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Optimization of preparation and application of activated carbon derived from cypress cones

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ABSTRACT/RESUME

Abstract: *The present paper concerns the valorization of a botanic solid waste to synthetize an activated carbon from the cypress cones (Cupressus sempervirens cones) that grows spontaneously in the north region of Algeria. The goal and the novelty of this study is the feasibility of chemical activation with orthophosphoric acid of cypress cones as a new low-cost precursor. The performance of this activated carbon is tested in batch adsorption of the basic dye (methylene blue) from aqueous solutions. An experimental factorial design was used to determine the interaction effects of the operating conditions for both steps activation and carbonization. The maximum 97.29 % of dye elimination was obtained with the optimal activated carbon (AC) produced under the operating conditions, impregnation mass ratio of 1:1 for 5 hours and carbonization at 873 K for 4 hours. The effects of pH solution, initial dye concentration, mass adsorbent, and temperature on the adsorption of methylene blue on optimal AC are also studied. The adsorption kinetics were determined from aqueous dye solution and correctly described by the pseudo-second-order model. The adsorption isotherms were modeled with the Langmuir, Freundlich, Temkin and Jovanovic models, it was found that Freundlich and Temkin models are the best models to describe the adsorption mechanism. The efficiency of industrial textile wastewater treatment by adsorption on the optimal activated carbon gave a good elimination of COD, color, and TSS over 50% of removal.*

I. Introduction

Reliable access to clean and affordable water is considered one of the most basic humanitarian goals, and remains a major global challenge for the current century. Industrial activities play an ever-greater role in exacerbating water scarcity by contaminating natural water sources[1], and the responsible of more than a half of global water consumption and water pollution[2]. Dyes are among the pollutants that have severe restrictions on disposal because the worldwide annual production of dyes is more than 7 10^5 tonesand the its loss in the dying process can be as high as 50% [3,4]. During the last decades, researchers have strived to remediate polluted water. In this regard, conventional treatment processes, including adsorption with different types of the adsorbents, coagulation, ion exchange, advanced oxidation, biodegradation have been developed [5-8]. Adsorption is commonly employed as a polishing step to remove organic and inorganic contaminants in water and wastewater treatment [9], this technology should be applied to processes that have

low concentrations of pollutants or when the adsorbent has a low cost or can be easily regenerated. Different adsorbents have shown potential for pollutant removal in wastewater treatment but, thanks to its high internal surface area and porosity, and it surface chemical properties, activated carbonisbyfarthe most widely used[2]. Activated carbons are made from materials rich in carbon through activation and carbonization process. The porous structure and the adsorbent properties of an activated carbon are obtained throughout its activation, which can be divided into two distinct groups: Physical and chemical activation. During physical activation, the carbonization of raw material is carried out in an atmosphere of CO_2 or steam. This process is preferred because it is environmentally friendly and cheaper[10]. But the chemical activation process produces activated carbon with bigger surface area and high mesoporous structure [11]. A variety of agricultural waste was used to prepare activated carbon in laboratories as indicated in numerous scientific articles, such as avocado [12], grape waste [13], mango [14], banana's peels and coffee husk [15], corncob wastes [16], almond shells [17], helm oak [18], kenaf core fiber [19] olive and apricot stones [20,21] and carob processing waste[22]. The latest studies showed that fluoride in water, Acid Red 97, Reactive Orange 122 dyes, hexavalent chromium and nickel (II) could be easily removed by carbons produced from banana peel and coffee husk [15]. Similar efficiency in the removal of basic dye was proved using broccoli stems, prickly pear peels, and white sapote seeds AC-based [23].

Since 2006, the natural fiber based activated carbons have increasingly got attention to be used as adsorbents to purify polluted gaseous and liquid effluents [23,24]. Methylene blue (MB), a rather big heterocyclic aromatic dye, is a good choice for testing the performance of adsorbents whose mesoporosity suggests their application for adsorption of liquid pollutants. Therefore, MB value is the most popular parameter used to appropriately measure the adsorption capacity of the mesoporous structure of activated carbons[25]. In addition to mentioned above the presence of MB dye in effluents of textile and other industries represents a source of environment contamination [26].

In this work a novel cypress cone based activated carbon is prepared by chemical activation. The preparation is optimized using an experimental design used to investigate the effect of different operating parameters on methylene bleu adsorption in aqueous solution, the kinetic an isotherm behavior was modeled and an industrial application to treat textile wastewater is performed to test the efficiency of this mesoporous material.

II. Materials and methods

II.1. Mathematical modeling

The empirical first-order polynomial model in (Eq 1) explains the behavior of the system.

$$\boldsymbol{Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k-1} \sum_{j=2}^{k} \beta_{ij} x_i x_j + \varepsilon} \qquad (\mathbf{1})$$

Where, Y is the predicted response, x_i, x_j,..,x_k are the input variables that affect the response and $x_j x_k$ are the interaction effects, β_0 is the intercept term, β_i (i = 1,2. ., k) is the linear effect, β_{ij} (i = 1, 2 …, k; j = 1, 2 …, k) is the interaction effect and ε is a random error. Regression analysis was used in order to fit the response function to the experimental data and to recognize the relevant terms of the model [27].

The finest model and the significance of each coefficient were determined by analysis of variance (ANOVA), including the sequential F-test, and other adequacy measures. The greater the magnitude of the F-value, and therefore the smaller the P-value, the higher significant of the corresponding coefficient [27].

The expressions of RMSEP (Root Mean Square Error of Prediction) and RMSPD (Root Mean Square Prediction Difference), which are usually used as the main criteria to assess the model performance, are shown in eq (2) and eq (3) respectively[27].

$$\boldsymbol{RMSEP = \sqrt{\frac{\sum_{i=1}^{n} (y_{pred(i)} - y_{ref(i)})^2}{n}}} \qquad (\mathbf{2})$$

$$\boldsymbol{RMSPD = 100 \sqrt{\sum_{i=1}^{n} \frac{(y_{pred(i)} - y_{ref(i)})^2}{(y_{ref(i)})^2} \times \frac{1}{n}}} \qquad (\mathbf{3})$$

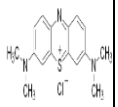
Where $y_{pred(i)}$ is the predicted value for sample i, $y_{ref(i)}$ is the reference value for this sample, and n is the number of samples [27].

II.2. Materials

The cones of local cypresses used for investigation in this study were collected after maturity from the region of Mila in the north east of Algeria, washed several times with distilled water to remove dust and other residues, dried during 24 h at 333K, and cut in small pieces of 10 mm.

A basic dye of analytical grade was used for adsorption experiments: Methylene Blue (basic blue 9, C.I. 52015) purchased from Panreac Quimica S.A.U (Table 1).

Table 1. Characteristics of Methylene Blue [28]

Dye	λ_{max}	Molecular weight ($g.mol^{-1}$)	Chemical formula	Chemical structure
Methylene blue (cationic)	664 nm	319.85	$C_{16}H_{18}ClN_3S$	

Orthophosphoric acid isused in the activation process with a purity of 85-87% (CAS n°7664-38-2 M.W. 97.995) purchased from CARLO ERBA REAGENTS.
Textile wastewater recovered from the outlet of pretreatment plant of an Algerian textile company, is treated by adsorption on prepared activated carbon. Table 2 includes the characteristics of this effluent before treatment.The pollution parameters are respectively: total organic carbon, electrical conductivity, chemical and biological oxygen demand, and total suspended solid (Table 2).

Table 2.*Characteristics of industrial textile wastewater effluent*

Parameter	*pH*	*TOC (mg/L)*	*EC (mS/cm)*	*COD (mgO_2/ L)*
value	10	344	4.86	919
Color (Pt/CO Unit)	*BOD_5 (mgO_2/L)*	*TSS (mg/L)*	*Ca^{2+} (mg/l)*	*Cl^- (mg/L)*
354	141	122	36	1567

II.3.Construction of Experimental design

The experimental data were statistically and graphically analyzed using the JMP Statistical Discovery Software 11.0.0 (SAS Institute Inc.). Full Factorial Design with two central points for checking was used to characterize the interaction between the variables of preparation process and the response.
Preliminary experiments were performed to determine the independent variables and their experimental ranges to design the experimental tests. Based on the preliminary results, the four most important operating variables, which affect the efficiency of AC prepared AC during dye removal are mainly:
(A) Impregnation rate of the precursor in the chemical agent of orthophosphoric acid activation whose mass varies from 1:1 to 1:5 m/m;
(B) Impregnation time: 2h to 5h at equilibrium temperature 358 K under stirring speed of 300 rpm;
(C) Temperature of carbonization: the heating process slope of 10 K/min between 673 K and 873 K;
(D) Period of carbonization: 1h to 4h in an electric furnace (Nabertherm SN 306352).
The combination between the different levels of activation parameters is established by the application of a full factorial design by considering in response the percentage of dye removal of the prepared AC; 16 tests with one central point were performed twice according to data gathered on table 3. The produced activated carbon was washed with deionized water until the pH of the solution approached the neutrality, and then dried at 353 K in an oven for 24 hours. The adsorption experiments were carried out by contacting 0.1g of each prepared AC with 100 ml of Methylene Blue solutions with concentration 5 10^{-5} $mol.L^{-1}$ during 24 hours.
The color removal percentage considered as the response for the mathematical model was calculated from the residual Methylene Bleu concentration measured by UV absorbance (UV/Vis SAFAS MONACO SP 2000 model).

II.4. Batch Adsorption Experiments

A stock solution of 1 $g.L^{-1}$ were prepared by dissolving the necessary amount of methylene blue (MB) on deionized water then diluted to obtain the desired dye concentration. The parameters that have effect on adsorption performance were studied: time of contact, pH of the solution, the initial concentration of MB, and finally the temperature of adsorption. The pH effect on dye adsorption was studied in the range of 2 to 12. Solutions of different pH were prepared with distilled water and adjusted with HCl and NaOH solutions at 0.1 $mol.L^{-1}$.
Quantities of 0.05 g of optimal AC were added to 50 mL of 50 $mg.L^{-1}$ MB solutions for 24 hours to reach equilibrium, the samples are then centrifuged for 20 min at the speed of 4000 rpm in UNIVERSAL centrifuge 320R Model. The residual concentrationofdye in thesupernatant was measuredby UV-Visanalysis at a constantwavelengthof 664 nm in a double-beam spectrophotometer (UV/Vis SAFAS MONACO SP 2000 model). The effect of temperature was investigated at free pH of MB solutions at concentration 50 $mg.L^{-1}$, 50 ml was shakenwith 50 mg ofthe optimal AC for 24h at different temperatures (293-323K) thencentrifuged and the residual dye concentration was measured.
The kineticexperimentswereperformedbymixing 0.05 g of optimal AC with 50 mLof 50 mgL^{-1} MB

solutions, individually, at a constant stirring rate of 400 rpm at room temperature. Samples were withdrawn at appropriate time intervals and the residual dye concentration in the supernatant was measured after centrifugation. The percentage of dye removal and its adsorbed amount at the equilibrium are expressed in eq (4) and eq (5) respectively.

$$\%\ \boldsymbol{Dye\ removal} = \frac{(C_0 - C_e)}{C_0} * 100 \quad (4)$$

$$Q_e = \frac{(C_0 - C_e) * V}{m} \quad (5)$$

C_0: initial dye concentration ($mg.L^{-1}$)
C_e: residual dye concentration at equilibrium ($mg.L^{-1}$)
Q_e: quantity of adsorbed dye by mass unit of adsorbent ($mg.g^{-1}$)
V: volume of the solution (L)
m: quantity of AC added as adsorbent (g).

For the solid-liquid system, adsorption isotherm describes the adsorption behavior. The experimental results are correlated with adsorption model to explain the adsorption mechanism, the heterogeneity of the adsorbent surface and gives further information for the design of adsorption systems.

The equilibrium isotherms of adsorption were obtained by mixing a mass of optimal AC 30 mg with 50 ml of different initial concentration ranging from 0.2 to 0.9 $g.L^{-1}$ of MB solutions during 24 hours under an agitation speed of 500 rpm at free pH and 293K temperature. Then, the residual concentration of MB is measured. In this study, the Langmuir, Freundlich, Temkin, and Jovanovic models are used. Table 3 gives the equation of each model and its linear formula.

Table 3. *The forms of the used isotherm models [29]*

Models	Forms	Linear form	Significance
Langmuir	$Q_e = \frac{Q_e k_L C_e}{1 + k_L C_e}$	$\frac{1}{Q_e} = \frac{1}{Q_{max} k_L C_e} + \frac{1}{Q_{max}}$	Adsorption occurs on homogeneous monolayer without interactions between adsorbed molecules, and all sites of adsorption surface have the same energy.
Freundlich	$Q_e = k_f C_e^{1/n}$	$\ln Q_e = \ln k_F + \frac{1}{n} \ln C_e$	The Freundlich isotherm is based on a heterogeneous adsorption surface with sites of different adsorption energies.
Temkin	$Q_e = \frac{RT}{B_T} \ln(K_T C_e)$	$Q_e = \frac{RT}{B_T} \ln K_T + \frac{RT}{B_T} \ln C_e$	The Temkin model shows the effects of indirect adsorbate/ adsorbent interactions on the adsorption isotherm.
Jovanovic	$Q_e = Q_{max}(1 - e^{-K_j})$	$\ln Q_e = \ln Q_{max} - K_j C_e$	The model is based on the formation of monolayer without side interactions.

Where Q_e (mg/g) equilibrium capacity; C_e (mg/L) equilibrium concentration; Q_{max} (mg/g) maximum capacity; K_L (L/mg) Langmuir constant; K_F the relative adsorption capacity, n the degree of adsorption dependence on the equilibrium concentration; B_T (J/mol) the variation of adsorption energy; K_T (L/mg) Temkin constants; K_J (L/mg) Jovanovic constant.

Based on the values of adsorption conditions reported in previous works [30], the operating conditions of the preliminary adsorption are: 1g of AC/Liter of wastewater, mixed for 120 min at temperature 303 K and 300 rpm of stirring speed, in order to measure the uptake of pollutant from textile wastewater.

III. Results and discussion

III.1. Modelizationofdyeremovalandstatisticalanalysis

The experiments of synthesis are gathered in Table 4 with results of dye removal percentage and mass of AC resulted from 20 g of precursor for each essay.

Table 4. *Experimental design based on full factorial design (FFD)*

Test	Encoded conditions	(A) R	(B) t_a (H)	(C) T(K)	(D) t_{car}(H)	Mass (g)	Color removal %
1	−−−−	1	2	673	1	9.88	70.27
2	−−−−	1	2	673	1	9.98	70.50
3	−−−+	1	2	673	4	4.35	77.79
4	−−−+	1	2	673	4	4.25	76.73
5	−−+−	1	2	873	1	6.37	84.25
6	−−+−	1	2	873	1	6.51	87.07
7	−−++	1	2	873	4	2.11	94.00
8	−−++	1	2	873	4	2.14	97.53
9	−+−−	1	5	673	1	9.42	77.79
10	−+−−	1	5	673	1	9.51	84.48
11	−+−+	1	5	673	4	6.40	96.12
12	−+−+	1	5	673	4	6.43	98.35
13	−++−	1	5	873	1	6.22	88.24
14	−++−	1	5	873	1	6.27	91.06
15	−+++	1	5	873	4	2.73	97.17
16	−+++	1	5	873	4	2.76	97.29
17	+−−−	5	2	673	1	9.87	93.77
18	+−−−	5	2	673	1	9.90	95.06
19	+−−+	5	2	673	4	7.37	77.20
20	+−−+	5	2	673	4	7.51	80.49
21	+−+−	5	2	873	1	8.41	73.91
22	+−+−	5	2	873	1	8.39	74.61
23	+−++	5	2	873	4	5.70	87.30
24	+−++	5	2	873	4	5.49	85.89
25	++−−	5	5	673	1	13.20	92.94
26	++−−	5	5	673	1	13.25	89.42
27	++−+	5	5	673	4	10.53	90.59
28	++−+	5	5	673	4	10.59	93.77
29	+++−	5	5	873	1	8.79	94.59
30	+++−	5	5	873	1	8.83	82.72
31	++++	5	5	873	4	4.71	79.43
32	++++	5	5	873	4	4.75	70.27
Central points	0000	3	3.5	773	2.5	7.90	94.47
	0000	3	3.5	773	2.5	7.96	93.88

From data in table 3 experimental runs 8, 12, 15 and 16 gave the maximum percentage of dye removal. The application of Standard Least Squares (SLS) method gave the dye removal percentage as a function of the rate of impregnation (A) , the duration of impregnation (B), the temperature of carbonization (C) and the period of carbonization (D).

$$y = 85.961 - 0.833A + 3.058B + 0.627C + 1.538D - 1.465AB - 4.659AC - 2.045BC - 3.543AD - 0.179BD + 0.488CD \quad (6)$$

The estimated values of the color removal percentage, using the model in eq (6) are plotted versus the actual values in figure (1). It appears that the predicted values from the polynomial expression in eq (6) fitted the actual values experimentally performed with R^2 equal to 0.69, RMSEP estimated at 6.036 and the RMSPD value is 5.98%.

The test of model adequacy given by the analysis of variance (Table 5) indicated that the probability value 0.0015 is small enough to show a very convincing significance so the model fits the experimental results better than a simple mean.

Table 5. ANOVA analysis

Source	**DF**	**Sum of Squares**	**Mean Square**	**F Ratio**
Model	10	1717.9908	171.799	4.6462
Error	21	776.5096	36.977	**Prob > F**
C. Total	31	2494.5004		0.0015*

It can be assumed that the model is correct when the residuals are without structure. They should be unrelated with the fitted values and should be randomly distributed. In our analysis, as shown in Figure 2, the curve does not reveal any obvious pattern, and therefore, it can be concluded that the residuals have a constant variance and the model is very significant.

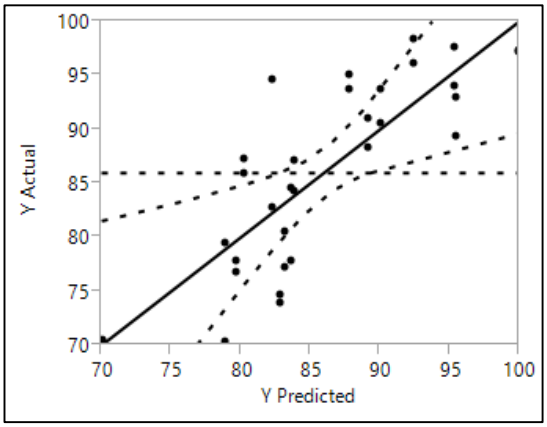


Figure 1. *Predicted versus actual values for color removal percentage*

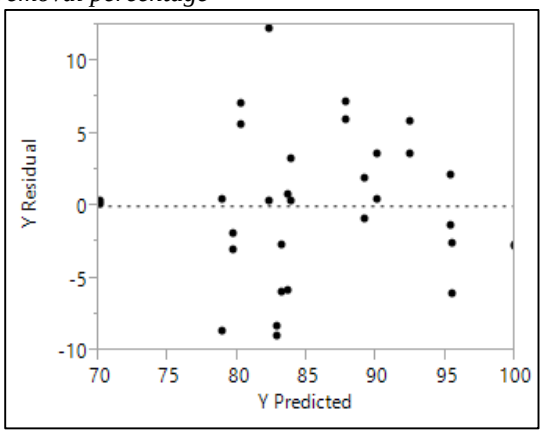


Figure 2. *Residuals versus thepredictedvaluesforcolorremovalpercentage*

The evaluation of each independent parameter influence on the response model is made throughout the p-value that indicates the probability of getting an even more extreme statistic since the real value tested is of hypothetical value, which is usually zero. So the smallest p-value shows a significant influence of the parameter. The most important parameters of this study are the duration of impregnation (B), the interaction between the ratio of impregnation (A) and the temperature of carbonization (C) in one hand and the period of carbonization (D) in another hand with respective p-values of 0.0097, 0.0003 and 0.003.
The numerical optimization of the desirability function gave the optimal preparation conditions to obtain activated carbon with a maximum percentage of dye removal. The optimization results are plotted in Figure 3 and the optimal conditions are reported in Table 6. In comparison with previous works using the conventional activation with H_3PO_4 for different precursors, the values of impregnation rate and temperature of carbonization are in agreement with the results in literature [31, 32], but a longer activation period.

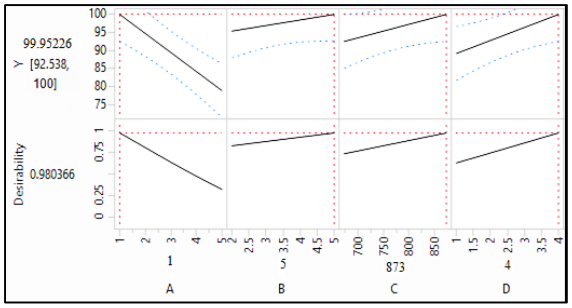


Figure 3.*Prediction profiler at maximal desirability*

Table 6. *Optimal conditions of activated carbon preparation*

Conditions	Value
Ratio of impregnation (A)	1
Duration of impregnation (B)	5 hour
Temperature of carbonization (C)	873K
Duration of carbonization (D)	4 hour

III.2. Adsorption kinetic and effect of the solution's initial pH and temperature on dye removal

As all transfer phenomenon in adsorption, the contact time is one of the most important parameters. The investigation of the contact time effect on the percentage of dye removal is shown in Figure 1, which points that, the dye adsorption of increases rapidly during the first minutes. According to the experimental data, the equilibrium was reached after 60 min.

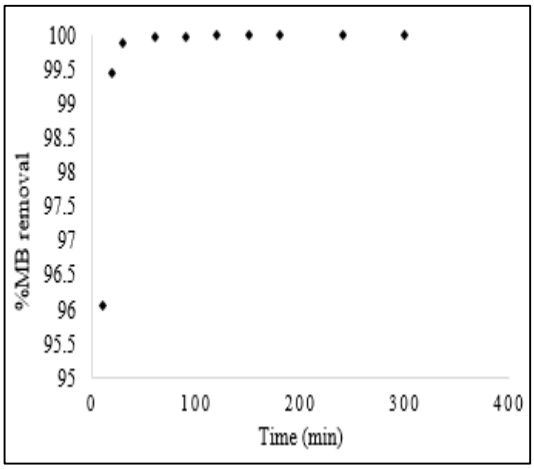


Figure 4.*Effect of contact time on MB removal*

The pH of aqueous solution is an important control parameter in the adsorption of cationic and anionic dyes, because of its impact not only on the adsorbent surface binding sites, but also on the ionization process of the dye molecules. The impact of solution's initial pH on dye removal percentage is shown in figure 5.

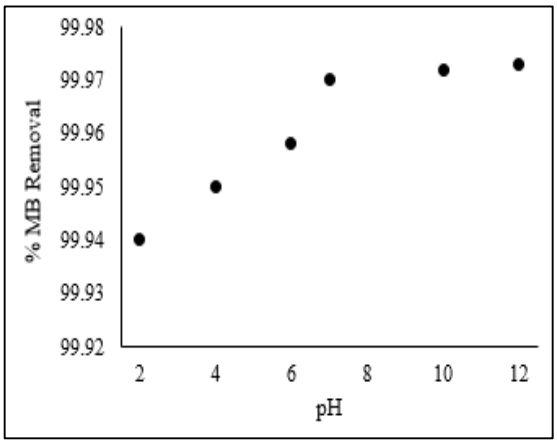


Figure 5.*Effect of solution's initial pH on MB removal*

The adsorption of MB increases with the pH of solution. When the pH value increases from 4 to 8, the dye removal percentage initially increases sharply and then reached a constant value at the maximum of dye removal around 99.97% at pH 9. The electrostaticinteractionbetweencationic MB moleculesandnegativelychargedcarbon was strengthenedwith increasing Ph because of the pH of zero charged point of the activated carbon that was 3.4. The optimal pH value for MB adsorption is similar to the values of initial pH solution previously reported using artichoke leaves based AC [33] and corncob based AC [34].
The temperature influence is an important factor on dye adsorption especially because textile dyes are

mostly prepared at high temperatures. The evolution of dye removal percentage at different temperatures is shown in Figure 6.

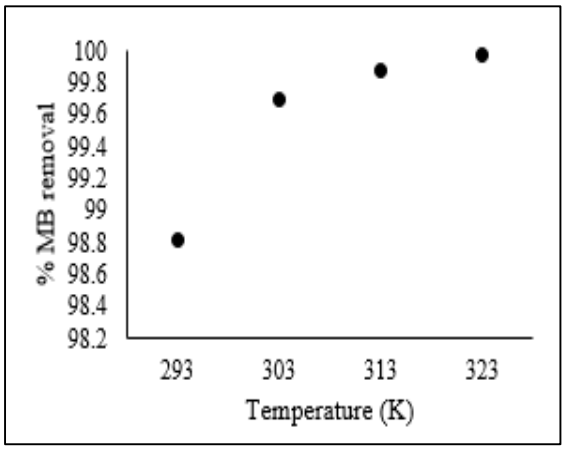


Figure 6.*Effect of temperature MB removal*

The percentage removal of MB expands from 98% to 99.99%, when the temperature of solution rises from 293 to 323K, such observations were reported by Lin et al [35]. This increase may be due to

(i) The penetration of dye molecules into the pores of adsorbent owing to the growth in their mobility at high temperature.
(ii) The chemical interactions between the dye molecules and the AC surface.

In order to reduce the cost of process, the adsorption is not always operated at high temperature, and as the dye removal percentage is acceptable at 313K, this would be the optimal temperature for MB adsorption.

III.3. Kinetic models of dye adsorption

The adsorption kinetics describes the adsorption rate and control the equilibrium time. In order to study adsorption's kinetics of MB, two models were used to fit the experimental data. Linear expressions of the pseudo-first-order and the pseudo-second-order models are respectively expressed in eq (7) and eq (8). The linear plots of the two models are shown in Figures (7, 8) and the kinetic parameters with correlation coefficients are listed in Table 7.

$$log(Q_e - Q_t) = log(Q_e) - \frac{k_1}{2.303}t \qquad (7)$$

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^{\,2}} + \frac{1}{Q_e}t \qquad (8)$$

The pseudo-first-order model is generally used to describe phenomenon that occurred at the beginning of the adsorption process where the pseudo-second-order model is used to describe the kinetic of adsorption process for a longer time interval.

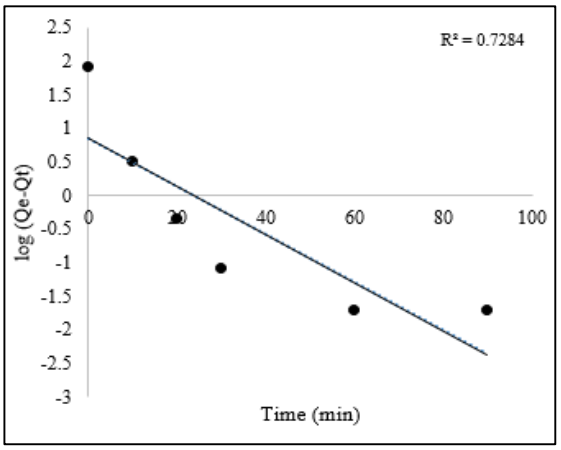


Figure 7.*Adsorption kinetic using pseudo-first-order model*

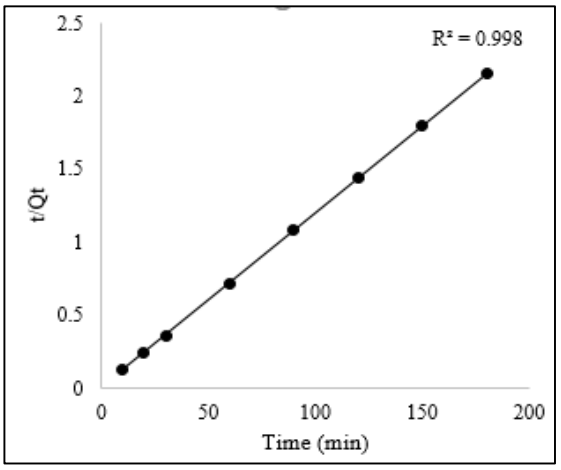


Figure 8.*Adsorption kinetic using pseudo-second-order model*

The pseudo-second-order model is more suitable for adjusting the kinetic of MB adsorption on the optimal activated carbon with high correlation coefficient R^2 equal to 0.9935 (Table 7). This modelindicatesthatthe rate-controlling stepischemisorptioninvolvingvalenceforcesthroughtheexchangeorsharingofelectronsbetween MB moleculesandthesurfaceof adsorbent [36]

Table 7. *Estimated kinetic model constants of MB adsorption on the optimal activated carbon*

Initial dye concentration ($mg.L^{-1}$)	Pseudo-first-order model	Pseudo-second-order model
50	k_1=0.0822 min^{-1} Q_e=7.10 $mg.g^{-1}$ R^2=0.7284	K_2=0.0576 $g.mg^{-1}$ min^{-1} Q_e= 83.33 $mg.g^{-1}$ R^2=0.998

where k_1 is the rate constant of the pseudo-first-order model, k_2 the rate constant of second-order model, Q_e and Q_t are the amount of MB adsorbed at equilibrium and time t respectively.

III.4. Adsorption isotherms

The adsorption isotherms are studied to determine the maximum quantity adsorbed by the material and to identify the type of adsorption. The experimental results are treated by the models previously summarized in Table 4. The adsorption isotherms for the MB are shown in Figures 9 (a, b, c, d). The linear data analysis listed in Table 8 shows that the isotherm of adsorption is better fitted with Freundlich and Temkin models which correlate the equilibrium data with R^2 greater than 0.91. The heterogeneous surface adsorption is at maximum capacity of 230 mg/g**.** Results of correlating the isotherm data are in accordance with the study reported by Yang and Qiu [37]. Table 9 presents a comparison of maximum MB adsorption capacities of AC prepared from different agricultural precursors. Negative value of the n in Freundlich model can be explained with the possibility of other competitive phenomenon like precipitation to occur simultaneously with adsorption. This is clearly confirmed with comparison of SEM analysis of the adsorbent surface before and after adsorption shown in figures 10 (a, b).

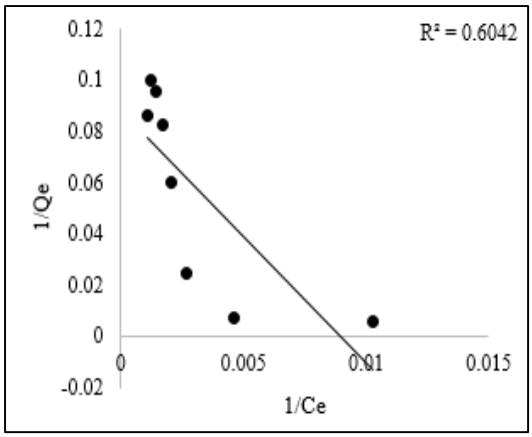


Figure 9(A).*Adsorption isotherms: Langmuir*

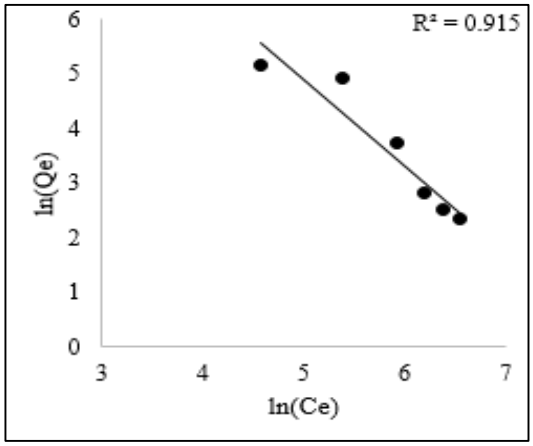


Figure 9(B).*Adsorption isotherms: Freundlich*

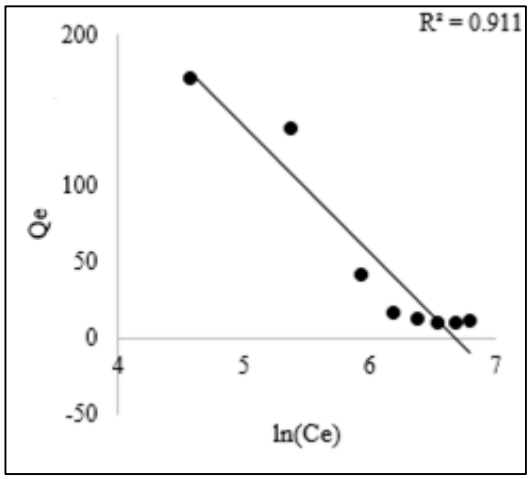


Figure 9(C).*Adsorption isotherms: Temkin*

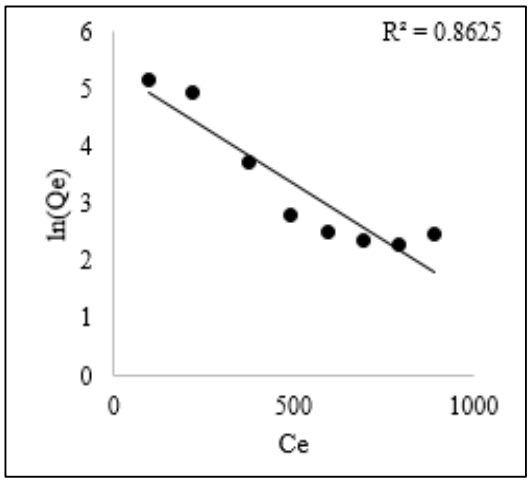


Figure 9 (D).*Adsorption isotherms: Jovanovic*

Table 8. *Linear data analysis of adsorption isotherm*

Langmuir		
K_L=-0.008 (L/mg)	Q_{max}= 11.36 $mg.g^{-1}$	R^2=0.604
Freundlich		
K_F=230	n=-0.66	R^2=0.914
Temkin		
K_T=0.0012 (L/mg)	B_T=-29.87	R^2=0.911
Jovanovic		
K_J=-0.003 (L/mg)	Q_{max}=204.17 $mg.g^{-1}$	R^2=0.865

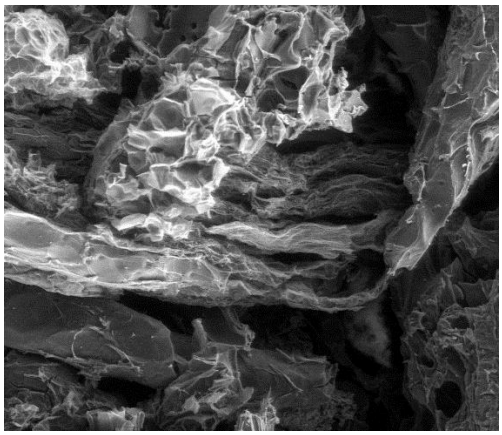


Figure 10 (a). Surface morphology of Cypress Cones based Activated carbon (at 800x magnification) Before adsorption, (b) After adsorption

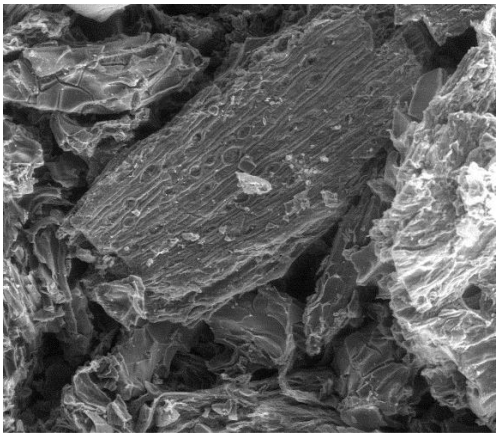


Figure 10 (b) Surface morphology of Cypress Cones based Activated carbon (at 800x magnification) after adsorption

Table 9 gave a comparison of the maximum adsorption capacity of the present activated carbon with previous works that used the same activation agent and the same synthesis method.

Table 9. MB adsorption capacities of AC prepared from different agricultural precursors

Activated carbon precursor	**Activation agent**	**Q_{max} (mg/g)**	**References**
Cypress cones	H_3PO_4	230	This work
Corncob	H_3PO_4	226.6	[16]
Jute fiber	H_3PO_4	225.6	[38]
Euphorbia rigida	H_2SO_4	114	[39]

III.5. Adsorption of the industrial textile wastewater

The application for the treatment of industrial textile wastewater shows a good efficiency in adsorption and a net decrease of several pollution parameters (COD, color and TOC) listed in Table 10. The best percentage of removal was observed for the color with 70%. Obtained results are promising to applicate this material in industrial wastewater remediation.

Table 10. *Estimation of pollution's parameters removal after adsorption on AC*

Parameter	Before adsorption	After adsorption	% Removal
Color (Pt/CO Unit)	354	106	70%
COD (mg/L)	919	367	60%
TOC mg/L)	344	172	50%
TSS (mg/L)	122	46.4	62%

III.6. Economicalstudy

According to the technical-economic study of the laboratory-scale production of activated carbon from Cypress cones, the production yield is about 140 Kg of AC per ton of natural precursor. The cost of commercial AC goes from 700 to 5000$ per ton depending on its quality [13]. Whereas the estimated cost of AC preparation from Cypress cones was determined to be around 300$ per ton, which explains that the selected precursor is a cost effective natural source to prepare commercial activated carbon.

IV. Conclusion

The activated carbon of cypress cones was obtained by a chemical activation method. Optimal conditions of preparation were determined using an experimental design. The effect of each parameter was investigated and proved that, the imbibition time and the interaction between imbibition ratio, time and temperature of carbonization have the most important impact on adsorption capacity of the prepared material.

Adsorption studies proved that the temperature has a strong and proportional effect in the MB adsorption on the optimal activated carbon, whereas the solution's pH had less influence. Kinetic studies indicated that the optimal time of contact was about one hour and the pseudo second-order model is the most suitable to explain the experimental data. The Freundlich and Temkin models explain the mechanism of adsorption with a maximum MB adsorption capacity of 230 mg/g of activated carbon. The preparation of activated carbon from local cypress cones is the cost-effective solution.

The results of textile wastewater adsorption on the produced activated carbon could be used in detailed study to enhance the treatment efficiency and simulation of the continuous process.

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