

## **Pomegranate Peels Precursor Used in the Synthesis of Activated Carbon: Application in the Wastewater Treatment**

Wafa Saadi\*, Souad Najar Souissi, Abdelmottaleb Ouederni

*National School of Engineers of Gabes, University of Gabes 6029 Gabes, TUNISIA*

*Received March 12, 2016; Accepted September 12, 2016*

**Abstract:** Activated carbon based pomegranate peels with potassium hydroxide as activating agent has been undertaken in the present study. Experiments were conducted to investigate the influence of different process parameters: the impregnation ratio, the temperature and the time of activation, followed by optimization. Activated carbon prepared in the optimum conditions with high specific surface area of  $1403 \text{ m}^2\text{g}^{-1}$  and total pore volume of  $0.7 \text{ cm}^3\text{g}^{-1}$  was evaluated for its ability to remove the 2-Nitrophenol from an aqueous solution in a batch process. Equilibrium studies were conducted in the range of 100-500 mg/L initial 2-Nitrophenol concentrations at temperature of  $30^\circ\text{C}$ . The experimental data were analyzed by the Langmuir, Freundlich and Temkin isotherm models. The kinetic models studies were also conducted. The pseudo-second order equation was the best applicable model to describe the adsorption process of 2-Nitrophenol onto optimized activated carbon compared to the commercial material.

**Keywords:** *Pomegranate peels, activated carbon, potassium hydroxide, adsorption, 2-Nitrophenol.*

### **Introduction**

Due to Nitrophenols harmful effects, wastewaters containing phenolic compounds must be treated before being discharge to receiving water bodies (Chern & Chien, 2002). They are frequently used as intermediates in the manufacture of explosives, pharmaceuticals, pesticides, pigments, dyes, rubber chemicals and so on (Uberoi & Bhattacharya, 1997). The 2-Nitrophenol (2NP) especially is used mainly as an intermediate for the production of dyestuffs, pigments, rubber chemicals, and fungicides (Burseay & Pellizzari, 1982). It poses significant health risks since it is highly toxic to mammals, microorganisms and anaerobic bacteria. Its toxicity is thought to be due to the nitro group being easily reduced by enzymes to a nitro anion radical, nitroso and hydroxylamine derivatives (Uberoi & Bhattacharya, 1997; Karim & Gupta, 2001, 2002). Many treatment methods have been applied to remove phenolic compounds from aqueous solution, such as biological treatment, catalytic wet oxidation, adsorption technology, air stripping, incineration, ion exchange and solvent extraction (Girish & Murty, 2012).

Activated carbon (AC) has become one of the most technically and widely used adsorbent because of its high adsorptive capacity. In general, it can be produced either by chemical or physical activation. Chemical process only involves single step in heating process to activate the carbon. This process needs chemical activating agent such as  $\text{ZnCl}_2$ ,  $\text{KOH}$ , and  $\text{H}_3\text{PO}_4$  (Basar, 2006; Hameed *et al*, 2009; Ruiz *et al*, 2015; Yakout & Sharaf El-Deen, 2011) to enhance carbon yield and produce micropores on the surface of the carbon. Physical activation involves carbonization of carbonaceous materials followed by activation of the resulting char in the presence of activating agents such as  $\text{CO}_2$  or steam (Sudaryanto, 2006).

Activated carbon can be prepared from different raw materials such as: apricot waste (Basar, 2006), lignocellulosic wastes obtained from the extraction of tannins (Ruiz *et al*, 2015), cassava peel (Sudaryanto, 2006), pistachio nut shell (Yang & Lua, 2003; Lua *et al*, 2004), olive stone (Ouederni *et al*, 2005). However, there are few publications reporting on the preparation of effective adsorbents from pomegranate peels (Ghaedi *et al*, 2012; Venckatesh *et al*, 2010; Bhatnagar & Minocha, 2009; Amin, 2009; El Nemer, 2009; Negi *et al*, 2003). Normally, these peels are used in the preparation of dyes, cosmetics, medications and cooking recipes (Yahiaoui, 2012).

The major novelty of this work is the production and optimization of activated carbon, from potassium hydroxide impregnated pomegranate peels samples by chemical activation process. The activated

---

\*Corresponding: E-Mail: saadiwafa@yahoo.fr;

carbon prepared was tested on the removal of 2NP from aqueous solutions. Our study presents the effect of impregnation and carbonization parameters on the yield and the textural properties of prepared activated carbons. In the other hand, the adsorption isotherm and kinetics of 2NP onto the optimum activated carbon is evaluated.

## **Materials and Methods**

### **Raw material**

Pomegranate peels (PP) was used as the precursor for the preparation of activated carbon. The collected peels were cleaned, dried, crushed and sieved to get the particles of size between 1.5 and 5 mm. The powdered sample was then examined by an elemental analyzer to determine the contents of C, H, N, and S (Table 1). The proximate analysis of precursor is shown in the table 2. The moisture content was found by oven-drying test method (TGA-LECO 701). In addition, an initial weight of 5g of PP are heated at temperature of 600°C in a Pyrolabo type muffle furnace in an oxidizing atmosphere to evaluate the thermal behaviour of the powder peels. The thermal stability of raw material was tested by measuring the mass loss during a heating ramp rate.

### **Activated carbon preparation**

The peels particles were impregnated with a potassium hydroxide solution with different impregnation ratio. This parameter is defined as:

$$\tau_{\text{imp}} = (\text{weight of KOH solution}) / (\text{weight of pomegranate peels}) \quad (\text{Eq.1})$$

The mixtures boiled under total reflux during an impregnation time ranges between 2- 4 hours at 102°C. At the end of this step, the grains are separated from the solutions by simple filtration without any washing.

The impregnated pomegranate peels are placed in a fixed bed in a tubular reactor with length of 25.5 cm and diameter of 6 cm. This reactor is placed in a horizontal electric furnace maintained at a controlled temperature. The pyrolysis is carried out under nitrogen flow.

The carbonization reaction produces the incondensable gases and tars. The solid is recovered after cooling by a slow nitrogen gas flow. During the activation process, the influence of parameters such as, the impregnation ratio between pomegranate peels/KOH solution, activation time, and activation temperature on the porosity development was examined.

In the first case, 1/2 to 1/5 impregnation ratios were used. While the carbonization temperature (700°C) and the activation time (2.5h) were kept as constants. Then, the impregnation time was ranged between 1 to 4 hours. The impregnation ratio 1/4 and time of 3h were fixed. In the second case, the carbonization temperature was varied from 500 to 900°C and the activation time was changed from 1 to 4h. All the activation processes were executed at the specified conditions under nitrogen atmosphere. Finally, the activated samples were washed with hot water for pH neutralization and dried at 110°C for 24h in a vacuum drier. The yield of activated carbon ( $\eta$ ) was calculated based on the weight of pomegranate peels on a dry basis from the following equation (Eq.2):

$$\eta = (\text{weight of activated carbon} / \text{weight of pomegranate peels}) \quad (\text{Eq.2})$$

## **Characterization of activated carbon**

### ***Textural properties***

The specific surface area and the pore volume of the activated carbon were determined from the nitrogen adsorption isotherms at 77 K using Brunauer-Emmett-Teller (BET) equation and Quantachrome Autosorb-1 instrument. The Dubinin-Radushkevich (DR) equation was used to calculate the micropore volume. The total pore volume was estimated to be the liquid volume of the adsorbate ( $N_2$ ) at a relative pressure of 0.99.

## **Nitrophenol Adsorption study**

### ***Adsorption equilibrium***

Equilibrium studies were done by contacting a 0.05 g sample sales placed in a series of Erlenmeyer flasks with 50 mL of the 2NP solution with different initial concentration varies between

20 and 500 mg L<sup>-1</sup>. The suspensions still stirring for 5 hours at ambient temperature and an agitation rate of 300 tr min<sup>-1</sup>. When the adsorption equilibrium is reached, the liquid phase is decanted for 24 hours. Then, the concentrations of 2NP in the samples were analyzed subsequently with UV-visible Spectrophotometry Shimadzu type.

**Adsorption Kinetics**

Kinetics studies were done by contacting 1 L of the 2NP solutions for different concentration 100-500 mg/L with 1g of activated carbon with particle size 0.125-0.2 mm at 200 tr/min. Samples of 3 mL were then pipetted out at different time intervals. The collected samples were then analyzed for their concentrations of 2-Nitrophenol. The stirring rate is a physical process condition that has no relation with the chemical nature of the adsorbent used. In the case of a solid-liquid system, the stirring role is to homogenize the particles distribution and increase the diffusion in the liquid phase. The optimal stirring rate was determined ranging from 100 to 300 rev/min. Under the same conditions, we conducted the kinetic adsorption measurements of 2NP.

**Results and Discussion**

**Precursor characterization**

Results of the ultimate and proximate analysis of the pomegranate peels are given in table 1 and table 2. The higher carbon content in pomegranate peels suggests the suitability of this material for the preparation of activated carbon.

**Table 1:** Chemical composition of pomegranate peels.

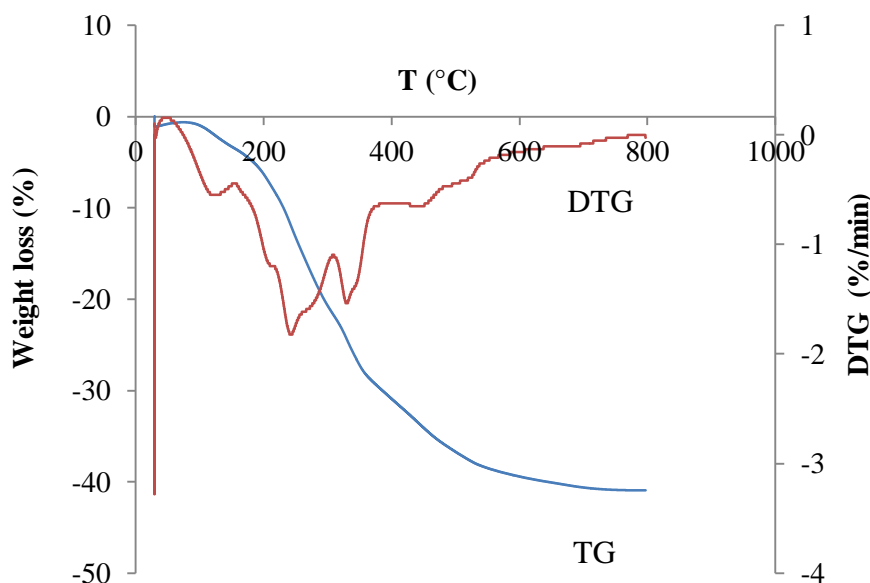
Ultimate analysis	C	H	N	S	O <sup>a</sup>
(Dry basis, wt %)	43.13	7.17	0.46	0.89	48.35

<sup>a</sup> Obtained by difference.

**Table 2:** Proximate analysis of pomegranate peels.

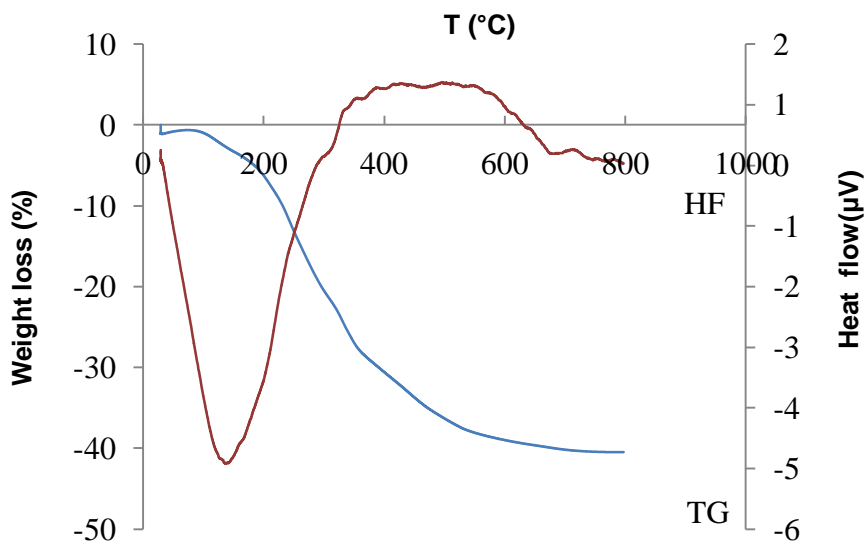
Proximate analysis	Moisture	Ash
(As received, wt %)	9.78	2.75

The mass loss curve (TG) and its derivative (DTG) of the dried powder of pomegranate peel in inert atmosphere, until temperature of 700 °C at heating rate of 10 °C min<sup>-1</sup> using a Setaram thermo-balance type are shown in Figure 1.



**Figure 1.** TG-DTG curves of PP

Through TG analysis can be observed three stages of mass loss. Until a temperature of 150 °C is related to loss of water in the sample; 150 °C to 350 °C has a loss of mass due to the decomposition of organic components, compatible to that described by Apaydin-Varol, they demonstrated that in this range of temperature, it is observed the decomposition of hemicellulose and cellulose. Then, from 350°C, there is the end of the decomposition of hemicellulose, predominantly below the decomposition of the cellulose. The mass loss to about 720 °C onwards is related to lignin degradation. Figure 2 illustrate the evolution of the heat flow generated during the pomegranate peels pyrolysis. It shows that the different steps proposed are exothermic.



**Figure 2.** TG-HF curves of PP

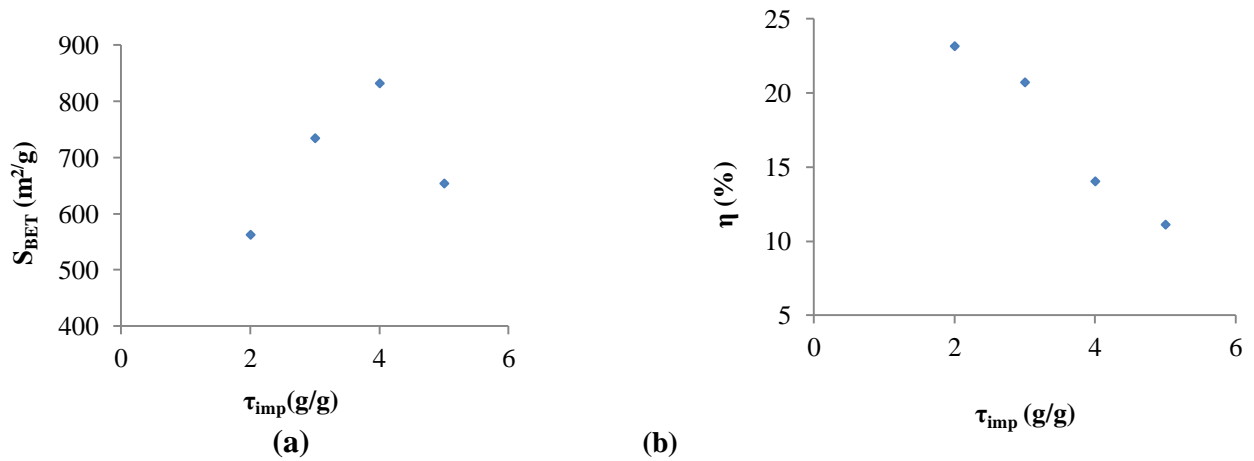
### Optimization of activated carbons preparation

#### *Effect of impregnation parameters on the specific surface area and the yield*

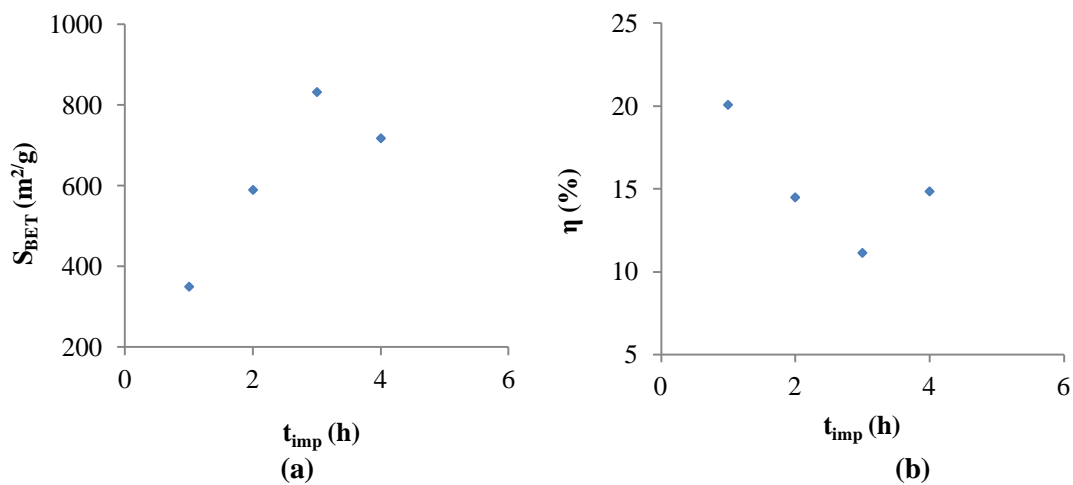
Activated carbon used in this part of the study were prepared by the impregnation with KOH aqueous solution using a different chemical ratio and then carbonized for 2.5 h at a temperature of 700°C. According to Fig. 3 (a), the increase of impregnation ratio ( $\tau_{imp}$ ) from 2 to 5 leads to more developed porosity, reaching a maximum specific surface area 833 m<sup>2</sup>/g at impregnation ratio equal to 4. So in this rate, the microporosity is well developed due to the presence of the hydroxyl group acts as the oxidizer for the C-KOH reaction, resulting in the consumption of carbon and the formation of pores within the internal (Yang & Lua, 2003). The microporosity development is mostly due to the intercalation of potassium metal in the carbon structure (Sudaryanto *et al.*, 2006). Beyond rate of 4, the specific surface area decrease may be due to the destruction of micropores and mesopores during their transformation.

It is seen from Figure 3 (b) that adding chemical agents to the precursor from 2 to 5, decreases the weight loss of the carbon products by 23.16% to 14.04%, because the potassium ions attached on the carbon surface acted as catalysts to accelerate gasification of the chars by CO<sub>2</sub>. Therefore, an increased amount of KOH enhanced this important function, resulting in an extensive C-CO<sub>2</sub> reaction and a larger weight loss due to carbon burn-off (Guo & Lua, 2002; Sudaryanto *et al.*, 2006).

Based to the maximum of specific surface area of activated carbon, we optimize the impregnation time, varying between 1 and 4 hours, shown in Fig.4 (a). According to this figure, it is clear that the time of about 3 hours in the KOH solution gives the highest specific surface area. This time is closely related to the broadcasting conditions of the chemical agent in the pomegranate peels grains. The evolution of the yield with the impregnation time is present in Fig.4 (b). It is noted that the yield decreases impregnation time by 1 to 3 hours. Beyond 3 hours, the yield increases may be this is due to the decrease of activated carbon micropores.



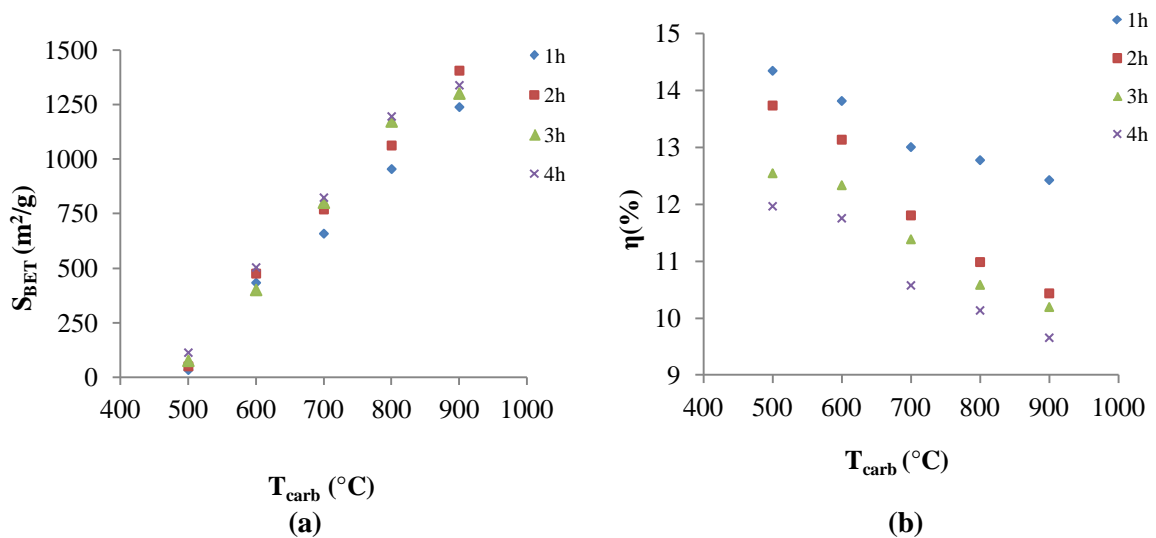
**Figure 3.** Effect of impregnation ratio on the BET surface area of AC (a) and the yield (b)



**Figure 4** Effect of impregnation time on the BET surface area of AC (a) and the yield (b)

***Effect of activation temperature on the yield and the textural properties of activated carbons***

Specific surface area evolution and the yield of activated carbons with varying activation temperature is shown in Figure 5.

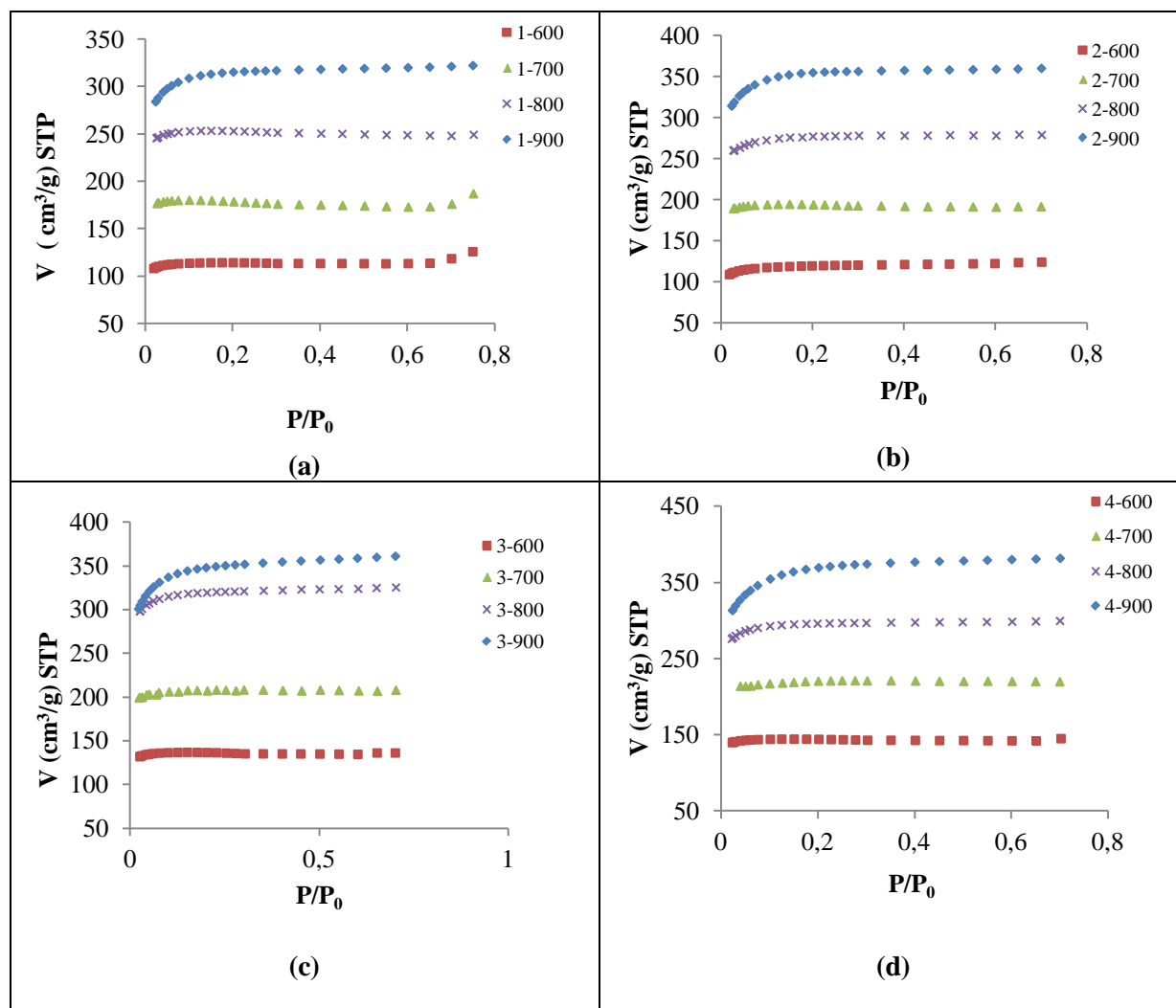


**Figure 5.** Effect of activation temperature on the BET surface area of AC (a) and the yield (b)

Specific surface area evolution and the yield of ACs with varying activation temperature are shown in Figure 5. The activation temperature has a significant influence on the development of porosity and the specific surface area of pomegranate peels activated carbons. According to Figure 5 (a), we can see that for the same activation time the specific surface area increase when temperature ranges between 500°C and 900°C. From activation temperature of 700°C, the specific surface area increase. Otowa et al. in 1993 indicated that high temperature and high KOH/carbon ratio produced large pores in the carbon structure, due to the presence of K<sub>2</sub>O, derived from KOH, and expanded the carbon atomic layers.

The activation temperature plays an important role in the performance of activated carbon. Fig.5 (b) shows that the increasing of activation temperature reduces the yields of the activated carbons continuously. This is expected since an increasing amount of volatiles is released at increasing activation temperature from 500 to 900°C. This decreasing trend in yield is paralleled by the increasing carbon consumption with increasing activation temperature due to the C-KOH reaction (Yang & Lua, 2003).

Figure 6 shows the N<sub>2</sub> adsorption isotherms at 77 °K on the chemically activated carbons generated at different activation temperatures. Generally, the shape of the isotherms changes with increasing activation temperature. For different activation time, the two nitrogen adsorption isotherms at 600-700°C and at 800-900°C show similar shapes. The isotherm increases at low relative pressure and tend to plateau in the long of relative pressure. It clearly indicate the type I isotherms, characteristics of microporous materials.



**Figure 6.** N<sub>2</sub> adsorption isotherm at 77 K on activated carbons prepared from pomegranate peels under different activation temperature, (a) t=1h, (b) t=2h, (c) t=3h, (d) t=4h

***Effect of activation time on the yield and the textural properties of activated carbons***

The activation time is another important process parameter for the C-KOH reaction. Fig.7 shows the effect of activation time on BET surface area and yield of prepared activated carbons. The results show that when the pyrolysis time increases from 1 to 4 hours, the specific surface area increases and the yield decreases. This result is probably due to the volatilization of organic precursor materials and the evolution of the C-KOH reaction, which leads to the formation of activated carbon. According to Fig.7 (a), we can see that the evolution of the specific surface area over time for different activation temperature from 500°C to 800°C is similar. For temperatures equal to 500°C and 600°C the specific surface area are very near when the activation time increases from 1 to 4h. It is clear that at temperature equal to 900°C proves the existence of a maximum specific surface area equal to 1403 m<sup>2</sup>/g for 2 hours.

The adsorption isotherm of activated carbons produced from pomegranate peels at activation time 1-4 h belong to a mixture of Type I and Type IV isotherms (see Figure 8). According to IUPAC classification, the Type I isotherm is associated with microporous structures and Type IV isotherm indicates mixture of microporous and mesoporous material. The plateau of this isotherm commences at high relative pressures (P/P<sub>0</sub>) and toward the end of isotherm, steep gradient is seen as the result of a limited uptake of nitrogen, indicating capillary condensation in the mesopores. Details of pore characteristics of activated carbon at different activation temperatures are given in Table 3.

**Table 3.** Textural properties of ACs on different activation temperature and time

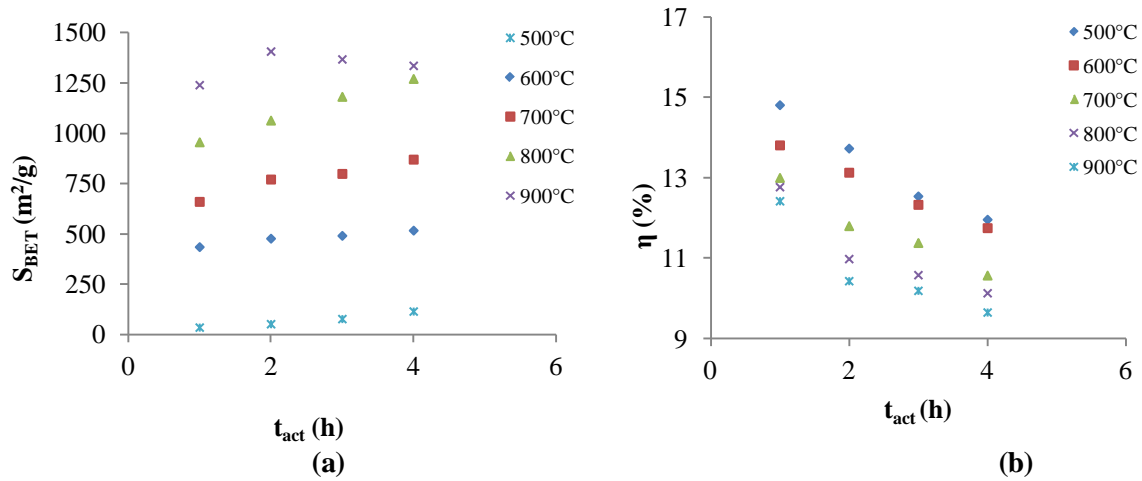
Activation conditions <sup>a</sup>	S <sub>BET</sub> (m <sup>2</sup> /g)	V <sub>mic</sub> (cm <sup>3</sup> /g)	V <sub>tot</sub> (cm <sup>3</sup> /g)	d (Å)
1-500	433	-	-	-
2-500	475	-	-	-
3-500	75	-	-	-
4-500	113	-	-	-
1-600	433	0.2734	0.4566	42.20
2-600	475	0.2020	0.2176	18.33
3-600	489	0.3263	0.529	27.34
4-600	515	0.2707	0.3519	43.29
1-700	659	0.4000	0.6086	37.01
2-700	769	0.306	0.3120	16.23
3-700	797	0.3323	0.3381	16.98
4-700	868	0.3681	0.4018	18.52
1-800	954	0.4202	0.4531	19.00
2-800	1062	0.4391	0.4411	16.61
3-800	1180	0.5227	0.6050	20.50
4-800	1269	0.5127	0.5246	16.53
1-900	1238	0.5292	0.577	18.65
2-900	1405	0.6017	0.617	17.57
3-900	1366	0.5939	0.6389	18.71
4-900	1334	0.5668	0.5809	17.42

<sup>a</sup> Note: a-b denote activation time (h)-activation temperature (°C).

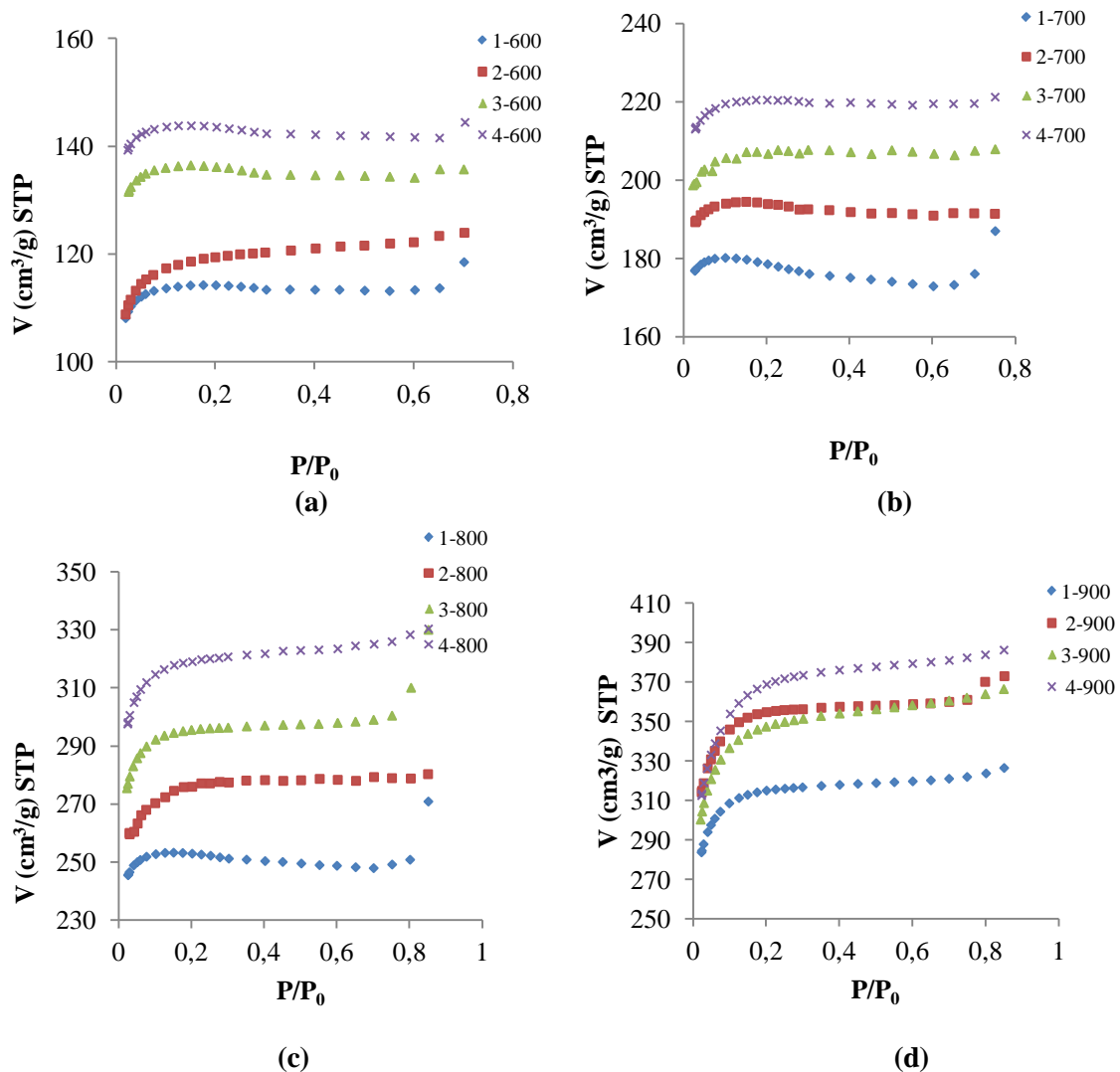
**Adsorption test**

***Determination of equilibrium time***

The variations of the adsorbed quantity for an initial concentration of 100 mg /L of 2NP are given in Figure 9. This figure shows that from 0.5 hour, the adsorbed quantity to an initial concentration of 100 mg/L remains constant. So a contact time of 2 hours is considered more than enough for the establishment of the equilibrium.

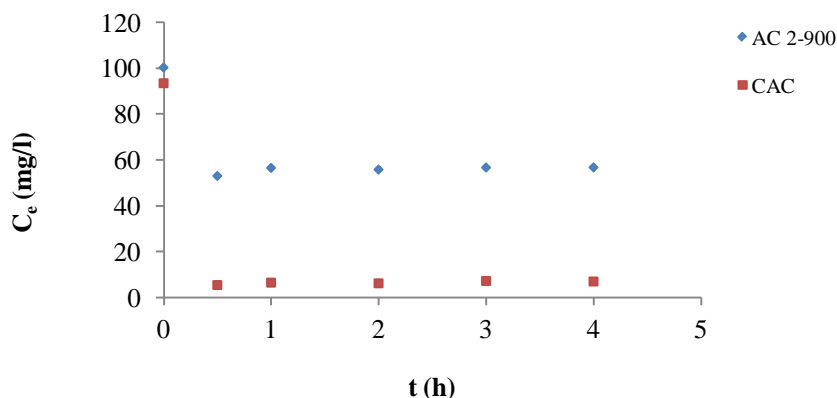


**Figure 7.** Effect of activation time on the BET surface area (a), and the yield of AC (b)



**Figure 8.**  $N_2$  adsorption isotherm at 77 K on activated carbons prepared from pomegranate peels under different activation time, (a)  $T=600^\circ C$ , (b)  $T=700^\circ C$ , (c)  $T=800^\circ C$ , (d)  $T=900^\circ C$ .

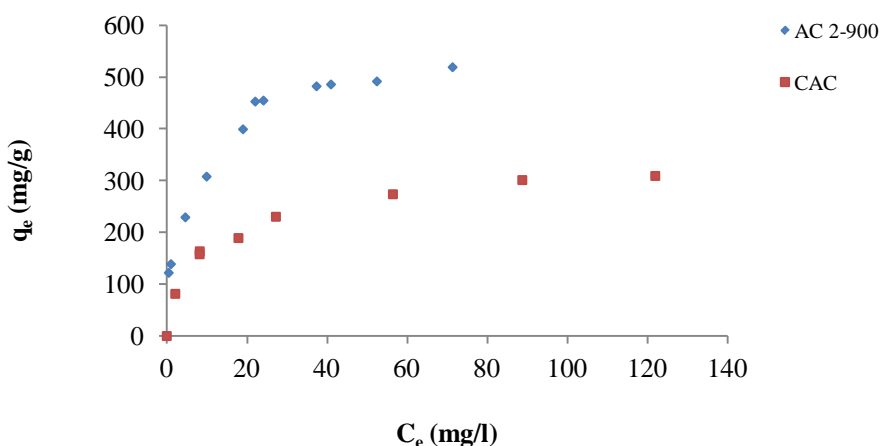




**Figure 9.** Evolution of the 2NP residual concentration on the two ACs as a function of time

**Adsorption isotherm**

Adsorption equilibrium models are a good way to explain the adsorption system. Its provide information about the adsorbate and adsorbent surface properties. There are several equilibrium isotherm models applied including, Freundlich, Langmuir and Temkin. The experimental adsorption isotherms of 2NP from aqueous solutions onto the optimum activated carbon based pomegranate peels (AC 2-900) and the commercial activated carbon (CAC) are presented in Figure 10.



**Figure 10.** Experimental adsorption isotherms of 2NP onto CAC and AC 2-900

According to the classification of Giles, MacEwan, Nakhwa & Smith (1960), the isotherm of 2-Nitrophenol displayed an L curve pattern. The L shape of the adsorption isotherm means that there is no strong competition between solvent (water) and the adsorbate (2NP) to occupy the adsorbents (AC 2-900 and CAC) surface sites. In this case, the longitudinal axes of the adsorbed molecules are parallel to the adsorbent surface (molecules adsorbed flat on the surface). The Langmuir class (L) is the most widespread in case of adsorption of phenolic compounds from water and it is characterized by an initial region which is concave to the concentration axis (Isichei and Okieimen, 2014). The same shape of isotherm was found by Isichei and Okieimen (2014), when they study the adsorption of 2NP onto water hyacinth activated carbon. The maximum adsorption capacities of the 2NP on both ACs are respectively 519 and 309 mg/g for AC 2-900 and CAC. In this study, Langmuir, Freundlich and Temkin isotherm models were used to describe the relationship between the amounts of 2NP adsorbed and its equilibrium concentration in solution at 30°C.

The Langmuir model (1916) can be represented by the following equation (Eq.3):

$$C_e/q_e = 1/K_L q_{max} + C_e/q_{max} \tag{Eq.3}$$

Where  $q_{max}$  and  $K_L$ (L/mg) are Langmuir constants related to adsorption capacity and rate of adsorption respectively. When  $C_e/q_e$  was plotted against  $C_e$ , a straight line was obtained.  $q_{max}$  was calculated from the slope whereas  $K_L$  was found from the intercept.

Hereby, a dimensionless constant, commonly known as separation factor ( $R_L$ ) defined by Webber and Chakkravorti (1963) can be represented as:

$$R_L = \frac{1}{1 + K_L C_0} \tag{Eq.4}$$

Where:  $C_0$  is the adsorbate initial concentration (mg/L). In this context, lower  $R_L$  value reflects that adsorption is more favorable. In a deeper explanation,  $R_L$  value indicates the adsorption nature to be either unfavourable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favourable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ).

The Freundlich model (1906) is given by the following equation (Eq.5):

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \tag{Eq.5}$$

Where  $C_e$  is the equilibrium concentration of the adsorbate (mg/L) and  $q_e$  is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g).  $K_F [(mg/g) (L/mg)^{1/n}]$  is the adsorption capacity of the adsorbent and  $n$  is a measure of adsorption intensity or surface heterogeneity. The plot of  $\ln q_e$  versus  $\ln C_e$  gave a straight line with slope of  $1/n$  whereas  $K_F$  was calculated from the intercept value.

Another popular equation (Eq.6) for the analysis of isotherms is Temkin and Pyzhev (1940) which are based on the supposition that the decline of the heat of adsorption as a function of temperature is linear rather than logarithmic.

$$q_e = B_1 \ln K_T + B_1 \ln C_e \tag{Eq.6}$$

Where  $B_1 = RT/b$  and  $K_T$  are constants.  $K_T$  is the equilibrium binding constant (L/mg) corresponding to the maximum binding energy and constant  $B_1$  is related to the heat of adsorption. A plot of  $q_e$  versus  $\ln C_e$  enables the determination of the isotherm constant  $K_T$  and  $B_1$ .

The parameters of models are calculated and summarized in table 4. It is clear from this table that the  $R^2$  values from both Langmuir and Freundlich isotherm describe the experimental data, but Langmuir isotherm model describes data better than Freundlich.

**Table 4.** Langmuir, Freundlich and Temkin parameters for 2NP adsorption on the Two ACs at 25°C

ACs	Langmuir			Freundlich			Temkin			
	$q_{max}$ (mg/g)	$K_L$ (L/mg)	$R^2$	$R_L$	$n_F$	$k_F$	$R^2$	A (L/g)	B (J/mol)	$R^2$
AC 2-900	555.55	0.16	0.994	0.143	3.01	145.61	0.984	5.11	88.24	0.961
CAC	333.33	0.10	0.997	0.150	3.16	75.23	0.955	1.89	57.66	0.993

**Adsorption kinetics**

The controlling mechanism in the adsorption of 2NP was examined using various kinetic models such as the pseudo-first order, pseudo-second order and intra-particle diffusion model.

Pseudo-first order model: The final integration of the Lagergren equation (7) is expressed in a linear form as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{Eq.7}$$

Where:  $q_e$  and  $q_t$  are the quantity adsorbed at equilibrium (mg/g) and at time  $t$ ;  $k_1$  is the rate constant of pseudo-first order adsorption ( $\text{min}^{-1}$ ); and  $t$  is the contact time (min). The plot of  $\ln (q_e - q_t)$  versus  $t$  should give a linear relationship with the slope equal to  $k_1$ .

Pseudo-second order model: The linear equation of the pseudo-second order is given by the following expression (8):

$$t/q_t = 1/k_2 q_e^2 + (1/q_e)t \tag{Eq.8}$$

Where:  $k_2$  is the rate constant of pseudo-second order adsorption ( $\text{g.mg}^{-1}.\text{min}^{-1}$ ).

The intra-particle diffusion model present by the theory of Weber and Morris (9).

$$q_t = k_i t^{0.5} + C \tag{Eq.9}$$

Or,  $k_i$  is the intra-particle diffusion constant ( $\text{mg/g min}^{1/2}$ ).  $q_t$  and  $t$  have the same meanings as given above; and  $C$  is a constant (mg/g), gives an idea about the thickness of the boundary layer.

All the kinetic parameters arising from the application of the three models to the data for the 2NP adsorption onto AC 2-900 and CAC are listed in Table 5. It clearly shows that the correlation coefficient values ( $R^2$ ) of the pseudo-second-order model for adsorbents greater than those obtained for the pseudo-first-order model. We can therefore conclude that the pseudo-second order model is more suitable to describe the 2NP adsorption process on both activated carbons.

The second-order rate constant  $k_2$  decreases with the increase of the initial concentration of the adsorbate. This may be ascribed to the enhancement of the pollutant molecules diffusion from the bulk of the solution to the sorbent surface as a result of the decrease of the number of water molecules holding each pollutant molecule compared to the number of water molecules in less concentrated solution (Sayed Ahmed et al., 2011).

The intra-particle diffusion constant  $k_i$  also shows a significant increase with the increase of the initial concentration, supporting thus the enhancement of the pollutant molecules on the surface located between adsorbent particles (Sayed Ahmed et al., 2011).

**Table 5:** Kinetic parameters for the 2NP adsorption onto AC 2-900 and CAC.

First order		Second order			Intra-particle diffusion			
$k_1$ ( $\text{min}^{-1}$ )	$R^2$	$k_2$ ( $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ )	$q_e$ (mg/g)	$R^2$	$k_i$ ( $\text{mg}\cdot\text{min}^{-1/2}\cdot\text{g}^{-1}$ )	C	$R^2$	
<b>AC 2-900</b>								
<b>Initial concentration (mg/L)</b>								
100	0.6922	0.9814	0.0194	114.9425	0.9952	18.828	87.726	0.9996
300	0.5443	0.9774	0.0087	322.5806	0.9975	33.224	218.95	0.9348
500	0.4637	0.9575	0.0036	476.1904	0.9938	70.811	249.23	0.9744
<b>Stirring rate (tr/min)</b>								
100	0.4762	0.9917	0.0032	312.5	0.9944	26.954	224.39	0.9716
200	0.5443	0.9774	0.0087	322.5806	0.9975	33.954	218.95	0.9348
300	0.5683	0.9826	0.0075	333.333	0.9972	36.918	219.8	0.9102
<b>CAC</b>								
<b>Initial concentration (mg/L)</b>								
100	0.7488	0.9209	0.2256	105.2631	0.9999	7.2974	87.912	0.4805
300	0.8479	0.9939	0.0217	256.4102	0.9974	20.768	193.78	0.8415
500	0.0364	0.9107	0.0338	384.6153	0.9998	13.787	346.13	0.5409
<b>Stirring rate (tr/min)</b>								
100	1.133	0.9899	0.0192	294.1176	0.9981	13.466	250.62	0.8987
200	0.8479	0.9939	0.0217	256.4102	0.9974	27.804	184.35	0.8542
300	0.5529	0.9429	0.03872	227.2727	0.9935	12.55	199.38	0.9928

## Conclusion

High surface area activated carbons were prepared from chemical activation of pomegranate peels with KOH solution. The pomegranate peels was found to be a good raw material for developing activated carbons with good pore characteristics. Under the experimental conditions studied, the optimum conditions for the preparation of activated carbon with high surface area and pore volume are: an impregnation ratio of 4, an activation hold time of 2 hours, and an activation temperature of 900°C. With these experimental conditions, an activated carbon with a BET surface area of 1403 m<sup>2</sup>/g and a total pore volume over 0.7 cm<sup>3</sup>/g was obtained. It is applied on the adsorption of 2-Nitrophenol in aqueous solution with adsorption capacity about 556 mg/g. better than the commercial one. So, the results proved that the prepared activated carbon was an effective adsorbent for the removal of 2-Nitrophenol from aqueous solution.

## References

- Amin NK, (2009) Removal of direct blue-106 dye from aqueous solution using new activated carbons developed from pomegranate peel: Adsorption equilibrium and kinetics, *J. Hazard. Mat.*, **165**, 52-62.
- Apaydin-Varol E, Putun AE, Putun E, (2007) Slow pyrolysis of pistachio shell, *Fuel* 86, 1892-1899.
- Basar CA, (2006) Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared waste apricot, *J. Hazard. Mat.*, **135**, 232-241.

- Bhatnagar A, Minocha AK, (2009) Adsorptive removal of 2,4-dichlorophenol from water utilizing *Punica granatum* peel waste and stabilization with cement, *J. Hazard. Mat.*, **168**, 1111-1117.
- Bursey JT, Pellizzari ED, (1982) Analysis of industrial wastewater for organic pollutants in consent decree survey, Contract No. 68-03-2867. Athens, GA: US EPA Environmental Research Laboratory 84.
- Chern JM, Chien YW, (2002) Adsorption of nitrophenol onto activated carbon: isotherms and breakthrough curves, *Water Res.* **36**, 647-655.
- El Nemer A, (2009) Potential of pomegranate husk carbon for Cr (VI) removal from wastewater: Kinetic and isotherm studies, *J. Hazard. Mat.* **161**, 132-141.
- Evans MJB, Halliop E, MacDonald JAF, (1999) The production of chemically-activated carbon, *Carbon*, **37**, 269-274.
- Freundlich HMF, (1906) Over the adsorption in solution, *J. Phys. Chem.*, **57**, 385-470.
- Ghaedi M, Tavallali H, Sharifi M, Nasiri Kokhdan SN, Asghari A, (2012) Preparation of low cost activated carbon from *Myrtus communis* and pomegranate and their efficient application for removal of Congo red from aqueous solution, *Spectrochimica Acta Part A: Molec & Biomol. Spect.* **86**, 107- 114.
- Giles CH, MacEwan TH, Nakhwa SN, Smith D, (1960) Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms and its use in diagnosis of adsorption mechanisms and in measurements of specific surface areas of solid, *J. Chem. Soc.*, **10**, 3973-93
- Girish CR, Murty VR, (2012) Adsorption of phenol from wastewater using locally available adsorbents, *J. Environ. Res. & Develop.* **6**.
- Hameed BH, Salman JM, Ahmad AL, (2009) Adsorption isotherm and kinetic modeling of 2, 4-D pesticide on activated carbon derived from date stones, *J. Hazard. Mat.*, **163**, 121-126.
- Ho YS, McKay G, Sorption of dye from aqueous solution by peat, (1998) *Chemical Engineering Journal* **70**, 115-154.
- Isichei TO, Okieimen FE, (2014) Adsorption of 2-Nitrophenol onto Water Hyacinth Activated Carbon-Kinetics and Equilibrium Studies, *Environment and Pollution* **3**, 99-111.
- Karim K, Gupta SK, (2001) Biotransformation of nitrophenols in up -flow anaerobic sludge blanket reactors, *Bioresource Technology* **80**, 179-186.
- Karim K, Gupta SK, (2002) Effects of alteration carbon sources on biological transformation of nitrophenols, *Biodegradation* **13**, 353-360.
- Langergren S, (1898) *Zurtheorie der sogenannten adsorption gelosterstoffe*. Kungligasuenska, vetenskapsakademiens Hanalinger, 241-39.
- Langmuir I, (1916) The constitution and fundamental properties of solids and liquids, *J. Am. Chem. Soc.* **38**.
- Lozano-Castello D, Lillo-Rodenas MA, Cazorla-Amoros D, Linares-Solano A, (2001) Preparation of Activated Carbons from Spanish Anthracite, I. Activation by KOH, *Carbon* **39**, 741-749.
- Lua AC, Yang T, Guo J, (2004) Effects of pyrolysis conditions on the properties of activated carbons prepared from pistachio-nut shells, *J. Analy. & Appl. Pyrol.* **72**, 279-287.
- Marsh H, Yan DS, O'Grady TM, Wennerberg A, (1984) Formation of active carbon from cokes using potassium hydroxide, *Carbon* **22**, 603-11.
- Moreno-Castilla C, Carrasco-Marin F, Lopez-Ramon MV, Alvarez-Merino MA, (2001) Chemical and physical activation of olive-mill waste water to produce activated carbons, *Carbon* **39**, 1415-1420.
- Negi PS, Jayaprakasha GK, Jena BS, (2003) Antioxidant and antimutagenic activities of pomegranate peel extracts, *Food Chemistry* **80**, 393-397.
- Otowa T, Mltoth RT, (1993) Production and adsorption characteristics of MAXSORB: high-surface-area active carbon, *Gas Separation & Purification* **7**, 241-245.
- Otowa T, Nojima Y, Miyazaki T, (1997) Development of KOH activated high surface area carbon and its application to drinking water purification, *Carbon* **35**, 1315-19.
- Ouederni A, Souissi-Najar S, Ratel A, (2005) Adsorption of dyes onto activated carbon prepared from olive stones, *J. Environ. Sci.* **17**, 998-1003.
- Ruiz B, Ruisanchez E, Gil RR, Ferrera-lorenzo N, Lozano MS, Fuente E, (2015) Sustainable porous carbons from lignocellulosic wastes obtained from the extraction of tannins, *Microporous and Mesoporous Materials* **209**, 23-29.

- Sayed A, Reham M, Abo El-enin M, El-Nabarawy Th, (2011) Adsorption properties of activated carbon prepared from pre-carbonized petroleum coke in the removal of organic pollutants from aqueous solution, *Carbon Letters*, , **12**, 152-161.
- Sudaryanto Y, Hartono SB, Irawaty W, Hindarso H, Ismadji S, (2006) High surface area activated carbon prepared from cassava peel by chemical activation, *Bioresource Technology* **97**, 734-739.
- Temkin MJ, Pyzhev V, (1940) Recent modifications to Langmuir isotherms, *Acta Physiochem. USSR* **12**, 217-222.
- Uberoi V, Bhattacharya SK, (1997) Toxicity and degradability of nitrophenols in anaerobic systems, *Water Environ. Res.* **69**, 146-156.
- Venckatesh R, Amudha T, Sivaraj R, Chandramohan M, Jambulingam M, (2010) Kinetics and equilibrium studies of adsorption of direct red-28 onto Punica granatum carbon, *Int. J. Eng. Sci. & Tech.* **2**, 2040-2050.
- Webber TW, Chakravorti RK, (1974) Pore and solid diffusion models for fixed-bed adsorbers, *Am. Inst. Chem. Eng. J.* **20**, 228-238.
- Weber WJ, Morris JC, (1963) Kinetic of adsorption on carbon from solution, *J. Sanit. Eng. Divis.* **89**, 31-59.
- Yahiaoui N, (2012) Etude de l'adsorption des composés phénoliques des margines d'olive sur carbonate de calcium, hydroxyapatite et charbon actif, Université Mouloud Mammeri Tizi Ouzou (Algérie).
- Yakout SM, Sharaf El-Deen GS, (2011) Characterization of activated carbon prepared by phosphoric acid activation of olive stones, *Ara. J. Chem.*
- Yang T, Lua AC, (2003) Characteristics of activated carbons prepared from pistachio-nut shells by potassium hydroxide activation, *Microporous and Mesoporous Materials* **63**, 113-124.