International Journal of Engineering Research & Technology (IJERT)
ISSN: 2278-0181
Vol. 8 Issue 08, August-2019

Adsorption Study of the Removal of Paraphenylenediamine (PPD) using Activated Carbon based Cameroonian Canarium Ovatum Shells Impregnated with $ZnCl_2$ and H_3PO_4

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***Abstract* :- The objective of this work is to prepare Activated Carbon (AC) from Canarium Ovatum shells by chemical activation with Zinc Chloride ($ZnCl_2$) and Phosphoric Acid (H_3PO_4) with best adsorption properties and apply them to reduction of paraphenylene diamine (PPD).**

**The prepared materials were characterized by Thermogravimetric Analysis (TGA);
FT-IR analysis and to determining the iodine index and methylene blue index. The study of adsorption allowed to discuss the effects of contact time, initial concentration and pH of the initial solution. Kinetic of adsorption process was studied by applying the isotherms pseudo-first-order and pseudo-second-order as well as intraparticle and Elovich isotherms. The adsorption equilibrium data were provided by Langmuir; freundlich; Dubinin-Radushkevich and Temkin isotherms.**

TGA indicated that the calcination temperature of our vegetal material is 450°C. Activated Carbons (AC) with Zinc Chloride are those which have both larger values of iodine and methylene blue index. However, the values of pH zero charge points reveal that all prepared Activated Carbon are acidic (pH_{PZC} <7). The isotherm models Freundlich and Dubinin Radushkevich are those best describe the dynamics of adsorption on the surface of these carbons (R^2>0,95) and the adsorption energies obtained from this isotherm are all above 8 KJ mol^{-1} corresponding to chemisorption while the isotherms models pseudo-first-order; Pseudo-second-order and Elovich best match the adsorption kinetics (R^2>0,96).

Keywords : Actived Carbon ; Activation; Paraphenylene diamine; Kinetics; Adsorption

I. INTRODUCTION

Water is a key issue for the present generations and those to come. It is used in all sectors: agriculture; industrial and domestic. However, it is racked with pollution phenomena due to chemicals effluents discharge from industrial activities. These chemicals effluents contain pollutants which can be inorganic such as heavy metals or organic include organic dyes such as paraphenylene diamine (PPD) which is mainly used in the cosmetics industry. Literature reports that exposure to that compound brings about kidney failure that can lead to death and also respiratory diseases, hepatic, digestive and nervous system [1; 2]. Faced with this situation different methods both physical and chemical were developed from which the coagulation and flocculation [3]; oxidation [4]; membrane separation [5] and adsorption [6]. However adsorption is processing technique increasingly studied because it seems to be the simplest and most effective for the removal of pollutants organic water [7]. This technique is based on capacity of a solid called adsorbent to fix the particles of a fluid called adsorbate on its surface. The different adsorbents far studied are geomaterials (zeolite, silica gel, clay ...) [8; 9] and activated carbon.

Activated carbons have advantage of having a wide range of application as many in the food industry in the field of health and remediation fluid [10; 11]. This versatile nature of activated carbon can be explained by their large specific areas, the presence of chemical functions on the surface of the latter and their variable porosity [12]. Several plant materials can be used as precursors of Activated Carbons including date stones [12]; olive pulp [13]; the oil palm waste [14]; coconut shells [15].

The main objective of this work is to prepare Activated Carbon from the stones of Canarium Ovatum by chemical activation with Zinc Chloride and Phosphoric Acid to reduce the PPD in an aqueous medium.

The various activated carbons prepared will be characterized and used for adsorption batch mode of para-phenylenediamine (PPD) by varying different parameters such as contact time; the initial concentration of PPD and the adsorbent mass. Isotherms of adsorption and kinetics will be studied to explain the adsorption process.

II. MATERIALS AND METHODS

The stone Canarium Ovatum were harvested in the locality situated in Mbouda Around west Cameroon at the foot of Bamboutos (5.623738 ° N 10.254815 ° E).

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ISSN: 2278-0181
Vol. 8 Issue 08, August-2019

2.1 Preparation of activated carbons

The extracts stones Canarium Ovatum were extensively washed with distilled water before being dried at room temperature for 72 hours; these have subsequently been crushed and then ground and sieved using a sieve electrical to obtain a powder homogeneous particle size of 63µm. The powder obtained was pretreated chemically with Phosphoric Acid and Zinc Chloride before being calcined at using an electric furnace.

- Chemical activation with phosphoric acid

The technique used is based on that used by Mbaye in 2014 [16]. It consists of stir in beakers accurate mass vegetable powder with phosphoric acid according to mass ratios activating / powder set (1/1, 2/1 and 3/1). The sets are homogenized and dried in a furnace at 110 °C for 48 hours. The dried mixtures were subsequently introduced into crucibles ceramic to be calcined at 450 °C in a Naberthern brand furnace with a speed of heating of 5 °C/min and a dwell time of 2 h at end having a porous structure sufficiently developed. Samples from this step are washed thoroughly with distilled water until a residual wash water having a pH equal to 7 to eliminate the residues of activating on the surface of activated carbon. Activated carbons thus obtained are dried again at 110 °C in an oven for 48h. These carbons activated with phosphoric acid will be named CAH_1; CAH_2 and CAH_3.

- Chemical activation with zinc chloride

Activation with zinc chloride was performed according to the method of Bénamraoui [17]. In three beakers of 250ml, a specific mass of powder is introduced into a volume of $ZnCl_2$ solution 50ml prepared from $ZnCl_2$ anhydrous claimed ratios mass activating / powder 1/1; 2/1 and 3/1. The mixtures were then stirred for 2 h at using a magnetic stirrer and then dried in an oven at 110 °C for 48h. The impregnated samples were then dried and introduced into a calcination furnace Naberthern brand; the temperature of the furnace was set at 450 °C with a bearing 2 hours and a heating rate of 5 °C/min. Activated carbons obtained at the end of this operation were washed in distilled water several times during 15 min. These have then washed with a volume of 250 ml of 3M Hydrochloric acid molarity repeatedly during 2 h, after decantation of the mixture, the supernatant solution Hydrochloric acid is extracted and the remaining activated carbons were again washed with distilled water until a pH in the range 6-7. After all these operations, the coal samples active were dried in an oven at 110 °C for 48h. We will name these carbons activated with zinc chloride CAZ_1; CAZ_2 and CAZ_3.

2.2 Characterization of active carbons obtained and the raw material

The calcination temperature of the powder canarium ovatum was determined by thermogravimetric analysis coupled to the differential thermal calorimetry and differential scanning. The chemical surface functions of different materials were determined by infrared Fourier transform analysis. IR-TF adsorption spectrum is registered in the area 4000 cm^{-1} to 400 cm^{-1} using an IR spectrophotometer. The powder of Canarium ovatum was analyzed as a combined tablet bromide potassium.

2.2.1. Ash content and moisture

The ash content is measured using the method described by J. Ahmad and SK Dhedan in 2012 [18]; 0.5g activated carbon mass dried at 110 °C in an incubator for 3h was introduced in a known mass of the crucible. The crucible was introduced into a furnace set at 800 °C with a dwell time of 3 hours at this temperature. Ash mass is then measured.

The ash content expressed in% is given by the formula: $\% T = \frac{M_2}{0,5} \times 100$ (1)

Where M_2 (g) represents the mass of ash obtained.

The humidity percentage is determined after drying a mass of 0.5 g activated carbon into the oven [19]. The adsorbent mass is introduced into a mass crucible known, the whole is weighed and dried at 110 °C repeatedly until the mass becomes constant.

The moisture content (% M) is given by the formula: $\% H = \frac{M_2 - M_3}{0,5} \times 100$

Where M_2: weight of the crucible filled before drying (g) and M_3: mass of the filled crucible after (2) (g)

2.2.2. Iodine Index

This parameter used to evaluate the adsorption capacity of the particles small size by activated carbon [19]. The process of determining the iodine index is derived from that used by Mamane et al in 2016 [20]; In a volume of 50 ml of an iodine solution (0.02 N), contained in the Erlenmeyer flask, 0.1 g of an adsorbent mass has been introduced; The mixture is stirred for 5 min then filtered. Thereafter, a volume of 10 ml of the filtered solution was taken and 2 drops starch were introduced to obtain a purple solution. A volumetric dosing was carried out with a concentration of 0.1N thiosulfate solution contained in the burette graduated to change the coloration of the purple color to a colorless solution.

$2NaS_2O_3 + I_2 \longrightarrow 2\ S_4O_6 + 2NaI$

The iodine index is given by the formula: $I_{I2} = \left(\frac{C_0 C_{th} V_{th}}{2V_{I2}}\right)\left(\frac{M_{I2} V_{ads}}{m_{ca}}\right)$ (3)

C_0: initial concentration of I_2 — M_{I2}: molar mass diiodine
C_{th}: concentration of thiosulfate — V_{ads}: adsorption volume of diiodine
V_{th}: volume of thiosulfate equivalence — m_{ac}: mass of activated carbon used

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V_{I2}: volume determined diiodine.
Knowledge of iodine value gives an approximation of the surface area by applying the relation: $S_{I2} = Q_e . \sigma N_A / M_{I2}$ ($m^2.g^{-1}$) [10] (4)
Q_0 being the maximum amount of diiodine adsorbed mg / g ; σ the maximum area occupied by the diiodine (σ = 21.3 Ă^2) and Mass diiodine M_{I2} is 126.9g / mol.

2.2.3 Methylene blue index

The determination procedure used is an adaptation of the European Center method federations of the chemical industry pulled out of Maazou's work performed in 2017 [19]. A 0.1 g mass of the dried powder was mixed with a volume of 100 ml of a solution of 25 mgl^{-1} of methylene blue contained in an Erlenmeyer flask. After stirring for 1 h, the mixture was filtered and the residual concentration was measured at 620 nm in using a UV-visible spectrometer. The methylene blue index given in mgg^{-1} is given by the formula:

$$Id_{BM} = \frac{C_0 - C_f}{0,1} \times 100 \quad (5)$$

C_0 represents the initial concentration of methylene blue
C_f is the concentration of methylene blue solution after adsorption.

The specific surface of the sample covered by the BM molecule (S_{BM}) is determined from the formula:

$$S_{BM} = \frac{q_m A_m N_A}{M_{BM}} \quad (6)$$

with:
q_m ($mg.g^{-1}$): the maximum amount of dye which can be adsorbed; A_m = 1.30 nm²: molecular surface of the BM; M_{BM} = 319.85: molecular weight of BM $g.mol^{-1}$.

2.2.4. Determination of pH of zero charge point (pH PZC)

It corresponds to the pH value for which there's so much negative charge than positive charge on the surface of the adsorbent. A volume of 50 ml of distilled water and pH 2; 4; 6; 8 and 10 adjusted by adding NaOH or HCl (0.1M) and controlled by a pH-meter are placed in five flasks. An activated carbon 0.05 g mass is introduced into each of these solutions. Mixtures are then kept in agitation at room temperature until the pH stabilizes and the final pH is then determined. The zero charge point is the intersection of the curve giving by (pH_f-pH_i) = f (pH_i) and the straight line passing through the origin [21]. This is important because it is a pollutant type of indicator that can be removed by activated carbon and depends the nature of the activating unused.

2.3. Adsorption Test

This test is performed using the adsorption method in batch. A mass of 0.1 g activated carbon is introduced into several flasks containing solutions of PPD to concentrations ranging from 100 mgl^{-1} to 800 mgl^{-1}, the whole is then stirred for a time accurate at room temperature. The different samples are filtered on filter paper wattman; the residual concentration of PPD at equilibrium (C_e) is determined using a BK spectrometer-UV-1600PC model at a maximum wavelength equal to 453 nm. The amount of contaminant remaining in solution per gram of coal is given by formula

$$q_e = \frac{V(c_0 - c_e)}{m} \quad (7)$$

C_0 and C_e represent the concentrations of the initial PPD and balance in mgl^{-1}; v the volume of the solution in ml and m the mass of activated carbon g.

2.3.1. Study of adsorption isotherms at fixed time

The adsorption equilibrium of PPD on different activated carbons prepared is studied by using the Langmuir isotherms; Freundlich; Temkin and Dubini-Radushkevich.

Langmuir isotherm:

The linear isothermal of this equation is: $\frac{C_e}{q_e} = \left(\frac{1}{q_{max}}\right) C_e + \frac{1}{q_{max} k_1}$ (8)

where C_e and Q_e represent the equilibrium concentration (mgl^{-1}) and the amount of pollutant at equilibrium adsorbent per unit mass (mgg^{-1}), K_1 is the constant Langmuir and Q_{max} is the maximum amount that can be adsorbed in a monolayer per unit mass of activated carbon
($mg\ g^{-1}$) [22].

Freundlich isotherm:

The linearization of the above equation gives: $\ln(q_e) = \ln(k_f) + {}^1/_n \ln C_e$ (9)

K_f and n are the kinetic constants and the adsorption efficiency of respectively for a given solute adsorbent; C_e is the equilibrium concentration (mgl^{-1}).

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Temkin isotherm:

The isotherm Temkin is expressed as: $q_e = (\frac{RT}{b_t})(lnk_t C_e)$ (10)

Or as: $q_e = B_1 lnk_t + B_1 lnC_e$ (11)

With B_1 in (J mol^{-1}), the constant Temkin on the heat sorption and k_t (l mg^{-1})

Isotherm of Dubinin-Radushkevich (DRK):

Here we consider that interaction between the adsorbent and the adsorbate is influenced by a potential field and the volume of adsorbate is only function of the potential of this ε field [23]. The linearization of the equation of this isotherm gives:

$lnq_e = lnX'_m - K'\varepsilon^2$ (12)

ε^2: Polanyi potential $\varepsilon = RT\ln(1 + \frac{1}{C_e})$ (13)

where q_e: amount of metal ions adsorbed by unit weight (mg g^{-1}); X'_m: capacity Adsorption (mg g^{-1}); C_e: concentration of metal ions in solution (mg g^{-1}) ; K': is a constant related to energy of adsorption (mol^2 K J^{-2})

The adsorption energy is obtained from K' values in the form: $E = \sqrt{2k'}$ (14)

2.3.4. Study of the adsorption kinetics

The adsorption kinetics was studied using pseudo first and second order models, intra-particle and the Elovich models.

Pseudo first order model:

The integrated equation of this model is ln (q_e - q_t) = ln q_e- k_1.t [24] (15)

Where: q_e and q_t represent respectively the adsorption capacity (mg g^{-1}) at equilibrium and time t; k_1 is the constant of rate of adsorption (mn^{-1})

Pseudo second order model:

After integration of the equation of the pseudo second order model and application of boundary conditions, we obtain the following integrated form: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e^2}$ (16)

q_e and q_t represent respectively the adsorption capacity (mg g^{-1}) at equilibrium and time t, respectively, and K_2 is the constant of rate of adsorption (g mg^{-1}.mn^{-1}).

Intra-particle model:

The intra-particle diffusion kinetics model is governed by the equation: $q=K_d.t^{1/2}$+ C (17)

Where: k_d is rate constant of the intra-granular diffusion (mg g^{-1} min$^{-1/2}$) and C: constant.

Elovich Model:

This kinetic model is generally used for chemical adsorption on adsorbent heterogeneous. The corresponding equation is as follows: $q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta} lnt$ (18)

Where: α is the initial adsorption capacity in g mg^{-1} min^{-1} and β is the regression constant in g mg^{-1}

III. RESULTS AND DISCUSSION

3.1 Material Characterization

3.1.1. TGA

The thermal behavior of the powder obtained form stones of Canarium ovatum given by the coupling the thermogravimétie, the thermogravimetric analysis and differential calorimeter is shown in Figure 1. We can see from this figure the decomposition of our plant material happens in three stages. The first observed at 82°C is a weight loss of 15.48%; it would correspond to the loss of water absorbed by the material in the form of moisture [25].

At 282°C we have a mass loss of 33.31% which corresponds according to the literature on structural water loss followed by decomposition of cellulose and hemicellulose. Between 417 and 433°C, the weight loss is 29.48°C which corresponds to the thermal decomposition range of the lignin; Soltes and Elder [26] set the decomposition of the latter between 280°C and 500°C. This is also the field flavoring which results in the end of the formation of the graphene layers so development of the pores; we therefore observe an intense endothermic peak. From 433°C, the evolution of the mass is constant which helped to set the temperature calcination at 450°C at the end to be sure to have a honeycomb-shaped graphene having a well structured.

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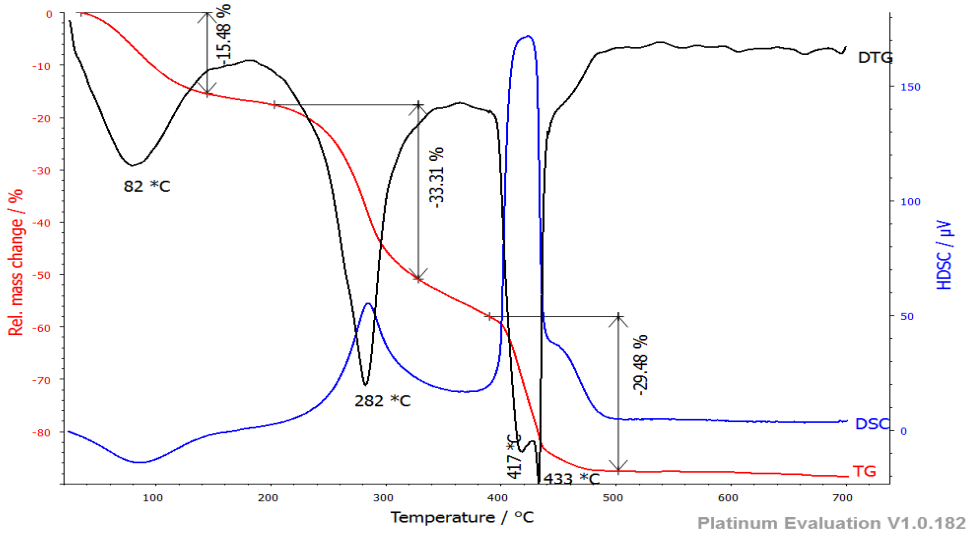

Figure 1: Thermal Analysis (TGA / HDSC / DTG) of powder

3.1.2. Determination of chemical surface functions by infrared analysis

The main chemical functions on the surface of activated carbons prepared and powder of Canarium Ovatum (PCO) are visible in Figure 2.

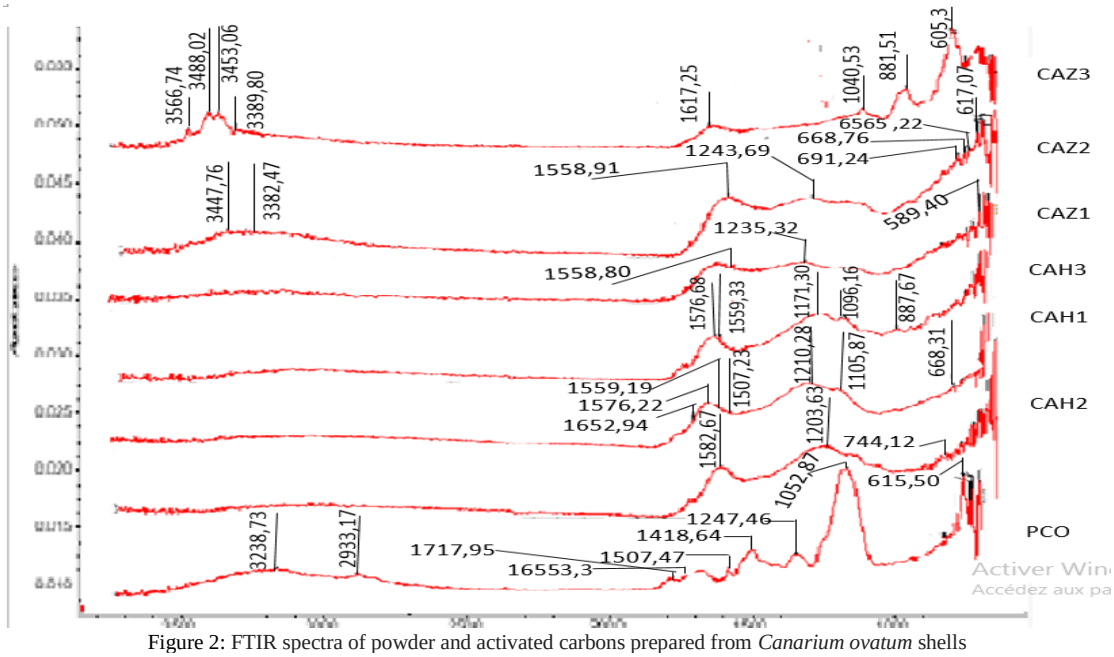

Figure 2: FTIR spectra of powder and activated carbons prepared from *Canarium ovatum* shells

The Fourier transform infrared spectroscopy shown in Figure 2 is used for determine the chemical functions on the surface of our different materials. The results reveal the presence of dark fruit powder spectrum of a wide band low 3238.73 cm^{-1} elongations corresponding to vibration of the hydroxyl group of acids carboxylic; alcohols; water molecules absorbed by the material [27], or of cellulose and lignin. [28] This group is absent in the spectra of activated carbons due to its disappearance at a certain temperature in the form of water vapor such as a provided the TGA. Band 1717,95 cm^{-1} and 1247,46 cm^{-1} respectively correspond to vibration elongations groups C = O and CO of the carboxylic acid compounds; esters or amides [29, 30]. Hypothesis of the presence of amide function is supported by the bands NH stretching vibrations of aromatic amides observed at 1418cm^{-1}

[31]. We can also observe the spectra of activated carbon to phosphoric acid (CAH_1, CAH_2 and CAH_3) the presence of bands corresponding to elongations aliphatic POC and COC in the POP chain situated respectively within the ranges [744.12 to 828.97 cm^{-1}] and [1171.3 to 1203.63 cm^{-1}]; these groups derived from phosphoric acid used. Regarding the activated carbon zinc chloride (CAZ_1, CAZ_2 and CAZ_3) among observable bands on their spectra we can especially notice the strips lying in the range [582,49-665,07cm^{-1}] corresponding to the vibrations deformation of the C-Cl [32] suitable for activation with zinc chloride. In addition to the bands mentioned characteristics, we also have to CAZ_2 coals and CAZ_3, bands corresponding to the stretching

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vibrations of the aliphatic primary amines located in the interval [3382,47-3488,02cm^{-1}] and bands of symmetrical vibration and elongations asymmetric primary aromatic amines located 3566,74cm^{-1} and 3389,8cm^{-1}.

3.1.3. Ash content and moisture

Table 1: shows the results obtained in functions of the activation a process used.

Table 1: Ash content and moisture content of the activated carbon with H_3PO_4 and $ZnCl_2$

	CAH_1	CAH_2	CAH_3	CAZ_1	CAZ_2	CAZ_3
Ash content %	2	2	4	20	28	30
Moisture content %	6	10	16	0	0	0

We can observe that the activated carbon with zinc chloride present considerably higher ash content which is a disadvantage because the ash is a inorganic material, it acts as impurities which will clog the pores on the surface of the adsorbent, thereby reducing the specific surface area; this results in the decreased activity of coals. On the other hand, we see that the rate of ash increases with the concentration of the activator; such high values for the activated carbon zinc chloride could be explained by the presence of chlorine on the surface of adsorbents after activation. Humidity levels obtained with our activated carbon for their defy widely those that have commercial activated carbons: they range from 6 to16 for coals activated with phosphoric acid and are zero for those activated zinc chloride. Obtaining humidity zero for activated carbon with Zinc chloride is an advantage for obtaining activated carbon high gross calorific [20] and an indicator of the quality of the obtained activated carbons; these values might also translate easy storage ability of these adsorbents because they do not easily capture moisture. We can deduce that the disadvantage of this enabling is to eliminate effectively to end after activation of having a reduced ash content.

3.1.4. Iodine value and methylene blue index

Table 2: Adsorption capacity of methylene blue for each adsorbent prepared

Activated carbons	***CAH_1***	***CAH_2***	***CAH_3***	***CAZ_1***	***CAZ_2***	***CAZ_3***
Iodine value (mg g^{-1})	380,70	507,60	507,60	697,95	761,40	793,10
Methylene blue value (mg g^{-1})	24,80	24,70	24,60	24,90	24,90	24,90
Adsorption capacity of methylene blue (%)	99,40	98,80	98,50	99,50	99,70	99,80
Specific area cover by methylene bue (S_{BM}) (m^2 g^{-1})	62,63	62,25	62,10	62,73	62,85	62,90
Specific area cover by iodine (S_{I2}) (m^2 g^{-1})	385,77	512,90	512,90	705,59	769,74	801,82

It is obvious from Figure 3 that the iodine value increases with concentration of the activator; however, these are the activated carbons with zinc chloride which possess the best adsorption capacities of diiodine with an iodine value reaching 793,1mg g^{-1} for the 3/1 ratio. In addition, the specific surface CAH_2; CAH_3; CAZ_1; CAZ_2 et CAZ_3 are between 512.90 and 801.82 m^{2}g^{-1} these lie in the range of 500 to 1500 m^{2}g^{-1} recommended for activated carbons used for the removal of micropollutants from aqueous solutions [33]. We can also see that the zinc chloride is more conducive to the development of a microporous surface Figure 3 also shows that methylene blue index increases with the activation ratio for activated carbon with zinc chloride while the phenomenon reverse was observed for the activated carbon with phosphoric acid. Furthermore, for methylene blue solution 25mg l^{-1}, we obtained adsorption capacities situated between 98% and 99% which may indicate that the prepared activated carbon present significant efficiency for the adsorption medium sized pollutants. However, Activated carbons with zinc chloride are those with better results adsorption capacity lying between 99.5% and 99.8% as shown in Table 2. These latter would therefore also effective for removing small contaminants for removing larger pollutants.

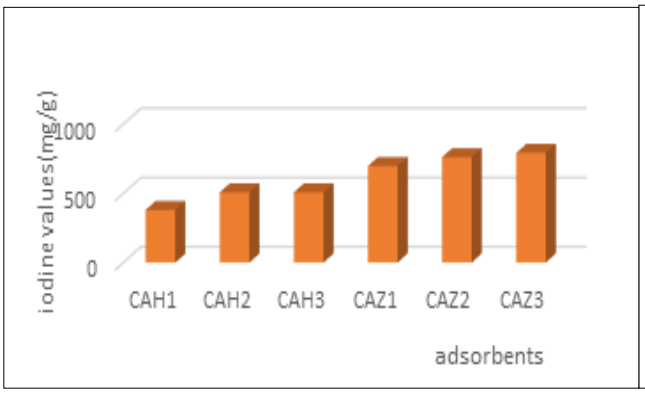

Figure 3 : Iodine values of carbons activated with H_3PO_4 et $ZnCl_2$

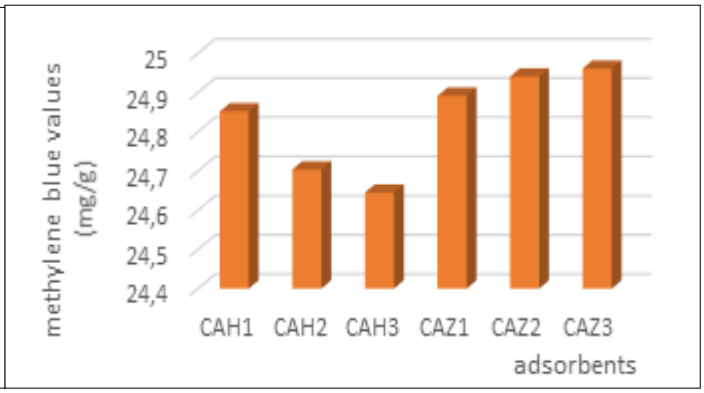

Figure 4 : Methylene blue values of carbons activated with H_3PO_4 et $ZnCl_2$

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3.1.5. Determination of pH at zero charge point (pH PZC)

The pH of zero charge point depends on the origin of the precursor and method activation; it is a good indicator of maximum adsorption area depending on the nature of the pollutant to eliminate. The load point pH values reported in Table 3 are obtained by determining the intersection points between the curves ΔpH = f (pHf-pHi) and a horizontal line passing through the origin as shown in Figure 5.

Table 3: Values of pH at zero charge point of the activated carbon with H_3PO_4 and $ZnCl_2$

Carbons	***CAH₁***	***CAH₂***	***CAH₃***	***CAZ₁***	***CAZ₂***	***CAZ₃***
pH_{PZC}	4,8	5,0	5,6	6,0	3,0	6,8

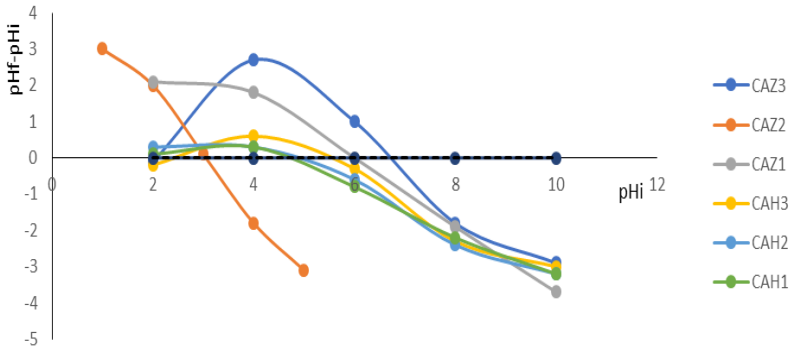
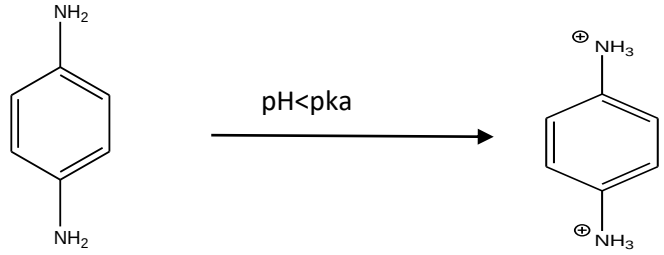


Figure 5: pH at zero charge point

The values obtained indicate that all the prepared activated carbons are likely acid. However, CAZ_3 has a pH of zero charge point close to 7 (6.8) could be ideal to use water treatment as its surface is almost neutral.

These pH_{PZC} values also predict the area conducive to adsorption of PPD. For each activated carbon, at pH lower than the pH_{PZC} surfaces activated carbons are protonated; so they become positively charged while in pH above this value, the hydroxide ions neutralize the positive site which makes this negatively charged surface [34]. However, at pH lower than pka of paraphenylenediamine (6.2), this one himself beneath made of paraphénylènediamonium causing repulsion with positive websites coals assets.



3.2. Study of the adsorption in batch

3.2.1 Effect of contact time

The evolution of the process of adsorption on the surface of different coals depending time is illustrated by the following figure.

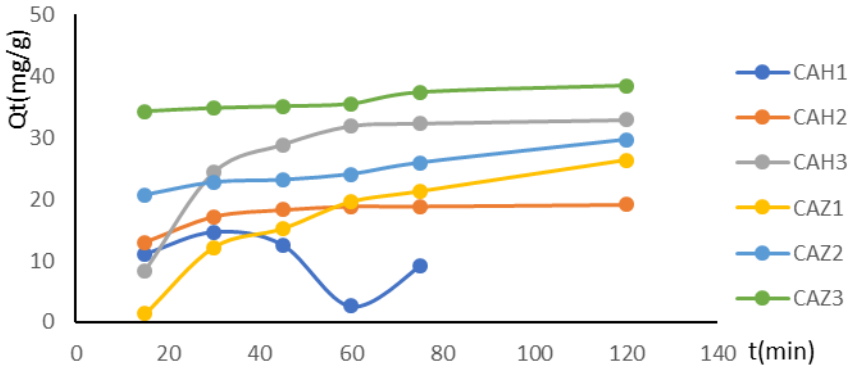


Figure 6: Influence of contact time on the adsorption capacity of PPD on the prepared activated carbon (m CA = 0.1g; C = 100 mg l^{-1}; V = 50ml)

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We can see from Figure 6 that the adsorption happens in three steps for CAH_2; CAH_3; CAZ_2 and CAZ_3:

- During the first thirty minutes, the amount of pollutant adsorbed believes quickly; this can be explained by the presence of a large number of binding sites vacant at the outer surface of the adsorbent which allows easy adsorption to this surface [35]

- After the thirty first minutes, the adsorption rate decreases and the process is slow. Other sites of the adsorbent reached saturation, the pollutant particles will migrate to the interior of the adsorbent; thereof being easily accessible, adsorption thus occurs slowly: the dissemination intra-particle [36].

- From eighty minutes we observe a landing; the adsorbent has reached its capacity Max. We can then say that the equilibrium time for these coals is 80minutes. However, the evolution curve of the amount adsorbed by CAH_1 shows considerable growth during the first thirty minutes, after these, the amount of pollutant adsorbed drops sharply: this would be a product desorption. This phenomenon is not visible to other coals; it could mean that the amount of pores available and bonding forces increase with the concentration of activating used, this is moreover verified with the values of iodine values and methylene blue. However for same ratio of $ZnCl_2$ desorption is not observed and we have instead a maximum time adsorption is de120min; this means that last provided a porous availability higher than H_3PO_4. So we set the adsorption time 30min to end easily conduct a comparative study of adsorption on the surface of our different coals.

3.2.2. Effect of the adsorbent mass

Figure 7 spring changes in adsorption with the increase in the mass adsorbent.

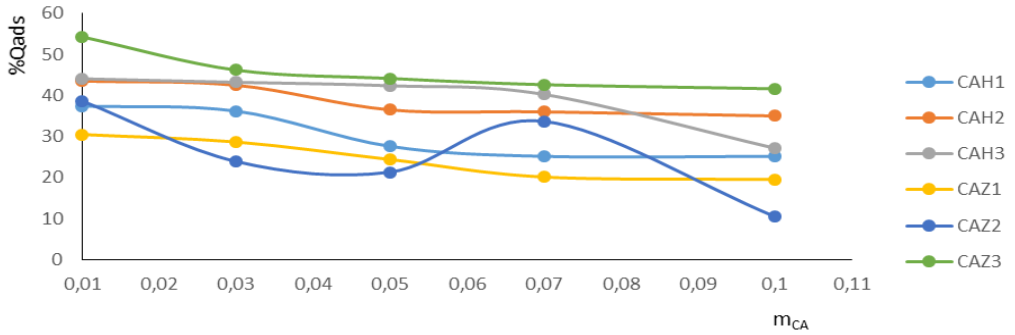

Figure 7 : Influence of the differents adsorbents mass on the adsorption capacity (V= 50ml; C=100mg l^{-1})

We can observe that the amount of pollutant adsorbed decreases increasing the mass of adsorbent. This could be explained by the fact that when the amount of adsorbent increases, the total surface area available for adsorption of the pollutant decreases due to the aggregation of adsorption sites. [37] From observation of the curves reflecting the influence of ACH_1 doses; CAH_2; CAH_3; CAZ_1; CAZ_2 and CAZ_3, it appears so that the adsorption is maximum when using the activated carbon which is minimum 0.01g.

3.2.3. Effect of initial concentration

The results obtained by varying the initial concentration of PPD are shown in Figure 8.

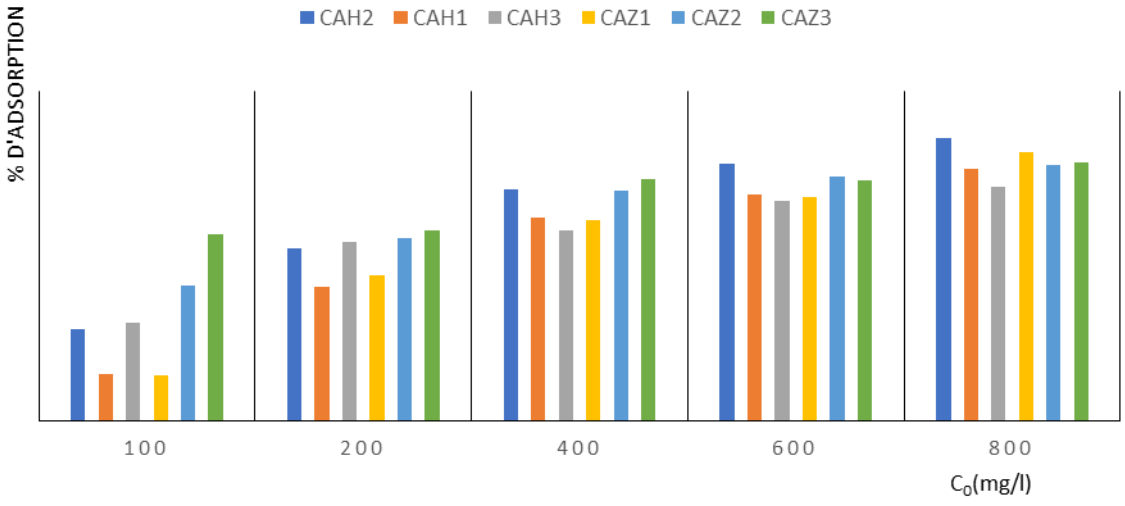

Figure 8: Adsorption capacity of the PPD as a function of the initial concentration PPD, conditions (m_{CA} = 0.1g; V = 50 ml; t = 30 min)

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Figure 8 shows the percentage of PPD adsorbed increases with initial concentration of the solution. This could be explained by the fact that the increase concentration leads to the creation of a large conveying force molecules pollutant on the surface of carbon; the quantity of molecules present at the surface increases and therefore promotes adsorption [35]. We can see that for the same ratio, the percentage adsorption of activated carbon to the $ZnCl_2$ is higher for low concentrations (100mg l^{-1} to 200mg l^{-1}) relative to that of activated carbon in H_3PO_4; this could push to conclude that the adsorption on the surface of activated carbon to $ZnCl_2$ is less favored by the transport phenomena that occurring on the surface of activated carbon in H_3PO_4.

3.2.4. Isotherm models of adsorption equilibrium

The adsorption isotherms studied are represented by the following figure:

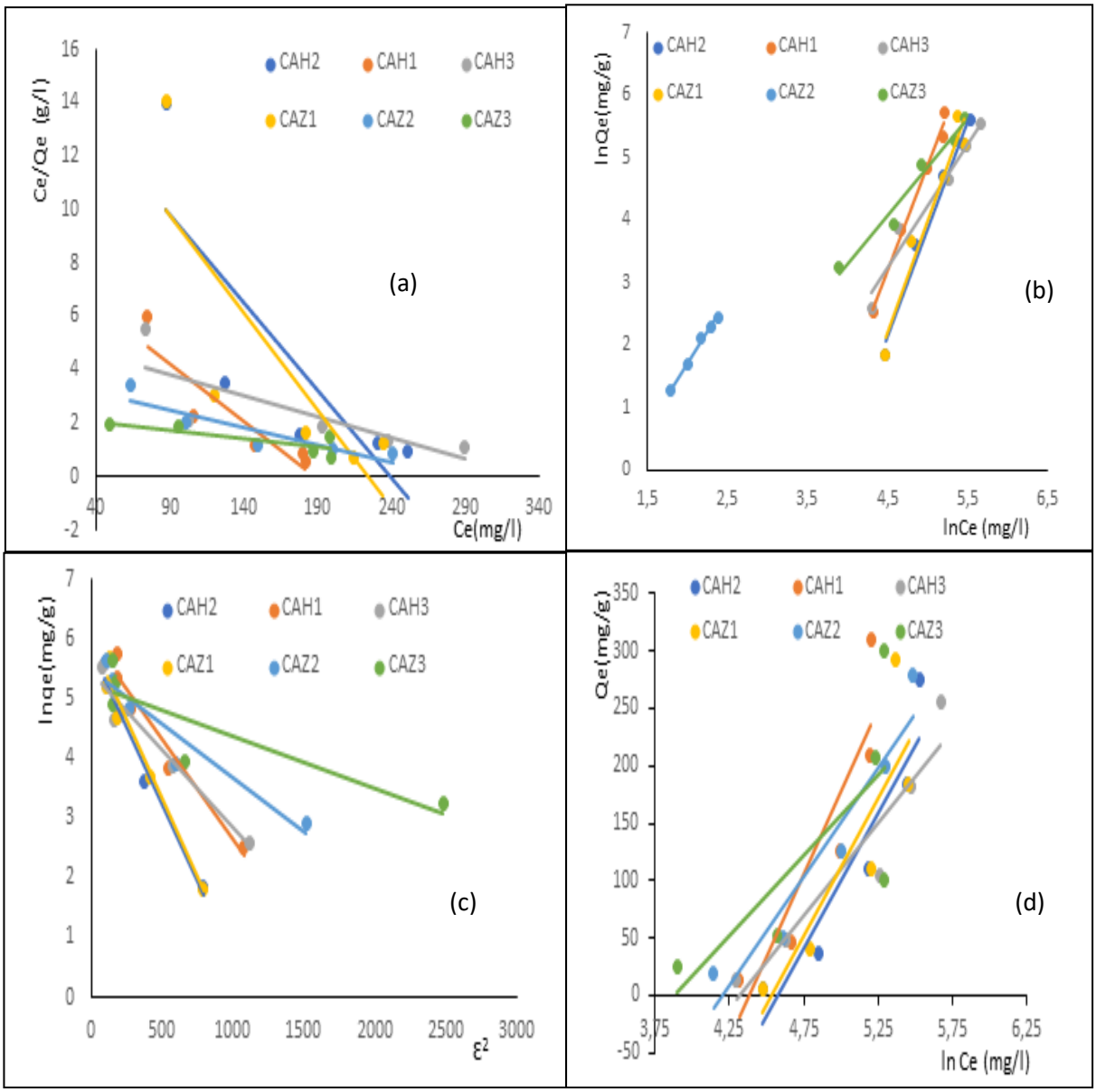

Figure 9: PPD adsorption isotherms on AC according to Langmuir (a); Freundlich (b) conditions; D-R-K (c) and Temkin (d) (m = 0.1 g, contact time t = 60 min, V = 30 ml, room temperature)

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Table 4: Isothermal time settings fixed different activated carbons

Models	*Paramèters*	*Adsorbents*					
		CAH_1	**CAH_2**	**CAH_3**	**CAZ_1**	**CAZ_2**	**CAZ_3**
Langmuir	**Q_{maxexp} (mg g^{-1})**	309,090	271,540	5255,170	292,860	279,000	300,560
	R^2	0,818	0,670	0,630	0,653	0,814	0,686
	Kl(l mg^{-1})	$-5,300.10^{-3}$	-4.10^{-3}	-5.10^{-3}	-4.10^{-3}	-3.10^{-3}	-2.10^{-3}
	Q_{max}(mg g^{-1})	-23,200	-15,100	-63,290	-13,71	-75,180	-153,800
Freundlich	**R^2**	0,988	0,979	0,958	0,941	0,996	0,973
	Kf	3.10^{-2}	1.10^{-4}	3.10^{-3}	8.10^{-7}	4.10^{-3}	5.10^{-2}
	1/n	3,370	3,440	1,98	3.59	2,04	1,54
D-R-K	**R^2**	0,954	0,979	0,958	0,968	0,914	0,766
	X'm(mg g^{-1})	394,880	341,89	227,120	379,820	238,360	185,400
	K'(mol_2 KJ^{-2})	33.10^{-4}	52.10^{-4}	26.10^{-4}	52.10^{-4}	18.10^{-4}	9.10^{-4}
	E(KJ mol^{-1})	14,74	9,800	13,860	9,800	16,660	23,570
Temkin	**R^2**	0,821	0,882	0,895	0,745	0,919	0,569
	B1(J mol^{-1})	288,500	235,6	160,500	241,200	190,100	140,100
	Kt(l g^{-1})	0,012	0,010	0,013	0,010	0,014	48,310
	bt(J)	0,028	0,035	0,051	0,034	0,043	0,059

The determination of the adsorption isotherm corresponding most to the process PPD adsorption to the surface of an activated carbon is performed from the value of R^2. We can deduce from the values of R^2 summarized in Table 8 that the Freundlich isotherm is the one who describes the more the adsorption process on the surface of CAH_1 carbons; CAH_2; CAH_3; CAZ_2 and CAZ_3 with correlation coefficients with respectively to 0.988 value; 0.979; 0.958; 0.996 and 0.973. The adsorption process the carbon surface CAZ_1 meanwhile is the DRK described by the model with R^2 equal to 0.968. The adsorption energies obtained from this isotherm are all above 8KJ mol^{-1} corresponding to chemisorption. Observation of different energies provided by the Temkin isotherm shows that the adsorption heats B_1 on the surface of Activated carbons with the acid are far superior to those of activated carbons with zinc chloride, however, the opposite phenomenon is observed for the binding energy the balance; this would mean that the PPD is more strongly absorbed on the surface of activated carbon zinc chloride than on the surface of activated carbon to phosphoric acid.

3.7. Isotherm models with variable time
These models are shown in Figure 10

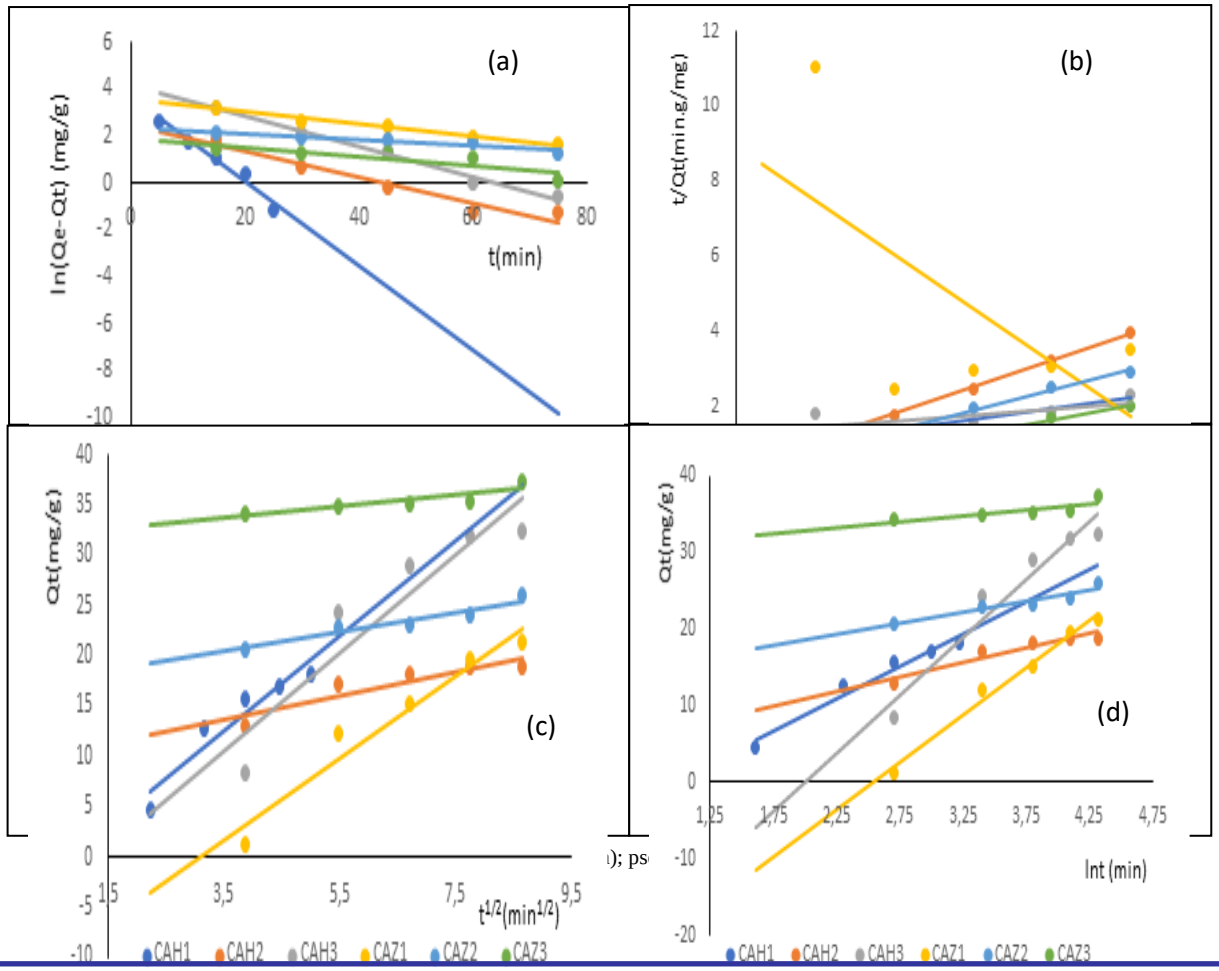

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Table 5 Kinetic parameters of activated carbons to H_3PO_4 and $ZnCl_2$

Models	*Parameters*	*Adsorbents*					
		CAH_1	**CAH_2**	**CAH_3**	**CAZ_1**	**CAZ_2**	**CAZ_3**
Pseudo first order	**Q_{exp} (mg/g)**	18,510	19,100	32,900	26,350	26,630	38,480
	R^2	0,967	0,945	0,985	0,985	0,923	0,726
	K_1 (min-1)	0,179	0,055	0,065	0,026	0,013	0,019
	$Q_{théo}$ (mg/g)	37,356	11,134	62,477	34,577	10,837	6,187
Pseudo second ordre	**R^2**	0 ,485	0,997	0,437	0,399	0,994	0,997
	K_2 (g/mg.min)	48.10^{-5}	57.10^{-4}	11.10^{-3}	1.10^{-3}	61.10^{-4}	1.10^{-2}
	Qthéo (mg/g)	51,282	21,186	89,285	10,350	27,174	37,879
Elovich	**R^2**	0,965	0,908	0,845	0,985	0,919	0,701
	β (g/mg)	11,880	0,267	0,084	0,081	0,350	0,630
	α (mg/g.min)	3,270	9,592	6,818	0,977	2,857	1,980
intra-particulaire Diffusion	**R^2**	0,909	0,831	0,865	0,952	0,944	0,778
	K_{di} (min^{-1})	4,771	1,201	4,900	4,090	0,973	0,563
	C	-4,244	9,392	-6,634	-12,600	17,012	31,741

From observation of the correlation coefficients shown in Table 5, we can see that the pseudo first order model best describes the kinetics adsorption to the surface of CAH_1 activated carbons; CAH_3 and CAZ_1 (R^2 = 0.966; 0,985 and 0.985) would mean that the rate of adsorption on the surface of these activated carbons depends of the behavior of the adsorption process during the first 20-30 minutes [38]. However, CAH_2 coals; CAZ_2 and CAZ_3 have correlation coefficients for the model pseudo second very satisfactory order (0.9974 respectively, and 0.9939 0.9970) with theoretical capacity of adsorptions (21,19; 27,17 and 37,87) near the experimental capabilities (19.1; 29.63 and 38.48) as presented in Table 5. The observation different adsorption and desorption speeds shown in Table 10 shows a desorption phenomenon is predictable for CAH_1 since its initial velocity adsorption (3,70mg $g^{-1}.min^{-1}$) is less than its initial desorption rate (11,88g mg^{-1}). This phenomenon is observable in any of activated carbon to zinc chloride.

CONCLUSION

The objective of this work was to prepare the Actived carbon from stone canarium ovatum by chemical activation with zinc chloride ($ZnCl_2$) and phosphoric acid (H_3PO_4) with best adsorption properties and apply them to the reduction of paraphenylene diamine (PPD).

TGA indicated that the calcination temperature of our vegetal material is 450°C. Activated carbons with Zinc Chloride are those which have both larger values of iodine and methylene blue index. However, the values of pH zero charge points reveal that all prepared activated carbon are acidic in nature (pH_{PZC} <7). The isotherm models Freundlich and Dubinin Radushkevich are those best describe the dynamics of adsorption on the surface of these carbons (R^2>0,95) and the adsorption energies obtained from this isotherm are all above 8 KJ mol^{-1} corresponding to chemisorption while the isotherms models pseudo first order; Pseudo second order and Elovich best match the adsorption kinetics (R^2>0,96).

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