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Preparation of activated carbon based on synthetic and agricultural wastes: application to the adsorption of methyl orange

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Abstract - *This study focus on the optimization of operating conditions for activated carbons preparation starting from synthetic waste (tires) and agricultural waste (date pits) by chemical activation. The experimental design was used in order to determinate the optimal conditions for the preparation of a precursor with high properties. The results show that a temperature of 550°C and particle diameter of 800 µm are interesting. The specific surface area reached 770 and 1030m^2/g respectively for the active carbons obtained from tires and date pits. In order to evaluate the efficiency of these adsorbents, we selected an anionic dye (orange methyl) as a pollutant. Kinetic results show that the adsorption equilibrium is reached at around 60 min with an adsorbed amount of 21.42 mg/ g and 38.83 mg/g for the TAC (Tire Activated Carbon) and the DPAC (Date Pits Activated Carbon) respectively. The different isotherms were well fitting by Freundlich model.*

Résumé - *Ce travail s'intéresse à l'optimisation des conditions opératoires pour la préparation des charbons actifs à base de déchets synthétiques (pneus) et de déchets agricoles (noyaux de dattes) par l'activation chimique. Le plan d'expérience a été utilisé afin de déterminer les conditions optimales pour la préparation d'un précurseur ayant des propriétés élevées. Les résultats montrent qu'une température de 550 ° C et un diamètre de particule de 800 µm sont intéressants. La surface spécifique a atteint 770 et 1030 m^2/g, respectivement, pour les charbons actifs obtenus à partir des pneus et des noyaux de dattes. Afin d'évaluer l'efficacité de ces adsorbants, nous avons sélectionné un colorant anionique (méthyle orange) comme un polluant. Les résultats de la cinétique montrent que l'équilibre d'adsorption est atteint à environ 60 min avec une quantité adsorbée de 21,42 mg / g et 38,83 mg /g pour le TAC (charbon actif à base de pneu) et le DPAC (charbon actif à base de noyau de datte) respectivement. Les différentes isothermes étaient bien ajustées par le modèle Freundlich.*

Keywords: Activated carbon - Tires - Date pits - Optimization - Experimental design - Dye adsorption.

1. INTRODUCTION

Coal, which is traditionally used as fuel for its specific properties, is also often used as adsorbent or in the manufacturing of electrodes, carbon fibers, and catalysts [1]. The increasing demand in adsorbent materials drives research towards the production of activated carbons from unconventional materials, such as synthetic and agricultural waste.

Several studies have shown the production and characterization of activated carbons from a wide range of materials of different origins [2-9].

Generally, the preparation of activated carbon can be divided into three categories such us: chemical activation with H_3PO_4 [10], physical activation with CO_2 and combined method using bothCO_2 and H_3PO_4.

The chemical activation is often preferred [11] due to several economic and structural reasons. The most important agents are used phosphoric acid [12], zinc chloride [13-15] and alkali metal hydroxides [16]. Phosphoric acid has been particularly used for several decades [17, 18] to prepare activated carbon with large specific surfaces [19]. Its role is widely described in the literature [20-22].It has also been demonstrated that the distribution of the porosity of the activated carbon in the H_3PO_4 is heterogeneous.

This work falls into a valorization context. Waste tires as well as agricultural waste (date pits) are used as precursors of activated carbons. The selected diameter is between 800-2500 µm and the temperature range is between 400-600 ° C.

Optimal experimental conditions were investigated to obtain activated carbons with interesting specific surface allowing them to be used as adsorbents [23].

Two steps have been undertaken, a screening step which determine among the factors identified by the experimenter who have a statistically significant influence on variations in response. This is done implicitly to a simplification of the problem. Research is why the answer varies (depending on what factors). In addition to influencing factors it is possible to identify interactions of factors that will have a significant influence on the response and the optimization step was to determine the optimal conditions of activated temperature, nature of three activating agents H_3PO_4 or CO_2 or combined H_3PO_4/CO_2 and the particle diameter for the preparation of activated carbons from tires and date pits.

These materials in clued various applications such as the purification of fluids by adsorption, storage of gas. They are also used in heterogeneous catalysis as carriers of the active phase. These adsorbents were evaluated for the treatment of industrial textile water by adsorption process.

2. METHODS AND MATERIALS

Waste tires used in this work come from tires of the same car (Michelin primacy HP). Concerning agricultural waste, the date pits (Deghlet-Nour) come from south Algeria, collected in 2010). The chemical agent used are H_3PO_4 (85%), CO_2 and H_3PO_4/CO_2 [24]. The two starting materials were washed with distilled water and dried in an oven at 105°C for 24 hours. They are then cut and ground and sieved to retain the granulometric fraction with diameter between 800 and 2000 µm.

2.1 Chemical pretreatment and preparation of activated Carbon

2.1.1 Using phosphoric acid

The technique consists to introducing in a reactor, a mixture containing a determined mass of the chosen granulometric fraction with 2 ml of H_3PO_4 (85%) per gram as proposed in [24]. The mixture was refluxed at 85°C during 2 h then carbonized in a quartz tubular reactor of a diameter of about 3 cm at 500°C under a flow of 20 l/h of nitrogen. To eliminate the excess of H_3PO_4, the prepared carbon has been washed with water in a Soxhlet extractor until a neutral pH was reached (20cycles). The sample was dried at 110°C in an oven [25].

2.1.2 Using carbon dioxide

In this activation, there are two steps which are the carbonization and the activation of the raw material. Carbonization is the thermal decomposition at high temperature under inert gas (here, nitrogen); the activation is carried out in a chamber preheated to 600°C under controlled flow of oxidant gases (here, carbon dioxide). Temperature is maintained for a period of 1 hour to obtain a dry residue. The latter is washed with distilled water under reflux until neutralization of the rinsing water.

2.1.3 Using carbon dioxide and phosphoric acid (H_3PO_4/CO_2)

In this activation, the particles of the selected diameter are first impregnated with 2 ml/g of H_3PO_4 (chemical activation), and then are subjected to a temperature rise of 10°C/min up to different temperatures (500-850°C) under a flow of 20 l/h of nitrogen. When the temperature is reached, the nitrogen is replaced by CO_2 (physical activation) and the activation persists during 1 hour.

2.2 Physicochemical characterization of activated carbon

The obtained materials were characterized by different methods. The surface area were determined from nitrogen adsorption isotherms measured at liquid nitrogen temperature using an ASAP 2010 sorptometer (Micromeritics) equipped by software for accessing to the specific surface (A_{sp}) according to classic Brunauer, Emmet and Teller (BET) [20].

The total pore volume was estimated from the adsorbed amount at a relative pressure of between 0.985 and 0.9990. The micropore volume is determined by the Dubinin *et al.* [26] model. The specific surface area determined by this analysis is the response used in the experimental design as described in the next section. The objective of this study is to optimize the parameters in order to reach a maximum of A_{sp}.

3. DESIGN EXPERIMENTAL METHOD

The experimental design method consists to investigate the effects of different factors to optimize the studied system with a minimum number of tests, based on mathematical equations. These expressions can model the responses of our system versus controlling factors. The quality of the models is statistically analyzed by the analysis of variance method (ANOVA) [27].

The experimental controlling factors which influence the activation of coals are characterized as follows:

-The activation temperature varied between 450°C and 850°C is considered as a quantitative controlling factor associated to the centered reduced variable X_1 which varies between -1 and +1.

-The nature of three activating agents H_3PO_4 or CO_2 or combined H_3PO_4/CO_2, is considered as a qualitative controlling factor with various levels associated to X_2 which is a vector with three levels {Eq. (1)}:

$$X_2 = \begin{bmatrix} H_3PO_4 \\ H_3PO_4/CO_2 \\ CO_2 \end{bmatrix} \qquad (1)$$

-The third factor which is the particle diameter (800 – 2000 μm) is a quantitative factor associated to X_3 which varies between -1 and+1.

According to the nature (discontinuous, multilevel and qualitative factors) of these factors, particularly the activating agent, an experimental design based on the screening objective is first necessary to determine the best value. After that, a second experimental design leads to the optimization of two other factors which are temperature and particle diameter.

For screening, the matrix of experiences responding to this type of strategy is D-optimal giving 18 trials, three of which are replicated. Note that the mathematical model is a linear interaction of order 1 {Eq. (2)}.

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_1X_2 + a_5X_1X_3 + a_6X_2X_3 \qquad (2)$$

Y is a three level response in a column vector form.

The next experiment design which is associated to the second optimization step consists to realize surface response modeling in order to maximize the A_{sp} value. Thus, a Composite Face Centered (CCF) has been selected from 11 trials, three of which are replicated. The selected factors are X_1: temperature in the range 550 and 600°C, and X_2: particles diameter varying between 800 and 2500 µm. The proposed mathematical model is polynomial of second degree with interaction of first order.

4. APPLICATION TO THE ADSORPTION

The study of the adsorption of methyl orange on the three powdered activated carbon (CAC, DPAC, TAC) clearly implies the determination of the contact time to reach adsorption equilibrium. This is an important step in any adsorption study.

Elimination of the kinetics of methyl orange on two activated carbons (DPAC, TAC) are made in aqueous dye solutions of 50 mg/l at 25 °C, then we add a mass of 0.05 g of activated carbon at pH of 6. The solutions were stirred for 6h using a type of shaker (Edmund Buhler Gmb HSM- 30) and then filtered. Lagergren's pseudo-first-order model, {Eq. (1)}, and Ho's pseudo-second-order model, {Eq. (2)} applied

$$q = q_e (1 - e^{-k_1 t}) \qquad (3)$$

$$q = \frac{q_e^2 \, k_2 \, t}{1 + q_e \, k_2 \, t} \qquad (4)$$

Where q_e and q (mg/g) are the amount of dye adsorbed at equilibrium and time t (min), k_1 (min^{-1}) is the pseudo-first rate constant and k_2 (g/mg.min) is the pseudo-second-order model. The adsorption isotherms are important in determining the maximum adsorption capacities and the design of new adsorbents, it is essential in our study to determine.

There are many theoretical models have been developed to describe the adsorption isotherms. In our study we used the most widely used isotherm models of Langmuir and Freundlich given by {eq. (5)} and {eq. (6)} respectively:

$$q_e = q_m \frac{k_L \times C_e}{1 + k_L \times C_e} \qquad (5)$$

$$q_e = K_F \times C_e^{1/4} \qquad (6)$$

5. RESULTS AND DISCUSSION

5.1 Screening phase

Before regression step (fit, modeling), mathematical adjustment of the two responses based on two controlling factors is considered. This is to analyze the correlation between the two responses to show dependencies or not. It appears a significant correlation between specific surface area A_{sp} and log (V_{mes}/V_{tot}).

It has been shown that both responses are strongly dependent with correlation coefficient of 93 and 95% respectively for tire and date pits activated carbons. Indeed an increase of surface area reduces mesoporosity. Thus, (V_{mes}/V_{tot}) ratio was not considered in order to keep only the independent responses [28].

The quality of the response surface model is then studied, with multilinear regression MLR by analysis of variance ANOVA. Note that the interaction between temperature (X_1) and diameter (X_2) is practically zero.

Table 1 shows the analysis of variance (ANOVA) for the A_{sp} response results. The quality of the response surface model in variance and prediction are related to the explained variance R^2 coefficient and the prediction coefficient Q^2 respectively. The coefficient R^2 equals 91 and 93% for the tire and date pits activated carbons respectively. This shows that the model is highly significant. In addition to that, Q^2 takes the values of 70 and 60 % for the two precursors, suggesting a good predictive model.

The ANOVA of this response showed that the model is highly significant as evidenced by the F value (the ratio of the regression mean square to the mean square of the actual error). F value equals 11.865 and 11.5601 respectively for the tire and the date pits carbonaceous materials and a very low probability value (P = 0.001) in all cases, which indicates that the model is statistically significant.

Table 1: Statistical parameters values of the ANOVA
for screening and optimization phase

A_{sp}(BET) m²/g	Screening phase					Optimization phase				
Tire char	0.913	0.70	11.865	0.001	18	0.926	0.646	12.46	0.008	11
Date pit char	0.923	0.59	11.560	0.001	18	0.976	0.786	39.89	0.000	11

This statistical analysis shows that the response surface model, A_{sp}, can be considered as representative and is written in vector notation:

- **For the tire activated carbon**

$$\mathrm{Log}A_{sp}(\mathrm{BET}) = \begin{bmatrix} H_3PO_4 \\ H_3PO_4/CO_2 \\ CO_2 \end{bmatrix} = 1.4866 - 0.2270\,X_1 + \begin{bmatrix} +0.1220 \\ -0.0057 \\ -0.1162 \end{bmatrix} X_2 - 0.02\,X_3 + \begin{bmatrix} -0.2366 \\ -0.0931 \\ +0.3298 \end{bmatrix} X_1 X_2 + 0\,X_1X_2 + \begin{bmatrix} -0.0543 \\ +0.0644 \\ -0.0050 \end{bmatrix} X_2 X_3 \quad (7)$$

- **For the date pits activated carbon**

$$\mathrm{LogA_{sp}\,(BET)} = \begin{bmatrix} \mathrm{H_3PO_4} \\ \mathrm{H_3PO_4/CO_2} \\ \mathrm{CO_2} \end{bmatrix} = 438 - 9.566\,X_1 + \begin{bmatrix} +132.69 \\ -39.077 \\ -93.613 \end{bmatrix} X_2$$

$$-66.164\,X_3 + \begin{bmatrix} -135.599 \\ +27.976 \\ +107.622 \end{bmatrix} X_1\,X_2 + 3.7384\,X_2\,X_3 + \begin{bmatrix} -32.14 \\ +26.009 \\ 6.1303 \end{bmatrix} X_2\,X_3 \qquad (8)$$

A/Effect of temperature on the surface area

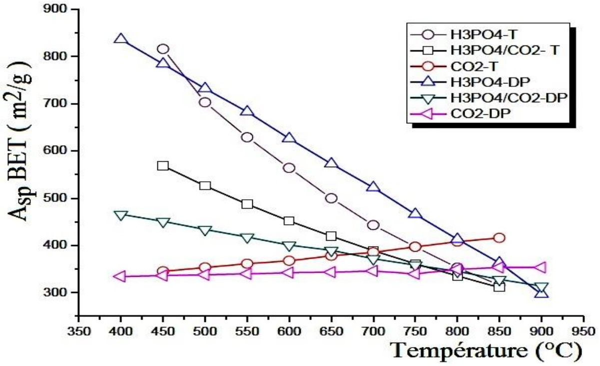

Fig. 1: Effect of temperature on the response of (**a**): TAC (**b**): DPAC

Figure 1 shows the effect of temperature on the specific surface area Asp according to the nature of the chemical agents. It appears that CO_2 does not promote the development of a good specific surface in the studied temperature range. In contrary, H_3PO_4 agent leads to an interesting specific surface area at low temperatures.

The combination of the two chemical agents CO_2/H_3PO_4 improves the surface values in the low temperatures field, but still insufficient by compared to specific surface area developed by H_3PO_4 alone.

B/Effect of particle size on the surface area for different activation agents

The effect of particle size on the surface area for different activation agents is reported on figure 2.

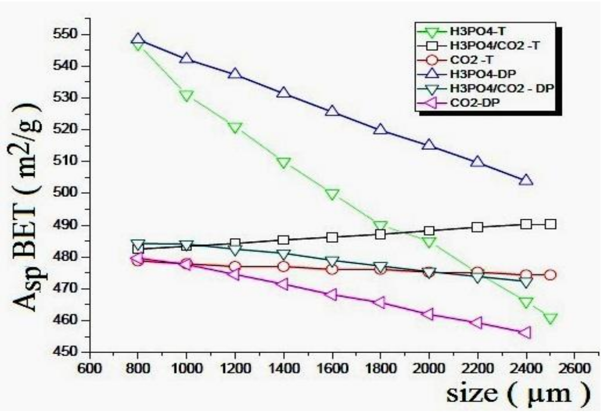

Fig. 2: Effect of particle size on the surface area of (**a**): TAC and (**b**): DPAC

Figure 2 shows the effect of the particle size on tire and date pits active carbon response in term of A_{sp}.

Concerning tire precursor, and when the particle size increases from 800 to 2500 µm, the behavior of A_{sp} value is different according to the type of activation. For CO_2 and H_3PO_4 used separately, the specific surface area decreases of about 16 and 7% respectively.

Nevertheless, when particle size equals 800 µm, the maximum surface area reached 550 m^2/g with H_3PO_4.

In contrary, when the activated carbon was prepared y the combined method (H_3PO_4/CO_2), the specific area rises slightly from 420 to 460 m^2/g in the range of diameter of 800 to 2000 µm.

Finally, H_3PO_4 is the chemical agent that generates the best A_{sp} at 550 °C for lowest particle size 800 µm. Thus, in the next step of the work H_3PO_4 is selected because of its excellent performance.

Concerning date pits precursor, the behavior of Asp versus the fraction diameter is the same for the three kinds of activation (CO_2, H_3PO_4 and the mix CO_2/H_3PO_4). Nevertheless, phosphoric acid seems to be more efficient to generate higher Asp values and particularly for lower particle size.

5.2 Optimization phase

The chemical agent H_3PO_4 was chosen because of its performance in terms of specific surface area. The characteristic parameters values of ANOVA were determined by regression following the partial least squares method [29], and are shown in **Table 1**. Based on the A_{sp} values, we can see clearly that the response surface model of specific surface area is statistically significant, because the probability, is lower than 0.05 [30].

The quadratic model which is associated to CFC experiences plan can be written:

- **For the tire activated carbon**

$$A_{sp}(BET) = 549.864 - 74.82X_1 - 60.47X_2 + 19.69\,X_1^2 - 32.25X_2^2 - 2.10X_1X_2 \quad (9)$$

- **For the date pits activated carbon**

$$A_{sp}(BET) = 544.579 - 23.833X_1 - 144.33X_2 + 349.553X_1^2 - 473X_2^2 + 45.25X_1X_2 \quad (10)$$

After determination of surface response model, a simulation of iso- curves form of A_{sp} surface versus centered variables is carried out figures 3-a, 3-b.

Figure 3 shows the presence of two separate domains of particle size. In the low domain (small than 2200 µm), specific surface area gradient is sensitive to the concomitant variation of temperature and particles size. This gradient is negative, suggesting that A_{sp} decreases when the two factors values increase.

Where the diameter is larger than 2200 µm, the A_{sp} gradient is negative and depends only to the temperature, particularly in the 550-580°C range. However, it was noted that the most interesting values of specific surface area are localized in the low temperatures range for small particle size of tire, contrary to the date pits, which show a different behavior.

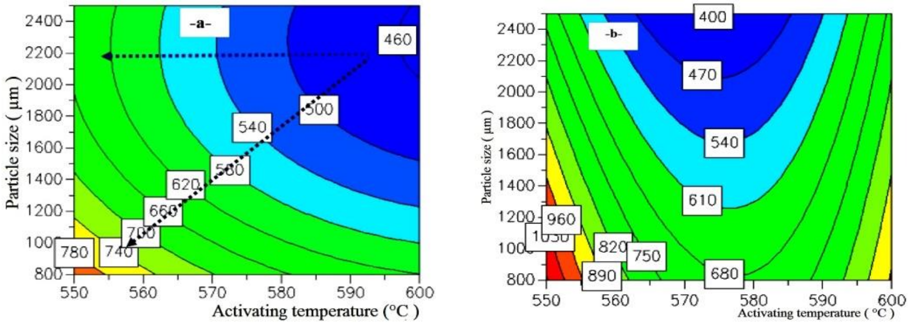

Fig. 3: Iso-response curves for H_3PO_4 – **-a-** TAC and **-b-** DPAC

Indeed in the range of 570 - 580 °C and when the particle size decreases, the surface area rises from 400 to reach 680 m^2/g for particle diameter comprised between 900-1300 µm.

Comparing to tire carbons and for a particle diameter of 970 µm and activating temperature of 550 °C, the surface area reaches 1030 m^2/g for the date pits, which corresponds to an increase of about 36%.

For temperatures less than 560 °C and for a size particle less than 1600 µm, the surface area increases, and the behavior is similar for temperature higher than 590 °C, while for the tire and under these conditions, the A_{sp} does not exceed 620 m^2/g.

6. APPLICATION TO ADSORPTION

Kinetic adsorption curves of the methyl orange onto the two prepared activated carbon (TAC, DPAC) compared to the commercial activated carbon (CAC) are presented as adsorbed amount versus time $(Q = f(t))$. According to figure 4 we can see clearly that for all kinetic curves that the amount adsorbed increases with stirring time and reach maximum values of 49, 48 and 46 mg/g for CAC, DPAC and TAC respectively.

In addition to this, the time of pseudo-equilibrium for the three kind of activated carbon was faster around 5 min, which indicated the efficiency of prepared activated carbon.

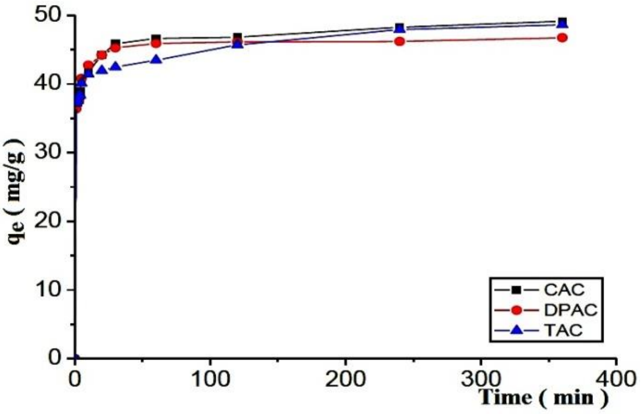

Fig. 4: Kinetic adsorption of orange methyl onto CAC, DPAC and TAC

Table 2: Kinetic adsorption constant from pseudo-first-order and pseudo-second-order model

	Pseudo-first-order model		Pseudo-second-order model	
	K_1 (min^{-1})	R^2	K_2 (g/mg.min)	R^2
CAC	1.468	0.920	0.132	0.720
NAC	1.503	0.940	0.118	0.820
TAC	1.781	0.93	0.227	0.600

Modeling results shows (**Table 2**) that the pseudo-first-order model properly depicts the adsorption process in agreement with the results of Cheknane *et al.* [31] for the adsorption of Basic Yellow 28 and Green Malachit onto granular pillared clay. The prepared activated carbon have a significantly higher rate constant ($K_1 > 1.50$ min^{-1}) compare than commercial activated carbon ($K_1 = 1.468$) this is can be explained by the structural proprieties of prepared activated carbon.

$$q_{CAC} = 104 \text{mg/g}, \; q_{TAC} = 96 \text{ mg/g} \text{ and } q_{NAC} = 86 \text{ mg/g}$$

Table 3: Freundlich parameter of used adsorbents

	Pseudo-first-order model		Pseudo-second-order model	
	K_1 (min^{-1})	R^2	K_2 (g/mg.min)	R^2
CAC	1.468	0.920	0.132	0.720
NAC	1.503	0.940	0.118	0.820
TAC	1.781	0.93	0.227	0.600

On the other hand we note that different isotherms obtained for the three adsorbents the types S curves according to Gilles classification. Which indicates that the adsorbed molecules promote the subsequent adsorption to other molecules (cooperative adsorption due to attractions between molecules of the solute by Van Der Waals forces)? Modeling results of obtained isotherms (**Table 3**) shows that the Freundlich model describe well our system, with values of $n < 1$ note the favorable adsorption and Freundlich equilibrium constant ($K_f > 12$ mg$^{1-1/n}$ L$^{1/n}$ g^{-1}) for all adsorbents.

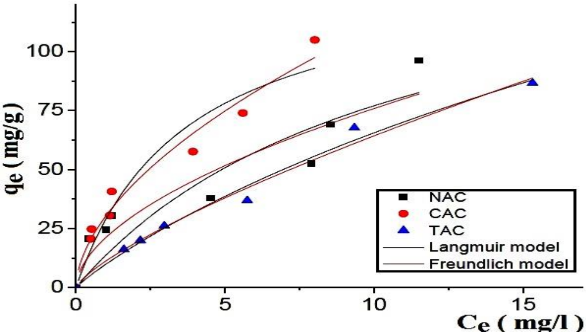

Fig. 5: Adsorption isotherm of orange methyl onto CAC, DPAC, and TAC

The maximum sorption values (q_{max}) in the present study were compared with other adsorbents (**Table 4**). It can see that prepared activated carbon based on synthetic waste (tire) and agricultural wastes (date pits) shows great potential as an adsorbent for orange methyl compare to other adsorbents.

In order to prove the efficiency of our adsorbents, we have done a comparison with other adsorbents of literature. The results were regrouped in **Table 4** where we have shown the adsorption capacities.

Table 4: Absorption capacity of some adsorbents

Sorbents	**Sorption capacity**	**pH**	**References**
Activated carbon powder and granular from eucalyptus wood	0.	/	[32]
Sugarcan bagasse	222	5	[33]
Activated carbon from rice husk	233	3	[34]
Activated carbon from eggshe	192	5	[35]
Biomass of maize stover	19	5	[36]
Tire activated carbon	96	66	This study
Date pits activated carbon	84	6	This study

7. CONCLUSION

Design of experiments (DOE) is used to analyze the influence of some parameters on the specific surface of a relatively new adsorbent.

Screening of experiments was carried out to limit the number of potentially sensitive factors following the observed response, namely the specific surface area. Chemical activation was performed to model the specific surface by DOE, according to the most important parameters such as temperature and particle size.

This model simultaneously quantifies the influence of each parameter on the maximum specific surface and shows the relationship between the various sensitive parameters. The values of F (Fischer parameter) and probability P show that the obtained model reflects very well the experimental results.

Preparation results show that waste tires and date pits are good precursors for the production of activated carbon with interesting textural properties.

In the optimization conditions, the activated carbon obtained from agricultural waste has a larger specific surface area of about 1030 m^2/g compared to that obtained from synthetic waste 770 m^2/g. Application of this new generation in the adsorption of orange methyl shows a great efficiency for methyl orange compare to other adsorbents with $(q_{max} > 86\ mg/g)$.

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