

CHAPTER IV RESULTS AND DISCUSSION

4.1 Characterization of Carbon Nanotubes

Carbon nanotubes can be obtained from many processes such as arc-discharge, laser ablation, and chemical vapor deposition. Therefore, the carbon nanotubes are characterized in order to relate their properties and the adsorption capacity. Raman Spectroscopy and BET surface area analyzer were exploited to characterize the carbon nanotubes in this study. The Raman spectra of the obtained MWNT and SWNT are shown in Figures 4.1 and 4.2, respectively. In Figure 4.1, the Raman spectra of MWNT show two peaks in disordered band (D Band) and Graphitic band (G Band). These two peaks indicate that the sample is multi wall carbon nanotubes (MWNT). In Figure 4.2, the single wall carbon nanotubes (SWNT) spectra show signal in the radial breathing mode (RBM) around 200 cm^{-1} , which is the characteristics of SWNT.

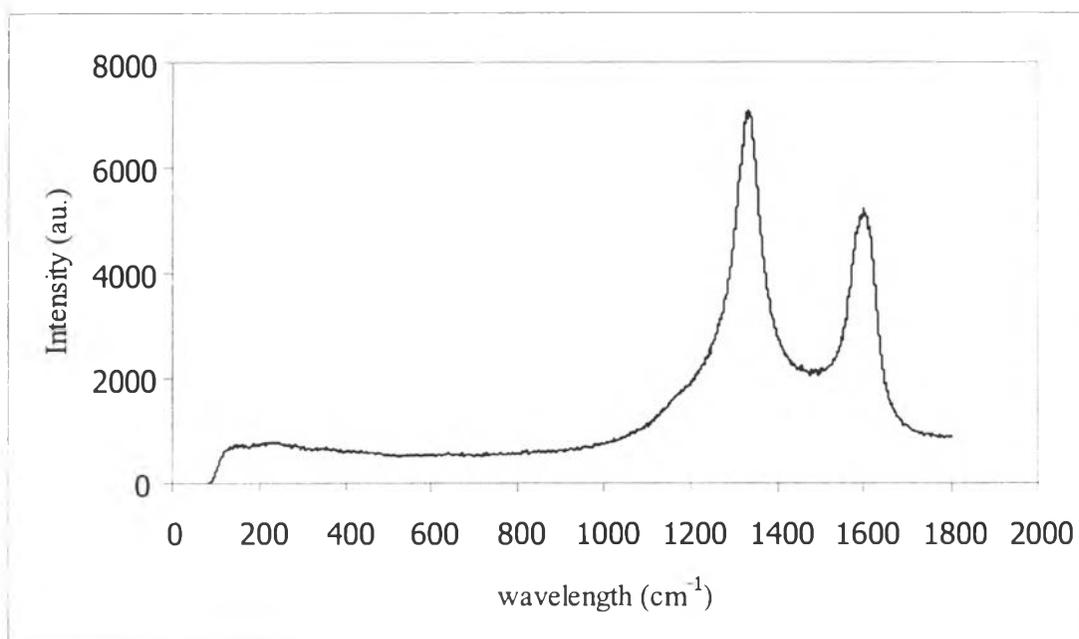


Figure 4.1 Raman Spectrum of multi-wall carbon nanotubes.

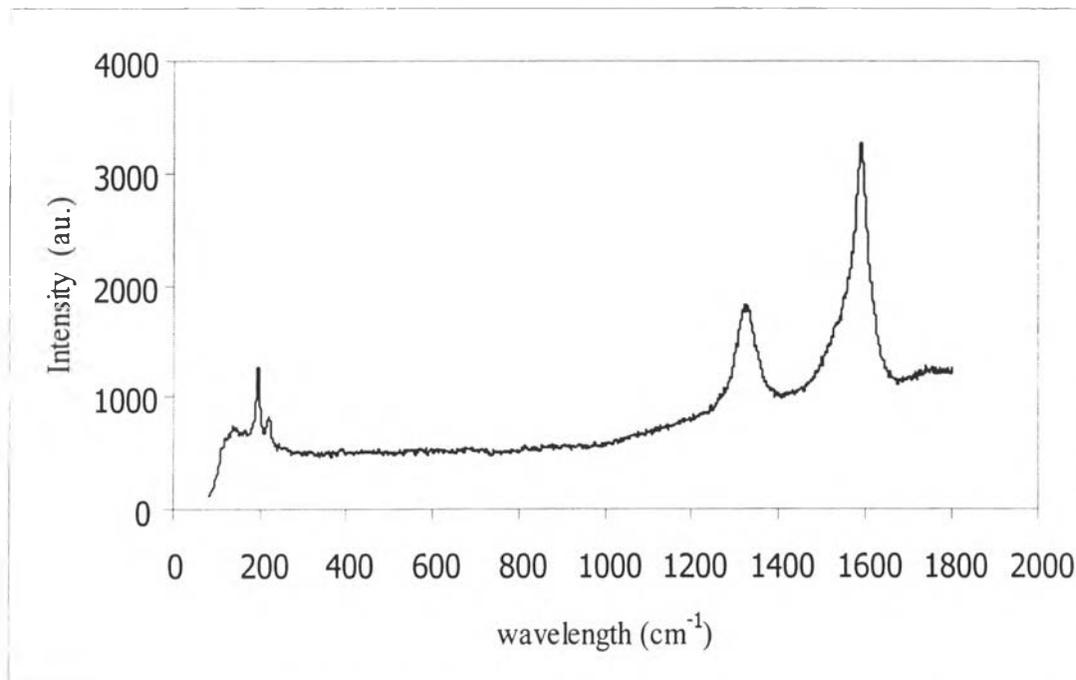


Figure 4.2 Raman Spectroscopy of single-wall carbon nanotubes.

The specific surface area, pore diameter and purity of carbon materials are shown in Table 4.1. The surface area and average pore diameters were obtained using a N₂ adsorption apparatus. SWNT has the BET surface area larger than MWNT. However, activated carbon has the highest surface area. The average pore size of SWNT reported by the BET apparatus is about 7.7 nm. Since the diameter of SWNT is around 1-2 nm, it suggests that the N₂ be adsorbed at the interstitial area in the bundles of SWNT.

Table 4.1 Some physical properties of the studied carbon materials

Physical parameter	SWNT	MWNT	Activated carbon
Surface area (m ² /g)	630 +/- 20	226 +/- 10	705 +/- 20
BET Pore diameter (nm)	7.7	n/a	n/a
Purity (%)	95.7	75.5	n/a

Note: n/a = not appreciable

4.2 Volume of Manifold and Sample Cylinder

The volume of manifold was obtained by performing the experiment of both blank test and known volume test with helium gas. Four runs of blank test (no sample) and the known volume test (stainless steel 5.01 cc) with the pressure varying from 140-1040 psia were selected for finding the manifold volume. The pressure was quickly steady after 10 minutes since there is no adsorption. The pressure was averaged for 10 minutes after helium expansion. Standard deviation of pressure was not greater than 0.2 % conforming to global error of pressure transducer.

The volumes of manifold and sample cylinder were calculated by matching the pressure from 2 systems, with/without adding a known volume. The result showed that the calculated volume of manifold was in range of 160-165 cm³ and in range of 51-52 cm³ for the sample cylinder. In conclusion, the average values of the calculated volumes of manifold and sample cylinder used to represent in this work are 162.43 cc and 51.88 cc, respectively.

4.3 Blank Test

The blank test was performed in order to check the leakage of the system. It was found that, when helium was pressurized into the system, the helium leakage was very small as shown in Figure 4.3. When using the initial pressure of helium at 826 psia, the pressure dropped for helium was 3.5 psia if the system was left for 6 hours. However, when the hydrogen was used, as shown in Figure 4.4, the pressure drop is very significant, for example, the pressure drop for hydrogen was 12.2 psia for 6 hours and 28.1 psia for 12 hours if the initial pressure was 826 psia as in the case of helium.

The system has been attempted to minimize the leak but it was found that it is not easy to prevent the hydrogen leakage from the system. Therefore, the data from the hydrogen adsorption experiment in the next section must be corrected with the leak.

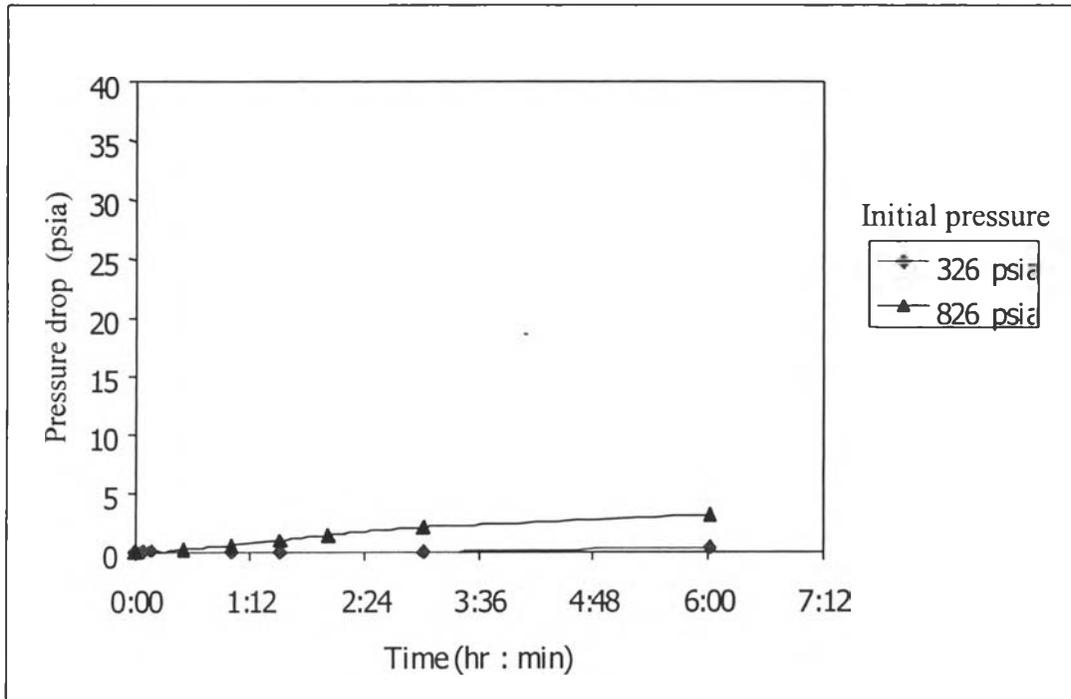


Figure 4.3 Pressure drop as a function of time in the helium blank test.

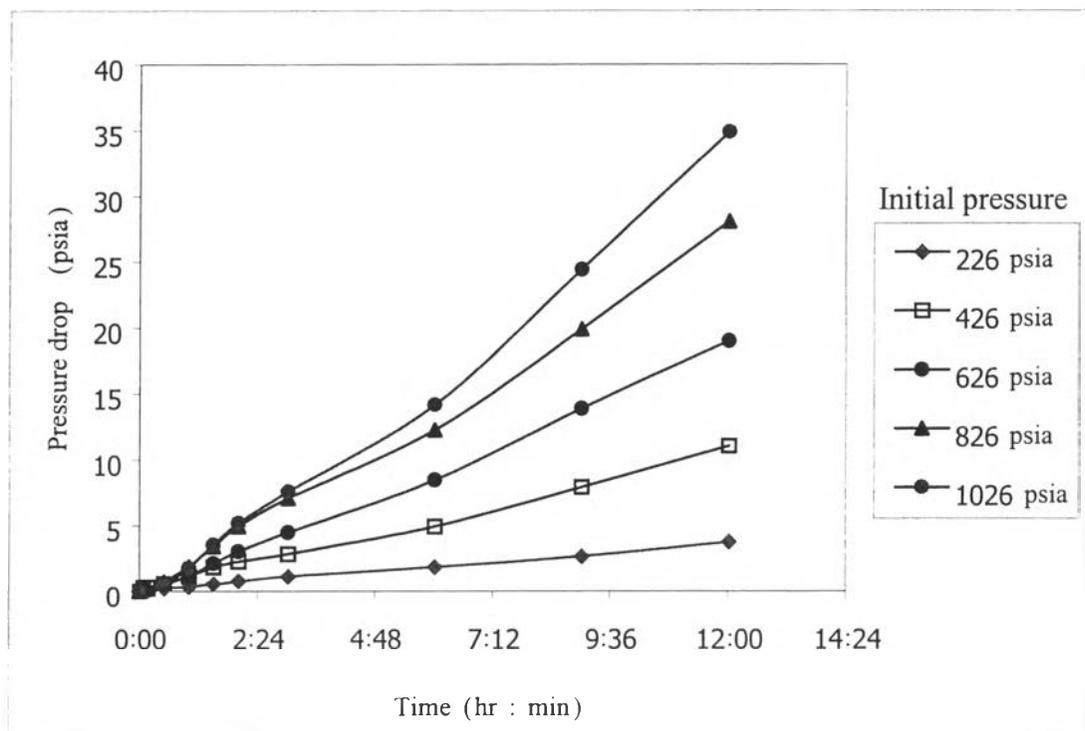


Figure 4.4 Pressure drop as a function of time in hydrogen blank test.

4.4 Approaches for Data Correction for Hydrogen Adsorption

Two approaches for correcting of the adsorption data are proposed and utilized in this study. The first approach is the subtraction method, which corrects the measured hydrogen pressure by subtracting the pressure drop obtained from the blank test from the measured pressure at the same initial pressure and time. Figure 4.5 shows the comparison of hydrogen adsorption at the initial pressure of 926 psia on the activated carbon between the data with correction and without correction by the subtraction method. It is obviously shown that the data correction must be taken into account.

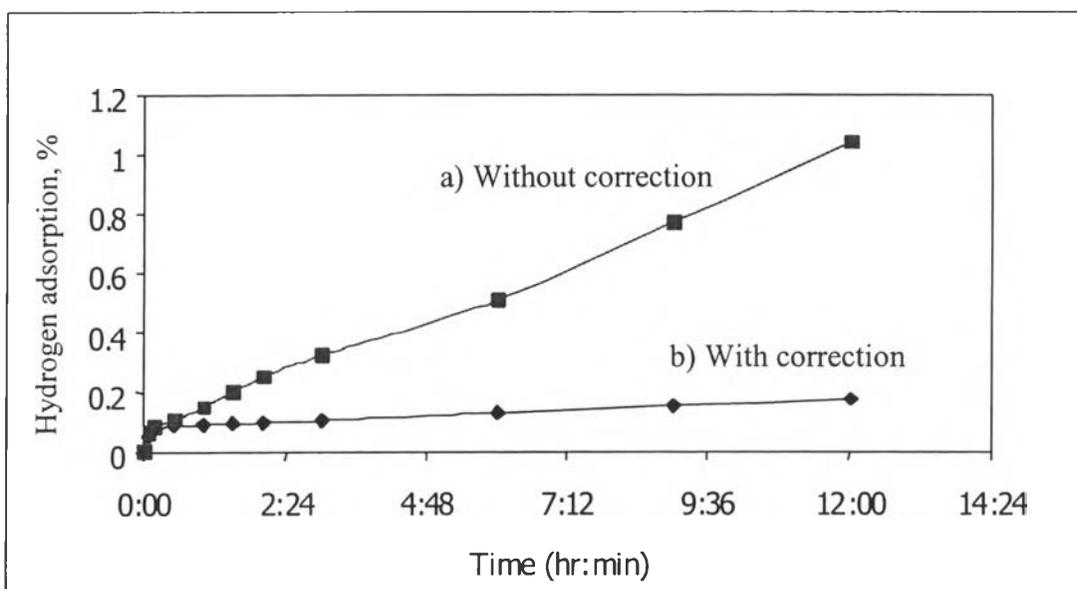


Figure 4.5 Comparison of hydrogen adsorption by 4g activated carbon at 926 psia initial pressure a) without blank test correction b) with blank test correction by subtraction method.

The second approach for data correction is the use of pressure correction factor. The pressure correction factor is the ratio of pressure at any time to the initial pressure obtained from the blank test. If there is no leakage, the pressure correction factor should be unity. The real pressure data were corrected by multiplying the pressure correction factor with the pressure obtained from the pressure transducer.

Figure 4.6 shows the comparison of hydrogen adsorption at the initial pressure of 926 psia on the activated carbon between the data with correction and without correction by the pressure correction factor.

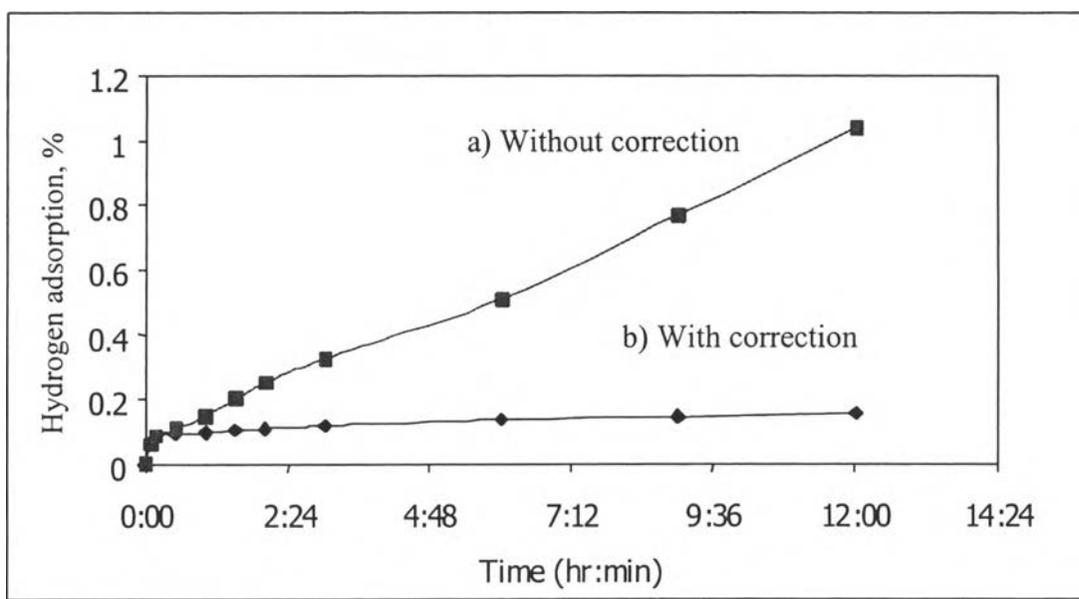


Figure 4.6 Comparison of hydrogen adsorption by 4g activated carbon at 926 psia initial pressure a) without blank test correction b) with blank test correction by the pressure correction factor.

It can be observed that both approaches for data correction provide similar results. From this point, the subtraction method were employed only because it was less complicated.

4.5 Stepwise and Continuous Adsorption

In this experiment, hydrogen adsorptions on carbon material were done by the two different methods, which are different in how hydrogen was pressurized. The first method was a stepwise adsorption, which started with the initial hydrogen pressure around 100 psia and left for equilibrium. Prior to the next higher pressure, the system was degassed and then the hydrogen was introduced into the system with higher initial pressure higher than the former run. The process was repeated with increment of hydrogen pressure about 100 psia until it reached around 1000 psia.

The second method is the continuous adsorption method. Unlike the stepwise adsorption method, the hydrogen pressure was increased continuously without the degassing step. The hydrogen pressure was kept increasing until it reached around 1000 psia.

Figure 4.7 shows the comparison results of stepwise and continuous adsorption methods. The initial pressure was increased from 140 to 1040 psia. The equilibrium hydrogen pressure was corrected by subtraction method. The continuous adsorption showed higher storage capacity than stepwise adsorption. This is due to the experimental error accumulating during the continuous adsorption. Therefore, from now on, the stepwise adsorption was selected for the later study.

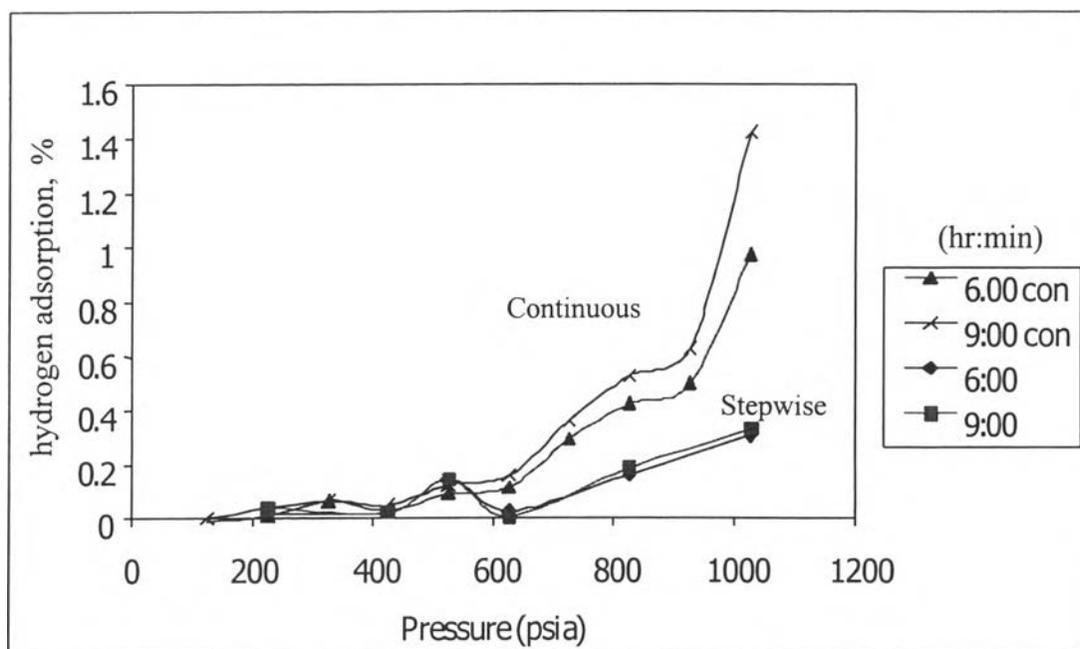


Figure 4.7 Adsorption isotherms of hydrogen at 298 K in MWNT as compared between stepwise adsorption and continuous adsorption.

4.6 Hydrogen Adsorption

The adsorptions of hydrogen by SWNT, MWNT and activated carbon are reported in this section. Figures 4.8, 4.9, and 4.10 illustrate the hydrogen adsorption isotherms on 1, 2 and 4 g of SWNT, respectively. At different amounts of SWNT, the amounts of hydrogen adsorbed per gram of SWNT are different. These results are not expected. In fact, the specific adsorption should be the same. However, the difference could be due to the leakage of hydrogen even though the pressure has been corrected by the subtraction method. Or, this is probably because, at higher amounts of SWNT, the surface of SWNT is not effectively exposed to the hydrogen.

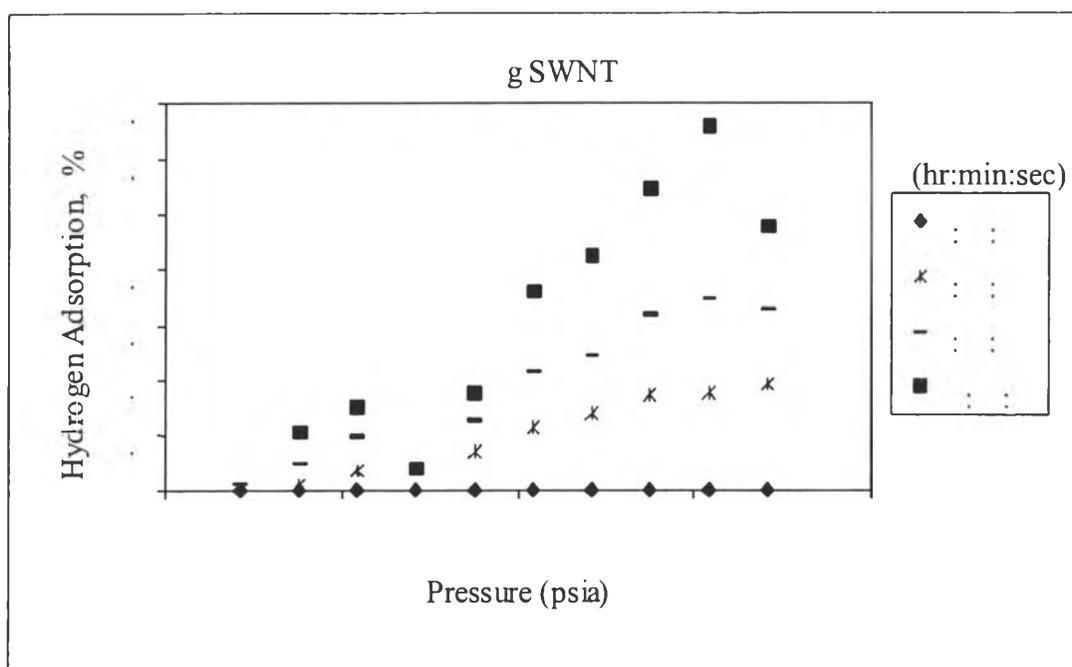


Figure 4.8 Adsorption isotherms of hydrogen on 1g SWNT obtained by Constant Volumetric Technique.

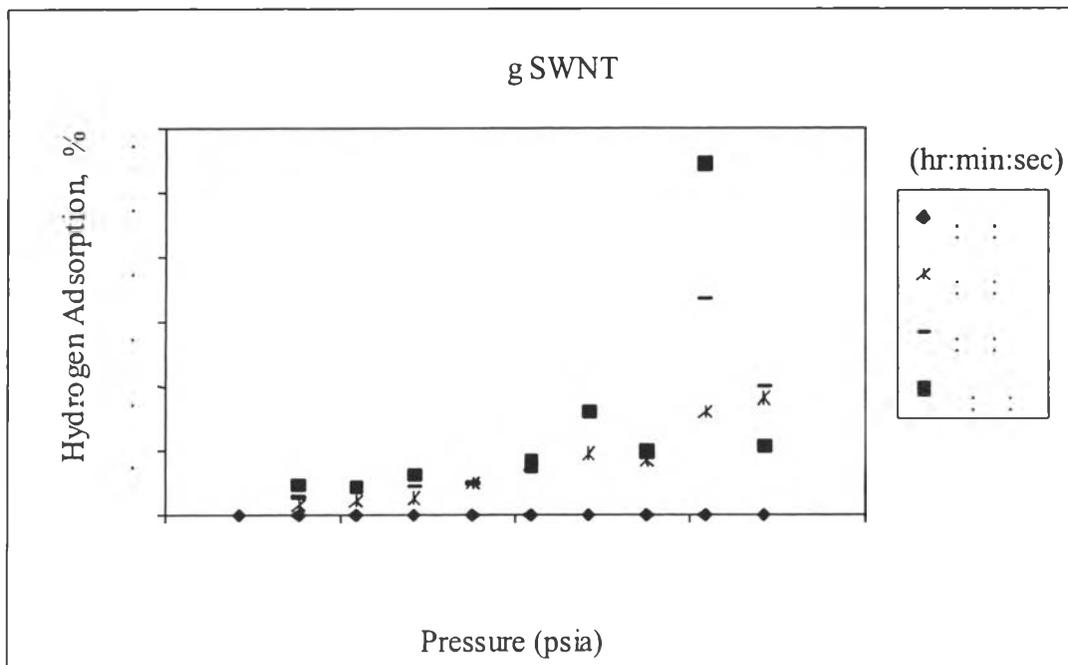


Figure 4.9 Adsorption isotherm of hydrogen on 2g SWNT obtained by Constant Volumetric Technique.

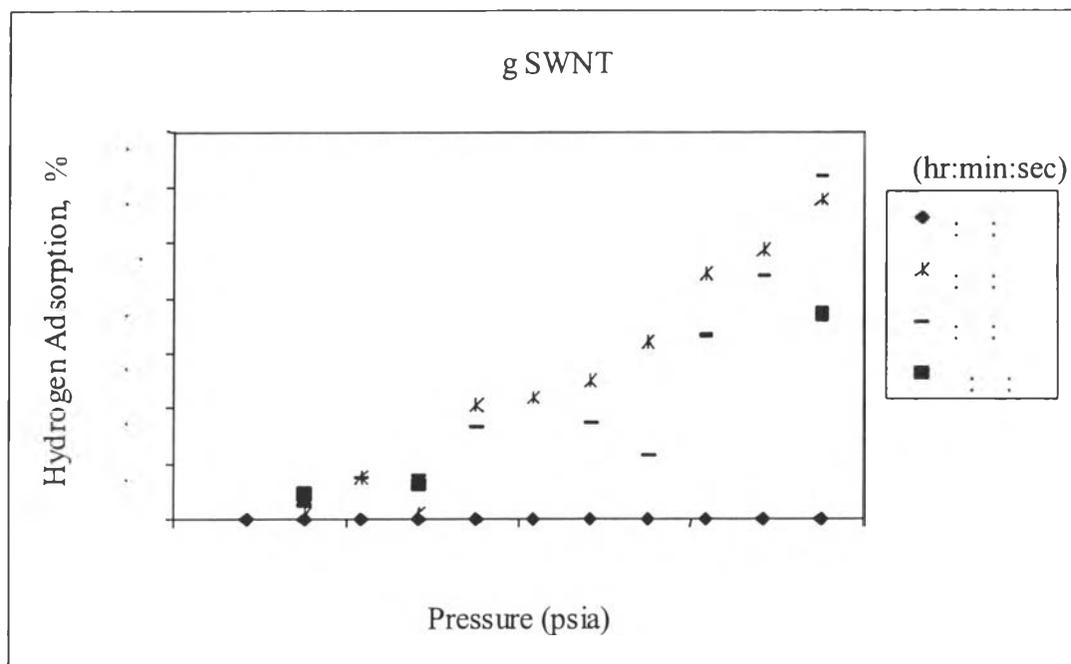


Figure 4.10 Adsorption isotherm of hydrogen on 4g SWNT obtained by Constant Volumetric Technique.

Figures 4.11 and 4.12 show the hydrogen adsorption isotherms on 2 and 4 g of MWNT respectively. For a given amount of adsorbent, the adsorption capacity of MWNT was lower than that of SWNT at any pressure. As observed for SWNT, the higher amount of MWNT resulted in less adsorption capacity for hydrogen. Based on a specific basis, the hydrogen adsorption capacity of 2 g MWNT was around twice of that of the 4 g MWNT.

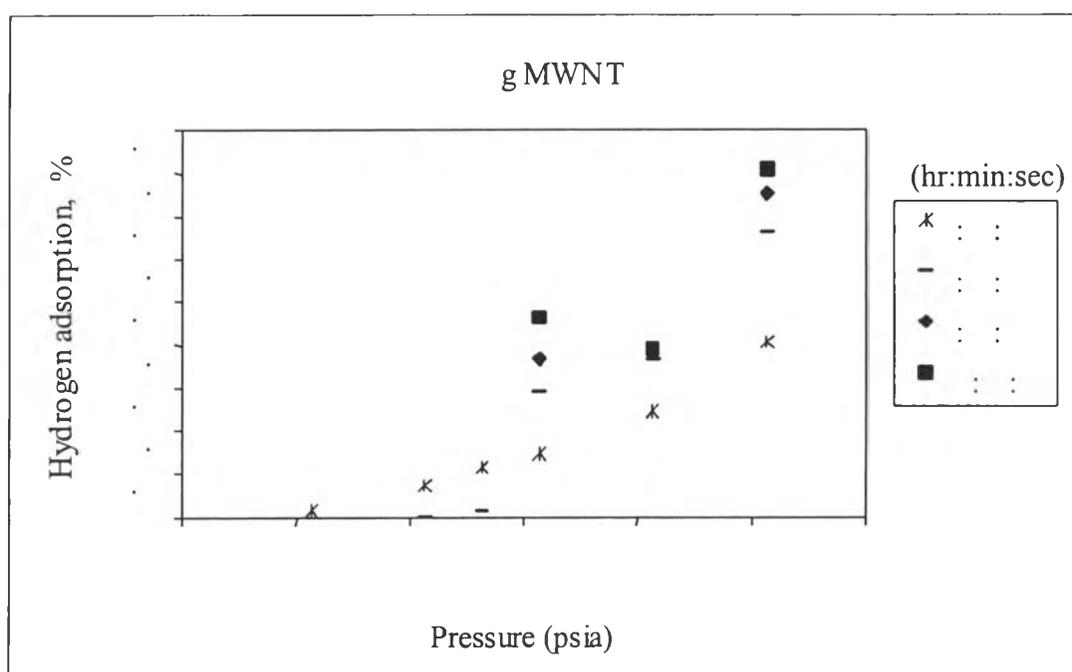


Figure 4.11 Adsorption isotherm of hydrogen on 2g MWNT obtained by Constant Volumetric Technique.

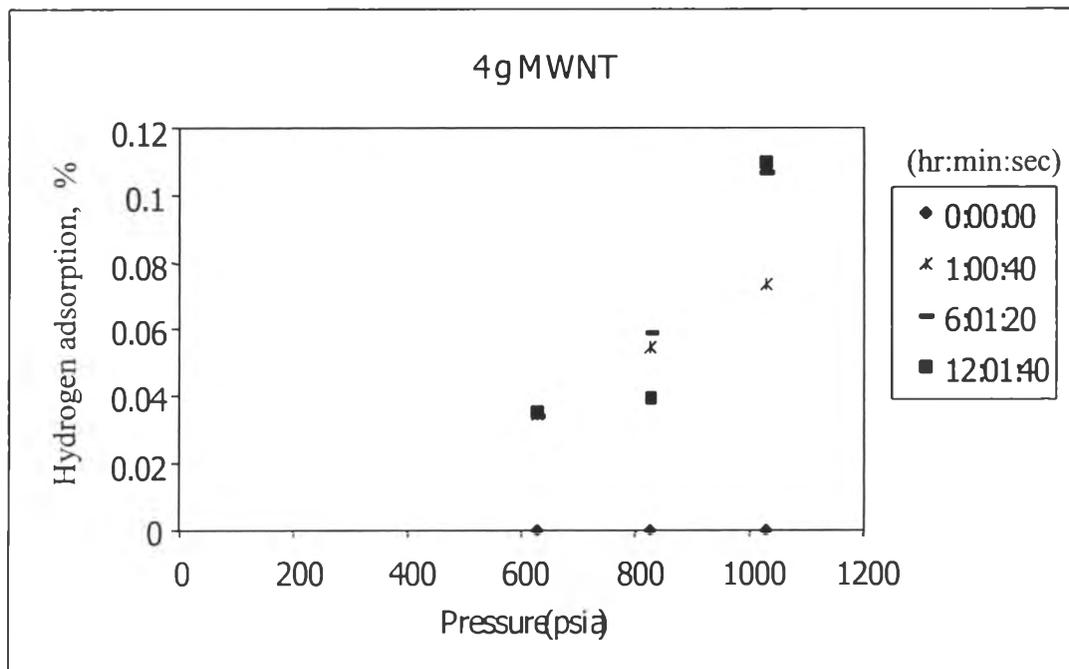


Figure 4.12 Adsorption isotherm of hydrogen on 4g MWNT obtained by Constant Volumetric Technique.

The adsorption isotherms of hydrogen on activated carbon are shown in Figure 4.13. Four grams of activated carbon was used. Since the amount of adsorbed hydrogen on activated carbon is relatively low, therefore no further experiment was performed.

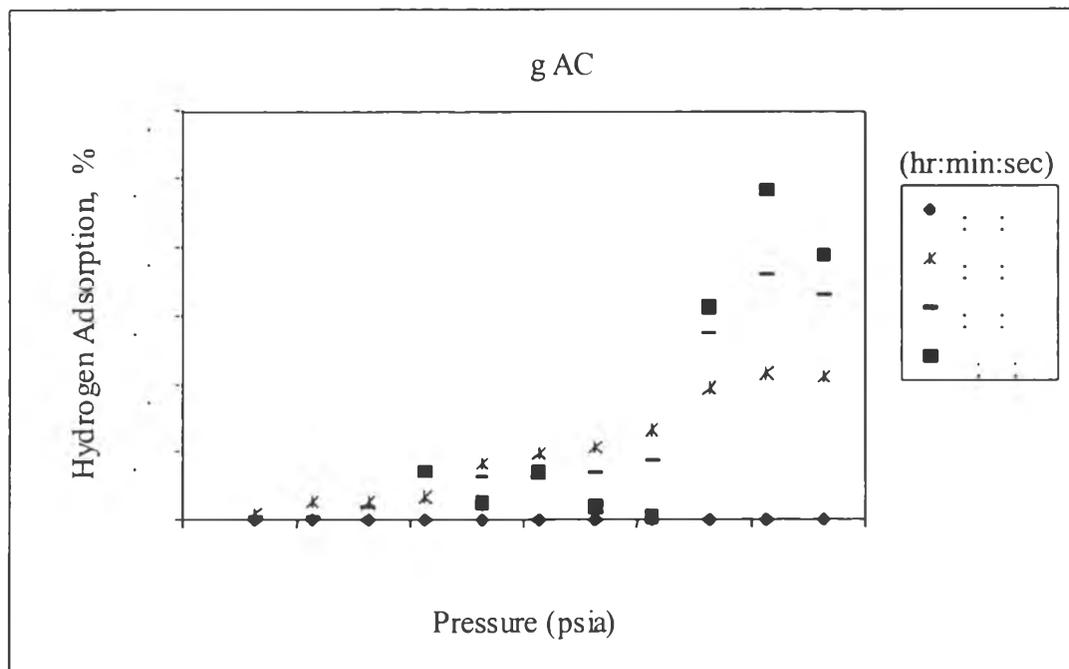


Figure 4.13 Adsorption isotherms of hydrogen on 4g AC obtained by Constant Volumetric Technique.

The maximum hydrogen storage capacities of SWNT, MWNT, and activated carbon are summarized in Table 4.2. The experiment of hydrogen uptake was performed in the range of 1-10 MPa using the constant volumetric technique at room temperature. The hydrogen adsorbed on 1g SWNT was 1.2 wt% at initial pressure of 10 MPa. The 2g MWNT adsorbed hydrogen at 0.33 wt % under initial pressure of 10 MPa. The 4 g activated carbon adsorbed hydrogen at capacity of 0.25 wt % at initial pressure of 10 MPa.

Table 4.2 Adsorption capacity of carbon materials at 10 MPa

Carbon materials	Adsorption capacity (wt%)
SWNT	1.20
MWNT	0.33
AC	0.25