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# Confrontation of various adsorption models for assessing the porous structure of activated carbons

Mirosław Kwiatkowski<sup>1</sup> · Vanessa Fierro<sup>2</sup> · Alain Celzard<sup>2</sup>

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## Abstract

Herein, a comprehensive analysis of DFT methods as a tool for evaluating the impact of the nature of the activating agent on the porous structure of activated carbons derived from hazelnut shells is given. The study was based on the use of NLDFT, QSDFT, and 2D-NLDFT methods applied to nitrogen adsorption isotherms, and the results were compared with those formerly obtained by using DR, BET, and LBET methods. Analyses conducted with NLDFT, QSDFT, and 2D-NLDFT revealed a very strong dependence of the results on assumptions about the specific pore model, which calls into question the reliability and credibility of these methods. However, if one takes into account the measurement errors that may occur during the determination of the adsorption isotherms, as well as the difficulty of selecting a representative sample in a batch of materials (most often non-homogeneous) to be analysed, some imperfections of the DFT methods become acceptable. The analyses in question revealed some limitations of the LBET method which became obvious when the analysis concerned bimodal porous materials with a considerable proportion of mesopores. In such cases, the LBET method, which was formerly designed for analysing microporous materials, may become less reliable.

**Keywords** Adsorption · Activated carbons · Porous structure · DFT methods

## 1 Introduction

Owing to their unique properties, including high specific surface area and adsorption capacity, porous carbonaceous adsorbents such as activated carbons are applicable to a broad range of industrial technologies and domains of daily life (Bahamón and Vega 2017; Ahmed et al. 2016; Acosta et al. 2016; Taslim et al. 2018). These materials are indeed mainly used in the adsorption processes for removing contaminants at very low concentration from liquids and gases. Thus, adsorption by activated carbons in the liquid phase is used, for instance, in the treatment of industrial and

municipal wastewaters, and for the decolourisation of sugar. The use of activated carbons for adsorption processes from the gas phase comprises the separation of gaseous mixtures, the purification of waste gases, the recovery of solvents, the removal of trace organic substances from air streams, the storage of natural gas and hydrogen, among others (Policchio et al. 2013; Zhao et al. 2012).

The substantially increased interest for activated carbons over the recent years and the intensification of research for improving their production processes result both from the growing demand in the traditional areas of application, as well as from the development of new technologies based on such materials.

Specific surface area, pore structure and pore size distribution of activated carbons are determined by the nature of their precursors, and by the way the latter are treated for producing those activated carbons. Consequently, it is possible to design the adsorptive properties of activated carbons to some specific applications by selecting the suitable raw material and method of preparation, and by controlling the conditions of the production process (El Qada et al. 2008). Virtually any substance characterised by sufficiently high carbon content and moderate ash content can be used as raw

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material for producing activated carbons. In many cases, precursors of activated carbons are hard (Lozano-Castello et al. 2001; Kopac and Toprak 2007; Sreńscek-Nazzal and Michalkiewicz 2011) and bituminous coals (Carrasco-Marin et al. 1996) as well as peat (Varila et al. 2017). Other materials include waste biomass, for example Kraft lignin (Fierro et al. 2006), rice straw (Basta et al. 2009), beer lees (Lee et al. 2011), palm kernel shells (Rashidi and Yusup 2017), walnut and pistachio shells (Kwiatkowski and Broniek 2012), wood (Kwiatkowski and Broniek 2013; Kilpimaa et al. 2015), apricot (Larbi et al. 2018) molasses (Młodzik et al. 2016) as well as coffee, tea, mint and rock rose grounds (Serafin et al. 2017). In the case of plant-derived biomass, the fractions of its main biopolymers (hemicellulose, cellulose and lignin) strongly influence the resultant porosity, because of their different carbon yields and different reactivities. All those raw materials can be easily activated and lead to high-quality activated carbons. Activated carbons can also be produced from anthracite (Byamba-Ochir et al. 2017), polystyrene (Gonsalvesh et al. 2016), ion-exchange resins (Kwiatkowski et al. 2012), etc.

The processes for preparing activated carbons having well-developed porous structure are generally categorised in two methods, namely physical activation and chemical activation (Moreno-Castillaa et al. 2001; Kuzmin et al. 2017). The production of carbonaceous adsorbents from an organic precursor by physical activation is usually carried out in two steps, i.e., carbonisation under inert atmosphere at 500–800 °C (Chen et al. 2018; Kwiatkowski 2008), followed by controlled gasification by either steam or carbon dioxide within the typical temperature range 700–1100 °C (Chen et al. 2018; Kwiatkowski 2008). The first step consists in eliminating water and removing volatiles, leading to the increase of carbon content in the material. The primary porous structure of the latter is also formed at this stage, which is essential for its further development and for the reactivity of the char, whereas at the same time a compact solid carbon tends to form. Such increase of reactivity is directly proportional to the development of porosity and inversely proportional to the degree of ordering of the carbon texture.

The controlled gasification which is carried out as a second step allows developing the porous texture further, and such development significantly depends on temperature, heating rate and time. The temperature of physical activation, which is one of the most important parameters of the process, must be selected with care for optimising gasification reactions at the surface of carbonise grains, resulting in the removal of carbon atoms and hence in the simultaneous creation of new pores and in the widening of pre-existing pores. At too high temperature, reactions mainly take place on the outer surface of the carbon grains; as a

result, the surface of the material is only consumed, without efficient formation of porosity.

The factors that influence the rate of physical activation include the concentration of active sites at the surface of the carbonise, the structural composition of the latter, the presence of inorganic impurities, and the diffusion of the activating agent to the active sites. The nature of the activating agent is also important, e.g. using carbon dioxide leads to a better development of micropores (<2 nm) and especially of ultramicropores (<0.7 nm), while steam spurs the development of a structure with a broader distribution of micropores and a higher fraction of mesopores (Moreno-Castillaa et al. 2001; Kuzmin et al. 2017).

In contrast, chemical activation consists in the simultaneous pyrolysis and activation of a raw material after mixing/impregnating it with an activating agent (Moreno-Castillaa et al. 2001; Kuzmin et al. 2017; Chen et al. 2018; Kwiatkowski et al. 2017). When the process is completed, the excess of activating agent and the by-products must be leached out in order to reveal the porous structure and to enable the practical use of the material. The factors that affect the formation of the porous structure upon chemical activation include the type of precursor, the activating agent, the process temperature, the atmosphere of the activation, and the impregnation ratio, i.e., the weight ratio of activating agent to precursor, on dry basis (Fierro et al. 2007; Lupul et al. 2015; Kwiatkowski et al. 2017). The impregnation ratio has a quite high impact on the resultant porosity; within some limits, a higher ratio usually leading to higher porosity and higher surface area of the product (Sreńscek-Nazzal et al. 2013; Lewicka 2017; Kwiatkowski et al. 2017).

One of the advantages of chemical activation is that it usually takes place at lower temperature and is shorter than physical activation. Moreover, chemically activated carbons usually have larger specific surface area and pore volume than those produced by physical activation (Fierro et al. 2007; Lupul et al. 2015; Sreńscek-Nazzal et al. 2013; Kwiatkowski et al. 2017). The effectiveness of chemical activation is also higher, since the chemicals used as activating agents are both desiccants and oxidisers, and reduce the production of volatiles. However, as mentioned above, chemically activated carbons need to be thoroughly washed for removing activation by-products, which can have an impact on the final chemical and textural properties of the activated carbon.

Either physical or chemical activation methods is used for producing adsorbents, depending on the intended application. Adsorption from the gaseous phase is more effective with adsorbents prepared by chemical activation, e.g. for the recovery of solvents or for the removal of trace amounts of organic volatiles. On the other hand, adsorption from the liquid phase, including water treatment, yields better results when carried out with carbons

produced by physical activation with steam. However, the basic methods for producing activated carbons can be combined. For instance, chemically activated adsorbents can undergo additional physical activation in view of modifying their porous structure.

The proper choice of the methods and/or conditions for activated carbon preparation requires a reliable assessment of the porous structure and related adsorption properties. Different techniques have been used to evaluate them, for instance mercury porosimetry, gas adsorption/desorption, and scanning microscopy, which is increasingly being used nowadays.

The most popular and employed method for the characterisation of porous solids is the physical adsorption of gases. Different adsorbates, like  $N_2$ ,  $CO_2$ , Ar, He,  $CH_4$ , benzene, nonane, etc., can be used for that purpose, but  $N_2$  adsorption at 77 K is the most common one. This is because it covers relative pressures from  $10^{-7}$   $P/P_0$ , which results in take into consideration adsorption process in the whole range of micropores and mesopores. It should be emphasised, however, that  $N_2$  adsorption at 77 K is used for the characterisation of microporous solids despite the occurrence of diffusional problems of this probe molecule inside the narrowest micropores. An additional experimental limitation comes from the need of using very low relative pressures of nitrogen for investigating such narrow microporosity.

Many studies are based on the analysis of adsorption isotherms for describing the microporosity of carbonaceous adsorbents. For that purpose, several theories and methods were developed, the most popular of them being the Brunauer–Emmett–Teller (BET) (Brunauer et al. 1938) and the Dubinin–Raduskevich (DR) (Dubinin 1960; Dubinin et al. 1991) methods. Their application, however, does not allow obtaining a broad spectrum of reliable information about structure of micropores and surface properties of the analysed materials. As a consequence, these methods are insufficient for today's technologists engaged in the production of high-quality microporous carbonaceous materials, or for engineers in charge of designing adsorption systems. Considering the above, new and more advanced methods for porous structure analysis have been devised, especially considerable progress was made in the recent years in porous materials research, giving rise to new methods for analysing and characterising porous structures based on computational technology. The most popular methods applied to porous structure analysis, in particular for the determination of pore size distributions (PSD), include the non-local density functional theory (NLDFT) (Evans and Tarazona 1984; Tarazona 1985; Tarazona et al. 1987; Seaton et al. 1989; Lastoskie et al. 1993; Olivier et al. 1994; Olivier 1998; Neimark et al. 2003; Thommes et al. 2006), the

quenched solid state functional theory (QSDFT) (Bhatia 2002; Ustinov et al. 2006; Ravikovitch and Neimark 2006; Neimark et al. 2009; Gor et al. 2012; Figueroa-Gerstenmaier et al. 2014), and the 2D-non-local density functional theory (2D-NLDFT) (Jagiello and Olivier 2009; Jagiello et al. 2011; Jagiello and Olivier 2013a, b). These methods assume the occurrence of, among other things, mechanisms of mobile adsorption in microporous materials because of the presence of a variable external potential, having an effect on the adsorbate molecules in the pores. Until recently, one of the most common methods for characterising micro- and mesoporous structures was the NLDFT (Lastoskie et al. 1993; Neimark et al. 2003; Olivier et al. 1994; Olivier 1998; Seaton et al. 1989; Thommes et al. 2006). The latter is based on a model of independent slit-shaped pores with ideal graphitic walls, and therefore it ignores the impact of, among other things, heterogeneity and deviations from such ideal structure in real porous materials. The NLDFT has generally been used for assessing pore size distributions and porosity of solid materials from the analysis data. Although the methods derived from the density functional theory were initially developed for activated carbons, the NLDFT is often recommended for the characterisation of ordered porous silica materials (Neimark et al. 2003; Thommes et al. 2006), due to the complexity and diversity of their porous structures. However, the NLDFT model has a significant drawback: in the case of carbonaceous materials having heterogeneous surfaces in terms of both energy distribution and geometrical characteristics, sometimes appear artificial gaps in the PSD (Neimark et al. 2003; Olivier et al. 1994; Thommes et al. 2006). Such discrepancy between the theoretical assumption of a smooth and homogeneous surface and the experimental situation is particularly obvious for microporous carbonaceous adsorbents having broad PSD. Works have also been carried out to improve the NLDFT itself. For instance, attempts were made to take the variability of pore wall thickness into account, but just led to a minor improvement in the reliability of the results (Bhatia 2002). Ustinov et al. (Ustinov et al. 2006) suggested a modification of Tarazona's version of the NLDFT and developed a model for the pore size analysis of carbons, which is based on a fit to a reference isotherm of non-graphitised carbon black. Their method was found to produce PSDs without false gap at  $\sim 1$  nm. Efforts were then made for developing new methods based on the density functional theory and, for instance, (Ravikovitch and Neimark 2006) proposed a new model called QSDFT, which is suitable for modelling adsorption in heterogeneous carbonaceous adsorbents with corrugated amorphous walls. The main idea behind the QSDFT method is to use a multicomponent DFT in which the solid is considered as a component having a fixed spatially distributed density. In the QSDFT

(Ravikovitch and Neimark 2006; Neimark et al. 2009; Gor et al. 2012; Figueroa-Gerstenmaier et al. 2014), the solid is modelled using a distribution of solid atoms rather than a source of external potential field. Consequently, the heterogeneity effect resulting from surface roughness can be explicitly accounted for, which is more realistic than the former NLDFT models considering porous carbons having flat and non-structured graphitic pore walls (Lastoskie et al. 1993; Neimark et al. 2003; Olivier et al. 1994; Olivier 1998; Seaton et al. 1989; Thommes et al. 2006). In turn, the QSDFT model is useful for analysing adsorption isotherms of carbonaceous materials having various degrees of pore wall roughness and surface defects. As often highlighted in the literature, the QSDFT method marked a meaningful step forward in the characterisation of the porous structure of carbonaceous adsorbents based on their adsorption isotherms, in particular in the low-pressure range. More specifically, the reliability of pore size distributions has increased significantly: the sharp minima in the NLDFT pore size distribution curve at ~1 and 2 nm don't appear anymore in QSDFT calculations (Ravikovitch and Neimark 2006; Neimark et al. 2009; Gor et al. 2012; Figueroa-Gerstenmaier et al. 2014). Considering the complexity of the porous structure of microporous carbons, attempts have been made to depart from the idealised image of heterogeneity in terms of geometrical characteristics and energy distribution. Davies and Seaton pointed out that the model pore shape definitely affects the characterisation results of porous carbonaceous adsorbents (Davies and Seaton 1998). Similarly, (Jagiello and Olivier 2009) demonstrated that a change of pore model allows better fits of the NLDFT to the experimental isotherms. As a consequence, those authors proposed a modification of the classical NLDFT method, namely the 2D-NLDFT, consisting in the introduction of a semi-complete two dimensional slit pore model (Jagiello et al. 2011; Jagiello and Olivier 2013a, b).

## 2 Materials and methods

The paper of Kwiatkowski and Broniek (2017) aimed at analysing the porous structure of activated carbons prepared from hazelnut shells by using various activation methods. Those materials were obtained either by physical activation with the use of steam ( $H_2O$ ) or carbon dioxide ( $CO_2$ ), as well as by chemical activation with the use of potassium hydroxide (KOH), potassium carbonate ( $K_2CO_3$ ), phosphoric acid ( $H_3PO_4$ ) or zinc chloride ( $ZnCl_2$ ). The corresponding activation conditions have been thoroughly detailed in (Kwiatkowski and Broniek 2017). For all activated carbons, nitrogen adsorption isotherms at 77 K were obtained with a Quantachrome

Autosorb 1-C automatic device using a manometric method, and the parameters of the porous structure were calculated by use of BET (Brunauer et al. 1938), DR (Dubinin 1960; Dubinin et al. 1991) and LBET methods (Kwiatkowski 2007, 2008, 2009, 2011; Kwiatkowski et al. 2016; Kwiatkowski and Hameed 2017). This former work showed that activated carbons having both high surface areas and a moderate degree of surface heterogeneity were those produced by activation with KOH, but the activated carbons characterised by the highest microporous surface area and the highest surface heterogeneity were those obtained with  $H_3PO_4$  and  $ZnCl_2$  (Kwiatkowski and Broniek 2017). In this context, this work demonstrated the considerable usefulness and reliability of the LBET method for analysing the adsorptive properties of activated carbons, including the assessment of the impact of the nature of the activating agent on porous structure formation (Kwiatkowski and Broniek 2017). Still, the LBET but even more the BET and the DR methods often proved to be insufficient to determine the optimal activation conditions for producing activated carbons for a given application, i.e., having a specific pore structure and pore size distribution.

In order to validate the aforementioned DFT methods and to check their usefulness in chemical technology research, a new series of tests aimed at analysing the porous structure of activated carbons derived from hazelnut shells by various activation methods is presented herein. Those tests incorporate the methods derived from the DFT, namely NLDFT, QSDFT and 2D-NLDFT. The corresponding results produced with the DFT methods were collected and compared with each other and with those from BET, DR and LBET methods carried out in former studies. Other models such as the well-known  $\alpha_s$  method were not considered herein, as they fail to consider the non-homogeneity of the materials surface.

## 3 Results and discussion

The results of all the analyses carried out using QSDFT and the BET, DR and LBET methods are presented in Table 1. In addition, Figs. 1, 2, 3, 4, 5, 6 present pore size distributions determined using NLDFT, 2D-NLDFT and QSDFT methods.

The results presented in Table 1; Fig. 1 suggest that the PSDs determined for the carbon activated with  $CO_2$  using NLDFT, QSDFT and 2D-NLDFT methods are similar. However, particularly noteworthy is the second peak within the pore range at ca. 2–3 nm and at ca. 3–4 nm determined by NLDFT and QSDFT methods, respectively, not seen with 2D-NLDFT. Nevertheless, all lead to the conclusion that narrow mesopores occur along with a prevalent microporosity.

These observations agree with the values of the parameters given in Table 1 such as micropore volume  $V_{DR}$ , total pore volume  $V_{Total}$ , surface area  $S_{BET}$ , parameters of the microporous structure obtained by the LBET method, together with the fast multi-variant identification procedure of adsorption systems, with implemented models of multilayer adsorption on heterogeneous surfaces. More specifically, comparing the micropore volume determined by QSDFT and DR methods ( $V_{QSDFT}=0.464 \text{ cm}^3/\text{g}$  and  $V_{DR}=0.393 \text{ cm}^3/\text{g}$ , respectively) with the total pore volume ( $V_{Total}=0.498 \text{ cm}^3/\text{g}$ ) and with the volume of the first adsorbed layer determined from the LBET equation ( $V_{hA}=0.417 \text{ cm}^3/\text{g}$ ), evidences the occurrence of micropores with a small proportion of mesopores in the analysed material. These conclusions confirm the accuracy of the PSD determined with the use of DFT methods. Moreover, earlier calculations carried out using the LBET method attested the formation of high and branchless clusters of adsorbate molecules ( $\alpha=0.74$  and  $\beta=1.02$ ) in the micropores of the analysed material, and to the substantial heterogeneity of its surface ( $h=5$ ) (Kwiatkowski and Broniek 2017).

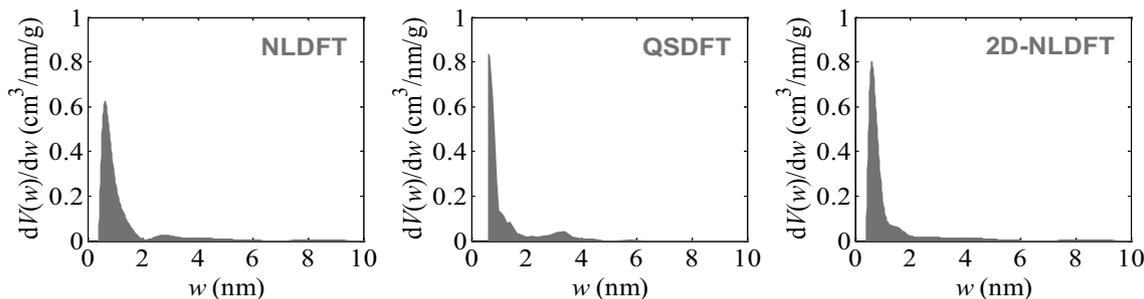
As for the activated carbon produced by physical activation with steam, the shapes of the PSDs obtained by use of DFT methods (see Fig. 2) point out a considerable proportion of broader micropores and mesopores in the range from 2 to 6 nm. It is also noticeable that the PSD from the QSDFT is more differentiated than those determined by NLDFT and 2D-NLDFT, and that there is no second peak in the distribution calculated with the 2D-NLDFT method. In addition, the analyses reveal a higher pore volume, i.e.,  $V_{QSDFT}=0.532 \text{ cm}^3/\text{g}$ , and a higher peak pore size, namely  $w=1.178 \text{ nm}$ , with respect to the former material activated by  $\text{CO}_2$ . The results obtained with the use of BET and DR methods, as well as based on the maximum nitrogen adsorption, coincide again with those derived from the DFT methods: the values of  $V_{DR}$ ,  $V_{Total}$  and  $S_{BET}$  agree with a higher proportion of larger pores, and with higher pore volume and surface area compared to those discussed before.

On the other hand, the results from the use of the LBET method are virtually identical with those obtained with the activated carbon produced by  $\text{CO}_2$  activation. This is not surprising as soon as one remembers that such method was

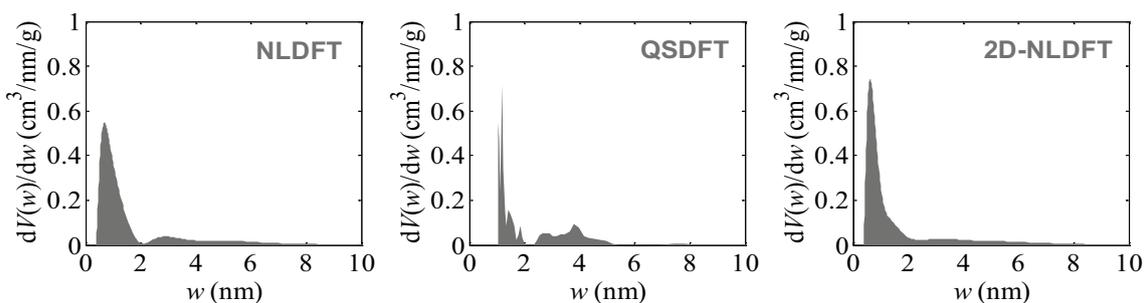
**Table 1** Results of the application of QSDFT, BET, DR and LBET methods to nitrogen adsorption isotherms of activated carbons prepared by physical or chemical activation of hazelnut shells

Sample	$V_{QSDFT}$ ( $\text{cm}^3/\text{g}$ )	$w$ (nm)	$S_{BET}$ ( $\text{m}^2/\text{g}$ )	$V_{DR}$ ( $\text{cm}^3/\text{g}$ )	$V_{Total}$ ( $\text{cm}^3/\text{g}$ )	LBET No.	$V_{hA}$ ( $\text{cm}^3/\text{g}$ )	$Q_A/RT$	$B_C$	$h$	$\alpha$	$\beta$
HAC/ $\text{CO}_2$	0.464	0.614	968	0.393	0.498	7	0.417	-13.60	3.34	5	0.74	1.02
HAC/ $\text{H}_2\text{O}$	0.532	1.178	1057	0.428	0.577	7	0.418	-13.81	3.28	5	0.75	1.00
HAC/ $\text{K}_2\text{CO}_3$	0.401	0.666	912	0.384	0.433	4	0.364	-11.13	6.91	3	0.38	1.52
HAC/ $\text{KOH}$	0.871	0.614	2031	0.783	0.930	22	0.833	-9.14	6.91	5	0.46	1.00
HAC/ $\text{H}_3\text{PO}_4$	0.991	1.096	1333	0.446	1.030	28	0.830	-10.03	2.82	9	1.00	1.00
HAC/ $\text{ZnCl}_2$	1.009	0.926	1643	0.589	1.058	13	0.1140	-10.51	5.30	9	1.00	1.00

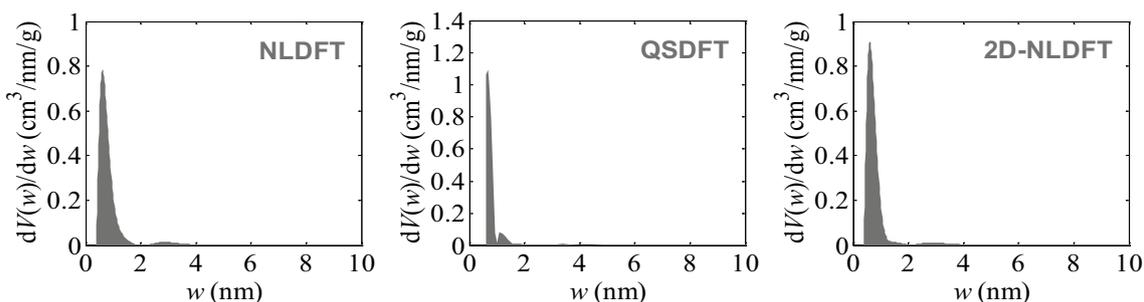
$V_{QSDFT}$  micropore volume determined by QSDFT method,  $w$  peak pore size,  $S_{BET}$  surface area determined by BET method,  $V_{DR}$  micropore volume determined by Dubinin-Raduskevich method,  $V_{Total}$  total pore volume determined at a relative pressure  $P/P_0=0.98$ , LBET No. the number of the best fitted LBET class model,  $V_{hA}$  volume of the first adsorbed layer determined from the LBET equation,  $Q_A/RT$  dimensionless energy parameter for the first layer,  $B_C$  dimensionless energy parameter for the higher layers,  $h$  heterogeneity parameter, the geometrical parameter of the porous structure determining the height of the adsorbate molecules clusters; the average number of sites provided by  $(n-1)$ th layer for the  $n$ th layer,  $n=2, k$ , averaged over all adsorbate molecules clusters ( $-1$  for narrow pores,  $>1$  for wider ones) (Kwiatkowski 2007, 2008, 2009, 2011; Kwiatkowski et al. 2016; Kwiatkowski and Hameed 2017)



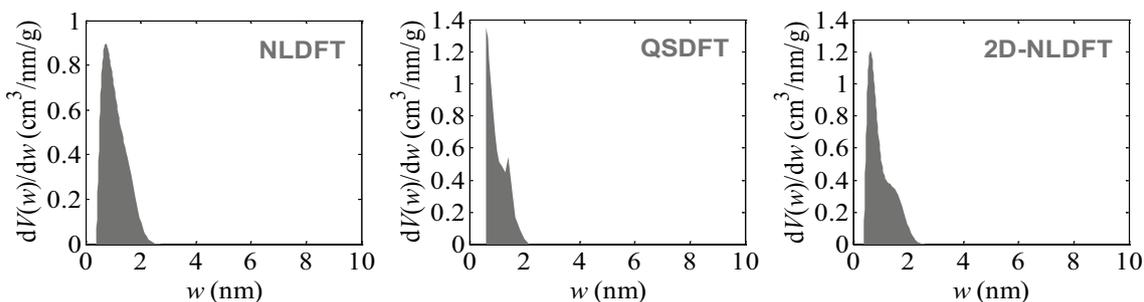
**Fig. 1** Pore Size Distributions (PSD) of activated carbon prepared by physical activation of hazelnut shells with  $\text{CO}_2$ , obtained by application of NLDFT, QSDFT and 2D-NLDFT methods to its nitrogen adsorption isotherm



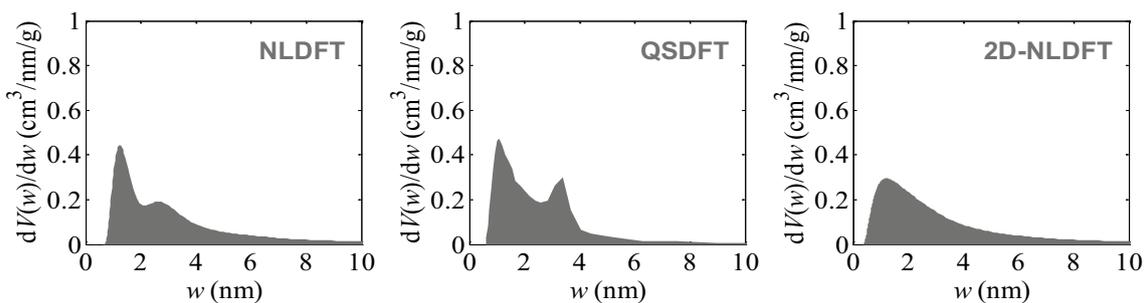
**Fig. 2** Same as Fig. 1, but for the activated carbon prepared by physical activation of hazelnut shells with steam



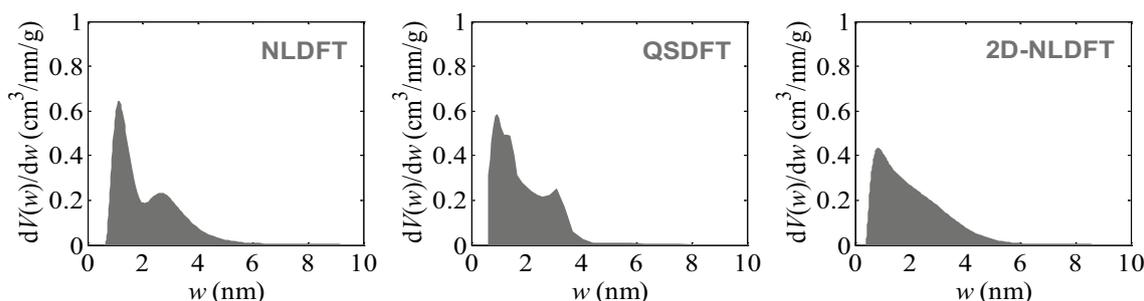
**Fig. 3** Same as Fig. 1, but for the activated carbon prepared by chemical activation of hazelnut shells with  $K_2CO_3$



**Fig. 4** Same as Fig. 1, but for the activated carbon prepared by chemical activation of hazelnut shells with KOH



**Fig. 5** Same as Fig. 1, but for the activated carbon prepared by chemical activation of hazelnut shells with  $H_3PO_4$



**Fig. 6** Same as Fig. 1, but for the activated carbon prepared by chemical activation of hazelnut shells with  $\text{ZnCl}_2$

developed for the analysis of microporous carbon materials. Therefore, it appears less reliable in terms of pore size categorisation when applied to materials with a large proportion of mesopores. This aspect must be taken into account in the analysis of bimodal porous materials such as the one activated with steam. This fact justifies a simultaneous analysis based on BET, DR, LBET and DFT methods, which should offer a more complete and reliable information on the porous structure of materials, as well as the possibility of verifying the results produced by the different methods.

The analysis of the activated carbon produced by chemical activation of  $\text{K}_2\text{CO}_3$  led to the narrow pore size distributions seen in Fig. 3. The one obtained by application of the QSDFT was somewhat different and even narrower than those derived from NLDFT and 2D-NLDFT. The latter two methods indeed evidenced a proportion of mesopores in the range 2–4 nm. As can be concluded from the results compiled in Table 1 and from the PSD, this material is characterised by poorer adsorption properties than those of the aforementioned activated carbons, the corresponding parameters  $V_{\text{QSDFT}}$ ,  $V_{\text{DR}}$ ,  $V_{\text{Total}}$ ,  $V_{\text{hA}}$  and  $S_{\text{BET}}$  being systematically lower. Moreover, the results of the analyses carried out by using the LBET method show that medium-sized and branched clusters of adsorbate molecules ( $\alpha=0.38$  and  $\beta=1.52$ ) are formed in the micropores of this material. The latter is also characterized by a lower surface heterogeneity ( $h=3$ ).

The activated carbon prepared by chemical activation with KOH presents rather narrow PSD, falling mainly in the micropore range, as seen in Fig. 4. The NLDFT method produced slight differences in the range of widths of ca. 1–2 nm with respect to both 2D-NLDFT and QSDFT. The prevalence of microporosity with a small fraction of mesoporosity is also reflected when comparing the parameters  $V_{\text{QSDFT}}$  and  $V_{\text{Total}}$  with  $V_{\text{DR}}$  and  $V_{\text{hA}}$ . Furthermore, the corresponding values, as well as that of  $S_{\text{BET}}$ , all evidently exceed those of the activated carbons cited above. As evidenced by former analyses, the surface of the material activated with KOH is heterogeneous ( $h=5$ ), and its pores contain medium-sized and unbranched adsorbate molecules clusters

( $\alpha=0.46$  and  $\beta=1.00$ ) (Kwiatkowski and Broniek 2017). Also, the energy parameters ( $Q_A/RT=-9.14$ ,  $B_C=6.91$ ) and the number of the fitted LBET class model (LBET No. 22) indicate obstruction to adsorbate molecules cluster growth, due to the geometrical limitations of the pores, which coincides with high adsorption energy on the layers  $n > 1$ . This observation corresponds to the results obtained using DFT, DR and BET methods.

The analysis of the porous structure of the carbon chemically activated with  $\text{H}_3\text{PO}_4$  points out a considerable proportion of mesopores, where the prevalent peak pore size is  $w=1.096$  nm (see Fig. 5). However, it is worth noticing that both NLDFT and QSDFT yielded two peaks in the PSD, against a single one for 2D-NLDFT.

Also, a comparison of the  $V_{\text{QSDFT}}$ ,  $V_{\text{Total}}$  and  $V_{\text{DR}}$ , and  $S_{\text{BET}}$  parameters confirms the above conclusions according to which a substantial fraction of mesoporosity exists in this material. Application of the LBET method show that the surface of this activated carbon is strongly heterogeneous ( $h=9$ ), with very high and unbranched adsorbate molecules clusters formed in its pores ( $\alpha=1.00$  and  $\beta=1.00$ ), their growth being a consequence of the geometrical constraints of the pores. Still, some of the results derived from the LBET method have to be considered with caution. Indeed, as evidenced by the results from both NLDFT and QSDFT, this material is characterised by a bimodal structure with a substantial proportion of mesopores. The case of the carbon activated with  $\text{H}_3\text{PO}_4$  thus reconfirms the necessity of analysing the porous structure simultaneously by using NLDFT, 2D-NLDFT, QSDFT, BET, DR and LBET methods, such an approach guaranteeing both the access to the whole range of information and a reliable verification of the results.

The comparison of the analytical results obtained for this activated carbon with those of the previous materials leads to the conclusion that activation with  $\text{H}_3\text{PO}_4$  has a clearly aggressive effect on hazelnut shells, destroying the walls between neighbouring micropores.  $\text{H}_3\text{PO}_4$  may therefore be applied to this precursor for obtaining a material having the highest possible total volume of pores. Obviously, however,

any modification of the activation conditions, namely temperature, time, impregnation ratio, as well as the application of pyrolysis prior to activation, may significantly alter the results.

The last analysed material of the series was the carbon chemically activated with  $\text{ZnCl}_2$ . The PSD obtained by application of the DFT methods coincide with that of the sample activated with  $\text{H}_3\text{PO}_4$  (see Fig. 6). Again, NLDFT and QSDFT methods produced two peaks on the PSD, unlike the unique peak found with 2D-NLDFT.  $\text{ZnCl}_2$  led to the activated carbon with the largest pore volume out of all other samples, as evidenced by the parameters  $V_{\text{QSDFT}}$  and  $V_{\text{Total}}$ , as well as by the rather high parameters  $V_{\text{DR}}$  and  $S_{\text{BET}}$ . Still, the value of the parameter  $V_{\text{HA}}$ , i.e., the volume of the first adsorbed layer, is strikingly low ( $V_{\text{HA}} = 0.1140 \text{ cm}^3/\text{g}$ ). When considered in the context of the aforementioned data, and taking into account the geometrical parameters  $\alpha$  and  $\beta$ , this finding suggests that expanded and unbranched clusters of adsorbate are formed in the micropores ( $\alpha = 1.00$  and  $\beta = 1.00$ ), and the expansion of those clusters results from the geometrical obstruction of the pores and from energetic limitations (LBET No. 13). Similarly to the material activated with  $\text{H}_3\text{PO}_4$ , the one prepared with  $\text{ZnCl}_2$  presents a strongly heterogeneous ( $h = 9$ ) surface.

## 4 Conclusion

The aims of this work were: (i) to analyse the porous structures of activated carbons prepared from a waste material of natural origin, hazelnut shells, submitted to various activation processes, by application of NLDFT, QSDFT, and 2D-NLDFT methods; and (ii) to compare the results with—and verify them against—those obtained in previous studies from BET, DR, and LBET methods.

The analyses carried out by using NLDFT, QSDFT and 2D-NLDFT indicated a very strong dependence of the results on the assumptions regarding the specific model of pores, which questions the reliability and credibility of those methods. However, if one considers errors of measurement that may occur when determining adsorption isotherms, as well as the difficulty of selecting a representative sample from a batch of (most often inhomogeneous) material to be analysed, certain imperfections of the DFT methods become acceptable.

The analyses in question revealed some limitations of the LBET method that become evident when the analysis concerns bimodal porous materials with a considerable proportion of mesopores. In such cases, the LBET method, which was formerly designed for analysing microporous materials, may become less reliable.

Considering the above, it is advisable to perform concurrent analyses using all together NLDFT, 2D-NLDFT, QSDFT, and BET, DR and LBET methods, which—provided that the results of analyses are correctly interpreted—may yield complementary and reliable information on the analysed porous structure and corroborate the results obtained using different methods. Only after information has been completed and checked this way, optimum methods and conditions can be selected to produce activated carbons and other carbonaceous adsorbents through state-of-the-art industrial processes with well-chosen preparation conditions.

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