CHAPTER 6

DEVELOPMENT AND PREDICTION OF HYDROGEN ISOTHERM DATA

6.1 Introduction

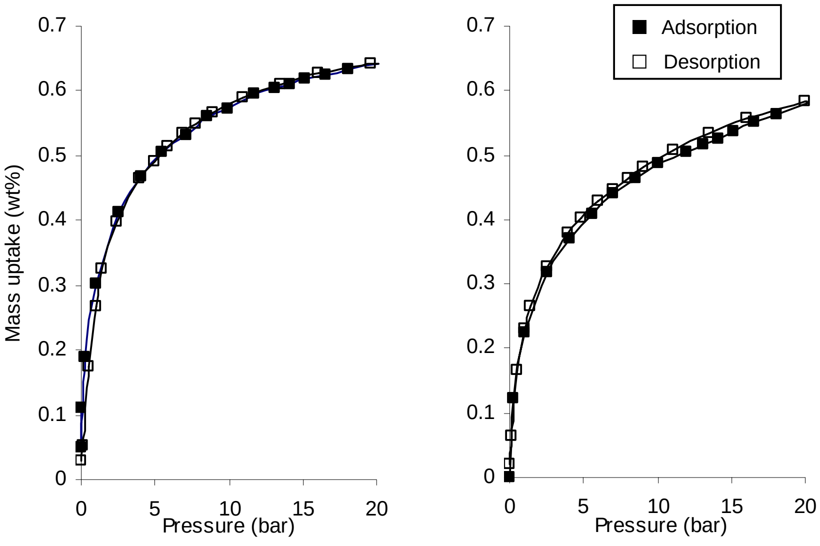
The developed CNTs and GNFs were tested for the feasibility in adsorbing hydrogen. There are two parts of hydrogen measurement that were carried out in the studies. The first part is to run hydrogen adsorption studies at 77 K and pressure up to 20 bar using intelligent gravimetric adsorption or IGA while the second part is to run hydrogen adsorption at 298 K and pressure up to 150 bar using magnetic suspension balance (MSB). These two techniques were used in order to compare the hydrogen uptake at low temperature (77 K) and room temperature (298 K). Due to some limitations, only selected CNTs and GNFs based on the surface area were used for running the hydrogen adsorption measurement. In addition, the commercial SWNTs were used in the both parts of adsorption measurement for comparison. The results of hydrogen isotherm data were then used to predict the hydrogen isotherm data for different surface areas using Nero-fuzzy system.

6.2 Hydrogen isotherm: experimental data

All hydrogen adsorption measurements were done using gravimetric measurement that is IGA and MSB. Although the technique of both measurement is similar, IGA operating pressure could not go beyond 20 bar since it would affect the measurement in the balance as been discussed in Chapter 3. Unlike IGA, MSB could be operated as high as 150 bar since the microbalance is isolated from the gas adsorption chamber. However, IGA could be operated at temperature as low as 77 K by immersing the sample vessel in the liquid nitrogen. This technique could not be done by MSB due to equipment limited capacity.

6.2.1 Hydrogen adsorption measurement using intelligent gravimetric analyzer (IGA)

Two developed samples that are iron-based and nickel-based GNFs were used to run adsorption and desorption of hydrogen at 77 K and pressure up to 20 bar as indicated in Figure 6.1(a) and (b), respectively. From the figures, both adsorption and desorption line show hysteresis indicating most of adsorbed hydrogen molecules are fully desorbed from the sample. The line is curve and agrees with the Langmuir model for isotherm Type I (Yürüm et al., 2009). This trend of curve is in good agreement with other findings which used different carbon materials at temperature of 77 K (Ansón et al., 2004; Ansón et al., 2006; Takagi et al., 2004; Xu et al., 2007)



(a) (b)

Figure 6.1 Hydrogen adsorption-desorption hysteresis of (a)iron-based; and (b)nickel-based GNFs at 77 K using IGA

Initially, the hydrogen uptake increases rapidly up to pressure 5 bar. At this stage, the hydrogen molecules fill in all micropores. Then the hydrogen uptake increases gradually up to 0.6 wt% up to a pressure of 20 bar. It is believed that more hydrogen could be adsorbed at higher pressure since the isotherm line has yet to reach plateau.

For comparison, the results of hydrogen uptake are compared with the commercial SWNT as given in Figure 6.2. The SWNT has properties with a specific BET surface area of 407 m^2/g and a true density of 2.1 cm^3/g. This value is almost twice higher than that of developed GNFs that are 248 and 293 m^2/g for nickel- and iron-based GNFs, respectively. The SWNT was chosen for comparison since the material has known to be one of the most potential mediums in storing hydrogen. As a result, the hydrogen uptake has the highest uptake approximately 1.1 wt% for the commercial of SWNT. This is because higher surface area of SWNT allows more hydrogen molecules to be adsorbed onto the surface including the inner surface of the nanotubes.

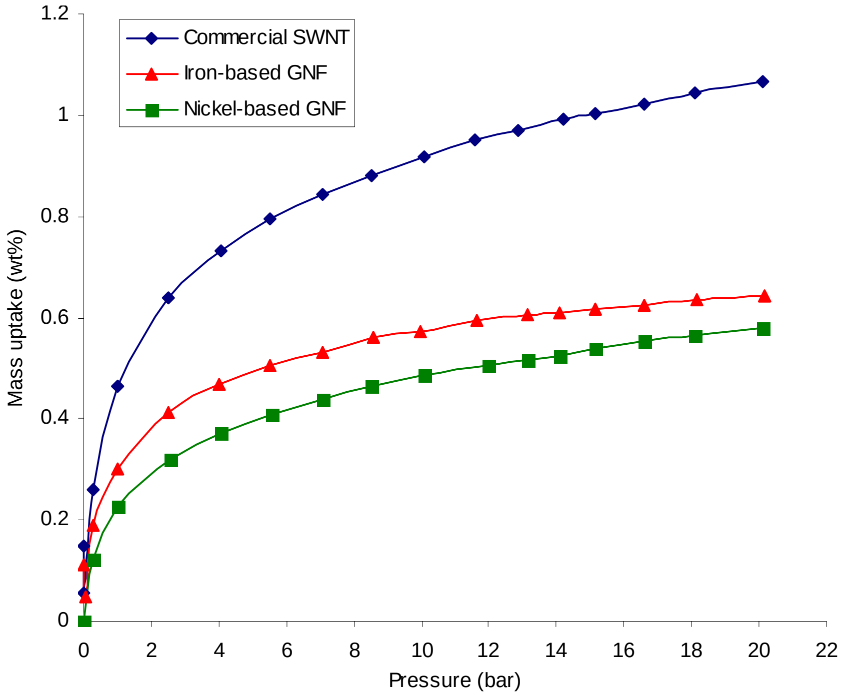
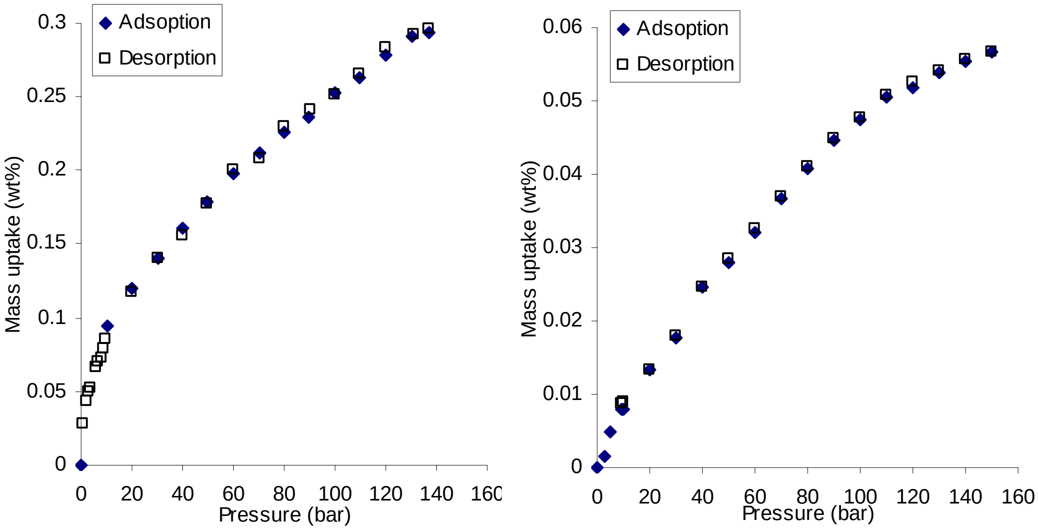


Figure 6.2 Comparison of hydrogen uptake using developed GNFs and commercial SWNT at 77 K

As for GNFs, the iron-based GNF provides more hydrogen uptake that is 0.64 wt% as compared with nickel-based GNF which has an uptake of 0.58 wt%. This is because the iron-based GNFs have more open edges in the nanofibers. Each of the open edges provides an interlayer space of 0:337 nm which would favor hydrogen sorption (Schur et al., 2002). However, if the edges of the fiber are closed, the hydrogen adsorption would be restricted and less adsorbed could be adsorbed onto the carbon surface. The low hydrogen uptake that is less than 1 wt% is acceptable for the given specific BET surface area. This is because even a carbon material with surface area of 2000 m^2/g has been reported to store hydrogen only up to 3.0 wt% at 77 K and l atm (Gogotsi et al., 2005). Hence, it is expected that at 77 K, the hydrogen uptake could not reach the target value that is 6.0 wt% even though the surface area of the adsorbent exceeds 2000 m^2/g.

6.2.2 Hyrogen adsorption measurement using magnetic suspension balance (MSB)

The next hydrogen adsorption measurement was done using magnetic suspension balance (MSB) at 298 K and pressure up to 150 bar. Based from Figure 6.3(a) and (b), the isotherm curve for each sample does not follow Langmuir model as in hydrogen adsorption at 77 K. When the temperature is increased at room temperature (i.e. 298 K), the mass uptake of hydrogen is found to vary almost linearly with pressure. This can be found especially at low pressure where initially a linear–like line follows Henry's Law. At this stage, the interaction is between single molecules and the carbon surface while interaction between adsorbed molecules can be neglected (Ansón et al., 2004). As the pressure increases, the isotherm line is slightly curve. This is due to the increase of intermolecular interactions. Similar trend of curve is also obtained by several researchers using different carbon materials as adsorbents (Jordá-Beneyto et al., 2007; Poirier et al., 2001; Takagi et al., 2004; Xu et al., 2007). The hydrogen capacity is lower at higher temperature. This could probably due to the thermal motion of hydrogen molecules that overcome van der Waals force which provides weak physiosorption of molecular hydrogen (S. E. Hong et al., 2007). In addition, other claims that hydrogen uptake by physisorption are found not to exceed 1 wt% when it is quantified by ion beam analysis (Yürüm et al., 2009). Only physical adsorption involved and no chemical process was taken place since at this condition since C and H atoms are in high chemical stabilization (Ning et al., 2004).



(a) (b)

Figure 6.3 Hydrogen adsorption-desorption hysteresis of (a)iron-based; and (b)nickel-based GNFs at 298 K and 150 bar using MSB

The surface area of an adsorbent is one of the factors that affect the mass uptake in adsorption process. It is thought that the higher the surface area, the higher the amount of hydrogen could be adsorbed since there would be more interaction between hydrogen molecules and the surface of the carbon. However, for hydrogen adsorption, the uptake value does not follow the predicted behavior as predicted by BET surface area (D'Elia et al., 2009). This is because (Poirier et al., 2001) claimed that some nanopores are unseen by nitrogen molecules during surface area measurement. Thus, the value of BET specific surface area does represent the actual surface area.

Apart from surface area, the hydrogen capacity is proportional with the micropore pore volume. The narrow micropore is preferable in physical adsorption of hydrogen (Xu et al., 2007). The microporosity is essential in assessing volumetric capacity whereas mesopores are used in determining the total pore volume (Yürüm et al., 2009). According to (Rzepka et al., 2005) the best achievable hydrogen storage is with the slit pore of size 0.7 nm while other claimed that the optimum pore size for adsorption in porous carbon that allows two layers of adsorbed molecules is 0.6 nm (Rzepka et al., 2005). This shows that microporosity is essential in hydrogen adsorption. Thus, the relation between hydrogen mass uptake and micropore surface area must be taken into account and not limited to the total surface area which includes mesopres and micropores.

Figure 6.4 depicts the isotherm curve of hydrogen adsorption with various micropore surface areas and micropore volume of an iron-based and two nickel-based GNF samples. The micropore surface area and volume are calculated using Barrett-Joyner-Halenda (BJH) method. As expected, the highest hydrogen uptake (about 0.3 wt%) is obtained from an iron-based GNF sample (symbol '■') that has the highest surface area and pore volume that are 809.9 m^2/g and 0.231 cm^3/g, respectively.

However, the second highest uptake of hydrogen is from a nickel-based GNF sample (symbol '◆') which has the lowest micropore surface area that is 84.8 m^2/g and not the other nickel-based GNF sample (symbol '▲') which has higher micropore surface area that is 207.7 m^2/g. This proves that the total hydrogen uptake does not proportional with the total surface area of the adsorbent. Similar finding has been recorded by (Sharon et al., 2007) where higher surface area gives less hydrogen uptake. Other researcher stated that the more active surface area that a sample has, the more uptake the sample could take (Ansón et al., 2004)

Figure 7.5(a), (b), (c) and (d) represent the adsorption-desorption hysterisis of samples L6Ni, 4NG, L7Fe and L5Fe, respectively. Figure 6.5(a) and (b) show a typical adsorption-desorption hysterisis where the desorption points slightly above the adsorption points. This indicates that during desorption process, several hydrogen molecules are still trapped inside the pores. If the desorption points are on the adsorption points, it is assumed that all hydrogen molecules are completely removed from the sample (as in Figure 6.3).

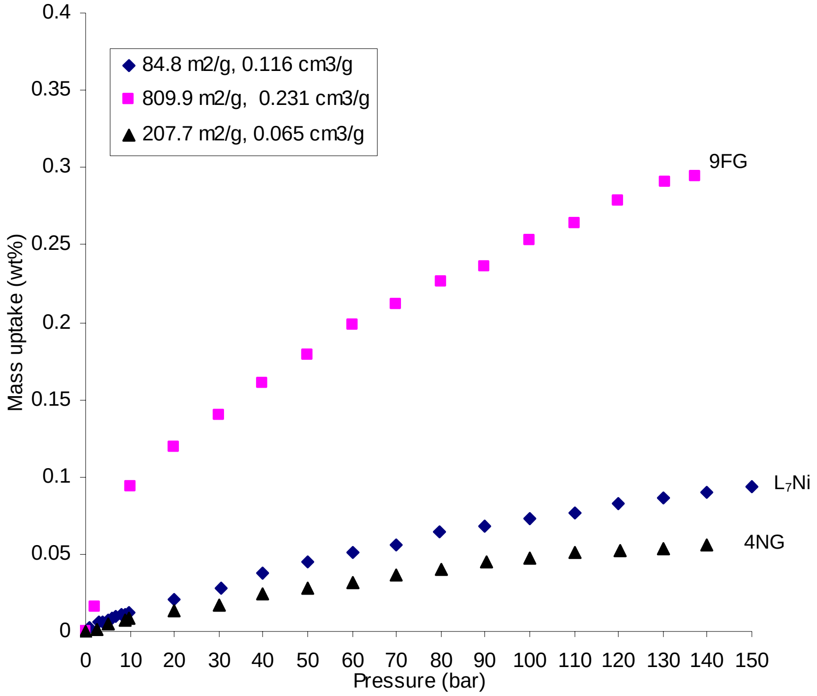
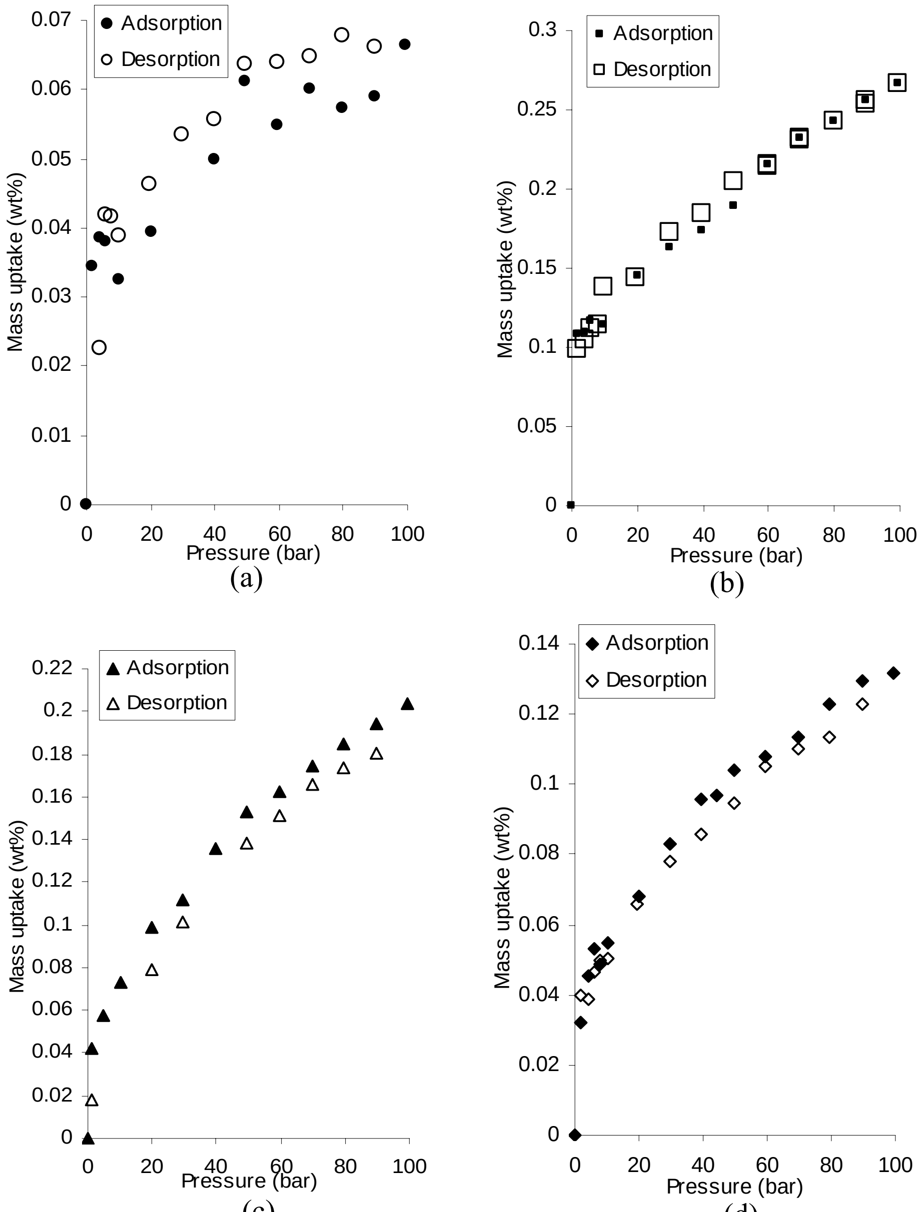


Figure 6.4 Comparison of hydrogen uptake using developed GNFs at 298 K at different micropore area (m^2/g) and micropore volume (cm^3/g)

However some samples like L_7Fe and L_5Fe as in Figure 6.5(c) and (d) have desorption points below adsorption. This could be due to kinetic problems in adsorption (Ansón et al., 2004) and such phenomenon does not imply any irreversibility. The four samples' results in Figure 6.5 are then compared to that of Figure 6.6. It can be seen that sample 4NG with the highest surface area of 250 m^2/g gives the maximum hydrogen uptake that is 0.27 wt%. The next highest uptakes are from iron-based GNF that are samples L_7Fe and L_5Fe.

Although these two samples have surface area around 130–147 m^2/g, but the difference in the hydrogen uptake is significant about 0.07 wt%. This could probably due to more micropore volume is present in sample L_7Fe. The lowest uptake that is 0.07 wt% is found in sample L_6Ni with the smallest surface area of 110 m^2/g. The details results of the adsorption and desorption points can be referred in Appendix D.



(a)

(b)

(c)

(d)

Figure 6.5 Hydrogen adsorption-desorption hysteresis of samples (a)L6Ni; (b)4NG; (c)L7Fe; and (d)L5Fe at 298 K and 100 bar using MSB with filled symbols as adsorption and open symbols as desorption.

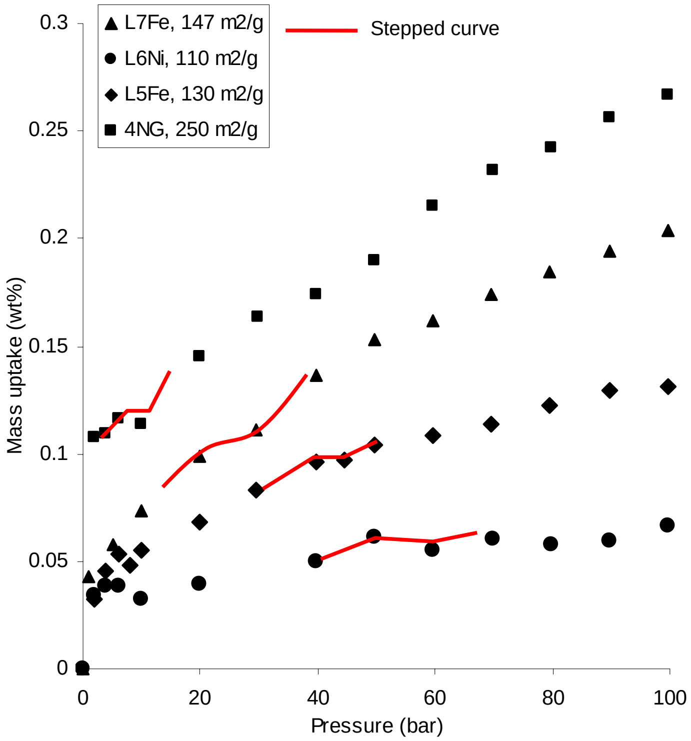
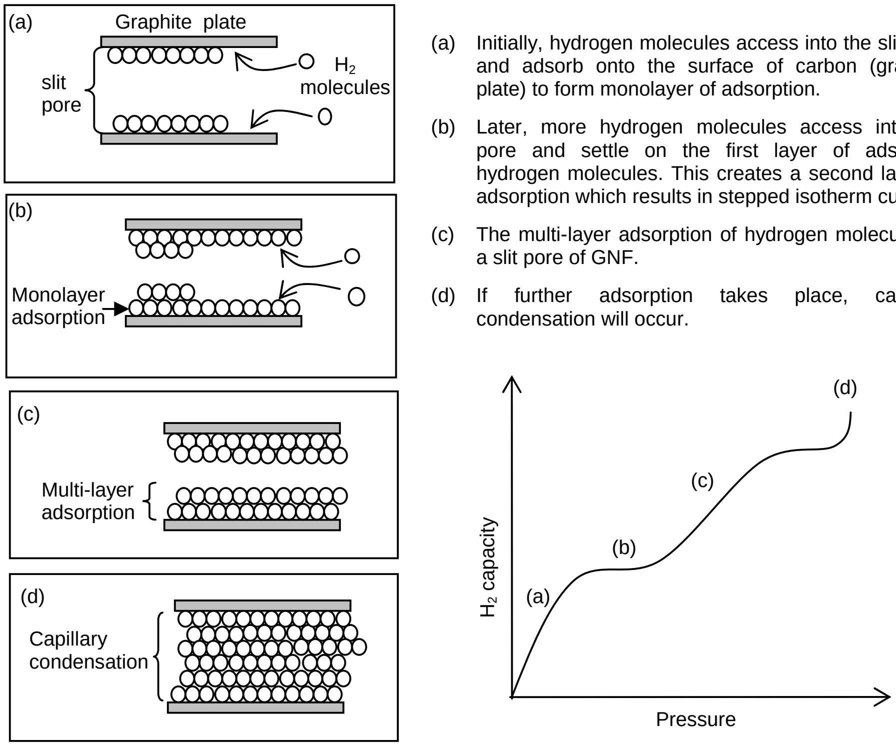


Figure 6.6 Comparison of hydrogen uptake using developed GNFs at 298 K at different specific BET surface area (m^2/g)

An interesting finding has been discovered at the hydrogen isotherm curves in Figure 6.6. As indicated by the ‘red line’ a stepped curve can be observed in each isotherm curve. For higher surface area, the stepped curve occurs at higher pressure. It is believed that the stepped curve is due to layer-by-layer adsorption occurs on a uniform planar graphite surface. At higher surface area, the next layer of adsorption occurs earlier at lower pressure than that of lower surface area which occurs at higher pressure. The theory of layer-by-layer adsorption incident can be illustrated in Figure 6.7. The hydrogen isotherm curve trend corresponds to the molecules adsorbed onto the carbon surface. It is believed that at high pressure, further adsorption will result in capillary condensation. Such observation has been reported by (Lim et al., 2007) for N_2 adsorption isotherm but no study has been reported for hydrogen adsorption isotherm either in gravimetric or volumetric measurement technique.



(a) Initially, hydrogen molecules access into the slit pore and adsorb onto the surface of carbon (graphite plate) to form monolayer of adsorption.

(b) Later, more hydrogen molecules access into the pore and settle on the first layer of adsorbed hydrogen molecules. This creates a second layer of adsorption which results in stepped isotherm curve.

(c) The multi-layer adsorption of hydrogen molecules in a slit pore of GNF.

(d) If further adsorption takes place, capillary condensation will occur.

Figure 6.7 Stepped isotherm curve corresponds to hydrogen molecules adsorbed onto the carbon surface (Fletcher, 2008; Nackos, 2006)

6.3 Hydrogen isotherm: prediction data

Hydrogen isotherm is predicted based from the experimental data obtained. The hydrogen isotherm prediction is categorized into two parts that are isotherm data at 77K and at 298 K. The importance of hydrogen prediction is that the capacity of hydrogen at a particular surface area can be estimated. For simplification, only data with total surface area proportional with mass uptake would be taken.

6.3.1 Hydrogen adsorption isotherm at 77 K

The prediction is done at two different areas that are at 248 and 407 m^2/g with pressure range between 0 and 20 bar. There are thirty-one (31) points of adsorption data to generate the isotherm model. The model was reviewed in order to achieve targeted relative error of less than 8 %. The relative error could not be taken less than 5 % since not many points are available to generate the model. Hence, 8 % is acceptable. The final limits of range for all parameters contributed to the prediction of hydrogen adsorption isotherm are as follow:

For area (Input 1), the membership function was divided into five terms that were:

I. Very low: 240 – 280 m^2/g
II. Low : 270 – 320 m^2/g
III. Medium : 300 – 350 m^2/g
IV. High : 340 – 390 m^2/g
V. Very high: 370 – 410 m^2/g

For pressure (Input 2), the membership function was divided into five terms that were:

I. Very Low : 0 – 5 bar
II. Low : 5 – 9 bar
III. Medium : 7 – 13 bar
IV. High : 11 – 17 bar
V. Very High : 15 – 20 bar

For mass uptake (Output), the membership function also was divided into five terms that were:

I. Very Low : 0 – 0.3 wt%
II. Low : 0.1 – 0.5 wt%
III. Medium : 0.3 – 0.7 wt%
IV. High : 0.5 – 0.9 wt%
V. Very High : 0.8 – 1.2 wt%

After the prediction of the adsorption isotherm curve was developed (refer to Appendix E), both modeling data and experimental data were compared between each other in order to test the reliability and accuracy of the system (refer to Figure 6.8). In addition, the prediction of isotherm at other surface area (293 m^2/g) within the model range is well acceptable.

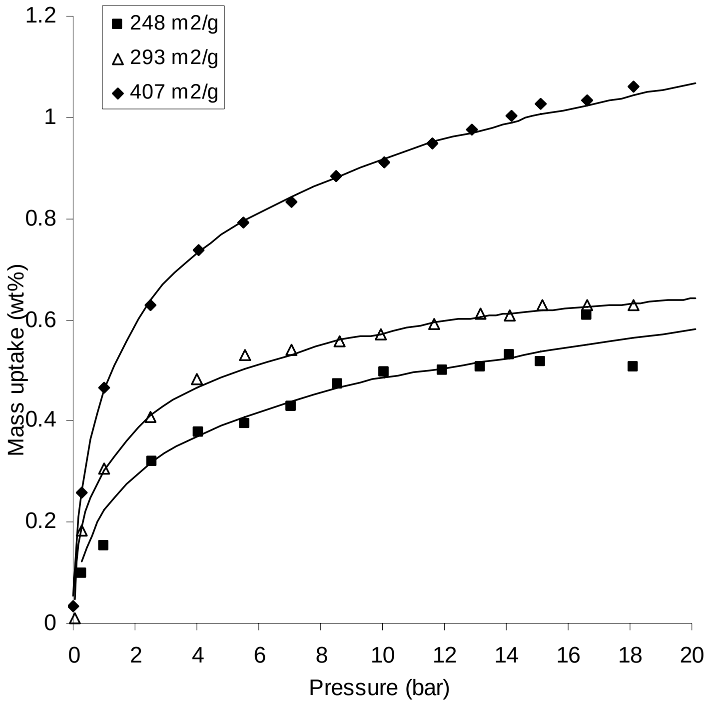


Figure 6.8 Model development of hydrogen isotherm at 77 K using Neuro-fuzzy at surface areas of 248 and 407 m^2/g (filled symbols) as well as model validation of hydrogen isotherm at surface area of 293 m^2/g (open symbols).

The relative errors for areas of 240, 293 and 407 m^2/g are 6.14, 5.85 and 0.03 %, respectively, that are less than 8 %. This indicates that the assumption-free model of Neuro-fuzzy system is applicable for predicting adsorption isotherm curve. This is comparable with other assumption-free model developed by artificial neural network (ANN), which gave MARE of 8.19% for adsorption isotherm (Basu et al., 2002).

6.3.2 Hydrogen adsorption isotherm at 298 K

The prediction of isotherm curve at 298 K is done at two different areas that are at 110 and 250 m^2/g with pressure range between 0 and 100 bar. There are twenty-five (25) points of adsorption data to generate the isotherm model. The final limits of range for all parameters contributed to the prediction of hydrogen adsorption isotherm are:

For area (Input 1), the membership function was divided into five terms that were:

I. Very low: 100 – 150 m^2/g
II. Low : 130 – 170 m^2/g
III. Medium : 160 – 200 m^2/g
IV. High : 190 – 230 m^2/g
V. Very high: 220 – 260 m^2/g

For pressure (Input 2), the membership function was divided into five terms that were:

I. Very Low : 0 – 20 bar
II. Low : 15 – 40 bar
III. Medium : 35 – 60 bar
IV. High : 55 – 80 bar
V. Very High : 75 – 100 bar

For mass uptake (Output), the membership function also was divided into five terms that were:

I. Very Low : 0 – 0.06 wt%
II. Low : 0.05 – 0.12 wt%
III. Medium : 0.11 – 0.18 wt%
IV. High : 0.17 – 0.24 wt%
V. Very High : 0.23 – 0.3 wt%

The results of the model development of isotherm and model validation using Neuro fuzzy are depicted in Figure 6.9. The relative errors for areas of 110, 130, 147 and 250 m^2/g are 7.78, 4.62, 7.34 and 1.60 %, respectively. The errors are acceptable since the values are less than 8 %. The detail results of the prediction isotherm can be referred in Appendix D.

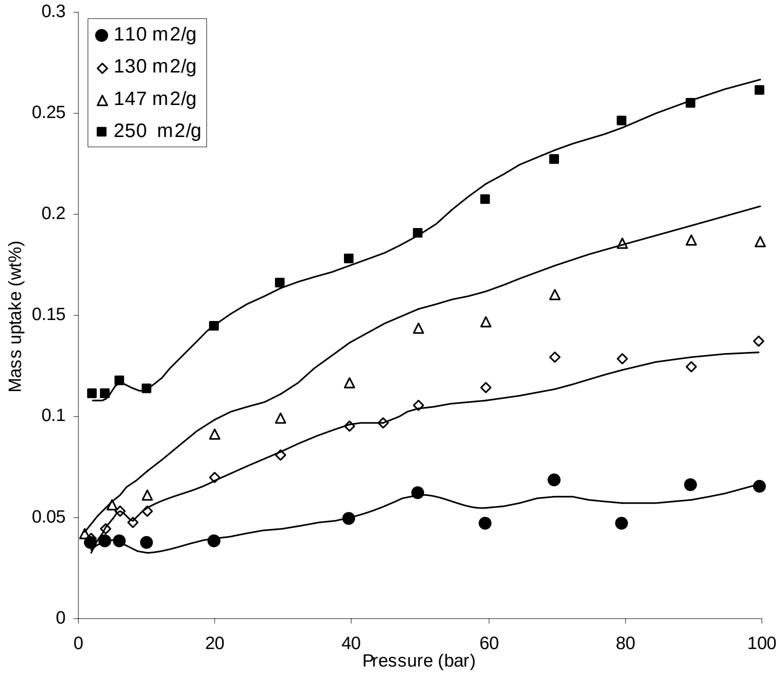


Figure 6.9 Model development of hydrogen isotherm at 298 K using Neuro-fuzzy at surface areas of 110 and 250 m^2/g (filled symbols) as well as model validation of hydrogen isotherm at surface areas of 147 and 293 m^2/g (open symbols).

6.3.3 Adsorption active site

Further analysis can be done to determine the number of adsorption active sites in the GNF. This was done by using Langmuir equation since the first step of the stepped isotherm followed Type I isotherm. The expression of Langmuir is:

$$q = \frac{q_o P_i}{K + P_i} \tag{6.1}$$

where q is amount of adsorbate per adsorbent, q_o maximum amount of adsorbate per adsorbent, P_i is partial pressure of adsorbate and K is constant.

In addition, the rate of adsorption, r_{ads} can be expressed as:

$$r_{ad\,s} = k_+ P A_v - k_- A_o \tag{6.2}$$

where k_+ and k_- are constants for adsorption and desorption process, respectively, A_v is vacant active site of adsorbent and A_o is the occupied active site. k_+/k_- can be written as K_{ads} and the total active site, A_t is can be expressed as A_v+A_o. at equilibrium, r_{ads} is zero, thus Equation (6.2) can be reduced as:

$$P_i A_v = \frac{A_o}{K_a} \tag{6.3}$$

Since at equilibrium A_v=A_t, thus Equation (6.3) can be rearranged and expressed in term of A_o as:

$$A_o = \frac{K_a P_i A_t}{(1 + K_a P_i)} \tag{6.4}$$

By assuming each H_2 molecule occupies one adsorption active site, q can be defined as:

$$q = A_o \times \mathrm{A}_{BET} \times \mathrm{m}_{H_2} \tag{6.5}$$

where A_{BET} is specific surface area of adsorbent and m_{H2} is mass of H_2 per molecule. Substitute Equation (6.4) into Equation (6.5) and rearrange the equation gives:

$$\frac{1}{q} = \frac{1}{(A_t \times m_{H_2} \times A_{BET})K_a P_i} + \frac{1}{A_t \times m_{H_2} \times A_{BET}} \tag{6.6}$$

By plotting $1/q$ versus $1/P_i$, a linear plot could be obtained and the number of the adsorption active sites, A_t can be obtained from the gradient of the linear line. An example of linear plot can be seen in Figure 6.10.

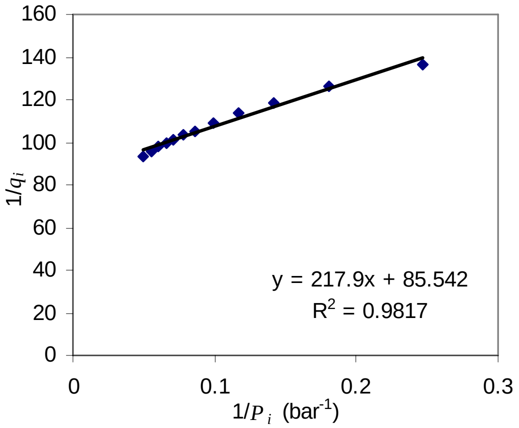


Figure 6.10 A linear plot of $1/q$ versus $1/P_i$ to obtain number of adsorption active site

The results of number of adsorption active sites for different specific BET surface area of adsorbent can be seen in Table 6.1 below. From the table it can be concluded that the number of adsorption active sites is proportional to the specific BET surface area of the developed material.

Table 6.1 Number of adsorption active sites in hydrogen adsorption onto GNF

Specific BET surface area (m^2/g)	Number of adsorption active sites
407	8.650×10^{18}
293	7.090×10^{18}
250	6.908×10^{18}
147	6.237×10^{18}
130	3.656×10^{18}
110	1.868×10^{18}

6.4 Summary

At 77 K and 20 bar conditions, the hydrogen adsorption capacities using the developed GNFs are found to be between 0.58–0.64 wt% as compared with a commercial SWNTs that give a hydrogen uptake of 1.07 wt%. Adsorption measurement at room temperature results in low hydrogen uptake. At 150 bar, the weight percentage of the adsorbed hydrogen using GNFs is ranging from 0.06–0.30 wt% while at 100 bar, the capacities ranging from 0.07–0.27 wt%.

The hydrogen uptake is proportional to the total surface area (i.e. BET specific surface area). However, certain isotherm results show that some samples with lower surface areas give higher hydrogen uptake. This is due to the higher micropore volume which provides more rooms for multi layer adsorbed hydrogen. Adsorption at cryogenic temperature (77 K) and moderate pressure (20 bar) provides higher uptake as compare to condition at room temperature (298 K) and at high pressure (100 bar). However, in reality the storage of hydrogen should be done at room temperature with pressure not more than 300 bar for safety reasons. The hydrogen adsorption measurement results are compared with the previous work from other researchers as in Table 6.2 and 6.3 for adsorption at 77 K and room temperature (298-303 K), respectively.

For adsorption at 77 K, with lower operating pressure, the hydrogen uptake of 0.64 wt% is higher than that of Kayiran, S.N. *et al* (Kayiran et al., 2003). This is due to higher surface area that is 293 m^2/g as compared with 112.7 m^2/g of Kayiran, S.N. *et al.*

Table 6.2 Comparison studies of hydrogen adsorption at 77 K

Researcher(s)	Technique	Adsorbent/ surface area	Pressure (bar)	H_2 capacity (wt%)
Sufian, S. (2009)	Gravimetric	GNF/ 293 m^2/g	20	0.64
Gogotsi, Y., et al. (2005)	Gravimetric	Carbide derived carbon, 2000 m^2/g	1.01	3.00
Ning, G.Q., *et. al.* (2004)	Volumetric	MWNT/ NA	120	2.27
Kayiran, S.N., *et al.* (2003)	Volumetric	GNF/ 112.7 m^2/g	170	0.22
Nishimiya, N., et. al. (2002)	Volumetric	SWNT, 504 m^2/g	1.08	2.37

In addition, the use of gravimetric measurement instead of volumetric could precisely determine the exact amount of adsorbed hydrogen as compared with Kayiran, S.N. *et al*. However, the measured result is less than what obtained by other research works that have higher surface area between 500 to 2000 m^2/g (Gogotsi et al., 2005; Nishimiya et al., 2002).

For adsorption of 298 K, at a pressure more than 100 bar, the measured result is in good agreement with other GNFs produced by other researchers which have higher surface area of materials (Blackman et al., 2006; S. E. Hong et al., 2006; Lueking et al., 2005). Other materials like Ni plated CNF, activated carbon and palladium loaded MAXSORB have much higher surface area but the adsorption uptakes are not so high (less than 2.5 wt%). It shows that higher surface area is not the only key factor to have better adsorption but the micropore volume and pores size also play important roles in determining the hydrogen uptake.

Table 6.3 Comparison studies of hydrogen adsorption at 298 K

Researcher(s)	Technique	Adsorbent/ surface area	Pressure (bar)	H_2 capacity (wt%)
Sufian, S. (2009)	Gravimetric	GNF/ 293 m^2/g	137	0.294
Kim, B.J., *et. al.* (2008)	Gravimetric	Ni plated CNF, 1310 m^2/g	100	2.2
Jin, H., *et. al.* (2007)	Volumetric	Activated carbon/ 2800 m^2/g	100	0.85
Ansón, A., *et, al.* (2006)	Volumetric	Pd loaded Maxsorb carbon/ 508 m^2/g	90	0.7
Hong, S.E., *et. al.* (2006)	Gravimetric	GNF, 477 m^2/g	80	0.18
Blackman, J.M., *et. al.* (2006)	Volumetric	GNF, 475 m^2/g	100[a]	0.35
Lueking, A.D., *et. al.* (2005)	Gravimetric	GNF, 555 m^2/g	20[b]	0.29

[a] adsorption conducted at 303 K

[b] adsorption conducted at 300 K

For relative errors for hydrogen isotherm model at 77 K, 20 bar and 298 K, 100 bar are acceptable since the value are less than 8%. It is believed that the errors could be reduced if more number of experimental data points could be obtained from the hydrogen adsorption measurement.