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Development and characterization of microwave-assisted activated carbons from *Parkinsonea aculeata* wood

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Abstract Activated carbons from invasive *Parkinsonia aculeata* wood sawdust were developed by microwave assisted H_3PO_4 acid activation varying the radiation time (2–10 min). Their main physicochemical characteristics were determined, and compared with those of a sample previously obtained by conventional heating using the same precursor, chemical agent, and impregnation ratio. The activated carbons developed for radiation times of 5 and 10 min showed higher BET surface areas (~ 1300 m^2/g) and total pore volume (1 cm^3/g) than those obtained at 2 min (~ 710 m^2/g) or by conventional heating (~ 970 m^2/g). Microwave assisted activation also led to activated carbons with higher total amounts of acidic oxygen and basic functionalities in comparison with the sample arising from conventional heating. Phenol adsorption capacity for all the samples was also evaluated from determination of the adsorption isotherms and their proper description by the Freundlich model. The adsorption capacity for the activated carbons obtained at 5 and 10 min was almost twice that measured for the samples prepared at 2 min and by conventional heating, in agreement with the higher BET surface areas characterizing the former. Compared with conventional heating, the process assistance by microwave energy not only reduced operation time, but also improved the characteristics of the resulting activated carbons.

Keywords Activated carbon · Microwave assistance · H_3PO_4 acid activation · Phenol adsorption

1 Introduction

Activated carbons (ACs) are used worldwide in a huge number of applications, including gas storage, removal of pollutants from aquatic environments, gas purification and separation, in catalysis, and in pharmaceutical and medical uses. The world demand for ACs is expected to increase more than 10 % per year over the next years, mainly due to stricter pollution regulations and increased production of consumer goods (Valente et al. 2013). Novel precursors as well as sustainable and energy efficient processes are being continuously investigated in order to satisfy the expected higher demand (Hasan and Ani 2014; Nowicki et al. 2015).

The properties of ACs, and consequently their applications, are largely dependent on the kind of precursors, the activation process, and the conditions employed in the activation stage (Cukierman 2013). The two main routes for ACs preparation are physical or chemical activation. The latter usually leads to higher product yield and better developed pore structure. In recent years, microwave assistance for the thermal treatment stage has been successfully employed as an alternative to conventional thermal heating for the preparation of high surface area ACs (Ahmed and Theydan 2013). Selective heating and higher

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heat transfer rates result in low energy consumption, short treatment time, and compact processing equipment for ACs production (Li et al. 2009; Hesas et al. 2013a; Motasemi and Afzal 2013; Hasan and Ani 2014).

Use of easily available, renewable precursors for ACs manufacture has been emphasized to address environmental and waste disposal problems (Kázmierczak et al. 2013). In this sense, several biomasses have been investigated to produce ACs by microwave heating, such as palmstone (Guo and Lua 2000), waste tea (Yagmur et al. 2008), pine wood (Wang et al. 2009), cotton stalk (Deng et al. 2010), pistachio nut shells (Foo et al. 2011), grapevine rhytidome (Hejazifar et al. 2011); coconut husk (Foo and Hameed 2012a), wood sawdust (Foo and Hameed 2012b), orange peel (Foo and Hameed 2012c), banana frond (Foo et al. 2013), pumpkin seed hull (Njoku et al. 2013), and waste apple (Hesas et al. 2013b), among others. The processes investigated for ACs production by microwave assistance include impregnation of either the precursor or of the char, i.e. the carbon enriched product arising from a previous carbonization stage of the precursor (Hasan and Ani 2014). In the former case, the precursor is impregnated with an activating agent prior to microwave heating, with carbonization and activation of the precursor occurring simultaneously in a single stage. Instead, the latter firstly involves the precursor's carbonization in an inert or oxygen—depleted atmosphere to yield the char. In a second stage, the char previously impregnated with the activating agent is subjected to microwave heating to obtain the ACs. Alkaline hydroxides and carbonates, phosphoric acid, and zinc chloride are commonly employed as activating agents. In particular, H_3PO_4 acid has been widely used for ACs preparation from lignocellulosic feedstocks by conventional heating since it presents some advantages, such as non-polluting character and ease of elimination by extraction with water, in comparison with other reagents, i.e. $ZnCl_2$ (Yagmur et al. 2008). It also enables direct impregnation of the precursor and, therefore the process takes place in a single stage. However, to the best of our knowledge, only a few works have been devoted to explore H_3PO_4 acid activation by microwave assistance (Yagmur et al. 2008; Liu et al. 2010; Hesas et al. 2013b; Emami and Azizian 2014; Kundu et al. 2015). Most of the reported studies involve K_2CO_3 or KOH as activating agents (Deng et al. 2010; Foo and Hameed 2011, 2012a, b, c; Ahmed and Theydan 2012, 2013; Foo et al. 2013; Njoku et al. 2013; Gupta et al. 2014; Chayid and Ahmed 2015). Use of these reagents usually introduces a previous carbonization step of the precursor in order to improve product yields. This step is generally conducted at high temperatures (~700 °C) by applying conventional heating under inert atmosphere, overall lowering the benefits associated with microwave heating. Besides, evaluation of ACs developed by microwave assistance in specific applications is still scarce.

Within this scenario, the aim of the present study is to examine the viability of applying microwave energy to produce ACs by single-stage H_3PO_4 acid activation of wood sawdust from the worldwide invasive arboreal species *Parkinsonea aculeata*, almost unexplored as precursor, and to compare the resulting ACs with own samples previously obtained by using the same precursor, chemical agent, and conventional heating (Nunell et al. 2012). The influence of the radiation time on yield and physicochemical characteristics of the microwave-assisted ACs is investigated. Moreover, assays towards phenol removal are conducted for the ACs obtained by microwave and conventional heating in order to assess their ability in the adsorption of this priority pollutant of known toxicity, frequently used as model adsorbate. Widespread prevalence of phenolic compounds in industrial wastewater results from their rampant use in chemical and petrochemical industries, oil refinery, ceramic and steel plants, disinfectant manufacturing, or metal refining (Gupta et al. 2014).

2 Experimental

2.1 Materials

Parkinsonia aculeata debarked trunks were obtained from a rural area located in Buenos Aires province, Argentina (Nunell et al. 2012). They were sun dried, crushed, milled, and screen-sieved. Fractions of average particle diameter of 750 μm were selected for preparation of the ACs. Sawdust fractions were then washed and dried at 60 °C up to constant weight.

2.2 Preparation of the activated carbons

Sawdust fractions were impregnated with a H_3PO_4 acid solution (50 wt%), using an acid/precursor weight ratio of 2. For thermal treatment by conventional heating, the impregnated sample was first dried in an oven at 110 °C for 2 h. Then, it was heated to 450 °C for 0.5 h under a self-generated atmosphere. The detailed preparation procedure for the conventional thermal treatment has been reported in a previous work (Nunell et al. 2012). The activated carbon developed by the conventional method is designated as PA-C.

Microwave assisted activation was conducted in a 2.45 GHz commercial microwave oven (Moulinex® Microcheff 850 W). The impregnated sample, as detailed above, was directly introduced in a quartz container and located in the microwave oven chamber. Based on some

preliminary experiments and other reported results (Emami and Azizian 2014; Kundu et al. 2015), the power level was set at 850 W and irradiation times used were 2, 5, and 10 min. Temperature was measured employing a ceramic sheathed Chromel–Alumel (type K) thermocouple connected to a filter capacitor, in order to avoid interferences due to the microwave electromagnetic field (Zhang et al. 2013). During the experiments the temperature increased rapidly, reaching a quasi-stationary state at about 750 °C at radiation time of 2 min. To remove the excess of phosphoric acid, the so-obtained ACs were extensively rinsed with distilled hot water until neutral pH in the wash water was achieved. Afterwards, they were dried in an oven to constant weight. The activated carbons prepared by microwave assistance are designated as PA-M2, PA-M5, PA-M10, for radiation times of 2, 5, and 10 min, respectively. Yields were evaluated from weight differences.

2.3 Characterization of the ACs

2.3.1 Chemical characterization

Chemical characteristics of the wood sawdust used as precursor and of the ACs were determined by proximate and elemental analyses. The former were performed according to American Society of Testing and Materials (ASTM) standards with a thermal analyser TA instrument SDT Q-600. Elemental compositions of the samples were assessed using a Carlo Erba EA1108 elemental analyser.

The total and individual amounts of acidic/polar oxygen functional groups (OFG) on the surface of the derived ACs were determined following a modified procedure based on Boehm's method (De Celis et al. 2009; Nunell et al. 2012). It enables to quantify carbonyls, phenols, lactones, and carboxyl groups by titration with a series of bases of different strength. A total of 0.5 g of each sample was suspended in 50 mL of a 0.05 N solution of sodium ethoxide, sodium hydroxide, or sodium bicarbonate. The slurries were stirred for 24 h and afterward filtered. A 10 mL aliquot of the resulting solutions was added to 15 mL of a 0.05 N HCl acid solution. The solutions were subsequently back-titrated with 0.05 N NaOH. Values are expressed as milliequivalents per gram of sample. Likewise, the content of basic surface groups was determined by contacting 0.5 g of each activated carbon with 50 mL of 0.05 M HCl solution. The slurries were stirred for 24 h and afterward filtered. A 10 mL aliquot of the resulting solutions was subsequently titrated with 0.05 N NaOH.

Identification of the surface functionalities of the precursor, the ACs developed by microwave heating at different times, and the sample obtained by conventional heating was complementary performed by Fourier transformed infrared (FT-IR) spectroscopy. A Perkin–Elmer IR Spectrum BXII spectrometer was used, by the transmission method; employing KBr pellets. The spectra were recorded within the range 600–4000 cm^{-1} wave numbers.

To get information about the nature of the carbon surface of the samples, pH and pHzc were determined. The pH of the carbons was measured according to the following procedure: 1 g of carbon was contacted with 100 mL of distilled water, and the mixture was boiled for 5 min. The suspension was cooled down to ambient temperature and the pH was measured to the nearest 0.1 pH unit. The point of zero charge (pH$_{zc}$) of each sample was estimated from the pH of a concentrated dispersion as detailed elsewhere (Carrott et al. 2001). Briefly, 0.6 g of each activated carbon were added to 10 mL of a 0.1 M NaNO$_3$ solution. The suspensions were kept in a shaker thermostatically controlled with an external circulating bath at 25 °C (Lauda Ecoline E200), until equilibrium was attained. Afterward, they were filtered with 0.45 µm Nylon membranes and the equilibrium pH was measured with a Consort C860 pH-meter.

2.3.2 Textural and morphological characterization

N$_2$ adsorption–desorption isotherms at (−196 °C) for the precursor, the derived ACs, and the sample obtained by conventional heating were determined with an automatic Micromeritics ASAP-2020 HV volumetric sorption analyzer. Prior to gas adsorption measurements, the samples of 0.1–0.15 g were outgassed at 120 °C overnight under flowing Helium employing a Micromeritics Flowprep 060 degassing station. Textural properties were assessed from the isotherms, according to conventional procedures depicted in detail in own previous studies (De Celis et al. 2009; Nunell et al. 2012). The Brunauer–Emmett–Teller (BET) surface area (S$_{BET}$) was determined by the standard BET procedure. Total pore volumes (V$_t$) were estimated from the amount of nitrogen adsorbed at the relative pressure of 0.95 (P/P$_o$ = 0.95). The mean pore widths (W) were calculated from W = 4 V$_t$/S$_{BET}$. Pore size distributions (PSD) of the activated carbons were calculated from N$_2$ adsorption isotherm data using the DFT Plus Software (Micromeritics Instrument Corporation), based on the non-local density functional theory, that assumes slit pore shape.

Scanning electron microscopy (SEM) analysis was carried out to examine the surface morphology of the activated carbons. A scanning electron microscope (Zeiss Supra 40®) was used. The images were taken with an in-lens detector and 3 kV acceleration voltages. The samples were placed on an aluminum holder, supported on conductive carbon tape and sputter coated.

2.4 Phenol adsorption assays

Batch experiments were performed in order to examine the effectiveness of the ACs developed at the different radiation times and of the sample prepared by conventional heating, in the removal of phenol from model dilute solutions. For this purpose, a stock solution (22 mmol/L) was first prepared by dissolving the necessary amount of analytical grade phenol in distilled water. Afterwards, the stock solution was diluted as required to obtain standard solutions of concentrations ranging between 0.5 and 11 mmol/L. Phenol concentrations in solution were determined by means of a UV–visible spectrophotometer (Shimadzu UVmini-1240 model, Shimadzu Corp., Kyoto, Japan) at $\lambda = 270$ nm (Valente et al. 2009).

The effect of the sample's dose on the adsorption of phenol was first examined by contacting different weighed amounts of each activated carbon (0.05–1.5 g) with 50 mL of 1.6 mmol/L phenol solutions up to equilibrium. The pH was adjusted to pH = 6 by dilute NaOH or HCl solutions. The pH value was selected on the basis of previous research dealing with phenol uptake by other activated carbons (Valente et al. 2009; Beker et al. 2010; Soto et al. 2011). Capped glass flasks containing the slurries were kept in a shaker at 300 rpm and thermostatically controlled at 25 °C, with an external circulating bath, until equilibrium was attained. To check for any significant pH drift during the tests, the pH was recorded at the start and at the end of each experiment. No variations were determined with pH values maintained within 0.2 units. Once equilibrium was attained, the slurries were filtered through 0.45 μm membranes and phenol concentrations in solution were determined as described above. Phenol removal percentages were calculated as follows:

$$\text{Removal } (\%) = [(C_0 - C_e)/C_0] \times 100 \qquad (1)$$

where C_0 and C_e are the initial and equilibrium phenol concentrations in solution, respectively.

Adsorption isotherms of phenol onto the ACs were determined by contacting 0.5 g of each sample with 50 mL of phenol solution of varying initial concentrations (0.5–11 mmol/L). The general procedure depicted above was followed, keeping the same experimental conditions (T = 25 °C, pH = 6, 300 rpm). The amount of phenol adsorbed at equilibrium per mass of activated carbon, q_e (mmol/g), was calculated as follows:

$$q_e = (C_e - C_0)/D \qquad (2)$$

where D is the dose of sample used (g/mL). Equilibrium conditions in all cases were verified from preliminary assays for prolonged times.

All the experiments were performed at least twice. Differences between replicates were less than 3 % in all of

the cases. Average values are reported. Furthermore, solute and adsorbent blanks were simultaneously run for control in all the assays under the corresponding conditions.

3 Results and discussion

3.1 Yields and physico-chemical characteristics of the activated carbons

Chemical characteristics of the precursor, the ACs prepared by microwave assistance at the different radiation times, and by conventional heating are presented in Table 1. Yields are also included in the same table. As seen, yield for the ACs obtained at a radiation time of 2 min was slightly lower than that achieved for the sample prepared by conventional heating. A relatively more pronounced reduction in yield was attained for 10 min of exposure to radiation. The trend may be attributed to the higher temperature involved in microwave heating that in turn should increase reactions rates and volatile matter release (Foo and Hameed 2012d). Prolonging the radiation time induced increases in the fixed carbon and ash contents as well as a reduction in the volatile matter content. Increase in the radiation time from 2 to 5 min led to reduce % H and % O, and to increase % C. However, no noticeable changes were detected as the exposure time increased from 5 to 10 min. The absence of N content for PA-M10 may be attributed to the release of this element as part of volatile compounds. The ACs prepared by conventional heating possessed the lowest contents of volatile matter and ash, and the highest fixed carbon content. This could be due to the longer time

Table 1 Chemical characteristics of *Parkinsonea aculeata* (PA) wood, the activated carbons developed by microwave assistance at radiation times of 2, 5, and 10 min (PA-M2, PA-M5, PA-M10, respectively), and by conventional heating (PA-C), and yields

Samples	PA	PA-M2	PA-M5	PA-M10	PA-C
Proximate analysis		wt% (dry basis)			
Volatile matter	77.4	30.0	25.0	21.0	5.7
Fixed carbon*	21.2	60.0	61.0	65.0	86.0
Ash	1.4	10.0	14.0	14.0	8.3
Elemental analysis		wt% (dry and ash free basis)			
C	48.0	72.5	77.6	77.6	77.0
H	5.7	2.9	1.8	1.7	2.5
N	0.2	0.5	0.5	–	0.3
O*	46.1	24.1	20.1	20.7	20.2
pH	–	4.8	4.9	5.3	4.3
pH$_{zc}$	–	5.2	4.9	5.3	5.1
Yield (%)	–	45.5	41.3	34.9	47.0

* Estimated by difference

involved in conventional heating that should favor carbonization reactions and release of volatile compounds.

pH values determined for the ACs prepared at the different radiation times were very similar and slightly higher than that of the conventionally heated sample. pH_{zc} values for the ACs were equal or slightly higher than the corresponding pH values, pointing to an acidic nature.

The total and individual contents of surface acidic/polar oxygen and basic functional groups of the ACs produced by microwave assistance at the different radiation times and by conventional heating are illustrated in Fig. 1. As may be observed, the microwave-assisted ACs presented higher contents of surface acidic and basic functional groups than those of the sample obtained by conventional heating. The very short times involved in the microwave activation process might prevent thermal decomposition of some functional groups in spite of the higher temperature. Moreover, as radiation time increased from 2 to 10 min, the total content of acidic oxygen functional groups also increased, mainly due to a higher content of carbonyl groups, whereas a slight reduction in phenols and lactones and in basic functionalities was assessed. High amounts of acidic oxygen functional groups onto the surface of ACs are very desirable for applications involving adsorption of cationic species, since they provide anionic characteristics to the activated carbons surface, due to their dissociation and polarization (Basso et al. 2002).

FT-IR spectra for the precursor, the ACs developed by microwave heating at different times, and the sample obtained by conventional heating are comparatively illustrated in Fig. 2. The spectra for the microwave-assisted ACs obtained at different radiation times were quite similar but showed differences with respect to the sample prepared by conventional heating. For all the ACs a wide absorption
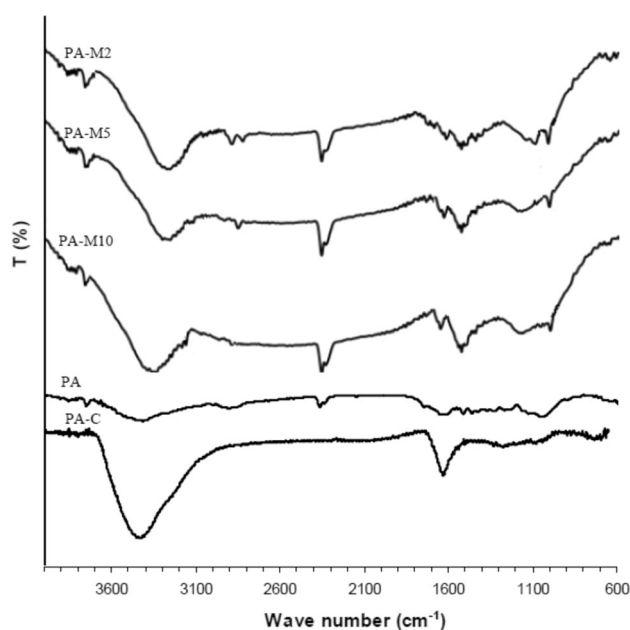
Fig. 2 FT-IR spectra of the precursor, the activated carbons prepared by microwave assistance at radiation times of 2, 5, and 10 min (PA-M2, PA-M5, PA-M10, respectively), and by conventional heating (PA-C)

band at 3200–3600 cm^{-1} may be noticed. It is assigned to O–H stretching mode of hydroxyl groups. The spectrum of the precursor also presented a weaker band at the same wavenumber range. The weak sharp bands at around ∼3750 cm^{-1} in the spectra of the precursor and the microwave-assisted ACs could be ascribed to isolated–OH groups (Puziy et al. 2002). These ACs also exhibited small peaks at 2900–2850 cm^{-1} due to C–H stretching in alkane structures. They became less noticeable with time prolongation and were not observed for the sample prepared by conventional heating. Functional groups, originally present on the precursor, could remain on the microwave-assisted ACs due to the shortened thermal treatment. The absorption peaks registered around 1700 cm^{-1} are usually assigned to C=O stretching vibrations of ketones, aldehydes, lactones or carboxyl groups. The spectra of the microwave-assisted ACs also showed a band at 1600–1580 cm^{-1}, due to aromatic ring stretching vibrations (C=C). Intensification of the peaks with time prolongation could be noticed. Broad absorption bands at 1300–1000 cm^{-1} for the spectra of the microwave-assisted ACs have been assigned to C–O stretching in acids, alcohols, ethers, phenols and esters (Durán Valle et al. 2005). The FT-IR spectrum of the PA-C seems consistent with the lower content of surface functionalities determined for this sample (Fig. 2).

Parts a) and b) of Fig. 3 show N$_2$ adsorption/desorption isotherms and pore size distribution for the ACs prepared by microwave assistance and conventional heating,
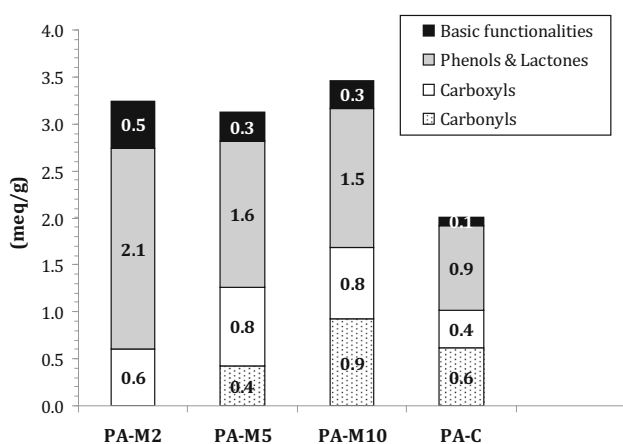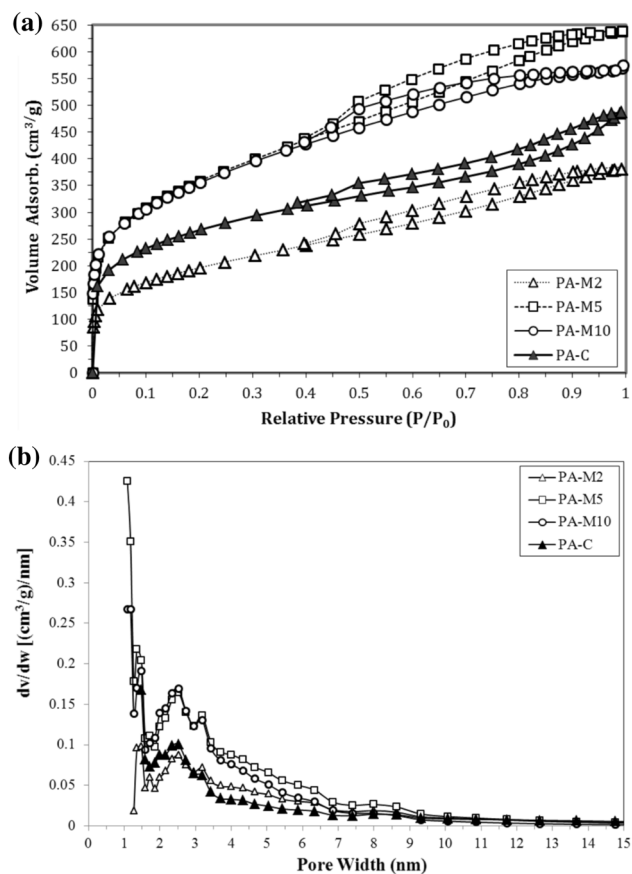

Fig. 1 Total and individual quantities of acidic and basic surface functional groups determined for the activated carbons prepared by microwave assistance at radiation times of 2, 5, and 10 min (PA-M2, PA-M5, PA-M10), and by conventional heating (PA-C)

(a)

(b)

Fig. 3 a N$_2$ adsorption–desorption isotherms, and **b** pore size distribution for the activated carbons prepared by microwave assistance at radiation times of 2, 5, and 10 min (PA-M2, PA-M5, PA-M10), and by conventional heating (PA-C)

respectively. As can be seen in Fig. 3a, N$_2$ adsorption isotherms for the ACs prepared by microwave assistance presented similar shapes to that of the sample obtained from the same precursor and activating agent by conventional heating (PA-C). They showed intermediate characteristics between type I and IV, according to the IUPAC classification, which are associated with the presence of both micropores and mesopores. Prolonging radiation time from 2 to 5 min led to increase more than twice the amounts of N$_2$ adsorbed, whereas a slight reduction was observed by prolonging the exposure time from 5 to 10 min. All the isotherms showed a hysteresis loop indicating capillary condensation in mesopores on the external surface (Rouquerol et al. 1999; Thommes et al. 2015). The pore size distribution of the ACs, ascertained by Density Functional Theory (DFT) model (Fig. 3b) evidenced that all the samples presented similar pore size distributions with most of the pores distributed between 2 and 6 nm. Textural characteristics of the ACs are shown in Table 2.

The results in Table 2 indicate that the ACs obtained at 5 and 10 min of exposure to microwave radiation had

surface areas and total pore volumes higher than those of the sample obtained by conventional heating. All the ACs showed a major contribution of mesopores. Prolonging the radiation time from 2 to 5 min induced an enhancement in the specific surface area, from ∼700 to ∼1300 m^2/g, likely due to an increase in the process reaction rate, thus intensifying the development of the porous structure. The slight drop in the surface area and total pore volume at 10 min suggests that formation of new pores became less important beyond 5 min of activation. Furthermore, thermal treatment for long times of exposure to radiation might produce local hotspots, leading to the ablation and shrinkage of the carbon structure. Similar results were previously reported by other authors for ACs obtained from different precursors using KOH or K$_2$CO$_3$ and microwave heating (Deng et al. 2010; Foo and Hameed 2012d; Ahmed and Theydan 2013).

SEM images of the surfaces of the precursor, and of the ACs obtained at radiation times of 2, 5, and 10 min are shown in Fig. 4. As can be seen, the morphology of the ACs derived at the different radiation times relatively retained the cellular structure of the parent material. The ACs obtained at 2 min (Fig. 4b) presented a quite similar morphology to that of the precursor (Fig. 4a), whereas differences became more pronounced as radiation time was prolonged from 2 to 10 min. The external surface of the ACs obtained at 5 and 10 min showed a lot of cavities and a honeycomb like shape. Prolonging radiation time from 5 to 10 min promoted some modifications in the surface appearance. PA-M5 presented a smooth surface almost clear of deposits, without evidence of structure deterioration (Fig. 4c). Instead, PA-M10 showed signs of structural deterioration, evidenced by the presence of large quantities of particles of different shapes and sizes that might be related to thermal decomposition of the precursor cell walls (Fig. 4d). These results were in line with those previously inferred from surface properties (Table 2).

Table 2 Textural characteristics of the ACs prepared by microwave assistance at radiation times of 2, 5, and 10 min (PA-M2, PA-M5, PA-M10, respectively) and by conventional heating (PA-C)

Samples	PA-M2	PA-M5	PA-M10	PA-C
S$_{BET}^a$ (m^2/g)	709	1297	1285	968
V$_t^b$ (cm^3/g)	0.58	0.98	0.87	0.70
V$_\mu^c$ (cm^3/g)	0.08	0.12	0.16	0.18
V$_m^d$ (cm^3/g)	0.50	0.86	0.71	0.52
W^e (nm)	3.25	3.01	2.71	2.91

[a] BET Surface area; [b] Total pore volume; [c] Micropore volume calculated by the DFT method; [d] Mesopore volume estimated by difference; [e] Mean pore width
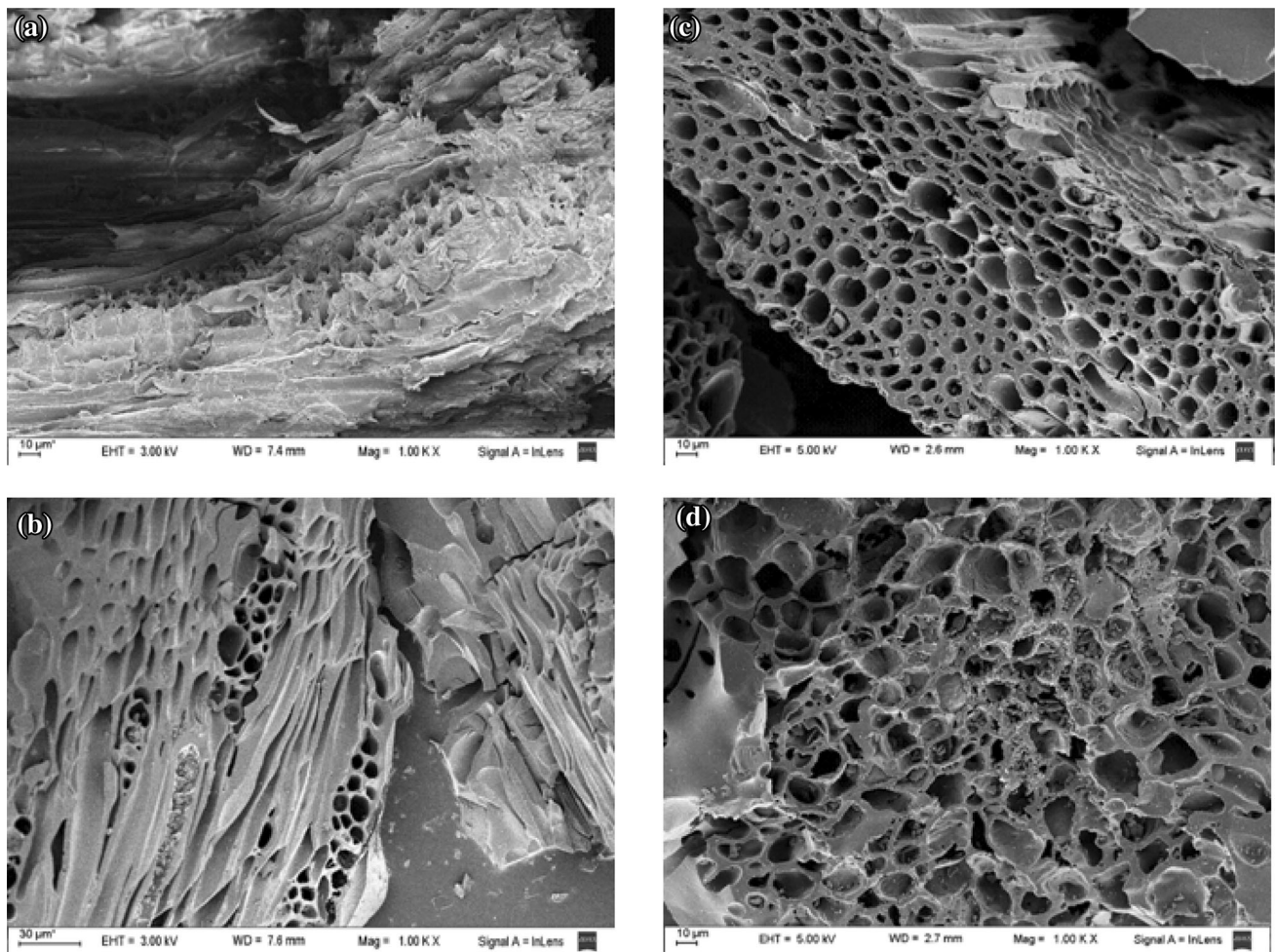
Fig. 4 SEM images of the precursor *Parkinsonia aculeata* (**a**) and the activated carbons obtained by microwave assistance at radiation times of 2 min (**b**), 5 min (**c**), and 10 min (**d**) Magnification: ×1000

3.2 Effectiveness of the activated carbons in phenol adsorption

The effect of the sample's dose on the removal of phenol from solutions of 1.6 mmol/L initial concentration is illustrated in Fig. 5. As expected, increasing the dose of the adsorbent led to enhancements in phenol adsorption for all the samples. The behavior may be attributed to the availability of more adsorption sites.

The isotherms for phenol adsorption onto all the ACs are depicted in Fig. 6. In this figure, the amount of phenol absorbed at equilibrium (q_e) versus equilibrium concentration of phenol, (C_e) is presented. The two-parameter Freundlich and Langmuir isotherm models were applied (Freundlich 1906; Langmuir 1918; Rouquerol et al. 1999). The Freundlich model is represented by:
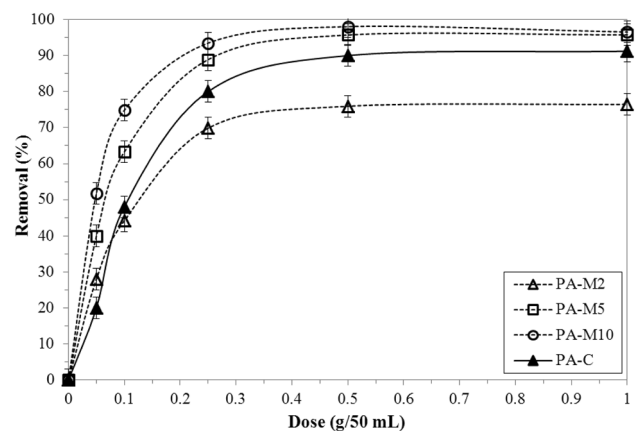
$$q_e = K_F(C_e)^{n_F} \tag{3}$$

Fig. 5 Effect of the dose of sample on phenol removal at equilibrium for the activated carbons prepared by microwave assistance at radiation times of 2, 5, and 10 min (PA-M2, PA-M5, PA-M10), and by conventional heating (PA-C). Conditions: T = 25 °C, 300 rpm, pH = 6, C_0 = 1.6 mmol/L. *Lines* are included only to guide the eyes

Fig. 6 Phenol adsorption isotherms for the activated carbons prepared by microwave assistance at different radiation times and by conventional heating. Comparison between the experimental data and predictions of the Langmuir and Freundlich models. Conditions: D = 0.5 g/50 mL; T = 25 °C, 300 rpm, pH = 6, C_0 = 0.5–11 mmol/L
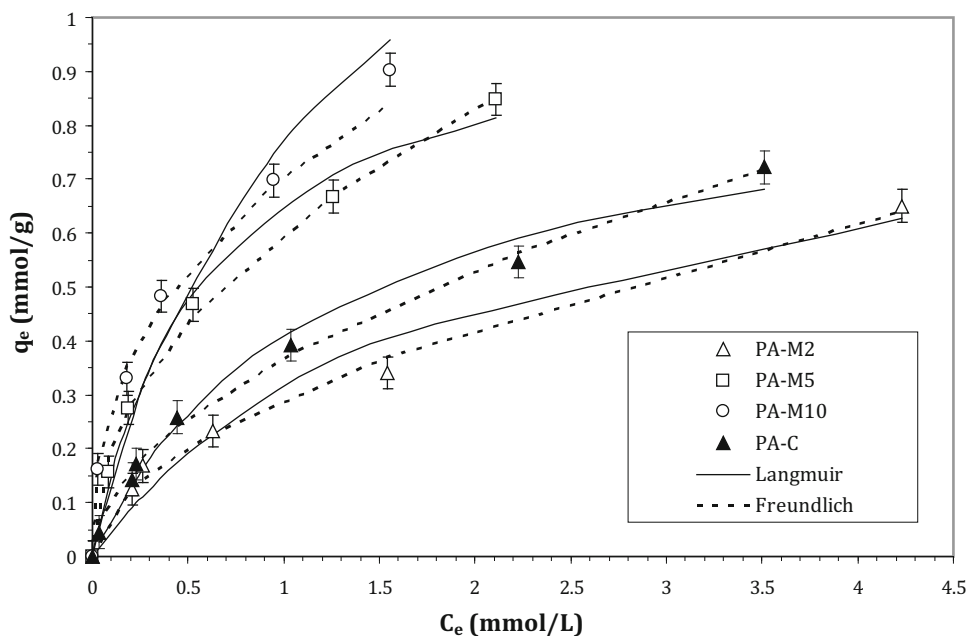
Table 3 Model characteristic parameters estimated for phenol adsorption isotherms onto the activated carbons developed by microwave assistance at radiation times of 2, 5, and 10 min (PA-M2, PA-M5, PA-M10, respectively), and by conventional heating (PA-C)

Model	Parameters	PA-M2	PA-M5	PA-M10	PA-C
Langmuir	X_{mL} (mmol/g)	0.91	1.04	1.70	0.93
	K_L (L/mmol)	0.52	1.67	0.83	0.79
	s (%)	4.6	3.5	9.9	3.2
	R^2	0.966	0.984	0.930	0.983
Freundlich	n_F	0.54	0.47	0.40	0.53
	K_F [(mmol/g)(L/mmol)^{nF}]	0.29	0.60	0.70	0.37
	s (%)	2.0	1.8	3.6	1.6
	R^2	0.994	0.996	0.991	0.996

where q_e is the amount of phenol adsorbed at equilibrium (mmol/g), C_e, the equilibrium concentration of the phenol, K_F and n_F, Freundlich constants; n_F provides an indication of how favorable the adsorption process is, and K_F (mmol/g (L/mmol)^{nF}) is related to the adsorption capacity of the adsorbent. The mathematical expression of the Langmuir isotherm is given by:

$$q_e = K_L X_{mL} C_e / (1 + K_L C_e) \quad (4)$$

where X_{mL} (mmol/g) and K_L (L/mmol) are the Langmuir constants related to the adsorption capacity and the energy of adsorption, respectively.

Model characteristic parameters were estimated by non-linear regression analysis for a 5 % significance level, by minimizing the following objective function:

$$O.F = \sum (q_{ei,\exp} - q_{ei,calc})^2 \quad (5)$$

The appropriateness of the model to represent the experimental data was examined from the standard deviation (s), which was estimated according to:

$$s = 100 \text{ x} \left[\sum_{i=1}^{N} (q_{ei,\exp} - q_{ei,est})^2 \Big/ (N - P) \right]^{1/2} \quad (6)$$

Results in Fig. 6 and Table 3 reveal that the Freundlich model provided a slightly better fit to the experimental data than the Langmuir one. Lower standard deviations and higher correlation coefficients were obtained in all cases. The relative adsorption capacities (K_F) estimated by this model, could be compared each other because the n_F values are quite similar. The K_F values indicate that the radiation time had a marked influence on the adsorption capacities of the ACs. It has been pointed out that physisorption of phenol depends on the porosity of the ACs and also that hydrophilic carbons may present a small but not negligible contribution of chemisorbed phenol depending on the extent of the functionalization (Velasco and Ania 2011). The results in Table 3 indicate that the adsorption capacities towards phenol increased almost twice by prolonging the radiation time from 2 to 5 min. Accordingly, the trend may be attributed to the great increment in the surface area

of the ACs developed for 5 min (Table 2). In turn, the slight increase in the adsorption capacity for the ACs obtained by prolonging the time to 10 min could be due to its relatively higher amount of carbonyl groups (Fig. 1) that should confer certain negative charges to the carbon's surface, thus improving phenol removal in the conditions studied. Moreover, the adsorption capacity for PA-M2 is quite comparable to that determined for the PA-C sample obtained by conventional heating, despite of the lower surface area of the former. This fact may be attributed to the higher amount of active surface functional groups on PA-M2. On the other hand, although meaningful, direct comparisons of X_{mL} values for different adsorbents are difficult since it should require data obtained under similar experimental conditions, it may be mentioned that, at least as an approach, phenol adsorption capacities estimated for the present microwave-assisted ACs, ranging from ~ 85 to 160 mg g^{-1}, are comparable or higher than others reported for some ACs also developed by microwave assistance (Gupta et al. 2014; Gokce and Aktas 2014).

4 Conclusions

Microwave assisted phosphoric acid activation of wood sawdust from the invasive species *P. aculeata* led to ACs with highly developed porous structures. The radiation time had a pronounced effect on the characteristics of the activated carbons. The sample obtained at a radiation time of 5 min showed the highest BET surface area (1297 m^2/g) and total pore volume (1.0 cm^3/g). Prolongation of the radiation time also exerted an influence on the surface chemistry of the ACs, affecting both the total content of acidic and basic groups and the relative proportions of the individual acidic functionalities present on the surface of the resulting ACs. Compared to the activated carbon obtained from the same precursor and activating agent by conventional heating, the microwave-assisted ACs possessed better textural properties as well as enhanced contents of basic and acidic functionalities on the surface. Microwave assistance also promoted ACs with higher phenol adsorption capacities than that determined for the sample resulting from conventional heating. As judged from modeling of the experimental adsorption isotherms, the relative phenol adsorption capacity for the ACs developed at radiation times of 5 and 10 min almost duplicated that determined for the conventionally heated activated carbon. Overall, the results indicate that microwave induced phosphoric acid activation could be applied for the effective development of ACs from *P. aculeata* wood with potentialities for phenolic pollutants removal, providing comparative advantages in terms of operation and product quality with respect to conventional heating.

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