 350°C and lignin degradation is between 200 and 500°C [25]. The latter is consistent with the thermal decomposition of lignin in eucalyptus sawdust.

We can conclude that our precursor material contains hemicellulose, cellulose and lignin thus confirming the lignocellulosic structure. Furthermore, this analysis allowed us to obtain the maximum calcination temperature of around 450°C. Beyond this temperature, we observe

stability on the thermogram which means that all the cellulose has decomposed as well as all the hemicelluloses.

#### Analysis of the FTIR spectra obtained

The FTIR spectra of the powder and activated carbon prepared from the recorded eucalyptus sawdust are shown in Figure 2 below.



Figure 2: FT IR spectra of eucalyptus sawdust powder and prepared activated carbon

The treatment of eucalyptus sawdust impregnated with ZnCl<sub>2</sub> causes an apparent effect on the infrared spectra, and a change in the structure of the eucalyptus sawdust. The peak at 3309 cm<sup>-1</sup> observed on the AC<sub>0</sub>, which corresponds to the valence vibration of the O-H bonds, undergoes a strong decrease in intensity until it disappears completely after impregnation. Since this peak corresponds to all hydroxyls, primary and secondary, the disappearance of the band can be explained by the conversion of some of the primary alcohols to carboxylic acid and the thermal decomposition of water. A vibration band detected at 1740 cm<sup>-1</sup> corresponds to the stretching of the carboxylic acid and ester (C-O) groups contained in raw eucalyptus sawdust [26]. This peak, which is related to the ester functions of hemicelluloses, gradually decreases until it disappears after modification of the eucalyptus sawdust. This suggests that the acid content has decreased resulting in the elimination of the carboxyl groups present in the hemicellulose. Monties (1980)

reports that hemicelluloses contain carboxyl groups that are absorbed in this region and are soluble in inorganic aqueous solutions [27]. It is not the same, the peak at 601 cm<sup>-1</sup> corresponds to the deformation of sulfonyl chlorides (SO<sub>2</sub>Cl<sub>2</sub>). However, there follows a peak at 1614 cm<sup>-1</sup> which can be attributed to the elongation vibrations of C = O of ketones, aldehydes, lactones, or carboxylic groups or C = N of amines. The absorption peaks observed at 1582-1573 cm<sup>-1</sup> correspond to the vibrations of elongation of C = C bonds in aromatic rings. Thus, the peaks at 1255-1227 cm<sup>-1</sup> which correspond to the C-O elongation of the acetyl groups of the C-O lignin of the aliphatic ring of cellulose undergo an increase after treatment [28]. An intense band at 1042 cm<sup>-1</sup> with a shoulder on AC<sub>0</sub> corresponds to the extremity of the stretching modes of the hydroxyl and ether groups CO These peaks are characteristic of the absorption of cellulose and appear to be changed after impregnation and calcination of eucalyptus sawdust. However, the corresponding bands at 478-442 cm<sup>-1</sup> could be the deformation of the C-O-C ethers of amines and C-N-C. Thus, the peaks at 425-421 cm<sup>-1</sup> correspond to the in-plane strain of Cl-C = O acid chlorides. These characteristic peaks could be due to the activator used as it is absent in eucalyptus sawdust.

It appears from all these changes in the FTIR spectra that treatment with zinc chloride has a significant influence on the structure of eucalyptus sawdust. The presence of lignin, hemicellulose, and cellulose in the eucalyptus sawdust ( $AC_0$ ) matrix confirms the lignocellulosic structure obtained at ATG.

# pH at zero charge point

The pH at zero charge point (pH<sub>ZCP</sub>) obtained for each mass ratio is compiled in Table 1 below.

Table 1: pH result at zero charge point of activated carbons

Activated carbon	AC1/1	AC1/2	AC1/3
pH <sub>PCN</sub>	2.9	2.4	2.1

The  $pH_{PCN}$  values obtained make it possible to determine the acidic or basic character of an AC and to know, depending on the pH of the solution, its net surface charge. It emerges from Table 1 that all the activated carbons prepared have an acidic character. This could be attributed to a high content of phenolic carboxylic acid groups and lactones present in the material. This was

confirmed by FTIR analysis. In addition, most authors agree in concluding that there is a decrease in pH<sub>PCN</sub> when the oxygen content of the carbons increases, which would tend to confirm that the basicity of the carbons is more linked to sites rich in  $\pi$  electrons than to functions of surface oxygenates [18,29]. Thus, for manipulations at pH = 2 and 3 all ACs will have their positively charged surface (pH<sub>PCN</sub> > pH) while at (pH<sub>PCN</sub> < pH), they will have a negatively charged surface. This can be of great importance in the interactions between molecules/adsorbent material in the liquid phase. This explains the high adsorption capacity of MO and Cr-VI at low pH values in the aqueous medium.

# Iodine and methylene blue number, specific surface area and ash content of activated carbon

The experimental results of iodine and methylene blue number, specific surface area and ash content of activated carbon are summarized in Table 2 below.

Table 2: Value	s of iodine an	d methylene	blue	number,	specific	surface	area and	ash	content	of
activated carbon	1		X							
			\ <b>\</b> .	1.10						

	4. S. Anadonikashi, J. F.		
Activated carbon	AC1/1	AC1/2	AC1/3
Iodine number (Q <sub>12</sub> , mg. g <sup>-1</sup> )	1269.00 A	1395.90	1395.90
Specific surface area ( $S_{12}$ , $m^2$ . $g^{-1}$ )	1282.90	1411.20	1411.20
Methylene blue number $(I_{MB}, mg. g^{-1})$	14.65	14.62	14.74
Specific surface area (S <sub>MB</sub> , m <sup>2</sup> . g <sup>-1</sup> )	48.26	48.20	48.61
MB rate (%)	97.64	97.45	98.34
Ash content (%)	1.80	0.80	2.60

The iodine value results presented in Table 2 show that the ZnCl<sub>2</sub> concentration influences the structure of eucalyptus sawdust. Indeed, the increase in the ZnCl<sub>2</sub> concentration promotes an increase in the iodine number of ACs, thus developing more micropores. By comparing these values (1269.00 for AC1/1 and 1395.90 for AC1/2 and CA1/3) with those found in the literature (550 mg/g) we can say that our activated carbons comply with the standards of iodine number of activated carbons and this justifies their good adsorbing power [30]. It appears that all our prepared activated carbons have their high iodine numbers as well as their specific surfaces and

therefore are more likely to adsorb small molecules (iodine) such as those responsible for tastes and odors [31].

The values of the methylene blue number given in Table 2 show that the increase in the ZnCl<sub>2</sub> concentration is not significant in the structure of eucalyptus sawdust. Activated carbons prepared from eucalyptus sawdust contain more mesopores and therefore are capable of efficiently absorbing large and medium-sized organic molecules. The values of the elimination rate ( $\geq$  97.45%) obtained are almost similar to those reported in the work of Tchieta *et.al* (2019) [32].

The ash levels obtained are relatively very low at around 2 % for all the activated carbons prepared. The low ash content implies that the biomass consists mainly of organic matter, and therefore of the majority element carbon. This parameter has a significant effect on the quality of AC. As a result, an increased ash content decreases the specific surface. This is because the pores of the carbonaceous structure are blocked by inorganic ash materials that make the activation process difficult [33]. The same results were obtained by Tchieta *et.al* (2019) [32].

# Adsorption of methyl orange and chromium (VI) on activated carbon in batch mode

# **Study of adsorption kinetics**



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**Figure 3:** Influence of contact time on the adsorption capacity of methyl orange (a) and Chromium (VI) (b) on activated carbon, experimental conditions ( $m_{AC} = 0.05$  g, C = 30 mg/L, V = 30 mL and T =  $25 \pm 2$  °C)

Because of these results, we can also note that the kinetics present two distinct stages. The first step is fast and corresponds to the external mass transfer while the second is slow and is related to the phenomenon of diffusion (internal mass transfer). During the first stage, there is a rapid increase in the adsorption capacity of MO and Cr-VI up to about 10 minutes for all three activated carbons. The high adsorption capacity of MO and Cr-VI on the three activated carbons could be due to the number of vacant sites available on the surface of the activated carbon as well as the pore size due to the fact that the activated carbon is mesoporous and microporous [34-35]. This ties in with the work of Le Cloirec (1985) which shows that organic compounds adsorb well on activated carbon [36]. The contact time for the adsorption of Cr-VI is similar to the work reported by Babel et. al (2004) on the adsorption of Cr-VI ) on commercial activated carbon and activated carbon from coconuts activated by the sulfuric acid [37]. In addition, during the second phase, the adsorption capacity of MO and Cr-VI increases more slowly and then reaches a level indicating saturation of the adsorbent of around 20 and 40 minutes for MO and Cr-VI, respectively. This could be justified by the fact that all adsorption sites become occupied in the presence of a high content of MO and Cr-VI [38]. Beyond that, the quantity adsorbed remains practically constant for up to 60 minutes of reaction. In the rest of our study, we will work with a time of 60 minutes.

To determine the kinetic model of adsorption of MO and Cr-VI on activated carbon, we applied the kinetic models of pseudo-first-order and pseudo-second-order adsorption and the intraparticle diffusion phenomenon.

The experimental results are shown in Figure 4. and the adsorption kinetics parameters including the correlation coefficient R<sup>2</sup> are compiled in Table 2 below:



**Figure 4.** A: Kinetic model of the pseudo first order adsorption of methyl orange (a) and chromium (VI) (b) on AC, experimental conditions ( $m_{AC} = 0.05$  g, C = 30 mg/L, V = 30 mL,T =  $25 \pm 2$  °C)



**Figure 4.B:** Kinetic model of the pseudo second order adsorption of methyl orange (a) and chromium (VI) (b) on AC, experimental conditions (mCA = 0.05 g, C = 30 mg / L, V = 30 mL, T =  $25 \pm 2$  °C)



Figure 4. C: Kinetic model of intra-particulate adsorption adsorption of orange methyl (a) and chromium (VI) (b) on AC, experimental conditions ( $m_{AC} = 0.05$  g, C = 30 mg / L, V = 30 mL, T =  $25 \pm 2$  °C)

**Table 3:** Kinetic parameters of adsorption of orange methyl and chromium (VI) on activatedcarbon and correlation coefficient  $R^2$ 

Madala	Doromtors	AC1/1-	AC1/2-	AC1/3-	AC1/1-	AC1/2-	AC1/3-	
Models	Paramers	ОМ	OM	OM	KD	KD	KD	
	<b>R</b> <sup>2</sup>	0.8465	0.9887	0.9785	0.3838	0.6968	0.9733	
	$K_1 (min^{-1})$	0.0462	0.0419	0.0372	0.0717	0.0531	0.0535	
	$Q_e$ (th) (mg/g)	0.1438	0.2070	0.1736	1.9090	1.6788	4.0947	
Pseudo-first	Qe max (exp)	17.0870	17 9817	17 9870	17.941	17.825	17 6516	
order	(mg/g)	17.9070	17.9017	17.9070	9	8	17.0510	
order	$t_{1,2}$ (min)	15,0000	16 5428	18 6320	16.032	16.140	13 5560	
	t <sub>1/2</sub> (mm)	15.0000	10.3420	10.0320	8	0	13.3300	
	40	17 8/132	17 7747	17 8133	9 6670	13.678	12 9560	
		17.0432	1/.//+/	17.0155	2.0070	8	12.9500	
	<b>R</b> <sup>2</sup>	1.0000	1.0000	1.0000	0.9996	0,.998	0.9998	
	K <sub>2</sub> (g/mg.min)	0.9090	0.5600	0.6200	0.0630	0.0632	0.0632	
	Qe (th) (mg/g)	17 9860	18.0200	17.9860	18.050	18.050	18.0500	
		17.9000	10.0200		0	0		
Pseudo-	Q <sub>emax</sub> (exp)	17 9860	17 9870	17 9870	17.941	17.825	17.6516	
second order	(mg/g)		110,010	1119010	9	8		
	ΔQ	0.0010	0.0330	0.0010	0.1080	0.2240	0.3980	
	h (mg/g.min)	294.06	181.8400	200.5600	0.8790	0.8766	0.8766	
	$t_{1/2}$ (min)	0.0611	0.0990	0.0896	20.525	20.590	20 5900	
	t1/2 (mm)				0	0	20.5700	
Intra- diffusion Particulate	<b>R</b> <sup>2</sup>	0.7854	0.9831	0.9881	0.7500	0.4908	0.9035	
	K <sub>d</sub>	0.0242	0.0292	0.0240	0 3978	0 4647	0.6100	
	$(mg/g.min^{1/2})$	0.0242	0.0272	0.0240	0.3770	0.4047	0.0100	
	I(mg/g)	17.8120	17,9551	17,7950	15.175	14.761	13,2740	
	- (	17.0120	11.7001	11.1750	0	0	10.2710	

It emerges from figure 4 (a) that, all the lines are not linear and table 3 gives the satisfactory values of the correlation coefficients ( $R^2 \ge 0.9733$ ) on the adsorption of methyl orange on AC1/2 and AC1/3 and chromium (VI) on AC1/3 but a large relative difference ( $\Delta q \ge 9.6670$ ) indicates the non-conformity of the experimental and theoretical values; the kinetic rate constant is low and the half-adsorption time is long. So the pseudo-first-order model does not better describe the removal of MO and Cr-VI on activated carbon.

As for the pseudo-second-order model, the results obtained show perfect linearity of the regression lines of all the activated carbons prepared, correlation coefficients are much better  $R^2 = 1$  for the MO on CA and  $R^2 \ge 0$ , 9996 for Cr-VI very close to unity, the different deviations ( $\Delta q \le 0.3980$ ) are small (the Qe calculated from the 2nd order kinetic equation are consistent with those obtained experimentally). We can conclude that the two adsorption mechanisms (CA/MO and Cr-VI is best described by the pseudo-second-order kinetic model, which is generally used to describe chemisorption phenomena, which is in agreement with the results obtained by the effect of pH on the adsorption of MO and Cr-VI [39].

However, the correlation coefficient associated with the intra-particle diffusion model ( $\mathbb{R}^2 \leq 0.9881$ ) for MO on AC1/2 and AC1/3 and  $\mathbb{R}^2 = 0.9035$  for Cr-VI on AC1/3 is quite significant, which implies that there are certainly intra-particle diffusion phenomena which occur during adsorption [40]. The existence of this intra-particle diffusion in the internal porosity of the activated carbon is supported by the presence of demonstrated mesopores which are known to promote the diffusion of the species which are then adsorbed in the micropores. Many studies reported in the literature are in agreement with these results [41].

# Effect of solution pH

The experimental results of adsorption of MO and Cr-VI on activated carbon are shown in Figure 5.



**Figure 5:** Influence of pH on the adsorption capacity of methyl orange (a) and Chromium (VI) (b) on activated carbon, experimental conditions ( $m_{AC} = 0.05$  g, C = 30 mg/L, V = 30 mL, t = 60 min, T = 25 ± 2 °C)

Figure 6 shows the influence of the pH of the solution on the adsorption capacity of MO and Cr-VI on the prepared AC. The trend of the curves is the same for methyl orange and chromium (VI) and it is clear for all the curves that the adsorption capacity is high for low pH values (pH = 2 for MO and pH = 3 for Cr-VI. This phenomenon confirms that the pH of the solution is an important factor that strongly affects the adsorption of metal ions and organic compounds to the surface of activated carbon. On the one hand, it affects the solubility of these ions and their speciation in an aqueous solution, and on the other hand, it controls the overall surface charge of

AC [42]. Indeed, activated carbons are materials of an amphoteric nature [42]. Their surfaces can be positively or negatively charged depending on the pH of the solution which governs the acidbase balances of the many surface functional groups located on the porous walls of the activated carbons. Furthermore, the analysis of pH<sub>PZC</sub> (Table 1) reveals that the three activated carbons AC1/1 (pH<sub>PZC</sub> = 2.9), AC1/2 (pH<sub>PZC</sub> = 2.4) and AC1/3 (pH<sub>PZC</sub> = 2.1) have an acidic character, which implies the presence of acidic surface functions (-OH, -NH<sub>2</sub> and -COOH) this was confirmed by the FTIR analysis. Therefore, the decrease in adsorption capacity of MO and Cr-VI with increasing pH can be explained by the fact that the further away from pH<sub>PZC</sub> to lower pH values, the greater the Positive charge density at the surface of the carbon increases and therefore promotes electrostatic interactions between C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>O<sub>2</sub>SO<sup>-</sup> ions, chromium ions (HCrO<sub>4</sub><sup>-</sup>,  $CrO_4^{2-}$ ) and the surface of activated carbon. In other words, as the number of H<sup>+</sup> ions increases with the lowering of the pH of the solution, this neutralizes the negative charge on the surface of the activated carbon and therefore limits the electrostatic repulsion of the ions and promotes their adsorption to the surface. The dominant form of orange methyl at pH = 2 is  $C_{14}H_{14}N_3O_2S-O^2$ , chromate ion at pH = 3 is HCrO<sub>4</sub>, which is, therefore, the form of MO and hexavalent chromium adsorbed on the surface of activated carbon at this pH. The decrease in the MO qnd Chromium adsorption capacity with increasing pH may be due to increased negative charge density at the surface of ACs as well as to increasing the number of OH<sup>-</sup> ions in solution that compete with C<sub>14</sub>H<sub>14</sub>N<sub>3</sub>O<sub>2</sub>S-O<sup>-</sup>, chromate and hydrogen chromate ions for adsorption. These observations confirm that the adsorption of MO and hexavalent chromium ions on activated carbon involves chemisorption phenomena, involving valence forces through the sharing or exchange of electrons between the surface of the activated carbon and ions, which is generally the case for the adsorption of metal ions on activated carbon [39]. The results obtained are similar to the work of Aboua (2013) on the removal of dyes and chromium ions in an aqueous solution on AC [42-43].

#### Absorption isotherms of MO and Cr-VI on AC

The experimental results are shown in Figure 6 below and the parameters of both isotherm models used including the correlation coefficient  $R^2$  are grouped in Table 3 below.



Figure 6: Adsorption isotherms of methyl orange (a) and chromium (VI) (b) on activated carbon according to Langmuir experimental conditions ( $m_{AC} = 0.05$  g, t = 60 min, V = 30 mL, T = 25 ± 2 °C pH = 2 for MO and pH = 3 for Cr-VI)



**Figure 6 B:** Adsorption isotherms of MO (a) and Cr-VI (b) on activated carbon according to Freundlich experimental conditions ( $m_{AC} = 0.05$  g, t = 60 min, V = 30 mL, T = 25 ± 2 °C, pH = 2 for MO and pH = 3 for Cr-VI)

Models	Donomitons	AC1/1-	AC1/2-	AC1/3-	AC1/1-	AC1/2-	AC1/3-
	Paramers	ОМ	ОМ	ОМ	KD	KD	KD
	$\mathbb{R}^2$	0.9935	0.9876	0.9854	0.9506	0.9216	0.9192
	$Q_{max}$ (mg/g)	-	-	-	-	-	-
Langmuir	K <sub>L</sub> (l/mg)	-	-	-	-	-	-
	R <sub>L</sub>	-	-	-	-	-	-
	$\mathbb{R}^2$	0.9749	0.9874	0.9859	0.9430	0.9612	0.9708
	$K_{\rm F} ({\rm mg}^{-1-(1/n)})$	0.8506	0.2856	0.7620	2.2020	2.0200	1.0000
Freundlich	Nf	0.9900	0.9380	0.9110	0.9430	0.9760	0.6670
	1/nf	1.0101	1.0655	1.0978	1.0606	1.0245	1.4989

**Table 4:** Parameters of the adsorption isotherms of methyl orange and Chromium (VI) and correlation coefficient R<sup>2</sup>

Regarding the Langmuir model, Table 4 gives the satisfactory values of the correlation coefficients ( $R^2 \leq 0.9935$ ) on the adsorption of MO and Cr-VI on all activated carbons. However, the maximum amount of MO and Cr-VI adsorbed  $Q_{max}$  could not be determined because the intercept is negative. This could be due to the weight of the isotherm points corresponding to the very low concentrations of MO and Cr-VI. In this case, the determination of  $Q_{max}$  is not possible because the absorption capacity  $Q_{max}$  cannot take negative values. Likewise, the K<sub>L</sub> parameter could not be determined because it is deduced using  $Q_{max}$ . The same for R<sub>L</sub> [44]. Similar results have been reported by **Tchieta and al (2019)** [32].

According to the Freundlich model, the values of the Freundlich parameter  $n_f$  are less than unity and between 0.6670 and 0.9900 (Table 4); indicating that the isotherms obtained for these adsorbents are of type L ( $n_f < 1$ ), a type characteristic of the microporous adsorbent (pore radius <20 A°). This, therefore, means a decrease in the available adsorption sites when the concentration of the solution increases. The adsorption of MO and Cr-VI is therefore not linear; and appears to be of the monomolecular type, the solid being saturated when filling the monolayer. There will therefore be weak interactions at the surface of these supports [45]. The values of  $k_F$  vary between 0.2856 and 2.2020. These data thus making it possible to classify the various activated carbons studied according to the adsorption capacity. The decreasing order is therefore as

follows: AC1/1 > AC1/3 > AC1/2 for MO and AC1/1 > AC1/2 > AC1/3 for chromium (VI). However, the values of the satisfactory correlation coefficients ( $R^2 \ge 0.9430$ ) indicate that the adsorption process of MO and Cr-VI on activated carbon is better described by the Freundlich model, while the negative constants Langmuir model imply its inadequacy for the adsorption of MO and Cr-VI on activated carbon.

#### Thermodynamic parameters

The experimental results of adsorption of MO and Cr-VI on activated carbon are shown in Figure 7 and the thermodynamic parameters are summarized in Table 5 below.



**Figure 7:** Representation of Ln (K<sub>d</sub>) as a function of (1/T) of methyl orange (a) and Chromium (VI) (b) on activated carbon, experimental conditions (mCA = 0.05 g, C = 30 mg / L, V = 30 mL, t = 60 min, pH = 2 for OM and pH = 3 for Cr-VI)

activated carbon	Temperature (°K)	$\Delta G^{\circ}$ (kj/mol)	$\Delta H^{\circ}$ (kj/mol)	$\Delta S^{\circ}$ (j/mol °k)	
	303.0000	-2.9955			
	308.0000	-3.2639		156 7190	
	313.0000	-3.5538			
AC1/1-KD	323.0000	-3.7960	45.0410	130./189	
	333.0000	-6.9756	7		
	303.0000	-3.1016			
	308.0000	-3.6827			
	313.0000	-4.0113			
AC1/2-KD	323.0000	-4.6859	46.5916	163.0456	
	333.0000	-6.9756			
	303.0000	-1.6756			
	308.0000	-2.8382	7		
	313.0000	-3.5538			
AC1/2 KD	323.0000	-4.3630	47.9734	156.0787	
AC1/3-KD	333.0000	-5.2000			
	303.0000	-16.7621			
	308.0000	-12.0438			
	313.0000	-13.1190			
AC1/1-OM	323.0000	-16.0050	-99.3689	-274.8774	
	333.0000	-4.5843			
	303.0000	-15.0140			
	308.0000	-15.2617			
	313.0000	-15.5095			
AC1/2-OM	323.0000	-13.5881	-46.1693	-100.7573	
	333.0000	-12.3213			
	303.0000	-12.6998			
	308.0000	-15.2617			
	313.0000	-15.5095			
AC1/3-OM	323.0000	-13.5381	-28.4172	-46.0437	
	333.0000	-12.3213			

**Table 5:** Thermodynamic parameters ( $\Delta G^{\circ}$ ,  $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$ ) of adsorption of MO and Cr-VI on AC

Negative values of the free enthalpy  $\Delta H^{\circ}$  indicate that the adsorption processes are exothermic; while, negative values of free energy ( $\Delta G^{\circ}$ ), indicate the feasibility and spontaneity of the adsorption process of methyl orange on all activated carbons; increasing these values with increasing temperature indicates that adsorption occurs better at lower temperatures [46]. On the

other hand, negative values of  $\Delta S^{\circ}$  entropy again indicate that the adsorption process is spontaneous, and justify an increase in order. This suggests that adsorption causes an increase in order and that MO molecules at the solid-liquid interface are more organized than those in the liquid phase.

On the other hand, the positive values of the free enthalpy  $\Delta H^{\circ}$  confirm that the adsorption processes are endothermic; however, negative free energy values ( $\Delta G^{\circ}$ ) indicate the feasibility and spontaneity of the Cr-VI adsorption process on all activated carbons; A decrease of these values with increasing temperature indicates that adsorption occurs better at higher temperatures. Therefore, positive values of  $\Delta S^{\circ}$  entropy denote an increase in disorder at the solution/solid interface during the adsorption process. This reflects the good affinity of Cr-VI to AC and indicates the randomness at the solid/liquid interface during Cr-VI adsorption on the different ACs used [47].

Moreover, the examination of the values of the enthalpies of absorption ( $\Delta H^{\circ} > 42 \text{ kJ/mol}$ ) for the adsorption of Cr-VI on all the ACs shows that it is chemisorption; in agreement with the results obtained on the influence of pH, while it is physisorption for the adsorption of methyl orange on all CAs Car, the adsorption of physical type is characterized by the heat of adsorption ( $\Delta H^{\circ} < 42 \text{ kJ mol}^{-1}$ ) [48].

#### CONCLUSION

The objective of this work was to prepare AC from eucalyptus sawdust, having an important pore structure and the best chemical properties for the reduction of MO and Cr-VI) in an aqueous medium.

As a result, an Analysis of the TG curve illustrates the presence of hemicellulose, cellulose and lignin, thus confirming the lignocellulosic structure. Samples AC1/1, AC1/2 and AC1/3 prove to be the best absorbents. The measurement of their iodine numbers gave, respectively I<sub>I2</sub> (1269.000, 1395.900 and 1395.900 mg/g) indicating a better microporosity and the specific surface area by iodine adsorption (S<sub>I2</sub>, 1282.900, 1411. 200 and 1411.200 m<sup>2</sup>/g) justifies the development of porosity. The pseudo-second-order kinetic model better describes the adsorption of MO and Cr-VI on AC with  $R^2 = 1$  for MO and  $R^2 \ge 0.9996$  for Cr-VI. The thermodynamic study gave the negative values of free energy which justify the feasibility and spontaneity of the

adsorption process of MO and Cr-VI on AC, the positive values of free enthalpy and entropy reflect that the process is endothermic and reflect the good affinity of Cr-VI on AC due to pore swelling, whereas, negative values indicate that the process is exothermic and indicate an increase in order at the solid / interface liquid. The heat of adsorption value ( $\Delta H^{\circ}$ > 42 kJ mol<sup>-1</sup>) indicates that the Cr-VI adsorption process on AC is chemical. On the other hand, the adsorption of MO on AC ( $\Delta H^{\circ} < 42$  kJ mol<sup>-1</sup>) is of the physical type.

#### REFERENCES

[1] Legube, B. (2017). La production d'eau potable, un enjeu majeur de santé publique, Encyclopédie de l'Environnement, http://www.encyclopedieenvironnement.org/?p = 4784.

[2] Khelili, H., achour, S. (2010). «Efficacité du sulfate d'aluminium et du charbon actif face à des polluants organiques aromatiques", *Larhyss Journal*, 9, 99-110.

[3] MAMANE, O. S., ZANGUINA, A., DAOU, I., I NATATOU, I. (2016). J. Soc. Ouest-Afr. Chim., 041, 59 – 67.

[4] Al Bahri, M., Calvo, L., Gilarranz, M., A., Rodriguez, J. J. (2012)." Activated carbon from grape seeds upon chemical activation with phosphoric acid: Application to the adsorption of diuron from water". *Chemical Engineering Journal*, 203, 348-356.

[5] Martínez de Yuso, A., Rubio, B., Teresa Izquierdo, M. (2014). "Influence of activation atmosphere used in the chemical activation of almond shell on the characteristics and adsorption performance of activated carbons". *Fuel Processing Technology*, 119, 74-80.

Cazetta, LA., Junior, PO, Vargas, MMA., Da silva, PA., Zou, X., [6] Asefa, Т., Almeida, CV. (2013). "Thermal regeneration study of high surface area activated carbon obtained from coconut Characterization shell: and application ofresponse surface methodology ". Journal of Analytical and Applied Pyrolysis. 101, 53-60.

[7] Girgis, BS., El-Hendawy, AA. (2002). "Porosity development in activated carbons obtained from date pits under chemical activation with phosphoric acid. Micropor. Mesopor ". *Mater*, 52 (2), 105-117.

[8] Attia, AA., Girgis, BS., Fathy, NA. (2008). "Removal of methylene blue by carbon derived from peach stones by H<sub>3</sub>PO<sub>4</sub> activation: batch and column studies ". *Dyes Pigments*, 76 (1), 282-289.

[9] Ahmed Hared, I., Dirion, JL., Salvador, S., Lacroix, M., Rio, S. (2007). "Pyrolysis of wood impregnated with phosphoric acid for the production of activated carbon: kinetics and porosity development studies". *J Anal Appl Pyrolysis.*, 79 (1), 101-105.

[10] Vargas, AMM. Cazetta, AL., Garcia, CA. Moraes, JCG. Nogami, EM. Lenzi, E.,Costa, WF., Almeida, VC. (2011). "Preparation and characterization of activated carbon from a new raw lignocellulosic material: Flamboyant (Delonix regia) pods". *Journal of Environmental Management*, 92 (1) 178-184.

[11] Suárez-García, F., Martínez-Alonso, A., Tascón, J. M. D. (2004). *Microporous and Mesoporous Materials*, 75 (1–2), 73–80.

[12] Rodriguez-Reinoso, F., Molina-Sabio, M. (1992). "Activated carbons from lignocellulosic materials by chemical and/or physical activation: an overview " *Carbon*, 30, 1111-1118.

[13] Carvalho, A. P. Gomes, M., Mestre, A. S. Pires, J., de Carvalho, M. B. (2004). Carbon, 42 (3), 672–674.

[14] Lei Yu, Yong-ming, luo. (2014)."The adsorption mechanism of anionic and cationic dyes by Jerusalem artichoke stalk-based mesoporous activated carbon". *J. Environ. Chem.* Eng, 2, 220-229.

[15] Perrin, A., Celzard, A., Albiniak, A., Kaczmarczyk, J., Marêché, J.F., Furdin, G. (2004). *Carbon*, 42 (14), 2855–2866.

[16] Derbyshire, F., Jagtoyen, M., Andrews, R., Rao, A., Martin-Gullon, I., and Grulke, E.A. In Radovic, L.R. (2001). Ed. *Chemistry and Physics of Carbon* 27, New York: Marcel Dekker, 1–66.

[17] **Mbaye, G. (2014).** "Développement de charbon actif à partir de biomasse lignocellulosique pour des applications dans le traitement de l'eau". Thèse de doctorat en technologie de l'Eau, de l'Energie et de l'Environnement. 2iE, Burkina Faso, 215.

[18] Lopez-Ramon, M. V., Stoeckli, F., Moreno-Castilla, C., Carrasco-Marin, F. (1999)."On the Characterization of acidic and basic surface sites on carbons by various techniques", *Carbon*, 37, 1215-1221.

[19] Adamson, A.W. (1982). *Physical chemistry of surfaces 4*<sup>ème</sup> Edition. John wiley and sons : New York.

[20] Barrett, B. E. P., Joyner, L. G., Halen, P. P. (1951). The Determination of Pore Volume and Area Distributions in Porous Substances. I. Computations from Nitrogen Isotherms. *J.Am. Chem. Soc.* 73: 373-380.

[21] Kannan, et al. (2001). "Kinetics and mechanism of removal of methylene blue by adsorption on various carbons-A comparative study". *Dyes Pigments*, 51, 25-40.

[22] Crank, G. (1933). "The mathematics of diffusion". Clarendon Press, London, New York. [23] Langmuir, I. (1918). "The adsorption of gases on plane surfaces of glass, mica and platinium", *Journal of Am. Chem.* Soc, 40.

[24] **Avom, J., Mbadcam, J. K., Matip, M. R. L., Germain, P. (2001).** "Adsorption isotherme de l'acide acétique par des charbons d'origine végétale"; African Journal of Science and Technology (AJST); Science and Engineering Series, 2 (2), 1-7.

[25] Tang, M.M., Roger, B. (1964). "Pyrolysis in Organic Chemicals from Biomass", Carbon, 2,211-220.

[26] **Haque, Md.M., Hasan, M., Islam, Md.S., Ali, Md.E. (2009).** "Physico-mechanical properties of chemically treated palm and coir fibre reinforced polypropylene composites". *Bioresour.Technol*, 100,4903–4906.

[27] Monties, B. (1980). Les polymères végétaux. Paris, France, 87–121.

[28] Sinha, S., Rout, S.K. (2008). "Influence of fibre-surface treatment on structural, thermal and mechanical properties of jute". *J. Mater. Sci.*, 43, 2590–2601.

[29] Fraga, MA., Jordão, E., Mendes MJ, Freitas, MMA., Faria, JL., Figueiredo, JL. (2002). "Properties of Carbon-Supported Platinum Catalysts: Role of Carbon Surface Sites". *Journal of Catalysis*, 209, 355-364.

[30] **Aravindhan, R., J.R. R., Nair, B.U. (2009).** "Preparation and characterization of activated carbon from marine macro-algal biomass". *Journal of Hazardous Materials*, 162, 688–694.

[31] **Ousmaila, S. M., Adamou, Z., Ibrahim D., Ibrahim, N. (2016).** Préparation et caractérisation de charbons actifs à base de coques de noyaux de Balanites Eagyptiaca et de Zizyphus Mauritiana J. Soc. Ouest-Afr. Chim, 21<sup>ème</sup>, 041, 59 – 67.

[32] Tchieta, P. G., Mbouombouo, J. B., Caroline, L. N. M., Charles, M. K., Harlette, P. Z. (2019). "Adsorption of Eriochrome Black T (EBT) Onto Activated Carbons Obtained from Cola Anomala Nut Shells by Chemical Activation with Phosphoric Acid (H3PO4)". *international Journal of Science and Research*, 8, 2319-7064.

[33] **Demirbas, A. (2004).** "Effect of initial moisture content on the yields of oily products from pyrolysis of biomass". *J. of analytical and applied pyrolysis*, 2, 803-815.

[34] Kara Gozo Glu, B., Tasdemir, M., Demirbas, E., Kobya, M. (2007). "The adsorption of basic dye (astrazon Lue FGrL) from aqueous solutions onto sepiolite, fly ash and apricot shell activated carbon : Kinetic and equilibrium studies". *J. Hazard. Mater.*, 147, 297-306.

[35] **Kifuani, K.M., Mukana, W.M., Noki, V., Musibono, E., Nzuzi, P., Pungi, P., Kunyima, B. (2004).** "Adsorption de bleu de méthylène en solution aqueuse sur charbon actif obtenu à partir des sciures végétales, préparation et caractérisation du charbon actif". *Rev. Sci.* 20, 1/2, 215-224.

[36] Le Cloirec, P. (1985). Etude des interactions soluté–charbon actif. Modélisation de réactions biotiques et abiotiques, Thèse de docteur Es Sciences Physiques, ENSCR, Université de Rennes, France.

[37] Babel, S., Kurniawan, T.A. (2004). "Cr(VI) removal from synthetic wastewater using coconut shell charcoalandcommercialactivatedcarbonmodifiedwithoxidizingagents and/or chitosan " Chemosphere, 54 (7), 951-967.

[38] Lei Yu, Yong-ming, luo. (2014). "The adsorption mechanism of anionic and cationic dyes by Jerusalem artichoke stalk-based mesoporous activated carbon". *J. Environ. Chem.* Eng, 2, 220-229.

[39] **Y.-S., H. (2006).** Review of second-order models for adsorption systems. *Journal of Hazardous Materials*, B 136, 681-689.

[40] **Dogan, et al. (2004).** "Kinetics and mechanism of removal of methylene blue by adsorption onto perlite". *Journal of Hazardous Materials*, B 109, 141-148.

[41] Nakagawa, et al. (2007). "Modification of the porous structure along the preparation of activated carbon monoliths with  $H_3PO_4$  and  $ZnCl_2$ ". *Microporous Mesoporous Mater*, 103, 29-34.

[42] Bishnoi, N.R., et al. (2004). "Adsorption of Cr (VI) on activated rice husk carbon and activated alumina". *Bioresource Technology*, **91**(3), 305-307.

**[43] Aboua, K. N. (2013).** Optimisation par le plan factoriel complet des conditions de productions de charbon actif et son utilisation pour l'élimination des colorants et métaux lourds en solution aqueuse. Thèse de doctorat. Université Félix Houphouët-Boigny.

[44] Lei Yu, Yong-ming, luo. (2014). "The adsorption mechanism of anionic and cationic dyes by Jerusalem artichoke stalk-based mesoporous activated carbon". *J. Environ. Chem.* Eng, 2, 220-229.

[45] Avom J., Ketcha Mbadcam J., Matip M. R. L., Germain P. (2001). J. African journal of science and technology, 2, 1-7.

[46] Lei Yu, Yong-ming luo. (2014). "The adsorption mechanism of anionic and cationic dyes by Jerusalem artichoke stalk-based mesoporous activated carbon". J. *Environ. Chem. Eng.*, 2, 220-229.
[47] Fytianos, K., Voudrias, E., Kokkalis, E. (2000). "Sorption-desorption behavior of 2, 4-dichlorophenol by marine sediments", *Chemosphere*, 40, 3–6.

[48] Barrow G. M., (1996). Physical Chemistry-sixth edition, McGraw-Hill Companies, 910.

