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Pomegranate Peels Activated Carbon by Phosphoric Acid Activation: Preparation, Characterization and Evaluation of Adsorptive Properties

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Abstract: Pomegranate peels, a by-product of agriculture are transformed by chemical activation with phosphoric acid into activated carbon. The raw material is impregnated with a H_3PO_4 solution with different ratios and impregnation time. The impregnated precursor is activated at different temperatures and times. The specific surface area was determined for all samples. The optimum activated carbon obtained is mainly microporous. Its BET specific surface area is approximately 1600 m^2/g and its pore volume is 1.118 cm^3/g which about 90% is micropores. The average pore diameter is about 3 nm. Boehm titration and IR spectroscopy show the presence of oxygen functions on the surface, essentially acidic. The adsorbent capacity of this carbon is tested using three model molecules phenol, nitrophenol and methylene blue. The adsorption isotherms of the three molecules follow well the Langmuir model. The maximum adsorption capacities obtained are 119, 286 and 588 mg/g for phenol, nitrophenol and methylene blue, respectively. The optimum carbon, thus, obtained has interesting characteristics comparable to others carbons derived from lignocellulosics materials and commercial activated carbons. It can serve as a very good adsorbent in the aqueous phase, especially, for the removal of cationic dyes.

Key words: Pomegranate peels, activated carbon, process optimization, phosphoric acid, characterization, adsorption

INTRODUCTION

Domestic, agricultural and industrial discharges are damaging to our environment in all its components, water, air and soil. These effluents contain toxic substances with variable contents of which a large part is not biodegradable. Finding solutions to pollution problems is becoming a priority for governments. The valorization of biomass wastes in particular those resulting from agriculture by transformation into activated carbon can contribute to the resolution of these environmental problems in particular in the fields of treatment of gaseous and liquid discharges.

Activated Carbon (AC) is a very porous carbon material. It exists in powder, granular or fiber form (Marsh and Reinoso, 2006). It can be used as adsorbent (Moreno-Castilla, 2004), catalyst or catalyst support (Lam and Luong, 2014). Its uses as adsorbent covers pollutants of organic or mineral origin. Its performance in adsorption depends on its textural characteristics such as surface area and porosity and its chemical functions on its surface (Prahas *et al*., 2008). The nature of the raw material and the process followed for its manufacture are largely responsible for these characteristics (Girgis and El-Hendawy, 2002). Two processes are adopted to prepare AC; the thermal (or physical) process and the chemical process (Caturla *et al*. 1991) the thermal process consists of pyrolysis of the raw material followed by activation in the presence of an oxidizing agent such as water vapor (Ouederni *et al*., 2006) or CO_2 (Nabais *et al*., 2013).

Chemical activation consists of the impregnation of the raw material with a chemical agent such as NaOH (Tongpoothorn *et al*., 2011), KOH (Saadi *et al*., 2016), $ZnCl_2$ (Miao *et al*., 2013), K_2CO_3 (Hayash *et al*., 2002) and H_3PO_4 (Lim *et al*., 2010) followed by activation of the impregnated material in inert atmosphere. The combination of two methods can also be applied (Budinova *et al*., 2006).

Recently, chemical activation is widely used because it has several advantages. On the one hand, it is carried out in a single step and at a reduced time and a lower temperature resulting in energy saving. On the other hand, the AC obtained by this type of process has a high

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specific surface area and a higher yield (Prahas *et al.*, 2008). Among the activating agents which appears effective for the impregnation of lignocellulosic precursors, there is the orthophosphoric acid H_3PO_4. This is because it is not polluting and easy to recover when washing the AC. The AC resulting from this process has applications in the food industry, pharmaceutical and the fine chemistry (Reddy *et al.*, 2012).

Different agricultural by-products have been tested to prepare activated carbon. Among these materials that are effecttive, we quote: coconut shells (Hayash *et al.*, 2002), almond shells (Nabais *et al.*, 2011), olive stones (Ouederni *et al.*, 2006), date stones (Ahmed, 2011), apricot stones (Aygun *et al.*, 2003), bagasse (Kalderis *et al.*, 2008), rice husk (Cheenmatchaya and Kungwankunakorn 2014), corn cobs (El-Sayed *et al.*, 2014) and cotton stalks (Girgis and Ishak, 1999).

In our recently published research Saadi *et al.* (2016), we used pomegranate peels to prepare chemically activated carbon using KOH as an activating agent. The resulting AC had very interesting textural and adsorption characteristics. This encouraging result and the reduced number of publications (Senthilkumar *et al.*, 2017; Serafin *et al.*, 2017) interested in the production of the AC from this precursor and still the availability of this waste of agriculture in our region (Saad *et al.*, 2012) pushed us to test this precursor for the preparation of AC by chemical activation using H_3PO_4 acid. We study the effect of the operating parameters on the specific surface area of the final product in order to optimize these parameters. The optimum product which having the high specific surface area is characterized physically and chemically and applied in the adsorption in aqueous solution of hazardous molecules such as phenol, 2-nitrophenol and methylene blue.

MATERIALS AND METHODS

Pomegranate Peels (PP) used for preparation of activated carbon were obtained from our region (Gabes) in the South of Tunisia. They were washed abundantly with distilled water then dried at temperature 105°C during 1 night. After that, they are crushed in to a number of particles with diameter of 1.5-5 mm.

The contents of dried pomegranate peels were as follows: moisture content, 9.78%, Ash, 2.75%, Carbon 43.13%, Hydrogen, 7.17%, Nitrogen, 0.46%, Sulfur, 0.89% and Oxygen (by difference), 48.35%.

Preparation of activated carbon: At the beginning, the PP/H_3PO_4 solution (50% in weight) were mixed at impregnation ratio (weight of activating agent solution/weight of raw material) varying from 2-5. The mixture is stirred at boiling for 3 h (about 112°C). After filtration, the solid is dried in the ambient for 24 h and then carbonized at the temperature of 400°C for 3 h. The impregnation ratio resulting in the AC with the highest specific surface area is fixed for the following experiments. Then, the impregnation time is varied from 2-4 h while maintaining the other parameters constant (impregnation ratio previously optimized, carbonization temperature 400°C, carbonization time 3 h). The same procedure is followed to optimize the carbonization parameters. The temperature is varied in the range 300-500°C and the time between 2 and 4 h. To prepare activated carbon, a weight of 25 g of acid-impregnated PP was carried out in a stainless steel tubular reactor (diameter of 21 mm and length of 375 mm) inserted in a vertical ceramic electrical furnace. It was heated in continuous nitrogen flow of 9 L/h at heating rate of 10°C/min up to desired temperature maintained at fixed time. After heating, the reactor is cooled with the same flow nitrogen until room temperature. The samples obtained were washed with hot distilled water and sodium hydroxide (0.1 N) until constant pH of the solution was reached. Finally, samples were dried at 110°C for 24 h and finally kept in tightly closed bottles for later experiment use. The yield of the prepared activated carbons was estimated using the following Eq. 1:

$$\text{Yield}(\%) = \frac{w_c}{w_0} \times 100 \qquad (1)$$

Where:

w_c = The weight of activated carbon

w_0 = The weight of pomegranate peels

The main characteristics and adsorption properties of the optimal activated carbon prepared were compared with those of a Commercial Activated (CAC) known as adsorbent in aqueous solution. This material derives from the chemical activation of wood with phosphoric acid.

Characterization methods

Thermal analysis: The thermogravimetric analyses of pomegranate peels and phosphoric acid impregnated pomegranate peels were evaluated by Setaram TGA-DTA Model which was carried out in nitrogen atmosphere at rate of 10°C/min and the temperature was between the ambient and 800°C for the raw PP and between the ambient and 500°C for impregnated PP.

Textural characteristics: Textural characterization of the AC was carried out using N_2 adsorption at 77 K using a Quantachrome Autosorb-1 apparatus. Before, the beginning of the experiments the sample was degassed at 300°C overnight under vacuum <0.05 mbar. The specific surface areas S_{BET} was determined from isotherms using BET equation at relative pressure in the range 0.01-0.1. The total pore volume, V_{tot} was estimated at a relative Pressure of P/P^0 near the unity. The micropore volume,

V_{mic} was determined using Dubinin Radushkevich equation and the mesopore Volume, V_{mes} was calculated from the difference between V_{tot} and V_{mic}. According to the relationship, $D_P = 4\ V_t/S_{BET}$, the mean pore Diameter (D_p) can be determined.

Chemical characterization: The surface chemistry characterization of the activated carbon was performed with Boehm titration, pH drift (pH_{pzc}) and FTIR spectroscopy.

The Boehm titration method can be described as follows: 1 g of activated carbon were placed to a series of flask which contain 50 mL of 0.01 N sodium bicarbonate ($NaHCO_3$), sodium carbonate (Na_2CO_3), sodium hydroxide (NaOH), sodium ethoxide ($NaOC_2H_5$) and hydrochloric acid. The flasks were sealed and shaken for 72 h. After this time, the solutions were filtered and the 10 mL of each filtrate was pipetted and titrated with 0.1 N sodium hydroxide or hydrochloric acid, depending on the nature of solution used. The amount of acidic groups on the activated carbon is calculated under the assumption that $NaOC_2H_5$ neutralizes all acidic groups; NaOH neutralizes carboxylic, lactonic and phenolic groups; Na_2CO_3 neutralizes carboxylic and lactonic groups; $NaHCO_3$ neutralizes only carboxylic group. The amount of basic groups was calculated from the amount of HCl which reacted with the carbon.

The pH_{PZC} (point of zero charge) of activated carbon was measured by the pH drift method. The procedure of this method can be described as follows: 50 mL of 0.01 mol/L NaCl were prepared and added into a series of Erlenmeyer's. Then their pH were adjusted in range 2-12 using 0.1 N HCl or 0.1 N NaOH solutions. 0.15 g of activated carbon was the added to each solution. The final pH achieved after 48 h of agitation was measured and plotted as a function of initial pH. The intersection of this curve with the first bisector gives the pH_{PZC} of the activated carbons.

The FTIR spectrum of the PP and PPAC were recorded between 4000 and 400 cm^{-1} using Spectrum Two Perkin Elmer spectrometer equipped with DTGS detector with a resolution of 2 cm^{-1} and 32 scans.

Iodine number: The Iodine Number (IN) expressed in mg/g gives an estimation of the surface area of adsorbant and is used to measure the porosity for pores larger than 1 nm in diameter (Wang *et al*., 2013).

Iodine number was measured by mixing 1 g of activated carbon with a particle size lower than 0.1 mm and dried with 10 mL of 5 wt.% HCl in a glass vessel. The latter is heated by a sand bath for 30 sec. After cooling the vessel to ambient temperature, 100 mL of iodine solution (0.1 mol/l) is introduced. The suspension is shaken during 30 sec and filtered using Whatman paper filter. The free iodine in the filtrate solution is titrated by a sodium thiosulfate solution (0.1 mol/L).

Adsorption experiments: The adsorption capacities of the carbons were tested using Phenol (Ph), 2-Nitrophenol (2NP) and Methylene Blue (MB). The chemicals used were of analytical grade and were purchased from Prolabo.

Phenol (chemical formula C_6H_5OH, MW: 94.11 g/mol) and 2-nitrophenol (chemical formula $C_6H_4NO_2OH$, MW: 139.11 g/mol) represent commonly encountered phenolic pollutants in water and wastewater treatment. A stock solution of phenol or 2-nitrophenol (1g/L) was prepared and suitably diluted to the required concentration.

Methylene blue is a basic dye (Chemical formula: $C_{16}H_{18}N_3SCl$, type: cationic, molecule dimensions in nm 1.43×0.61×0.40; MW: 319.85 g/moL). This dye was chosen because of its importance and wide applications in various fields such as analytical chemistry, aquaculture (antifungal) and biology (staining procedure) (Mahamad *et al*., 2015). In addition, the adsorption capacity of this molecule provides information on the presence of mesopores given that it is accessible to the pores which have diameters larger than 1.5 nm (Aygun *et al*., 2003).

A stock solution of methylene blue (200 mg/L) was prepared. Solutions at various concentrations are obtained by dilution.

The study of Ph, 2-NP and MB adsorption was performed at temperature 30°C under continuous shaking. To obtain the equilibrium isotherms, a series of 250 mL Erlenmeyers flasks were employed. Each flask was filled with 200 mL of solute solution of varying concentrations (20-500 mg/L for Ph, 2-NP and 10-120 mg/L for MB). A known amount of activated carbon was added into each flask. The mixtures were then shaken for 4 h, this time was considered adequate to reach equilibrium. At the end of this time, the content of each flask was filtered and the filtrate was analyzed by spectrophotometry absorption using a Shimatzu 1700 UV visible spectrophotometer at 270 nm (Ph), 350 nm (2-NP) and 660 nm (MB). The amount of solute adsorbed at equilibrium (q_e, mg/g) was calculated by the following Eq. 2:

$$q_e = \frac{V\left(C_0 - C_e\right)}{W} \tag{2}$$

Where:

C_0 and C_e = The initial and equilibrium concentration of the solute (mg/L)
V = Represents the solution volume (L)
W = The mass of adsorbent (g)

Adsorption isotherms models: Adsorption isotherm models were applied to determine the relationship between adsorbate and adsorbent at equilibrium. In this study three commonly models Langmuir, Freundlich and Temkin were applied. The Langmuir model is expressed by Eq. 3:

$$q_e = \frac{q_m K_L C_e}{1+K_L C_e} \tag{3}$$

The Freundlich model is expressed by Eq. 4:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{4}$$

The Temkin model is expressed by Eq. 5:

$$q_e = B_T \ln(A_T C_e) \tag{5}$$

where, C_e (mg/L) is the equilibrium concentration of solute in solution, q_e (mg/g) is the amount of solute adsorbed at the equilibrium time, q_m(mg/g) is the maximum capacity, K_L (L/mg) is the Langmuir constant, K_F ((mg/g).(L/mg)$^{1/n}$) is the constant of adsorption capacity and n is the adsorption intensity, A_T(L/min) is the equilibrium binding constant and B_T is the Temkin constant.

RESULTS AND DISCUSSION

Thermal analysis: Figure 1a shows TGA and Derivative Thermo Gravimetric (DTG) curves of raw permanganate peels. According to the figure, thermograms of untreated permanganate peels follow the usual shape for lignocellulosic materials, indicating three stages: the first one is below 150°C which is due to moisture loss. A weight loss of 5% is recorded. The main degradation is located in the temperature range from 150-400°C. This stage consists of a major loss of weight (about 35%). On DTG curves, two distinct peaks are clearly observed. The first, occurring at lower temperatures (150-300°C) could be mainly corresponds to the hemicellulose decomposition, associated with a weight loss of 22%. Meanwhile, the second peak (300-400°C) was attributed to the degradation of cellulose with a mass loss of 13%. After main decomposition, the weight loss decrease slowly indicating the third stage.

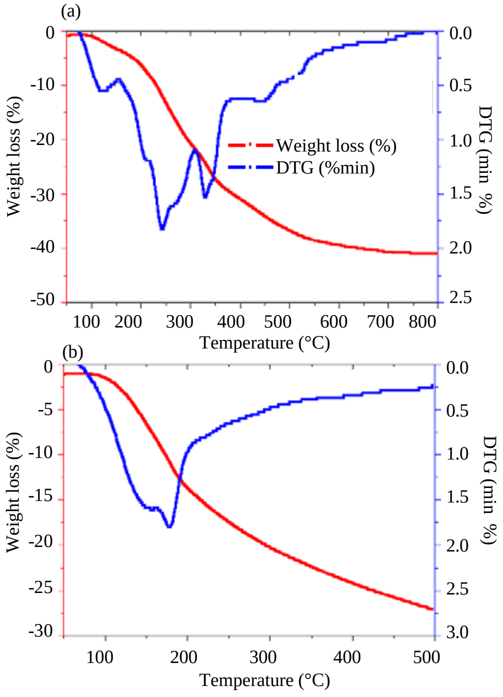

Fig. 1: TG-DTG of PP; a) and H_3PO_4 impregnated PP and b) pyrolysis under N_2 atmosphere at heating rate 10°C/min

In comparison to the untreated material, impregnation with phosphoric acid H_3PO_4 brings about remarkable modification to the pyrolysis of the precursor as shown in Fig. 1 b. With the impregnation by H_3PO_4, the weight loss stages shifted to lower temperature whereby the main degradation of impregnated pomegranate peels is observed at a temperature range of 70-225°C. These findings can be explained by the fact that H_3PO_4 acts as catalyst to promote the degradation of biopolymers, principally hemicellulose, cellulose and lignin (Zuo *et al*., 2012). In addition, the main degradation stage of impregnated permanganate peels involved only one step. This means that phosphoric acid removed impregnated materials from their origin shape of lignocellulosic biomass (Dobele *et al*., 1999).

In the other hand, the weight loss at 500°C of raw permanganate peels was 40%, whilst only 27% of weight loss for impregnated permanganate peels. It is anticipated that H_3PO_4 reduced the weight loss of decomposition of cellulose (Nada and Hassan, 2003).

Effect of operating parameters on produced carbons: In order to produce optimal AC from PP, the effects of the impregnation ratio of H_3PO_4 solution to PP, impregnation time, activation temperature and time on the specific surface area and iodine number were investigated.

Table 1: Effect of operating parameter on BET surface area and iodine number

Impregnation ratio (g/g)	Impregnation time (h)	Carbonisation temperature (°C)	Carbonisation time (h)	Sample	S_{BET} (m^2/g)	IN (mg/g)
2.0	3.0	400	3.0	AC2343	779	653
3.0	3.0	400	3.0	AC3343	1318	773
4.0	3.0	400	3.0	AC4343	1465	775
5.0	3.0	400	3.0	AC5343	1287	762
4.0	2.0	400	3.0	AC4243	1597	813
4.0	4.0	400	3.0	AC4443	1082	734
4.0	2.0	300	3.0	AC4233	1168	575
4.0	2.0	500	3.0	AC4253	1346	724
4.0	2.0	400	2.0	AC4242	1000	519
4.0	2.0	400	4.0	AC4244	1429	805

Table 2: Textural and yield of PPAC and CAC

AC	Activation agent	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)	D_p (nm)	Yield (%)
PPAA	H_3PO_4	1597	1.118	1.002	0.116	2.99	33.4
CAC	H_3PO_4	1377	1.23	0.905	0.325	3.84	-

Effect of impregnation parameters on BET surface area and iodine number: The objective of this part is to prepare an optimal activated carbon based on the measurement of the BET specific surface area and iodine number. The two impregnations parameters ratio and time were varied.

Table 1 summarizes the effects of impregnation agent on the BET surface area and the iodine number of the activated carbon.

From Table 1 when the impregnation ratio goes from 2-3, the specific surface area increases considerably. It passes from 779-1465 m^2/g. In this step, there will be development of the microporous structure of activated carbon. In fact, new micropores are created due to the dehydrating effect of the chemical agent (Mahamad *et al*., 2015), hence, the increase in the specific surface area. Also, the volatile matter decreased while the fixed carbon content increased due to the pyrolytic effect where most of the organic substances are degraded and discharged as gas and liquids leaving a material with high carbon content (Mahamad *et al*., 2015). Arriving at a certain content of the impregnating agent, there will be formation of mesopores and macropores which are due to the enlargement of the micropores (Kong *et al*., 2013) which causes a decrease in the specific surface area.

The iodine number follows the same variation as the specific surface area but its value expressed in mg/g is significantly lower than the specific surface area. This proves the presence of micropores with a diameter of <1 nm which are accessible to the nitrogen molecule but not accessible to iodine. Based on these results, we set an impregnation ratio 4.

The effect of the impregnation time in the range 2-4 h on surface area and iodine number of prepared activated carbon is shown in Table 2. An increase in the yield of activated carbon is observed which goes from 33.36% for duration of impregnation of 2 h to 36.22% for duration of impregnation of 4 h. Hence, an increase of 2.86%. The prolongation of the impregnation time facilitates the development of the mesoporosity shown by a reduction in the specific surface area from 1597 m^2/g for an impregnation period of 2 h to 1082 m^2/g for an impregnation period of 4 h. As for the iodine number, it follows the same variation as the specific surface area. We note, here that a few work has been studied the effect of impregnation time on surface area and iodine number.

Looking at the results commented above an impregnation time of 2 h was selected as the most suitable for preparing activated carbon do to the high specific surface area and iodine number. After the study of the impregnation step, we choose as working conditions: impregnation ratio of 4 and impregnation time of 2 h.

Effect of carbonization parameters on BET surface area and iodine number: The temperature and time of the carbonization step are key operating parameters of the operation.

The impregnated precursor is carbonized for 3 h. However, the heat treatment temperature is varied between 300 and 500°C to obtain the activated carbon with the high specific surface area. The optimum temperature obtained is applied in the optimization of the carbonization time between 2 and 4 h. The BET surface area increases with the increasing activation temperature from 300-400°C what can be attributed to the release of tars from the cross-linked framework generated by the chemical reagents treatment (Hsu and Teng, 2000). Increasing the temperature beyond 400°C, allows a drop in the specific surface area that can be attributed to the shrinkage in the carbon structure, leading to a reduction in porosity (Hsu and Teng, 2000). The same result has also been reported by Prahas *et al.* (2008). In general, the effect of the carbonization temperature on the microporosity and therefore, on the BET specific surface area, depends on the impregnation ratio (Girgis and Hendawy, 2002; Philip and Girgis, 1996).

Table 3: Textural characteristics of PPAC and some others ACs prepared from agricultural waste

Precursor	Activation agent	S_{BET} (m^2/g)	V_{tot} (cm^3/g)	V_{mic} (cm^3/g)	V_{mes} (cm^3/g)	D_p(nm)	References
Pomegranate peels	H_3PO_4	1597	1.118	1.002	0.116	2.99	This study
Pomegranate peels	KOH	1405	0.617	0.6017	0.0153	1.757	Saadi *et al*. (2016)
Pomegranate peels	H_3PO_4	686	0.5053	-	-	1.363	Senthikumar *et al*. (2017)
Coconut Shell	H_3PO_4	891	0.7233	0.2680	0.4546	-	Wang *et al*. (2013)
Jatrophacurcas fruit Shell	NaOH	1873	1.312	-	-	2.80	Tongpoothorn *et al*. (2011)
Olive stones	H_3PO_4	1218	0.6	0.5	0.1	1.1	Yakout and Sharaf
Sky fruit husk	H_3PO_4	1211.57	0.84	0.15	-	2.778	Njoku *et al*. (2014)
Soybean straw	$ZnCl_2$	2271	1.479	0.793	0.686	2.60	Miao *et al*. (2013)
Jackfruit peel	H_3PO_4	1260	0.733	0.471	0.262	-	Prahas *et al*. (2008)

Therefore, carbonization temperature of 400°C was considered as the optimum for further optimization process. In most of the research work interested on the production of activated carbon from biomass using phosphoric acid as activation agent, the carbonization temperature which results in a developed porosity is in the range 350-450°C (Reddy *et al*., 2012; Gonzalez-Serrano *et al*., 2004). The effect of optimum activation time was determined for 2-4 h. The highest specific surface area and iodine number were 1597 m^2/g and 812 mg/g, respectively. The sample having these characteristics was obtained at activation time 3 h.

As seen from the Table 1 while the activation time increased from 2-3 h, the S_{BET} and IN increased from 1000 to 1597 m^2/g and from 519-812 mg/g, respectively. However, the increase of activation time from 3-4 h, adversely affected the surface area and iodine number. Probably a high carbonization time causes the collapse of some pores resulting to lower pores volume and surface area (Saygili *et al*., 2015; Wang *et al*., 2011).

In summary, the activated carbon with the highest specific surface area and iodine number is named AC4243 in Table 1. Its specific surface area is 1597 m^2/g and its iodine number is 813 mg/g. The optimum conditions which are determined previously and resulting in this activated carbon are an impregnation ratio 4, an impregnation time 2 h, a carbonization temperature 400°C and a carbonization time 3 h. In the rest of the text, the optimal AC is called PPAC.

Characterization of the optimal activated carbon

Textural characteristics: Figure 2 illustrates the adsorption-desorption isotherm of nitrogen at 77 K onto PPAC. The isotherm is a mixture of type i at low pressure and type 4 at intermediate and high pressure based on IUPAC classification. Adsorption isotherm presents a sharp increase in the adsorbed volume up to a P/P$_0$ of 0.1 which was attributed to the presence of micropores. However, a progressive increase in this volume in the entire range of relative pressure could be attributed to the presence of mesopores. In addition the presence of the small hysteresis loop in the adsorption-desorption isotherms confirms the existence of this mesoporosity.

The adsorption isotherm of this AC showed a good agreement with those reports in the literatures (Tongpoothorn *et al*., 2011; Reddy *et al*., 2012).

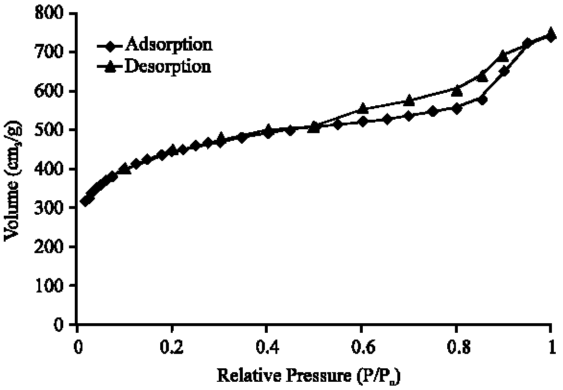

Fig. 2: Nitrogen adsorption-desorption isotherms of PPAC

The textural characteristics (BET surface area, pores volumes and average pore diameter) of PPAC obtained from adsorption-desorption isotherms were presented in Table 3. As shown from this table, PPAC has a S_{BET} near 1600 m^2/g which is over the acceptable range for commercial activated carbons (500-1500 m^2/g) (Tongpoothorn *et al*., 2011).

Regarding the porosity of this AC, it contains both microporous and mesoporous; nevertheless, the micropore volume (1.002 cm^3/g) is larger than mesopore volume (0.116 cm^3/g). Indeed, the fraction of the microporosity (ratio of the micropore volume to the total pore volume) is about 90%. However, the mesoporosity represents 10%. The average pore diameter of 2.99 nm confirms the presence of this mesoporosity.

Textural characteristics were comparable to those of other activated carbons prepared from agricultural waste by chemical process and even better in some cases.

Chemical characteristics of PPAC: The previous mentioned textural characteristics are not the only responsible for the effectiveness of the AC as adsorbent or catalyst but there are also the chemical characteristic (pH$_{pzc}$ and oxygenated groups at the surface).

The pH$_{pzc}$ and Boehm acid-base titration results for pomegranate peels and PPAC are shown in Table 4. As can be seen, PP has a pH$_{pzc}$ of 5.03 which shows its acidic nature. This being justified by the number of surface acid groups which is 3.9 meq/g. This acidity comes essentially from the presence of phenolic groups which is 3.1 meq/g.

Table 4: pHpzc and surface functional groups of PP, PPAC and CAC

	Acidic surface functional groups (meq/g)						
Materials	pHpzc	Carboxyl	Lactone	Phenol	Carbonyl	Acidic groups	Basic surface functional groups (meq/g)
PP	5.03	0.8	0.00	3.10	0.0	3.9	0.00
PPAC	2.80	0.5	0.30	0.40	0.2	1.4	0.15
CAC	5.00	0.1	0.35	0.45	1.1	2.0	0.05

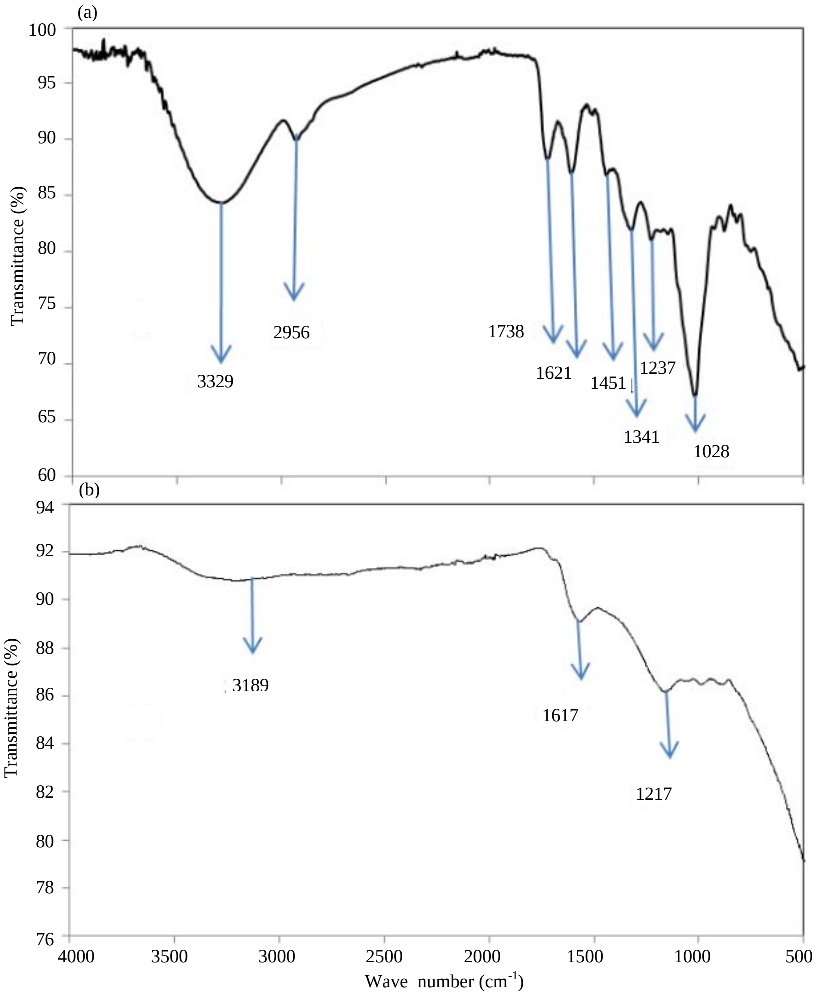

Fig. 3: a) FTIR Spectra for PP and b) PPAC

We note the presence of a small amount of carboxyl groups (0.8 meq/g) and the absence of lactone groups. As for the basic groups of surface, they are nonexistent. The impregnation of this raw material with phosphoric acid and its carbonization at 500°C reduces the number of acidic groups on the surface from 3.9-1.4 meq/g. Indeed, during the carbonization, there will be decomposition of certain functions in the form of CO and CO_2. This is due to the instability of acid groups at high temperature (Prahas *et al*., 2008). Compared to the lower carbonyl group number (0.2 meq/g for PPAC vs. CAC, it can be seen that the PPAC has a significantly 1.1 meq/g for CAC). The phenol and lactone contents are close to those of the prepared AC. A few number of basic groups appears in the PPAC (0.15 meq/g) due to thermal treatment of the raw material (Cazetta *et al*., 2011). This number is even lower in the case of the CAC (0.05 meq/g). The spectra of the pomegranate peels and its activated carbon are shown in Fig. 3. As seen in the Fig. 3, the spectra of the raw material show a strong wide

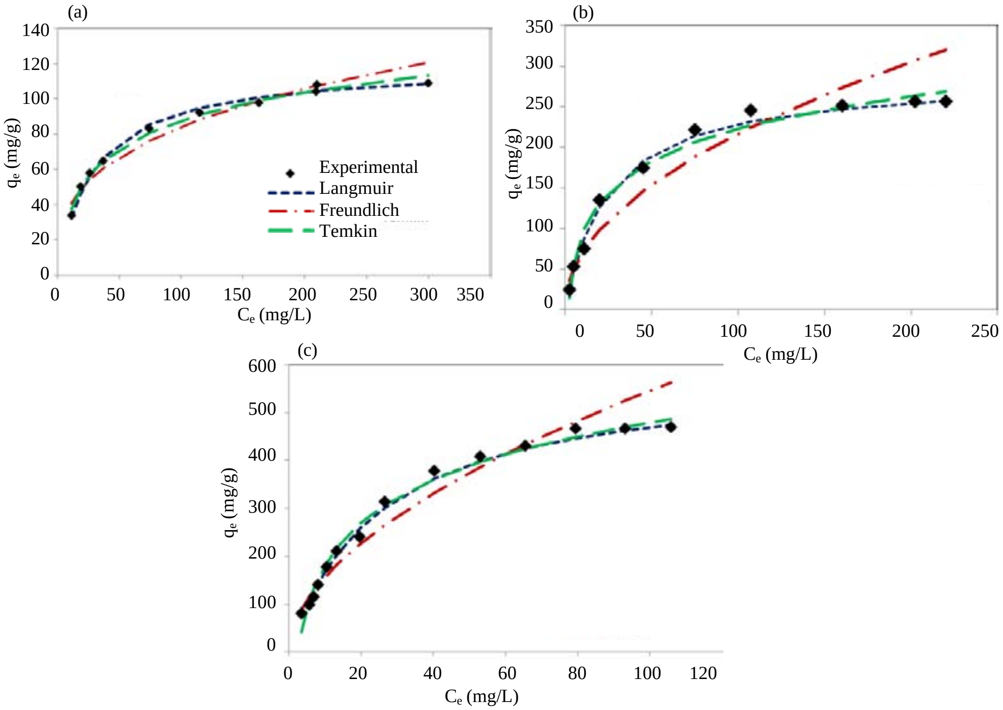

Fig. 4: a) Adsorption isotherms of Ph; b) 2-NP and MB and c) onto PPAC at 30°C

Table 5: Parameters of Langmuir, Freundlich and Temkin for the adsorption of Ph, 2NP and MB onto PPAC

	Langmuir			Freundlich			Temkin		
Adsorbate	K_L (l/g)	q_m(mg/g)	R^2	K_F	n	R^2	A_T	B_T	R^2
Ph	0.0341	119	0.9984	18.427	3.033	0.9516	0.4584	22.951	0.9922
2-NP	0.0398	286	0.9979	22.540	2.033	0.9359	0.519	56.562	0.9808
MB	0.0395	588	0.995	44.785	1.805	0.9648	0.397	130.44	0.9868

absorption band with a maximum at around 3329 cm^{-1}. It is attributed to hydroxyl groups (Gurten *et al*., 2012; Cazetta *et al*., 2011). The bands located at around 2956 cm^{-1} indicated the presence of C-H band stretching in carboxylic acids (Gao *et al*., 2016). The relatively band at 1733 cm^{-1} and 1621 cm^{-1} was ascribed to C = O stretching from aldehydes, ketones or carboxyls groups (Deng *et al*., 2010). The band at 1451 cm^{-1} was attributed to symmetrical angular deformation on the plane of methylene groups (Vargas *et al*., 2011). Finally, the region between 1350 cm^{-1} and 900 cm^{-1} is ascribed to C-O and C = O vibrations (Al-Bahri *et al*., 2012). PP spectra is similar to others lignocellulosic materials such as flamboyant pods (Vargas *et al*., 2011), cotton stalk (Deng *et al*., 2010) and grape waste (Saygili *et al*., 2015).

Figure 3b shows the FTIR spectra of PPAC. Compared to PP spectra (Fig. 3a), we can show the disappearance of the most absorption bands. This is due to the decomposition of functional groups as volatile matter in the carbonization and activation process at high temperature (Saygili *et al*., 2015). This result confirms Boehm's analysis of the raw material and activated carbon. The bands at 3211 cm^{-1} correspond to OH stretching in hydroxyl functional groups involved in hydrogen banding possibly due to the water adsorbed (Reddy *et al*., 2012). Two others small picks can be observed. The first peak appeared at 1617 cm^{-1} can be attributed to the C = O axial deformation of aldehyde, ketone, lactone and carboxyl groups and the second peak observed at 1217 cm^{-1} might be ascribed to the presence of C-O aliphatic esters (Mahamad *et al*., 2015).

Adsorption isotherms: Adsorption isotherms of Ph, 2NP and MB by PPAC are shown in Fig. 4. The experimental equilibrium data of three solutes are fitted by Langmuir (Eq. 3), Freundlich (Eq. 4) and Temkin (Eq. 5).

The fitted parameters of the Langmuir, Freundlich and Temkin equations are summarized in Table 5. Based on the correlation coefficient (R^2) obtained the Langmuir model with R^2 more than 0.995 is more suitable to describe the adsorption process of Ph, 2NP and MB onto PPAC than the other two models. This implied the homogeneous and the monolayer coverage of these molecules on the surface of AC (Deng *et al*., 2010). The

Table 6: Reported Ph, 2-NP and MB capacities of AC in literature

1.	Precursor	$q_{m,pH}$(mg/g)	$q_{m,\ 2\text{-}NP}$(mg/g)	$q_{m,MB}$(mg/g)References
Pomegranate peels	119			El-Naas *et al.*(2010)
Date- pits	262.3			Hameed and Rahman (2008)
Rattan sawdust	149.25			
Bituminous coal:				
Black Water	76.9			Teng and Hsieh (1999)
Mt Thorley	138			Teng and Hsieh (1999)
Olive stones	200			Bedoui *et al.* (2014)
Pomegranate peels		286		Altaher and Dietrich (2014)
Date pits		142.9		Gokturk and Kaluc (2008)
Commercial AC		256.41		Bedoui *et al.* (2014)
Olive stones		500		
Pomegranate peels			588	This study
Pomegranate peels			556	Saadi *et al.* (2016)
Commercial AC			333	Saadi *et al.* (2016)
Grape waste			417	Saygili *et al.* (2015)
Fir wood			579.97	Wu and Tseng (2006)
Corncob			28.65	El-Sayed *et al.* (2014)
Corncobs			208	El-Hendawy (2005)
Date palm pits			455	Reddy *et al.* (2012)
Pineapple waste biomass			288.34	Mahamed *et al.* (2015)
Olive stones			303	Najar-Souissi *et al.* (2005)

maximum adsorption capacity (q_m) of Ph, 2-NP and MB on the PPAC at 30°C were 119, 286 and 588 mg/g, respectively.

A comparison of the adsorption capacities for these molecules by other ACs is displayed in Table 6. As it can be shown, the pomegranate peels is a promising precursor for preparing AC mainly in the removal of organic dyes in solution.

CONCLUSION

The transformation of the pomegranate peels into activated carbons by a phosphoric acid chemical process was carried out for different operating parameters in order to determine the optimal conditions. The PPAC with the highest specific surface area is obtained for these conditions: 4:1 (w/w) H_3PO_4 (50%) to PP ratio, 2 h time of impregnation, 400°C carbonization temperature and 3 h carbonization time.

The optimal AC has S_{BET} of about 1600 m^2/g, V_{tot} 1.118 cm^3/g, V_{mic} 90%, V_{mes} 10%, D_p 30 Å and pH $_{pzc}$2.8. It contains acid functions at its surface of about 1.4 meq/g while the number of basic groups is very small (0.15 meq /g).

The PPAC is applied for the adsorption of two phenolic compounds: phenol and 2-nitrophenol and an organic dye methylene blue in the aqueous phase. The adsorption isotherms follow the Langmuir model for the three molecules. The adsorption capacities, q_m of phenol, 2-nitrophenol and methylene blue are 119, 286 and 588 mg/g, respectively. In conclusion, pomegranate peals can be good precursors for the preparation of activated carbon which can find its application in the field of waters and wastewater treatment particular for the treatment of cationic organic dyes.

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