

Estimation of the dimension of micropores and mesopores in single walled carbon nanotubes using the method Horvath–Kawazoe, Saito and Foley and BJH equations

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The adsorption isotherm of the single walled carbon nanotubes (CNTs) is measured. The mathematical models for calculating pore size distribution (PSD) are modified. The PSD of sample is determined using Horvath–Kawazoe (KH), Saito and Foley (SF) and Barrett–Joyner–Halenda (BJH) methods. An average potential function has been determined inside the slit-like and cylindrical pores. Since all of the regions of CNTs have same type that adsorbed nitrogen in the same conditions, the calculated PSDs from HK, SF and BJH models have same trend in both interior and exterior surfaces. By adding the adsorption term on outer surface, HK, SF and BJH models have been developed hence the pore volume increased.

1. Introduction: In recent years, carbon nanotubes (CNTs) have been intensively studied due to their importance as building blocks in nanotechnology [1]. The special geometry and unique properties of CNTs offer great potential applications, including nano electronic devices, energy storage, chemical probes and biosensors, field emission display, etc. [2]. Gas adsorption in CNTs and nanotube bundles is a vital issue for both fundamental research and technical [3].

Single-walled carbon nanotubes (SWNTs) are of interest as gas adsorbents because of their unique structural properties. Four different adsorption sites have been identified on bundles of SWNTs: internal (endohedral), interstitial channels (ICs), external groove sites, and external surface. Experimental gas adsorption data on SWNT bundles have been previously analysed in terms of an over simplified model of homogeneous nanotubes (all the same diameter) packed into perfect arrays. This analysis has led to the general conclusion that gases do not adsorb inside ICs. Real SWNT bundles contain SWNTs with a variety of different diameters (heterogeneous) [4].

The porous materials are usually supposed, in models, to have slit-like or cylindrical pores. IUPAC classifies the pores as micro (<2 nm), meso (2–50 nm) and macro (>50 nm). Several methods for the calculation of pore size distribution (PSD) from adsorption data have been proposed [5].

In mesopore range, Barrett *et al.* in 1951 [6], offered a technique for the estimation of volume and area of porous adsorbents based on Kelvin equation. In the micropore domain the Kelvin equation is not valid; therefore, Horvath–Kawazoe in 1983 [7], introduced a new method for slit pores, to calculate pore size and pore volume from isotherm data. This method allows one to evaluate the micropore size distribution by simple differentiation of the amount adsorbed (expressed as the volume of liquid adsorbate per unit mass of the adsorbent) with respect to the pore width. The values of the pore width are obtained by converting the equilibrium pressures of the adsorption isotherm by means of suitable theoretical relations [8]. Saito and Foley in 1991 [5] developed the cylindrical variation of the former method.

PSD has a decisive role in the adsorption behaviour of a porous material. In porous materials, determining PSD models have mathematical and physical complexity. The complexity of the porous materials would be more when appearing in nanostructures [9].

As far as we know, there is no new modification to improve relations for calculating PSD in some adsorbent such as CNTs with

special structure and geometry. In this paper, we try to propose three methods including Horvath–Kawazoe (HK), Saito and Foley (SF) and Barrett–Joyner–Halenda (BJH), which in meso and micro size, have different accuracies.

2. Theory: The presented mathematical models for the calculation of PSD, is acceptable for some adsorbents occurring inside pores, such as activated carbon. As mentioned, in CNTs samples, adsorption occurs in all regions that is shown in Fig. 1. The models need to be improved because of the regions [ii], [iii] and [iv] are not considered of the PSD.

2.1. Review on HK method: In this section, a short summary of Horvath and Kawazoe approach has been presented. By considering molar integral change of the free energy (Gibbs functions for constant temperature) and replacing the terms, the following relation is obtained [7, 9]:

$$RT \ln(p/p_0) = U_0 + P_a \quad (1)$$

where U_0 is the expression of the adsorbent–adsorbate interactions, and P_a is an implicit function of the adsorbate–adsorbate–adsorbent interactions [6].

The potential energy between two carbon layers filled with adsorbates is defined by [10]:

$$\emptyset = 3.06 \emptyset^* \left[-(\sigma/r)^4 + (\sigma/r)^{10} \right] \quad (2)$$

$$\emptyset^* = (N_a A_a) / (3.06)(2\sigma^4) \quad (3)$$

where σ is the distance between gas atom and the surface at zero interaction energy, r is the distance from the surface, N_a is the number of atoms per unit area of surface, A_a is a constant given by Kirkwood–Muller and London equations [9].

The potential function between two carbons layers filled with adsorbate is [7]:

$$\emptyset = \frac{N_a * A_a + N_A * A_A}{2\sigma^4} * \left[\left(\frac{\sigma}{l-r} \right)^4 - \left(\frac{\sigma}{r} \right)^4 + \left(\frac{\sigma}{l-r} \right)^{10} + \left(\frac{\sigma}{r} \right)^{10} \right] \quad (4)$$

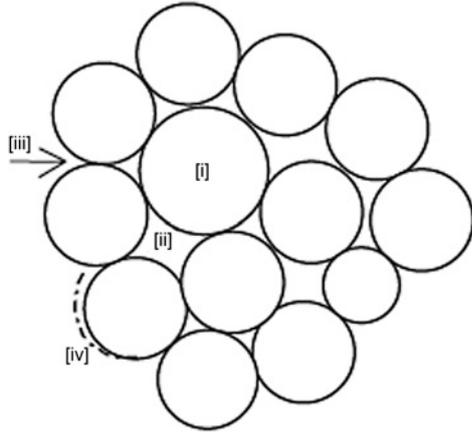


Fig. 1 Adsorption sites on a bundle of SWNTs with different diameters [4]

where l is the distance between the nuclei two layers and N_A is the number of molecules per unit area of adsorbate [7] and

$$A_a = \frac{6mc^2 \alpha_a \alpha_A}{(\alpha_a/\chi_a) + (\alpha_A/\chi_A)} \quad (5)$$

$$A_A = \frac{3mc^2 \alpha_A \chi_A}{2} \quad (6)$$

where m is the mass of electron, c is the velocity of the light, α_a is polarisability and χ_a is the magnetic susceptibility of an adsorbent atom, α_A and χ_A are polarisability and magnetic susceptibility of an adsorbate molecule [7].

Equation (4) consists of two parts. One of them, $N_A A_a / 2\sigma^4(L-d)$, multiplied by the expression in parentheses corresponds to U_0 (1), the other corresponds to P_a (1).

Having taken into account (1), an average potential value depending on the absolute values of distances between two layers can be calculated [5]:

$$RT \ln\left(\frac{p}{p_0}\right) = K \frac{N_a * A_a + N_A * A_A}{2\sigma^4(L-d)} \int_{d/2}^{l-d/2} \left[\left(\frac{\sigma}{l-r}\right)^4 - \left(\frac{\sigma}{r}\right)^4 + \left(\frac{\sigma}{l-r}\right)^{10} + \left(\frac{\sigma}{r}\right)^{10} \right] dr \quad (7)$$

where K is Avogadro's number, and

$$d = d_a + d_A \quad (8)$$

where d_a is the diameter of an adsorbent atom, and d_A is the diameter of the adsorbate molecule. Integration gives the following results:

$$RT \ln\left(\frac{p}{p_0}\right) = K \frac{N_a * A_a + N_A * A_A}{\sigma^4(L-d)} * \left[\frac{\sigma^4}{3(l-(d/2))^3} - \frac{\sigma^4}{3(d/2)^3} - \frac{\sigma^{10}}{9(l-(d/2))^9} + \frac{\sigma^{10}}{9(d/2)^9} \right] \quad (9)$$

where l should be greater than d [7] (Fig. 2).

Adsorption isotherm is a graph between the amounts of adsorbate (N_2) adsorbed on the surface of adsorbent (CNTs) and pressure at constant temperature. According to (19) and (22), each relative pressure is related to a pore size. Indeed, each carbon nanotube's pores are filled at specific relative pressure of N_2 . Thus, it can be

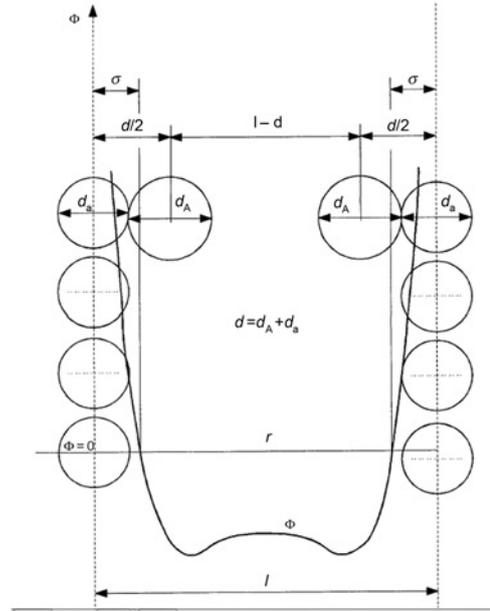


Fig. 2 Potential functions in a slit-like pore [10]

said that any pressure corresponding to distinctive pore size which adsorbed specified amount of adsorbate. Whatever the relative pressures are increased the smaller pores are filled. This tip is properly showed in (19) and (22).

In this step, there is an equation which defines pressure (P) as a function of l . Now using this equation and nitrogen isotherm adsorption data at 77 K, the effective pore distribution can be calculated [7].

2.2. Review on SF method: Saito and Foley [5] developed the cylindrical variation of the former method. A line averaged model, was examined the equation of cylindrical potential was taken from the works of Everett and Powl (for an explanation see Fig. 3):

$$\Phi(r) = \frac{5}{2} \pi \Phi^* \left[\frac{21}{32} \left(\frac{d_0}{r_p}\right)^{10} \sum_{k=0}^{\infty} \alpha_k \left(\frac{r}{r_p}\right)^{2k} - \left(\frac{d_0}{r_p}\right)^4 \sum_{k=0}^{\infty} \beta_k \left(\frac{r}{r_p}\right)^{2k} \right] \quad (10)$$

$$\bar{\Phi}_{LA} = \frac{\int_0^{r_p-d_0} \Phi(r) dr}{r_p - d_0} \quad (11)$$

$$\ln\left(\frac{p}{p_0}\right) = \frac{3}{4} \frac{\pi k}{RT} \frac{(N_a * A_a + N_A * A_A)}{d_0^4} \sum_{k=0}^{\infty} \left[\frac{1}{2k+1} \left(1 - \frac{d_0}{r_p}\right)^{2k} \times \left\{ \frac{21}{32} \alpha_k \left(\frac{d_0}{r_p}\right)^{10} - \beta_k \left(\frac{d_0}{r_p}\right)^4 \right\} \right] \quad (12)$$

where r_p is a pore diameter (in cylindrical shape).

2.3. Review on BJH method: The Kelvin equation provides the relationship between the pore radius and amount of adsorption at a relative pressure. Many researchers developed a method for the calculation of the PSD on the basis of the Kelvin equation with a correction term for the thickness of the multilayer adsorbed film. This method has been widely used for such calculations [6, 11].

$$r_p = r_k + t \quad (13)$$

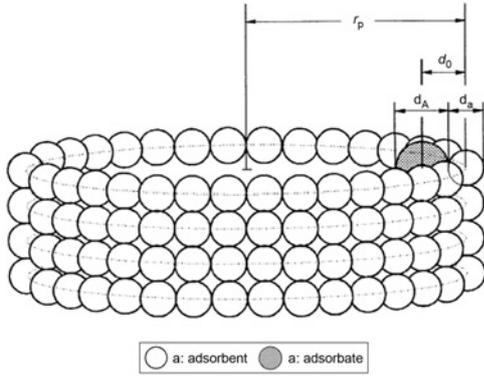


Fig. 3 Explanation of Saito-Foley model [10]

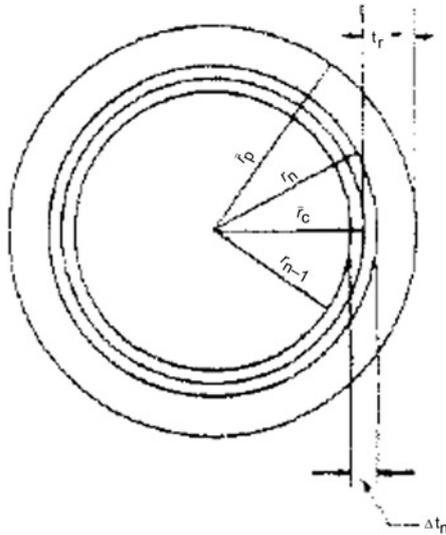


Fig. 4 Relation of $V\Delta t$ to r_p at n th step [12]

$$V_{pn} = R_n \Delta V_n - R_n \Delta t_n \sum_{j=1}^{n-1} C_j A_{p_j}. \quad (14)$$

In these equations, all parameters are functions of relative pressure (p/p_0), defined in the literature [6]. Therefore in any relative pressure, the pore size and pore volume as a point of PSD can be calculated.

The pore size (r_p) is defined as a distance between walls of the pore rather than the distance between centres of atoms, which form first layers of the opposite pore walls (Fig. 4).

2.4. Proposed modified models

2.4.1. Modified HK method: In CNTs sample, the nitrogen gas passes inside the tubes and outer surface of them, and adsorption occurs in both cases in same condition. The process of adsorption on outer surface of tubes has shown in Fig. 3. As shown in Fig. 1, the formation of tubes in a bundle makes small spaces between the tubes such as part [ii]. However, the calculation for PSD from mathematical models has not been studied. For this purpose, if the pores of the tubes are considered as slit and assumed a layer of adsorbed film on the outer surface of them, hence the atoms of adsorbed layer on the outer surface just have interaction between adsorbent and adsorbate. In this case, the interaction between next slit and the carbon layer can be neglected. The potential function over a graphite surface (interaction energy between a gas molecule and infinite graphite layer) is:

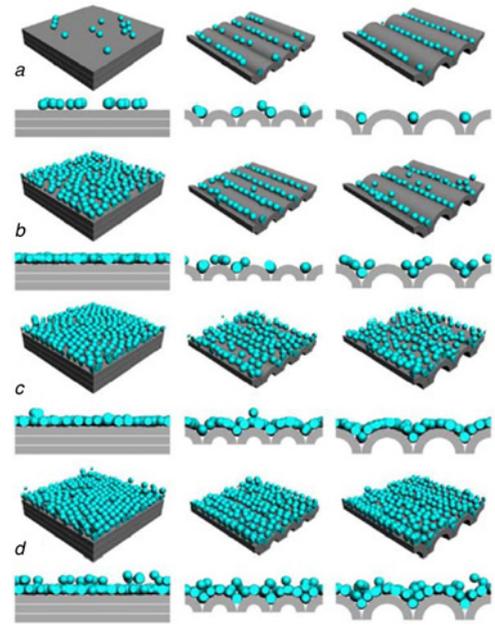


Fig. 5 Adsorption in CNTs [13]

$$\Phi_o = \frac{N_a A_a}{2\sigma^4} \int_{d/2}^{\infty} \left[-\left(\frac{\sigma}{r}\right)^4 + \left(\frac{\sigma}{r}\right)^6 \right] dr \quad (15)$$

$$\Phi_o = \frac{N_a A_a}{2\sigma^4} \left[-\frac{\sigma^4}{3(d/2)^3} + \frac{\sigma^{10}}{9(d/2)^9} \right]. \quad (16)$$

with this assumption, (1) can be rewritten as:

$$RT \ln p/p_0 = 2\Phi_o + \Phi_i \quad (17).$$

where Φ_o is the potential on the outer surface. Based on Φ axis in Fig. 2, considered the interaction between adsorbent and adsorbate of the outer layer and the potential energy of that can be doubled, because of the shape of pores (like slit) are symmetric.

As mentioned, if the next adsorbate interaction on the outer layer was neglected. Hence

$$RT \ln p/p_0 = 2(U_o) + (P_a + U_o) \quad (18).$$

By performed these changes in (9), the following relation is created

$$RT \ln\left(\frac{p}{p_0}\right) = K \left(\frac{N_a * A_a + N_A * A_A}{\sigma^4(L-d)} * \left[\frac{\sigma^4}{3(t-(d/2))^3} - \frac{\sigma^4}{3(d/2)^3} - \frac{\sigma^{10}}{9(t-(d/2))^9} + \frac{\sigma^{10}}{9(d/2)^9} \right] + \frac{N_a A_a}{\sigma^4} \left[-\frac{\sigma^4}{3(d/2)^3} + \frac{\sigma^{10}}{9(d/2)^9} \right] \right). \quad (19)$$

With this relation, the PSD is calculated by the HK method in inner and outer surfaces of tubes (Fig. 5).

2.4.2. Modified SF method: By applying the assumption of previous part (Section 2.4.1) on SF method, the following relations are obtained. As shown in Fig. 3, with supposing adsorbed film on the outer layer for calculating potential energy on the cylindrical form the band of integral should be changed. As mentioned, the next adsorbate interaction on the outer layer would be omitted (indicating infinite space such as $2r_p$). Hence

$$\bar{\Phi}_{LA_o} = \frac{\int_{r_p+d/2}^{2r_p} \Phi(r) dr}{\int_{r_p+d/2}^{2r_p} r dr} \quad (20)$$

$$\ln\left(\frac{p}{p_0}\right) = \frac{3}{4} \frac{\pi k}{RT} \frac{(N_a * A_a)}{d_0^4} \sum_{k=0}^{\infty} \left[\frac{1}{2k+1} \left[\frac{2^{2k} * 2r_p}{r_p + d_0} - \left(1 + \frac{d_0}{r_p}\right)^{2k} \right] \right. \\ \left. \times \left\{ \frac{21}{32} \alpha_k \left(\frac{d_0}{r_p}\right)^{10} - \beta_k \left(\frac{d_0}{r_p}\right)^4 \right\} \right] \quad (21)$$

$$\ln\left(\frac{p}{p_0}\right) = \frac{3}{4} \frac{\pi k}{RT} \frac{(N_a * A_a + N_A * A_A)}{d_0^4} \\ \times \sum_{k=0}^{\infty} \left[\frac{1}{k+1} \left(1 - \frac{d_0}{r_p}\right)^{2k} \left\{ \frac{21}{32} \alpha_k \left(\frac{d_0}{r_p}\right)^{10} - \beta_k \left(\frac{d_0}{r_p}\right)^4 \right\} \right] \\ + \frac{3}{4} \frac{\pi k}{RT} \frac{(N_a * A_a)}{d_0^4} \sum_{k=0}^{\infty} \left[\frac{1}{2k+1} \left[\frac{2^{2k} * 2r_p}{r_p + d_0} - \left(1 + \frac{d_0}{r_p}\right)^{2k} \right] \right. \\ \left. \times \left\{ \frac{21}{32} \alpha_k \left(\frac{d_0}{r_p}\right)^{10} - \beta_k \left(\frac{d_0}{r_p}\right)^4 \right\} \right] \quad (22)$$

with this relation, the PSD is calculated by the SF method in inner and outer surfaces of tubes.

2.4.3. Modified BJH method: For optimisation BJH method, such as HK and SF, adsorption layers with thickness t_0 on outer surface of the pores are considered. Now based on the added layer, radius, r_0 , can be calculated.

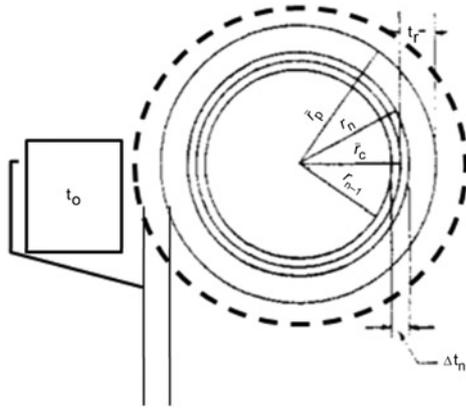


Fig. 6 Thickness of t_0 in outer surface

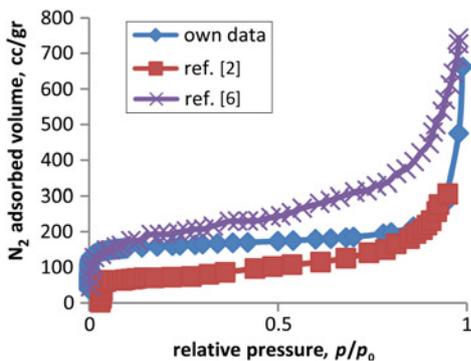


Fig. 7 N_2 adsorption isotherms of the CNT

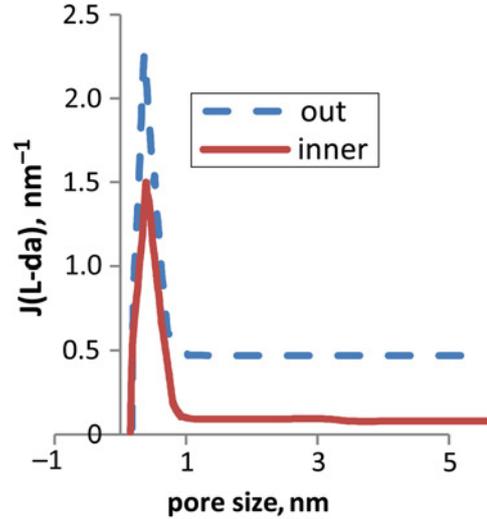


Fig. 8 PSD of CNTs from HK model

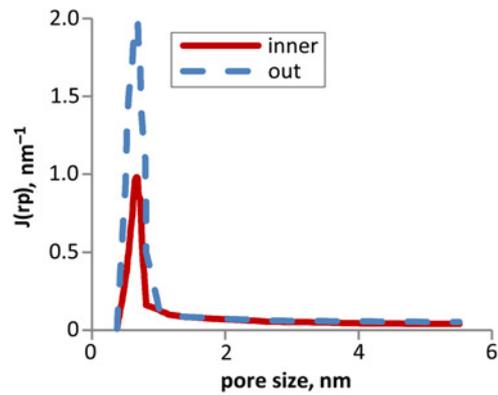


Fig. 9 PSD of CNTs from SF model

$$r_o = r_p + t_0 = r_k + t + t_0 \quad (23)$$

where r_p is the radius of pores to simplify calculation, assuming that the thickness t_0 is equal to t :

$$r_o = r_k + 2t \quad (24)$$

Now all the volume calculation is based on a new radius (Fig. 6):

$$V_{p_{n_0}} = R_{n_0} \Delta V_n - R_{n_0} \Delta t_n c \sum_{j=1}^{n-1} A_{p_j} \quad (25)$$

3. Results and discussion: Sample of single-wall CNTs used in this paper, has been synthesised in the University of California. The adsorption isotherm was measured by nitrogen adsorption at the temperature of 77 K with Autosorb B-1 apparatus (Quantachrome Corp.) shown in Fig. 7.

The PSD data of the samples is determined by programming in Matlab environment using the isotherm data and the relative equations.

3.1. Determining the PSD for CNTs in micropore range: In this paper, the PSD for CNTs in micropore range has been calculated from SF and HK models. At first, correlations between relative pressure and pore size from corresponding (19) and (22) have been calculated. After that, from adsorption isotherm data and

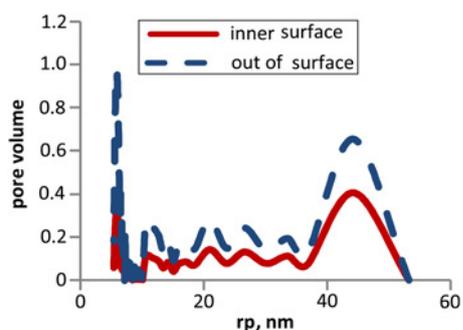


Fig. 10 PSD of CNTs from BJH model

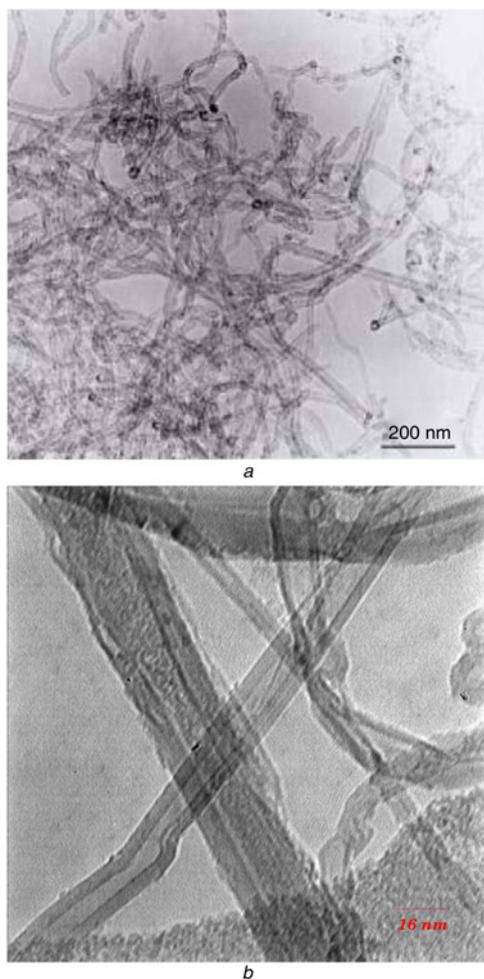


Fig. 11 TEM images of SWCNTs (with two different resolutions, 200 and 16 nm)

using HK PSD algorithm, differentiation is done on the adsorption isotherm.

After integration within the considered range, PSD interior surfaces of the sample are calculated and the results are presented in Figs. 8 and 9 (part inner).

Since all of the regions of CNTs have same type that adsorbed nitrogen in the same conditions (both interior and exterior surfaces), the calculated PSDs from HK and SF models have same trend in both interior and exterior surfaces that shown in Figs. 8 and 9.

By adding the adsorption term on outer surface, HK and SF models have been developed so the pore volume increased that is indicated in Figs. 8 and 9 (Vertical axis represents the pore volume.).

According to determined PSDs by different models in micropore scale, all of the pore sizes have same range (<1 nm) shown in Figs. 8 and 9. Figures show the accuracy of the proposed models and equations.

3.2. Determining the PSD for CNTs in mesopore scale: With similar arguments in Section 3.1, the PSD calculated from the BJH method (assuming just one layer in internal surface) have same trend in both interior and exterior surfaces that is shown in Fig. 10.

For developing PSDs calculated by BJH method, considered an adsorbed layer in outer surface are considered that added to inner surface, hence the pore volume increased.

TEM images of CNTs, which is shown in Fig. 11, have been confirmed the pore size range reported by modified models. In addition, it is compared with the work done by Byle *et al.* [14] and Li *et al.* [2].

4. Conclusions: One way to find the diameter of CNTs is to determine the PSD. In micro pore range both models are shown an approximately equal size. These results are confirmed the plausibility of the model's answers. Considering that the diameter of the PSD in all cases is less than 1 nm, as expected, the SF model has higher precision. By developing models, predictions of mathematical models are more accurate, considered the outer surface on predictions of the PSDs, the outer surface has affected on adsorption capacity about 60%.

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6 References

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