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# A Comparative Study of the Effects of Different Chemical Agents on the Pore-size Distributions of Macadamia Nutshell-based Activated Carbons Using Different Models

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**ABSTRACT:** The effects of the chemical activation agent and the chemical/nutshell ratio (ranging from 15–500 mass%) on the pore-size distribution (PSD) of macadamia nutshell-based activated carbons have been investigated in this study. The adsorption isotherm data of two series of activated carbons prepared from macadamia nutshell by chemical activation with potassium hydroxide and zinc chloride were used. The three widely used models of Dubinin–Stoeckli, Stoeckli and Horvath–Kawazoe were applied for characterizing these porous solids.

Although the results showed some differences amongst these models arising from the fundamental assumptions on which they are based, in general they were comparable. Thus, at the same chemical ratio, samples activated by  $\text{ZnCl}_2$  showed more adsorption capacity than those from KOH. Moreover, the pore volumes increased as the impregnation ratio in each series increased. In addition, with increasing impregnation ratio (up to 100%) in the  $\text{ZnCl}_2$  series, the micropores were widened and a further increase in  $\text{ZnCl}_2$  content caused the micropores to change to mesopores. In the KOH series, increasing KOH created more micropores in the carbon structure over the whole range of chemical/nutshell ratio studied.

## 1. INTRODUCTION

Activated carbons (ACs) obtained from different carbonization and activation processes exhibit various structures (Ahmadpour and Do 1995). Their adsorptive properties, such as high surface area, microporous structure and a high degree of surface reactivity, are the main reasons for the wide application of ACs in purification, recovery, decolorization, deodorization, dechlorination, separation, catalyst supports and methane storage. For this reason, adsorption by activated carbon is of interest in many economic sectors and concern areas such as the chemical, food, pharmaceutical, automobile, petroleum, petrochemical and gas industries (Bansal and Goyal 2005; Quirke 2006; Roque-Malherbe 2007).

One of the important characteristic of any carbonaceous adsorbent is its microporosity. The adsorption performance and efficiency of such an adsorbent will then be directly related to the sizes of the micropores. Hence, the determination of the pore-size distribution (PSD) of porous adsorbents is of particular interest and several models proposed by various workers have been used for this purpose. As a consequence, a large number of studies have been conducted during the past six decades to obtain the pore-size distributions of various porous adsorbents.

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A direct but cumbersome experimental technique for determining PSDs is to measure the saturated amounts of various probe molecules of different sizes adsorbed. However, there is uncertainty about this method because of the networking effects of some adsorbents, including activated carbons (Cheng and Yang 1994). Other experimental techniques usually employed for characterizing the pore structures of porous materials include mercury porosimetry, X-ray diffraction (XRD), small angle X-ray scattering (SAXS) and immersion calorimetry.

A large number of both simple and sophisticated models have been proposed in an attempt to obtain a realistic estimation of the PSDs of porous adsorbents. Relatively simple methods but of restricted application such as those of Barrett, Joyner and Halenda (BJH), Mikhail *et al.* (MP), Horvath and Kawazoe (HK), Jaroniec and Choma (JC), Kruk–Jaroniec–Sayari (KJS) and Nguyen and Do (ND) were presented from 1951 to 1999 for the determination of PSDs from experimental adsorption isotherms (Barrett *et al.* 1951; Mikhail *et al.* 1968; Horvath and Kawazoe 1983; Jaroniec and Choma 1986; Kruk *et al.* 1997; Nguyen and Do 1999). The HK model was developed for calculating the micropore-size distribution of slit-shaped pores. Extension of this theory for cylindrical and spherical pores was made by Saito and Foley (1991) and Cheng and Yang (1994). Some improved models for calculating the PSDs of porous adsorbents based on modifications to the HK theory have also been presented (Cheng and Yang 1994, 1995). From a variety of synthetic and experimental data, Gauden *et al.* (2007) extended the Nguyen and Do method to the determination of bimodal PSDs of various carbonaceous materials.

More sophisticated models which are grounded on statistical mechanics [e.g. the Monte Carlo and Density Functional Theory (DFT) methods] have also been proposed for calculating PSDs (Seaton *et al.* 1989; Aukett *et al.* 1992; Olivier 1995). The advantages of these models are that they can be applied to a wide range of pore widths and are therefore not limited to micropores. However, they only provide accurate PSD estimations for just some special shapes of adsorbate molecules.

There is also a different approach based on a single adsorption isotherm. Here, the total amount adsorbed, which is simply a summation of the adsorbed molecules on various adsorption sites, is equal to an integral of the local adsorption on particular sites multiplied by a PSD function, integrated over all pore sizes:

$$\theta(P) = \int_0^{\infty} \theta(L,P)f(L)dL \quad (1)$$

where  $\theta(L,P)$  is the local adsorption isotherm (kernel) evaluated at bulk pressure ( $P$ ) and local pore size ( $L$ ), and  $F(L)$  denotes the PSD of the heterogeneous solid adsorbent. The solution of the PSD function presents an ill-posed problem unless the form of function is defined. Different models such as the Dubinin–Stoeckli (DS) and Stoeckli which assume various kernels (Langmuir, BET, DR, ...) and mathematical functions (Gaussian, Gamma, ...) have been presented for PSD calculations (Dubinin and Kadlec 1987; Stoeckli 1995; Wang *et al.* 1997). Although PSD estimations from these models are experimentally convenient, they are unlikely to be of high accuracy because of the assumptions and empiricism involved (Cheng and Yang 1994).

Sun (2002) proposed a method based on the modification of the Dubinin–Radushkevich (DR) equation by introducing the adsorption density and correlating between the pore-filling pressure and the critical pore size for nitrogen adsorption at  $-196$  °C. The results obtained were comparable with those of popular PSD methods such as MP, JC, HK and DFT. In addition to uncertainty about the general performance of this model as a result of some assumptions in the model derivation, it is relatively complicated and the procedure for obtaining PSDs is cumbersome.

Some other models that describe PSDs over the mesopore and macropore ranges have also been proposed. The average diameter of mesopores is usually calculated from nitrogen adsorption data using the Kelvin equation (Do *et al.* 2001). The Kelvin equation is derived from thermodynamic considerations and is limited to mesopores and macropores. It becomes progressively less accurate with decreasing pore size. This is due to the enhancement of adsorption in micropores as a result of the overlap of the force fields created by the opposing pore walls. Recently, Shahsavand and Niknam (2011a,b) proposed two new methods based on the Kelvin equation for the reliable extraction of PSDs from adsorption and condensation isotherms. However, their results appear to indicate that both methods have some limitations similar to those advanced previously. Thus, the regularization technique used for obtaining the optimum value of the regularization parameter in these methods is challengeable. In addition, the basis of the methods is the Kelvin equation which is unlikely to provide reliable PSDs for microporous solids.

Thus, although many methods have been proposed to address the calculation of the PSD of an activated carbon, to date no general and reliable theory is available. Here, we have used the adsorption isotherm data for benzene at 30 °C onto two series of carbons from macadamia nutshell precursors chemically activated using KOH and ZnCl<sub>2</sub> to estimate and compare their PSDs. The PSD of each sample was obtained from the isotherm data using the three well-known models of Dubinin–Stoeckli (DS), Stoeckli and Horvath–Kawazoe (HK). The effects of the two chemical agents as well as the impregnation ratio on the porosities of the AC samples have been investigated. Finally, a comparison of the PSD results obtained from each model is also made for the KOH- and ZnCl<sub>2</sub>-activated carbon series.

## 2. METHODS

The correct determination of the pore-size distribution of porous adsorbents still remains the most important problem in the characterization of porous materials. Unfortunately, there is no convenient and accurate experimental method for this purpose. The lack of such a method is exasperated by the rapid development of new porous materials and their wide application in various fields. A large number of methods have been presented by many researchers for the determination of the PSDs of porous solids. However, the type of adsorbate, the adsorbent characteristics, the adsorption temperature, the range of applicable of pore sizes and the relative pressure range covered by each method are some of the important limitations that allow the models to be only applicable in specific situations. In the present study, the following three well-known models for PSD determination were used for two series of chemically activated carbons and the results obtained have been compared.

### 2.1. The Dubinin–Stoeckli (DS) method

In this method, the adsorption of vapours by microporous carbons was described by the following fundamental equation of Dubinin and Astakhov (DA) (Dubinin 1975, 1985; Bansal *et al.* 1988):

$$W = W_0 \exp[-(A/E)^n] \quad (2)$$

where  $W$  (mmol/g) represents the amount adsorbed at a relative pressure  $P/P_0$ ,  $W_0$  is the limiting amount of micropore filling and  $A$  denotes the differential molar work of adsorption at temperature  $T$  as defined by  $A = RT \ln(P_0/P)$ . At high pressures, the ratio  $P_0/P$  is replaced by the

fugacity ratio  $f_0/f$  and, for temperatures above the critical value, the saturation pressure is replaced by an expression given by Dubinin and Nikolayev (Dubinin 1985) based on  $T_c$ ,  $P_c$  and  $T$ . Finally,  $E = \beta E_0$ , where  $\beta$  is an affinity coefficient expressing the ratio of the characteristic adsorption energies of the test and reference vapour (benzene).

The micropore-size distribution can be assumed to take the following Gaussian distribution:

$$\frac{dW}{dx} = \frac{W_0}{\delta\sqrt{2\pi}} \exp\left[-\frac{(x-x_0)^2}{2\delta^2}\right] \quad (3)$$

where  $x_0$  is the half-width of a slit-shaped micropore which corresponds to the maximum of the distribution curve, and  $\delta$  is the variance.

From small-angle X-ray scattering experiments, the parameter  $E_0$  has been found to follow the following relationship with the micropore half-width (Dubinin 1989):

$$E_0 = k/x_0 \quad (4)$$

When benzene is employed as the reference vapour, the constant  $k$  is equal to 12 (kJ nm)/mol.

Assuming the exponent  $n$  in equation (2) is equal to 2 leads the well-known Dubinin–Radushkevich (DR) equation, and using the last equation we have:

$$W = W_0 \exp(-mx^2 A^2) \quad (5)$$

where  $m$  is a constant coefficient for a given vapour:

$$m = \left(\frac{1}{\beta k}\right)^2$$

Substituting  $dW_0$  from equation (5) into equation (3), we obtain the adsorption equation in an integral form:

$$W = \frac{W_0}{\delta\sqrt{2\pi}} \int_0^\infty \exp\left[-\frac{(x-x_0)^2}{2\delta^2}\right] \exp(-mx^2 A^2) dx \quad (7)$$

Upon integration, the Dubinin–Stoeckli (DS) adsorption equation for adsorbents with non-homogeneous microporous structures is obtained (Dubinin and Kadlec 1987):

$$W = \frac{W_0}{2\sqrt{1 + 2m\delta^2 A^2}} \exp\left(-\frac{mx_0^2 A^2}{1 + 2m\delta^2 A^2}\right) \left[1 + \operatorname{erf}\left(\frac{x_0}{\delta\sqrt{2}\sqrt{1 + 2m\delta^2 A^2}}\right)\right] \quad (8)$$

Using the above equation to fit the experimental data, the three parameters,  $W_0$ ,  $x_0$  and  $\delta$  can be extracted. Knowing these parameters, the micropore-size distribution in terms of volume can be calculated from equation (3).

## 2.2. The Stoeckli method

The second method for determining the PSDs of microporous materials from gas adsorption measurements which is also based on the Dubinin theory of volume filling of micropores (TVFM) is the Stoeckli method (Stoeckli 1995).

It is worthwhile pointing out that the use of  $n = 3$  rather than  $n = 2$  in equation (2) corresponds to much narrow PSDs and should, in principle, lead to a more flexible isotherm equation (Carrott and Ribeiro Carrott 1999; Stoeckli *et al.* 2002).

Stoeckli *et al.* (1990) showed that, for ideal slit-shaped microporous materials, good estimates of the overall mean micropore width of an activated carbon may be obtained from the relationship:

$$L_0 = 10.8/(E_0 - 11.4 \text{ kJ/mol}) \quad (9)$$

This is applicable over a range of pore size from 0.4 nm to 2.0 nm (Carrott and Ribeiro Carrott 1999). For simplicity, this expression is not used directly to estimate the mean micropore width ( $L = 2x$ ) of different pore groups, but this may be estimated from the expression:

$$L = K/E \quad (10)$$

where  $E$  is the characteristic energy of a particular pore group. Combination of these two last equations results in:

$$K = EL = 10.8E/(E - 11.4) \quad (11)$$

It is further assumed that, instead of using different values of  $K$  for each pore group, a mean value,  $K_0$ , corresponding to the mean characteristic energy,  $E_0$ , of the whole micropore system can be used. The value of  $K_0$  may be calculated from equation (11) by replacing  $K$  by  $K_0$  and  $E$  by  $E_0$ . With these assumptions, the local isotherm becomes:

$$W = W_0 \exp\left[-(AL/\beta K_0)^3\right] \quad (12)$$

For the pore-size distribution function, the existence of the following gamma-type distribution of the mean pore widths of the different pore groups is assumed:

$$\frac{dW}{dL} = \frac{3W_0 a^\nu L^{3\nu-1} \exp(-aL^3)}{\Gamma(\nu)} \quad (13)$$

where  $W_0$  denotes the total micropore volume. The constants  $a$  and  $\nu$  are related to the mean and the width of the distribution, respectively.

Combining equations (12) and (13) results in a well-known Laplace transform and leads to the following isotherm equation which is referred to as the Stoeckli equation (Stoeckli 1995; Stoeckli *et al.* 2002):

$$W = W_0 \left[ \frac{a}{a + (A/\beta K_0)^3} \right]^\nu \quad (14)$$

The model parameters can be obtained by using equation (14), following which application of equation (13) will give the pore-size distribution of a porous adsorbent.

### 2.3. The Horvath–Kawazoe (HK) method

A theoretical framework was developed by Horvath and Kawazoe (1983) for calculating PSDs from the steep-rise range of an adsorption isotherm. This model provides a simple, one-to-one correspondence between the pore size and the relative pressure at which the pore is filled. Using thermodynamic arguments, Horvath and Kawazoe derived the following expression:

$$RT \ln \left( \frac{P}{P_0} \right) = N_{AV} \frac{N_a A_a + N_A A_A}{\delta^4 (L - 2d_0)} \left[ \frac{\delta^4}{3(L - d_0)^3} - \frac{\delta^{10}}{9(L - d_0)^9} - \frac{\delta^4}{3d_0^3} + \frac{\delta^{10}}{9d_0^9} \right] \quad (15)$$

where  $L$  is the micropore width ( $L = 2x$ ),  $N_{AV}$  is Avogadro's number, and  $R$  and  $T$  are the gas constant and temperature, respectively. The terms  $A_a$  and  $A_A$  are dispersion constants characterizing the adsorbate–adsorbent and adsorbate–adsorbate interactions,  $N_a$  and  $N_A$  are the number of atoms per unit area of adsorbent and the number of molecules per unit area of adsorbate,  $d_0$  is the arithmetic mean of the adsorbate molecular diameter and the adsorbent atomic diameter, while  $\delta$  is the distance between a gas molecule and an adsorbent atom at zero interaction energy at a relative pressure of  $P/P_0$ .

From the amount adsorbed at a relative pressure of  $P/P_0$ , equation (15) yields the corresponding slit-pore width,  $L$ . Thus, a plot of the adsorbed volume versus  $L$  gives a cumulative pore volume curve whose slope gives the differential PSD.

### 3. EXPERIMENTAL

Activated carbons were prepared from macadamia nutshells by chemical activation with KOH and  $ZnCl_2$ . The influence of different chemical activating agents, viz. a strong base (KOH) and a Lewis acid ( $ZnCl_2$ ), on the structure of the prepared activated carbon was investigated. The detailed experimental procedure employed was reported in our previous work (Ahmadpour and Do 1997). In brief, 10 g of dried macadamia nutshell (MNS) was well mixed for ca. 5 min with a concentrated solution of KOH or  $ZnCl_2$  employing a chemical/nutshell ratio in the range of 15–500 mass%, following which the resulting homogeneous slurry was dried overnight at 110 °C. The resulting samples were placed in a quartz boat in a horizontal reactor and heated to the final carbonization temperature in a nitrogen flow of 150 ml (STP)/min. All samples were held at the final temperature (500 °C in the  $ZnCl_2$  series and 700 °C in the KOH series) for carbonization times of 1 h before cooling down under nitrogen. The products were washed sequentially with 0.5 N HCl, hot water and finally cold distilled water to remove residual organic and mineral matters, and then dried at 110 °C. In all experiments, the heating rate and nitrogen flow were kept constant, the nitrogen gas having been passed through a bed filled with copper turnings heated at 480 °C and a 4 Å molecular sieve bed to remove any traces of oxygen and water before entering the reactor.

After preparation, low-pressure benzene adsorption measurements on the samples were carried out at 30 °C using a conventional high-accuracy volumetric adsorption rig with multiple sample cells. A schematic representation of the experimental apparatus is given in Figure 1 overleaf. The rig was constructed of VCR components suitable for experiments at very low pressures. The pressure was measured with high-accuracy MKS-type pressure transducers (P.T.). The dosing section was first evacuated through one of the line in the analysis section. Prior to any adsorption experiments, liquid benzene in the reservoir was frozen with the aid of liquid nitrogen, followed

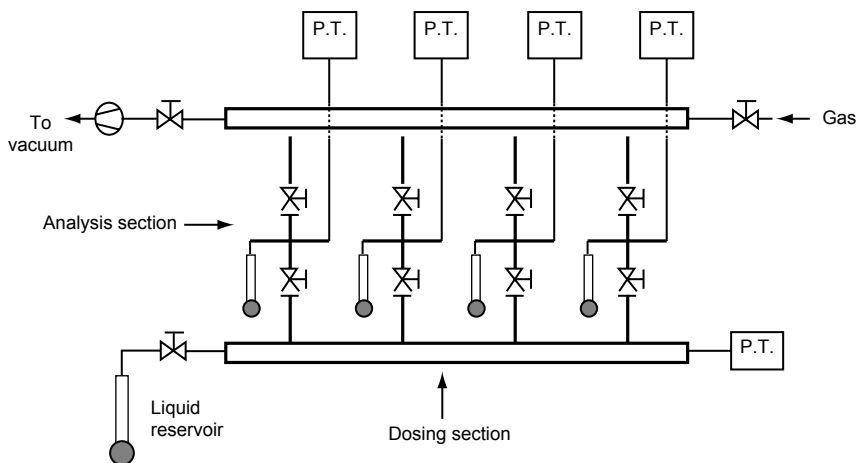


Figure 1. Schematic diagram of the volumetric adsorption rig employed.

by subsequent evacuation for removing any trapped air in the cell and then heating to room temperature. This procedure was then repeated three times. Adsorption of nitrogen at  $-196\text{ }^{\circ}\text{C}$  was performed on the prepared samples using a Quantachrome Autosorb-1 instrument.

#### 4. RESULTS AND DISCUSSION

Two series of activated carbons with different chemical/nutshell ratios of 15, 25, 50, 100, 200 and 500 mass% were prepared by chemical activation of macadamia nutshell with potassium hydroxide and zinc chloride. Figure 2 shows the benzene isotherms measured at  $30\text{ }^{\circ}\text{C}$  on samples prepared with different chemical/nutshell ratios. For the sake of comparison, the nitrogen adsorption/desorption isotherms with various nutshell/chemical ratio measured at  $-196\text{ }^{\circ}\text{C}$  are plotted in Figure 3 overleaf. It will be seen that a similar behaviour was observed for benzene adsorption to that for nitrogen adsorption.

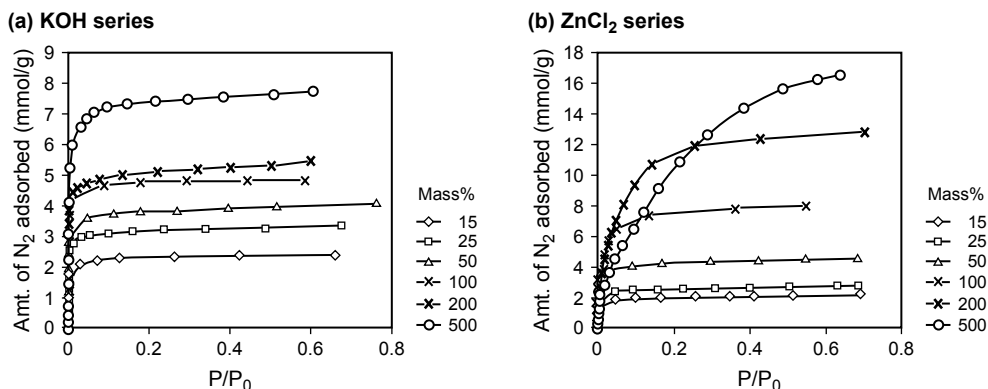
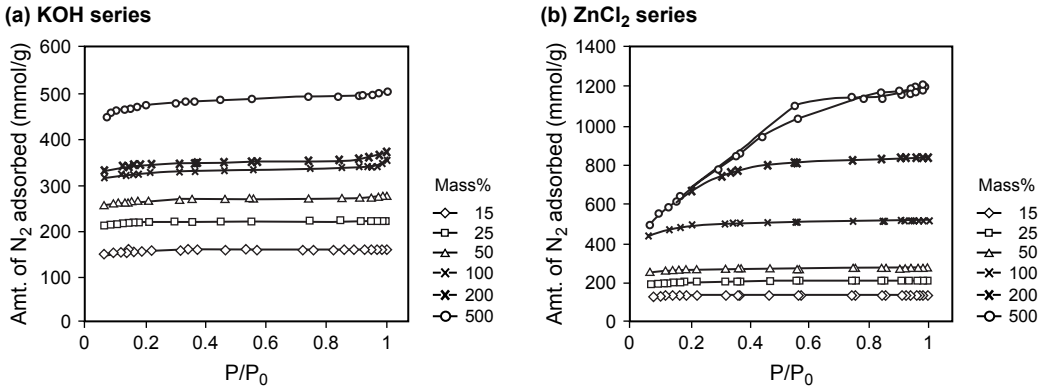


Figure 2. Benzene isotherms at  $30\text{ }^{\circ}\text{C}$  on the prepared samples with different chemical/nutshell ratios: (a) samples activated with KOH; (b) samples activated with  $\text{ZnCl}_2$ .

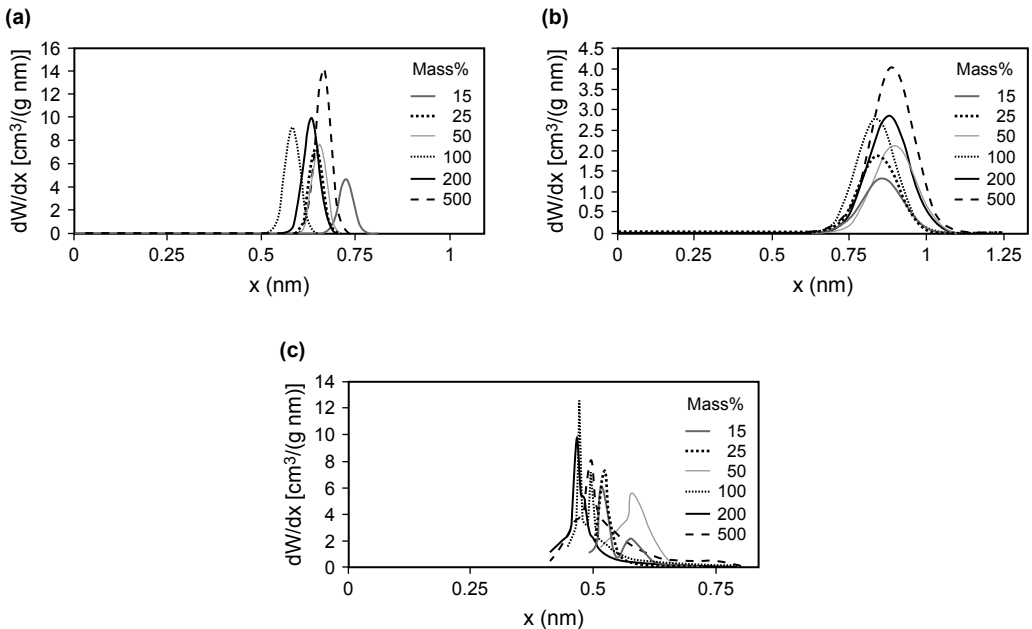




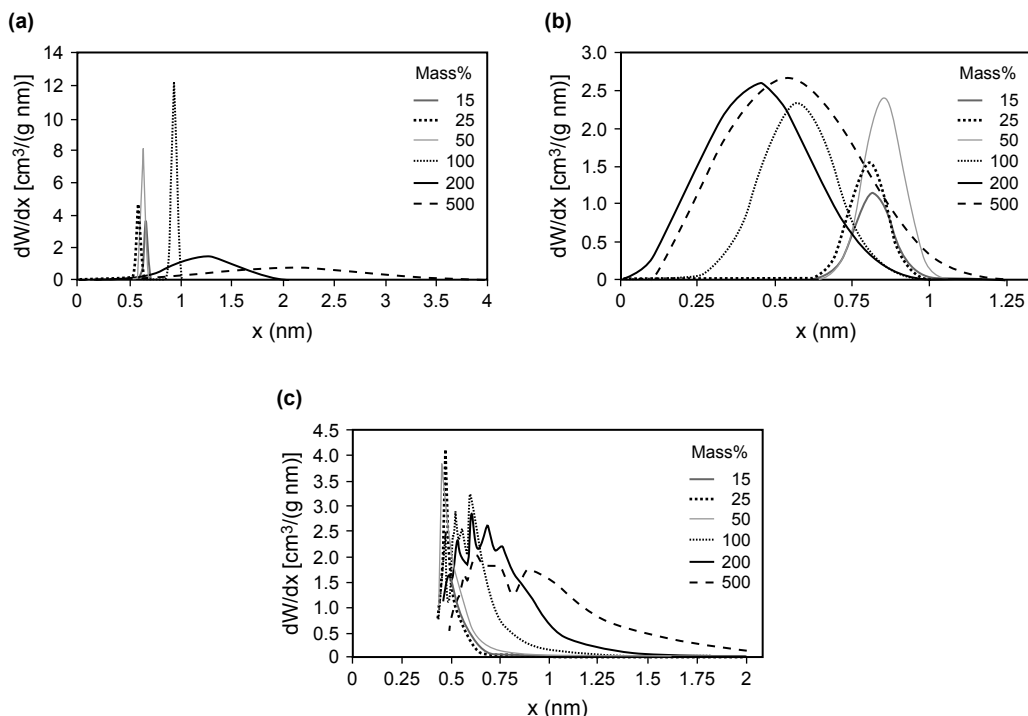
**Figure 3.** Nitrogen adsorption/desorption isotherms at  $-196\text{ }^{\circ}\text{C}$  on the chemically activated carbons with various chemical/nutshell ratios: (a) samples activated with KOH; (b) samples activated with  $\text{ZnCl}_2$ .

As can clearly be seen from Figures 2 and 3, the use of KOH for activation mainly created microporosity in the carbon samples over the whole range of chemical/nutshell ratios covered in our studies. Zinc chloride, on the other hand, produced a wide range of porosity, with a high ratio of this chemical changing the form of isotherm from Type I to Type II, which is an indication of the development of a mesoporous carbon as far as nitrogen isotherm data are concerned (Gregg and Sing 1982; Ahmadpour and Do 1997).

Based on the data for the benzene adsorption isotherms, the pore-size distributions for the prepared samples chemically activated with KOH and  $\text{ZnCl}_2$  at different chemical/nutshell ratios were calculated employing three of the above-mentioned models. These are presented in Figures 4 and 5,



**Figure 4.** Pore-size distribution of carbons chemically activated with KOH calculated using (a) the Dubinin–Stoeckli (DS) method, (b) the Stoeckli method and (c) the Horvath–Kawazoe (HK) method.



**Figure 5.** Pore-size distribution of carbons chemically activated with  $\text{ZnCl}_2$  calculated using (a) the Dubinin–Stoeckli (DS) method, (b) the Stoeckli method and (c) the Horvath–Kawazoe (HK) method.

respectively. In these figures, a comparison can also be made among the different models available for characterizing the AC porous structures. By fitting the DS and Stoeckli models to the experimental data, the model parameters were obtained and are listed in Table 1. The parameters of the HK model for benzene adsorption were taken from Terzyk and Gauden (2001).

The pore-size distributions of the prepared samples chemically activated by KOH as obtained from the DS, Stoeckli and HK models are presented in Figure 4. As expected from the benzene and nitrogen adsorption isotherms depicted in Figures 2(a) and 3(a), all the samples in the KOH series exhibited a microporous structure. Moreover, on increasing the KOH/nutshell ratio, the pore volumes also increased. However, there are some differences among the PSDs calculated using the DS, Stoeckli and HK models which are related to the specific assumptions employed in the description of the porous structure and/or adsorption mechanism.

The pore-size distributions calculated from the Stoeckli method were shifted to larger pore diameters in comparison with the DS method. However, a similar trend was observed for both models. Furthermore, it may be noted that the method proposed by Horvath and Kawazoe gave slightly lower pore diameters in comparison with the DS results (Figure 4).

The PSDs of the samples activated with  $\text{ZnCl}_2$  as calculated from the DS, Stoeckli and HK methods are presented in Figure 5. As seen from the figure,  $\text{ZnCl}_2$  activation led to larger pores than KOH activation which gave a mesoporous structure at higher chemical/nutshell ratios. In contrast to the results for the KOH-activated samples, the DS model indicated larger pore diameters in comparison with the Stoeckli and HK methods. In this case, the HK theory still indicated smaller pore diameters in comparison to the DS and Stoeckli models.

**TABLE 1.** DS and Stoeckli Model Parameters for the Various Prepared AC Samples

Impregnation ratio	DS model parameters			Stoeckli model parameters			
	$W_0$ (mmol/g)	$x_0$ (nm)	$\delta$ (nm)	$W_0$ (mmol/g)	$a$ (nm <sup>-3</sup> )	$v(-)$	$K_0$ [kJ/(nm mol)]
<i>KOH-activated samples</i>							
15	2.5178	0.7254	0.019	2.39	3.893	20	28.32
25	3.4374	0.6466	0.017	3.309	4.068	20	30.18
50	3.9	0.655	0.018	4.013	3.4	20	26.28
100	5.0975	0.5834	0.02	4.917	4.195	20	34.09
200	5.5505	0.6338	0.02	5.25	3.634	20	33.94
500	7.9576	0.6656	0.02	7.584	3.491	20	32.73
<i>ZnCl<sub>2</sub>-activated samples</i>							
15	2.0565	0.6619	0.02	1.98	4.395	20	29.74
25	2.6807	0.5871	0.02	2.6	4.678	20	33.33
50	4.5641	0.6335	0.02	4.337	3.896	20	32.9
100	8.4771	0.9345	0.025	7.936	1.581	2.751	14.83
200	13.3127	1.2411	0.3236	12.73	0.9034	0.9519	8.337
500	17.4575	2.0569	0.7732	16.46	0.5404	0.6979	5.135

It is clear from Figure 5 that the creation of micropores occurred mainly at low chemical/nutshell ratios. On increasing the chemical/nutshell ratio further in the ZnCl<sub>2</sub> series, pore widening became the predominant mechanism, while in the case of KOH the creation of micropores still played an important role over the entire range of chemical/nutshell ratios studied.

As can be seen from Figures 5(a) and (c), increasing the chemical/nutshell ratio (up to 100%) in the ZnCl<sub>2</sub> series led to micropore widening at a very rapid rate, while a further increase in ZnCl<sub>2</sub> content caused the micropores to change into mesopores. This behaviour was not seen in the results arising from the Stoeckli model, which may be a consequence of the fundamental assumptions made in that method. In fact, the Stoeckli method just seems to provide a powerful means of characterizing microporous solids. On the other hand, although the use of KOH created more micropores in the carbon structure, the pore width did not vary significantly as the KOH content increased.

Comparison of the data for the two activated carbon series (Figures 2–5) revealed that, at the same chemical ratio, samples obtained by ZnCl<sub>2</sub> activation had a greater adsorption capacity than those derived from KOH.

## 5. CONCLUSIONS

Activated carbon samples were prepared from the chemical activation of macadamia nutshell employing two chemical activation agents, viz. ZnCl<sub>2</sub> and KOH. The effects of the chemical agent and the chemical/nutshell ratio on the PSDs of the prepared samples were investigated using three well-known models (DS, Stoeckli and HK). According to our findings, some differences emerged

amongst the results derived from these models. These differences may be interpreted as being derived from the fundamental assumptions employed in each theory. The results obtained showed that samples prepared using  $ZnCl_2$  as the chemical agent possessed a greater adsorption capacity than those obtained via the use of KOH. Furthermore, increasing the chemical/nutshell ratio led to an increase in the corresponding pore volumes. In the KOH series, this increase could be associated with an increase in the number of micropores with an insignificant variation in the average pore size. However, the use of  $ZnCl_2$  led to the creation of wider pores with mesopores being developed in the carbonaceous structure after a specific impregnation ratio (100%) had been attained.

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