

## CHAPTER IV

### RESULTS AND DISCUSSION

This study was produced the Single Walled Carbon Nanotubes (SWNTs) by CoMoCAT<sup>®</sup> process and silica gel was used as the support metal catalyst. At first, we dissolved catalyst particles by hydrochloric acid because the SWNTs grew up from the metal catalyst particle then silica and SWNTs were separated. After that the froth flotation process was used to concentrate the SWNTs. The effects of sonication time, hydrochloric concentration, and reaction temperature were studied. The optimum conditions for the maximum percentage of catalyst dissolved were applied to the froth flotation experiments, which concerned in the effect of surfactant concentration, pH solution and air flow rate. The second way to purify SWNTs due to silica was the highest part in the SWNTs particle so we dissolved silica after catalyst particles by sodium hydroxide and also concentrated SWNTs by froth flotation process. The parameters that we studied were same as the first part. The Laser Raman spectroscopy was used for systematic screening of the all types of carbon products, the Temperature programmed oxidation (TPO) was used to confirm the forms of carbons presenting in samples and also to provide the amount of total carbon products and Scanning Electron microscopy (SEM) was used to observe the surface of the particle.

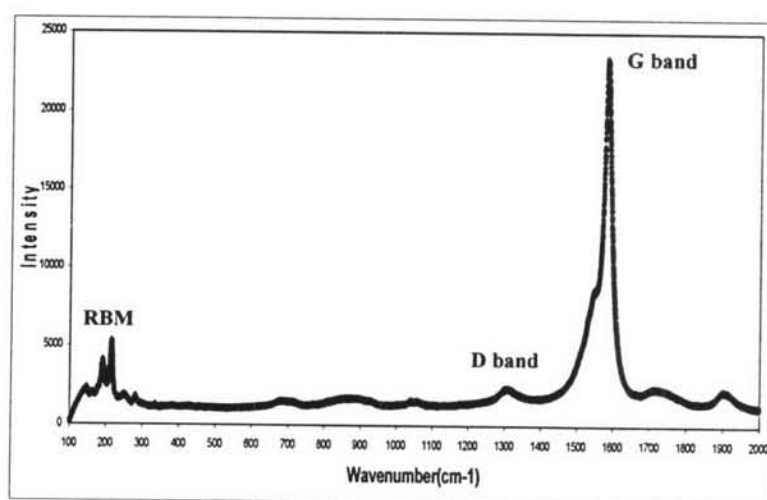
#### **4.1 The Production of Single-walled Carbon Nanotubes**

Single-walled carbon nanotubes (SWNTs) were produced by a disproportionation of carbon monoxide over cobalt-molybdenum catalyst, which called CoMoCAT, employs silica supported.

The total metallic loading in a catalyst was 6 wt%, with a Co:Mo molar ratio 1:3. Before the catalyst exposure to the CO feedstock, it was heated to 500°C in a flow of gaseous hydrogen and further heated to 850°C in flowing helium. The SWNTs were grown by this method remained mixed with the spent catalyst.

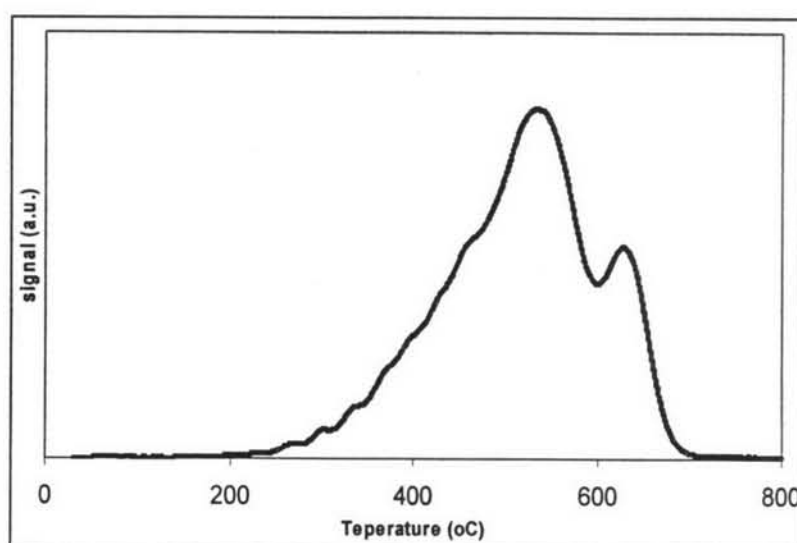
For the carbon nanotubes characterization, this thesis employs the Raman Spectroscopy technique for a systematic screening of catalyst (Figure 4.1). It can

provide information about purity, distribution of tube diameters, and electronic properties. The result give three important modes, namely graphite-like tangential mode (G-band), disordered carbon band (D-band), and the radial  $A_{1g}$  breathing mode frequency range (RBM). The tangential modes or G-band locates at around  $1570\text{ cm}^{-1}$ , which are the characteristics of both carbon nanotubes and graphite. The latter band at  $1350\text{ cm}^{-1}$  (D-band) corresponds to the disorder or amorphous carbon. The presence of the RBM, which locates at frequencies below  $300\text{ cm}^{-1}$ , can provide information about the existence of SWNTs in the sample. The intensity of D-band relative to that of G-band can be used as a qualitative measurement for the formation of undesired forms of carbon. Moreover, the D-band to G-band (D/G) intensity ratio also provides a relative amount of disorder carbon to graphite-like carbon. Typically, if the relative intensity ratio (D/G) is low, this can indicate that the formation of disorder carbon is lower than graphite-like carbon, so it means that carbon mostly consists of graphite-like forms such as SWNTs, MWNTs, and nanofiber. On the contrast, if the relative intensity ratio (D/G) is high, this can imply that the sample is mainly in disorder carbon form.



**Figure 4.1** Raman spectra of SWNTs produced by CoMoCAT at 1:3 mole ratios over silica supported with CO at  $850^{\circ}\text{C}$ .

The Temperature Programmed Oxidation (TPO) was employed to confirm the types of carbonaceous deposits on spent catalyst. Carbon with different morphology was oxidized at different temperature so examining the oxidation temperature helps in identify the types of carbon products (Figure 4.2). It has been reported that the oxidation of amorphous carbon on this type of catalyst under the particular condition used in this work has a range of 300 to 400°C, while SWNTs and MWNTs have shown peaks around 495-530°C and 600-700°C respectively (Kitiyanan *et al.*, 2000). According to both of the Raman and TPO results, most of products obtained are SWNTs. The carbon yield is estimated about 3 wt%.



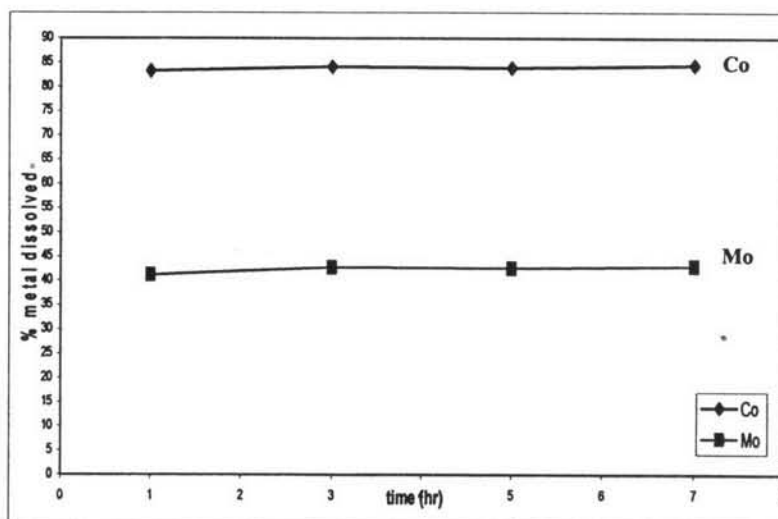
**Figure 4.2** TPO profile of as-prepared carbon produced from CoMoCAT<sup>®</sup> process.

## 4.2 Catalyst Dissolution Results

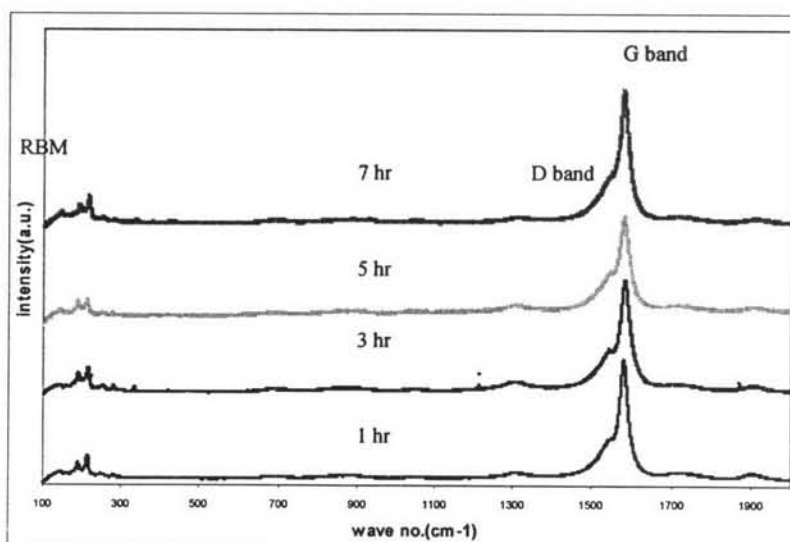
### 4.2.1 Effect of Sonication Time

The SWNTs 0.1 g were dissolved by hydrochloric acid, which a concentration at 10 M about 5 ml and placed into the sonication bath at 70°C. In this step, we used sonication to enhance the dissolution reaction. An atomic analysis spectroscopy (AAS) was used to determine the concentration of dissolved catalyst

particles. Figure 4.3 summarizes the result of percentage of catalyst dissolved at different sonication time.



**Figure 4.3** The effect of sonication time to dissolve catalyst particles.

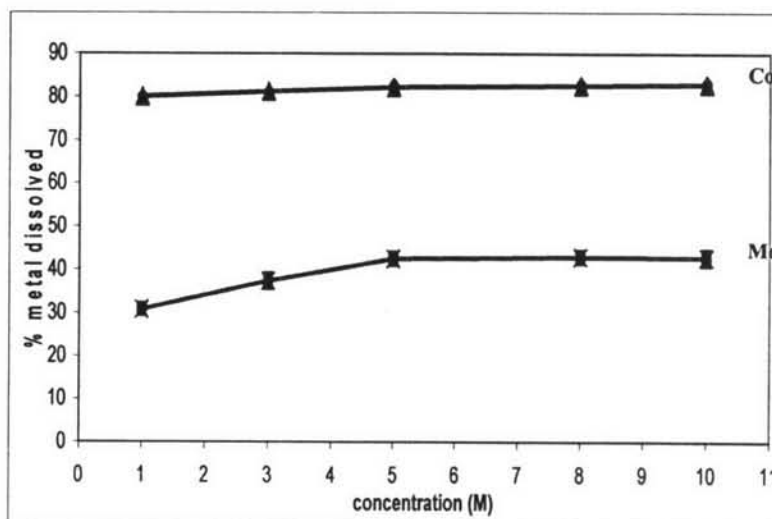


**Figure 4.4** Raman spectra of SWNTs treated by HCl with different sonication time at 70°C.

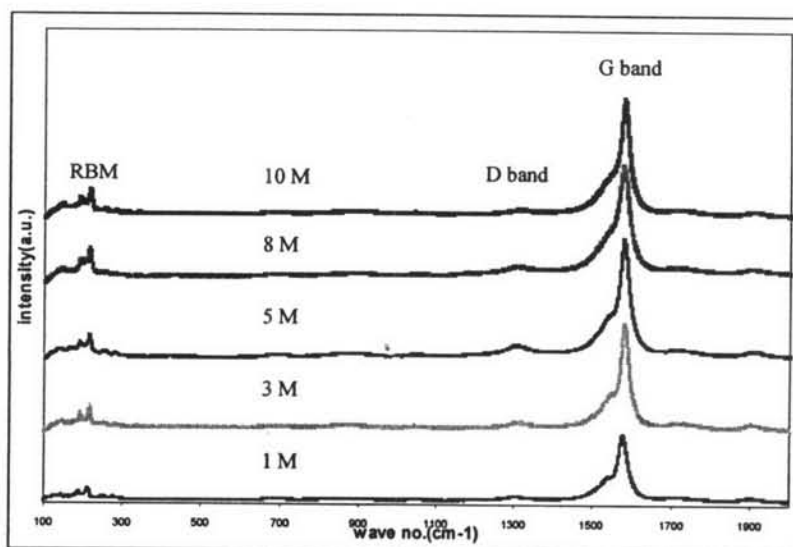
From Figure 4.3, the percentage of Co dissolved was higher than Mo dissolved because the SWNTs were grown up from Co particle and Mo as the stabilizer so the Mo molecule was hard to expose to the acid. If we consider in the effect of time, when the time increased the percentage of catalyst dissolved was changed a little so the time did not significant. From the Raman spectra in Figure 4.4, all peaks of G-band, D-band and RBM were found in all samples indicated the carbon structure was not destroyed by the HCl treatment. Then, in the next part we did the experiment by sonicated for 3 hour to make sure the highest metal was dissolved

#### 4.2.2 Effect of Hydrochloric Concentration

In this part was sonicated at 3 hr and operated at 70°C. The same procedure as mentioned above was done. We also used AAS to determine the dissolved catalyst particles and the result was shown in Figure 4.5.



**Figure 4.5** The effect of HCl concentration to dissolve catalyst particles.

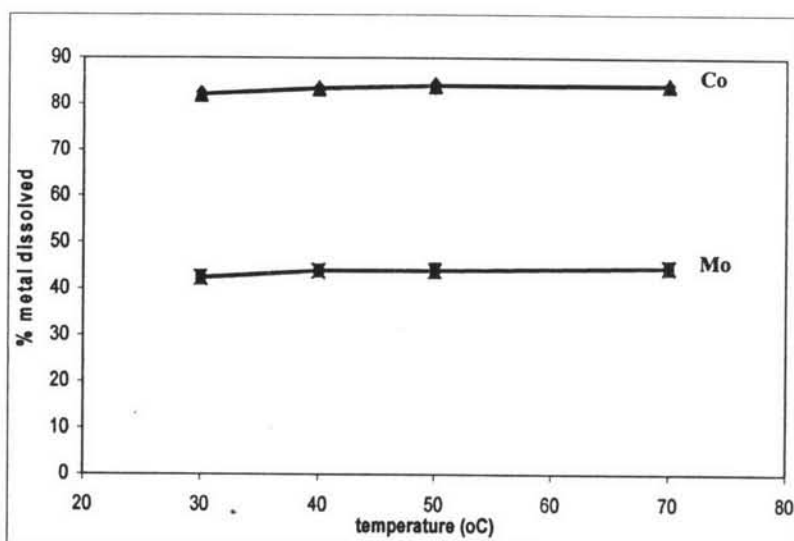


**Figure 4.6** Raman spectra of SWNTs treated by HCl with different concentration at 70°C.

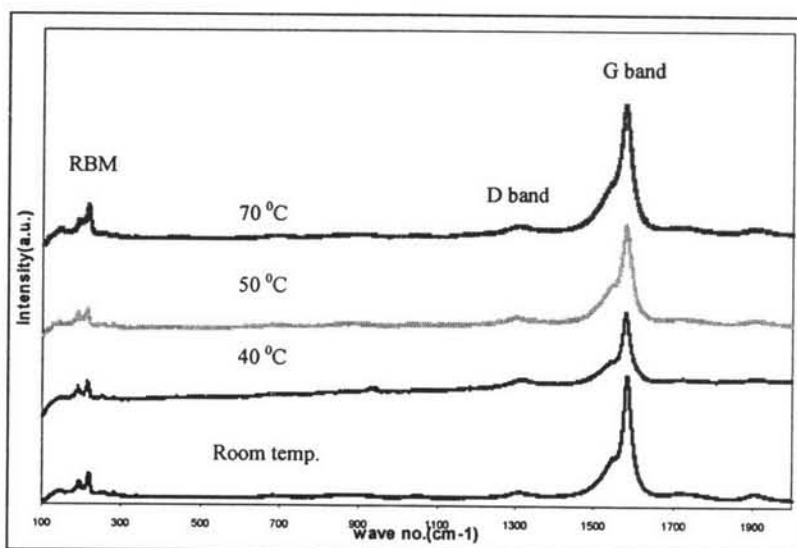
From Figure 4.5 showed the effect of HCl concentration, when the concentration increased the percentage of catalyst dissolved was increased too. The Raman results (Figure 4.6) suggest that HCl did not change the carbon structure of the SWNTs and the reason of the percentage of Co dissolved was higher than Mo was described in section 4.2.1. Hence, the optimum HCl concentration, 6M, was used in next experiments.

#### 4.2.3 Effect of Reaction Temperature

The experiment procedure was same as above but this part was done in the different reaction temperature. In this section was operated at 6 M of HCl and sonicate for 3 hour. The AAS result of catalyst dissolved was shown in Figure 4.7.



**Figure 4.7** The effect of reaction temperature for dissolve catalyst particles.



**Figure 4.8** Raman spectra of SWNTs treated by HCl with different temperature.

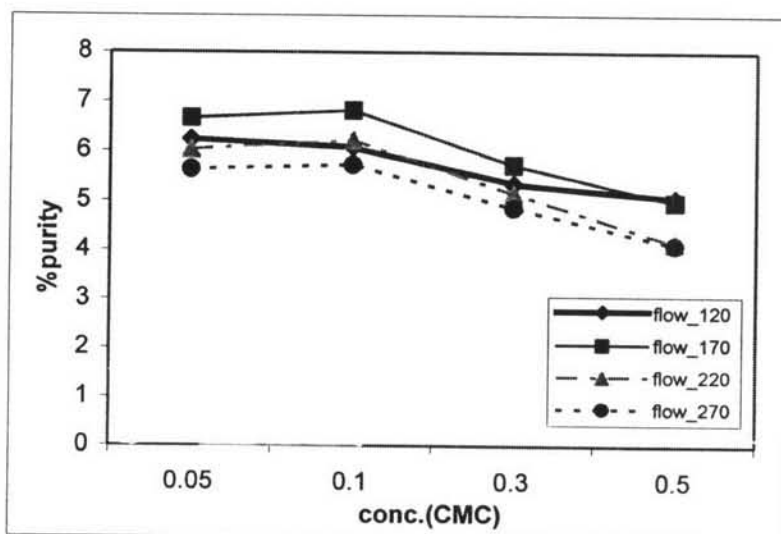
The effect of reaction temperature was expressed in Figure 4.7. As we can see, when the temperature increased the percentage of catalyst dissolved was increased too but after 50°C was changed a little. From the Raman spectra in Figure 4.8 illustrated the temperature did not destroyed the structure of SWNTs. The optimum reaction temperature was 50 °C.

### 4.3 Froth Flotation Results (After dissolved catalyst particles)

In this section, the SWNTs produced by the CoMoCAT<sup>®</sup> process which silica was used as catalyst support contained 1 to 25 wt% carbons, 1 to 6 wt% catalyst and 69 – 98 wt% silica. In the catalyst dissolution step, we used sonication to enhance the dissolution reaction. The froth flotation was further used to concentrate the SWNTs after the catalyst dissolution. For the carbon nanotubes characterization, Temperature programmed oxidation (TPO) technique was employed to determine the quantity of the samples after the froth flotation.

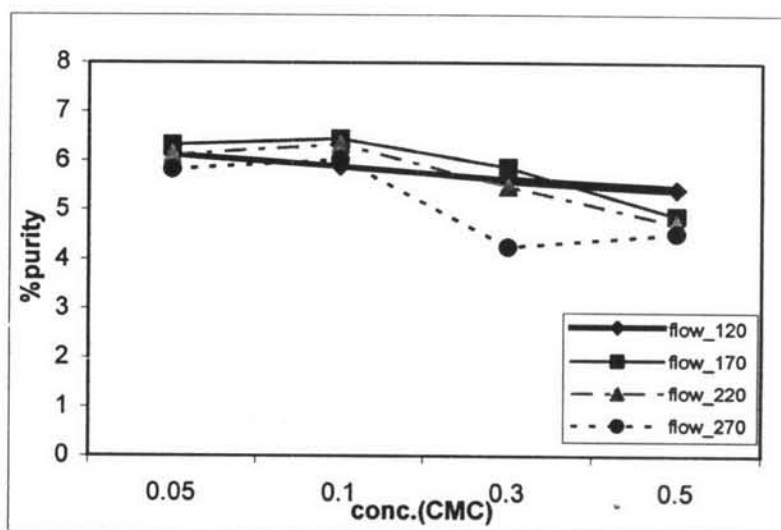
#### 4.3.1 Effect of Surfactant Concentration

After dissolved catalyst particles with HCl, the SWNTs and the silica particles were separated then froth flotation process was applied to concentrate the SWNTs. In this study we use an anionic surfactant, sodium dodecylbenzensulfonate, to separate the SWNTs from silica remaining. Figure 4.9 showed the results in terms of carbon purity of SWNTs at different surfactant concentration.

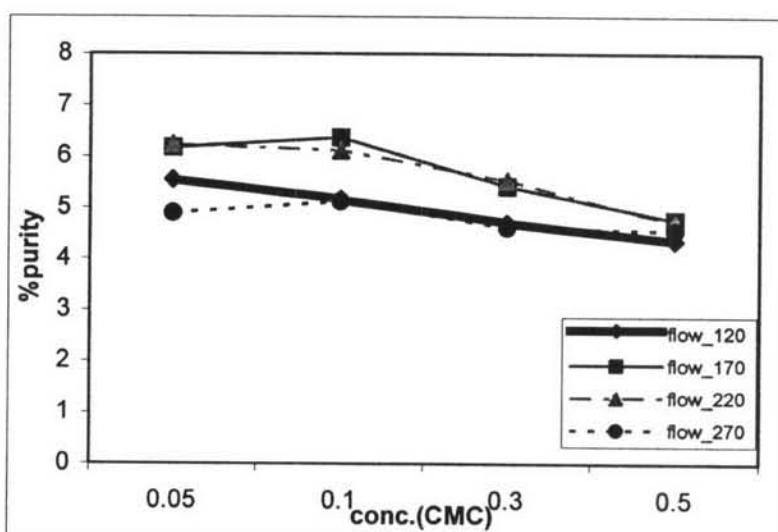


(a)





(b)



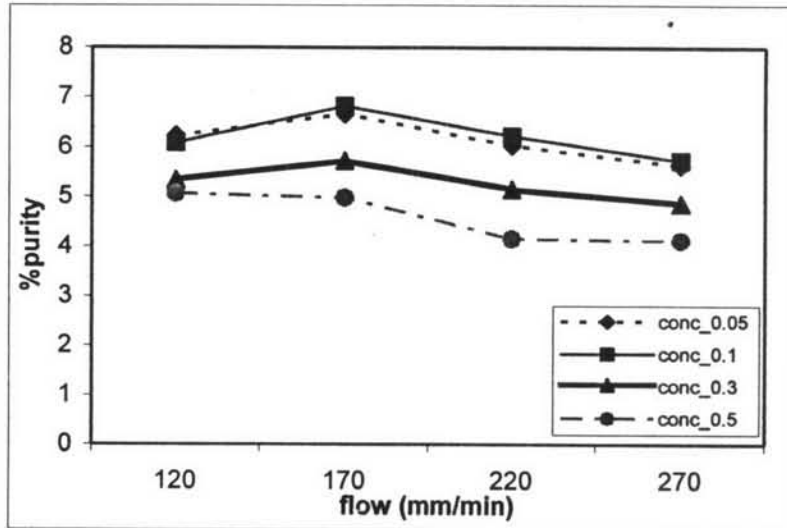
(c)

**Figure 4.9** Effect of surfactant concentration at (a) pH 3, (b) pH 5, (c) pH 7.

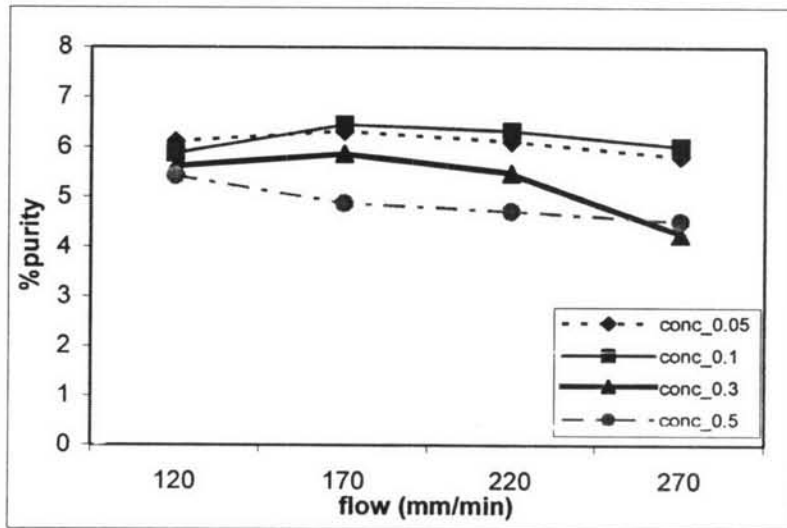
As can be seen in Figure 4.9 the percentage of carbon purity decreased with increasing surfactant concentration. The deterioration of carbon purity with increasing surfactant concentration was due to the ability of surfactant to remove the particle in the solution. The higher surfactant concentration, the higher particle can remove. So at high concentration both SWNTs and silica particle were removed to the top of the column then the carbon purity was decreased.

4.3.2 Effect of Air Flow Rate

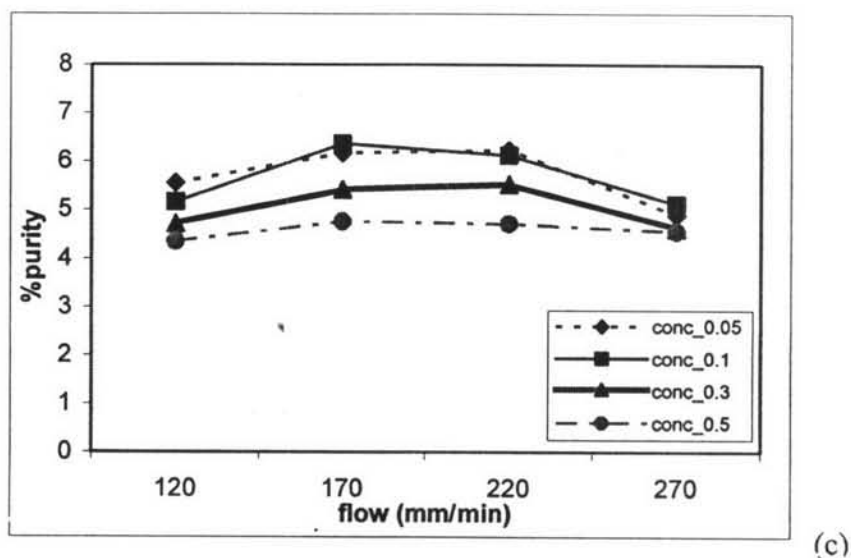
The air flow rate is the key of separation. This factor was corresponded with the foam generation and the ability of particle removed. This section was studied in the different air flow rate, 120 ml/min, 170 ml/min, 220 ml/min and 270ml/min.



(a)



(b)

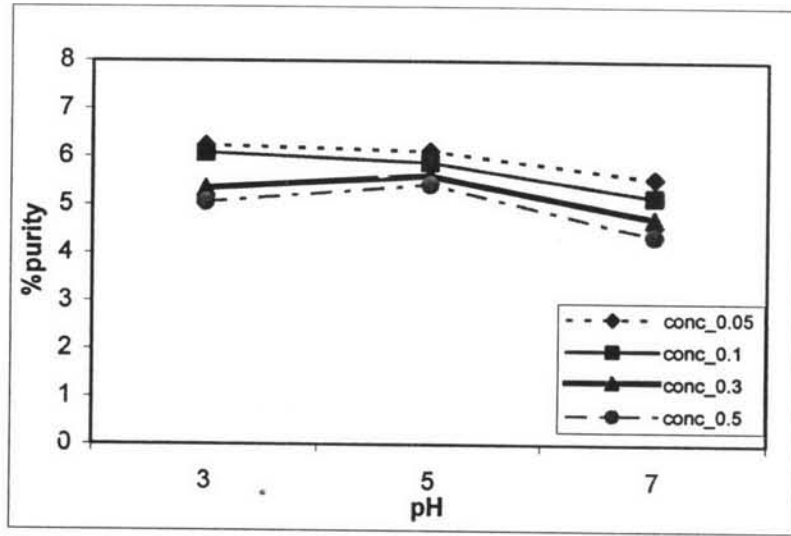


**Figure 4.10** Effect of air flow rate at (a) pH 3, (b) pH 5, (c) pH 7.

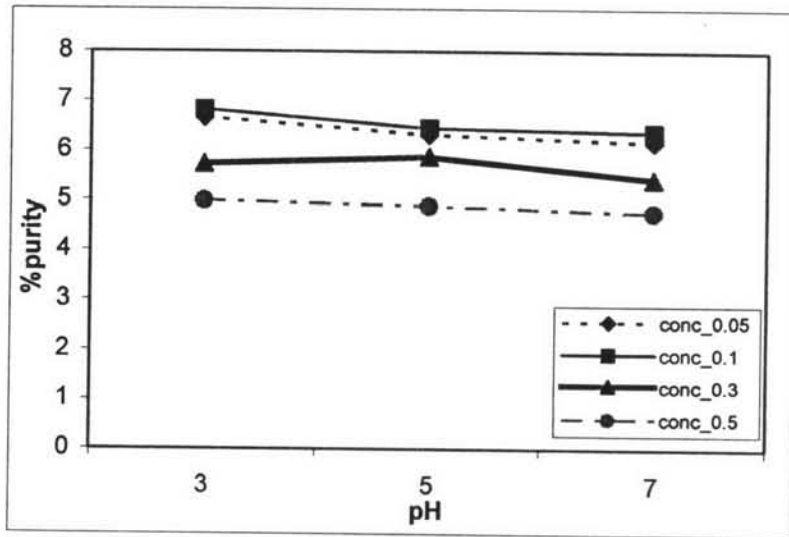
The Figure 4.10 expressed the effect of air flow rate with different pH solution. The air flow rate related to the power of the air to remove the particle, the foam at flow rate 120 ml/min has low ability to remove the SWNTs, so the percentage of carbon purity was lower than flow rate 170 ml/min. But at flow rate 220 and 270 ml/min can remove other impurities then the purity was less than 170 ml/min, too. So the optimum flow rate was 170 ml/min.

#### 4.3.3 Effect of pH Solution

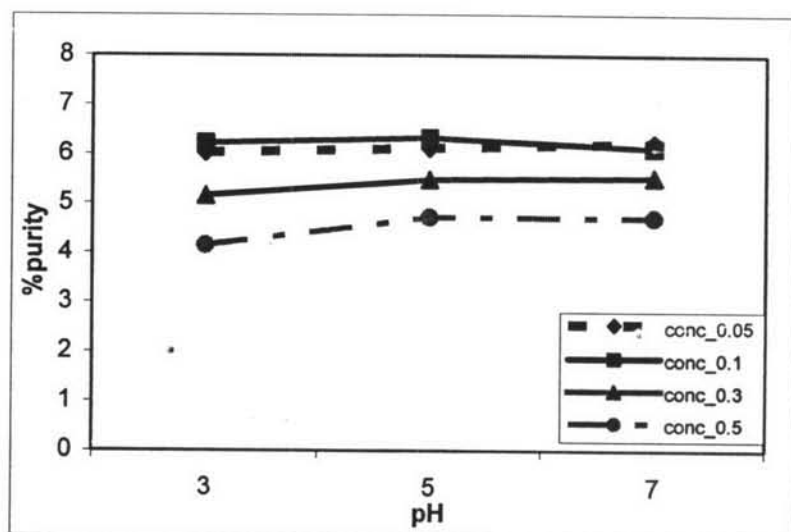
The pH solution can change the charge of particle. Since the point of zero charge (PZC) of silica and SWNTs was different so in this part use the pH solution as the key of separation.



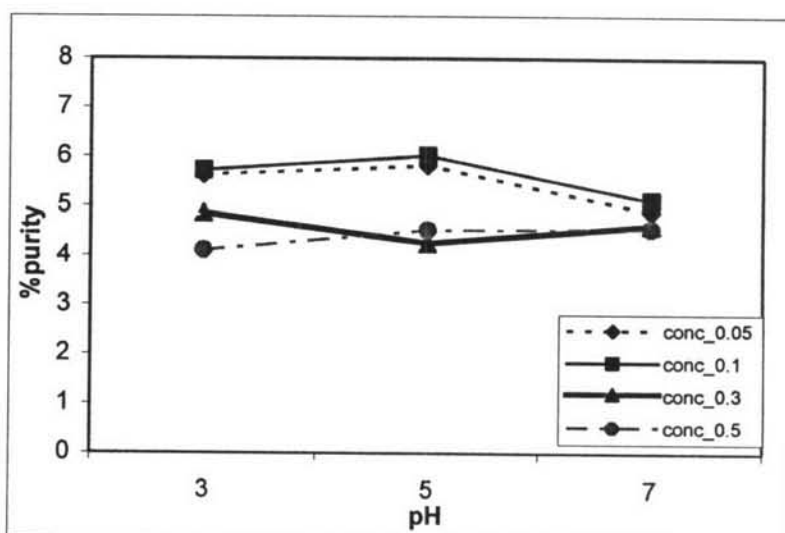
(a)



(b)

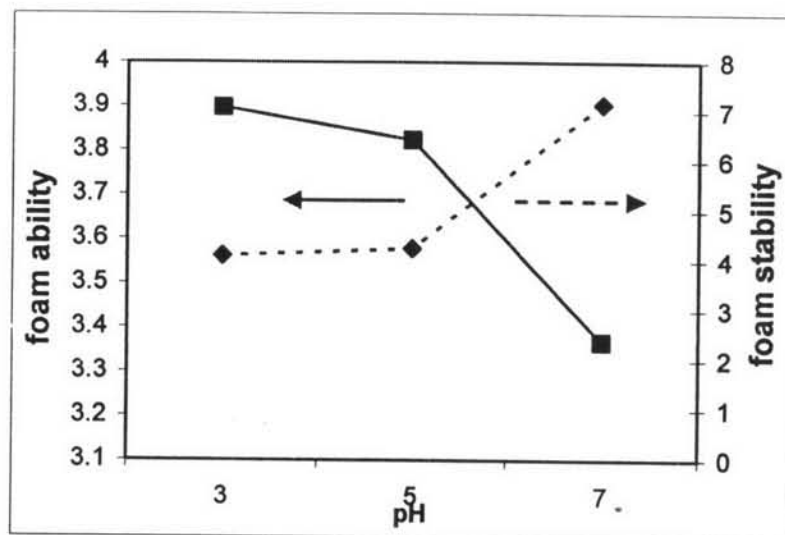


(c)



(d)

**Figure 4.11** Effect of pH solution (a) air flow rate 120 mm/min, (b) air flow rate 170 mm/min, (c) air flow rate 220 mm/min, (d) air flow rate 270 mm/min.

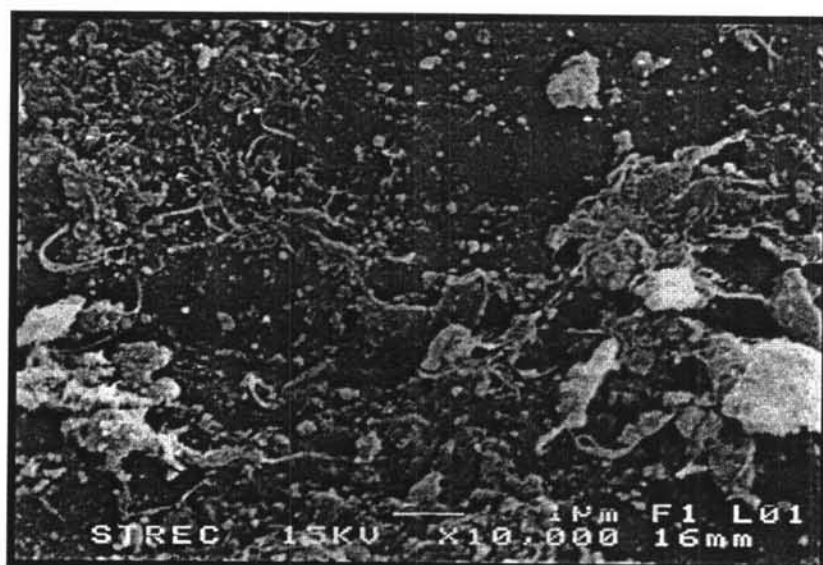


**Figure 4.12** Foam ability and foam stability at different pH solution.

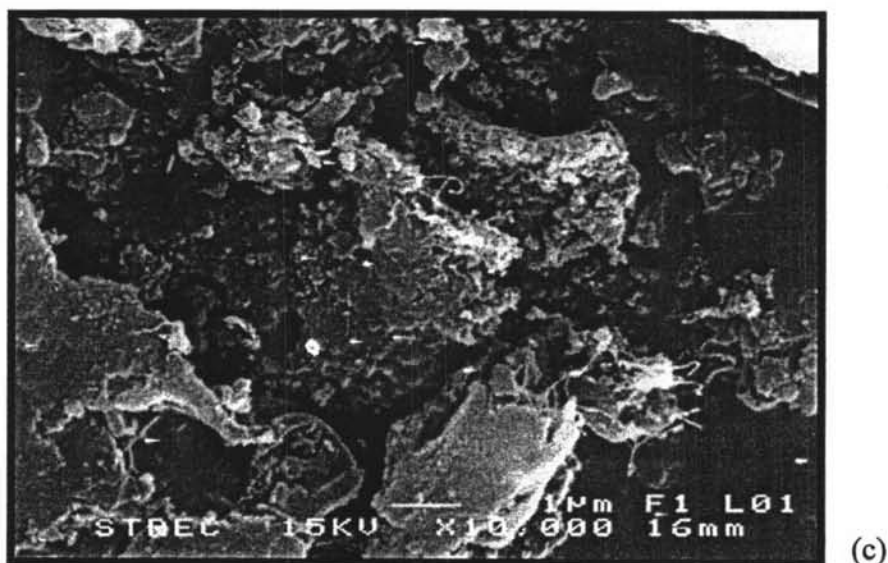
Since the PCZ of silica and SWNTs were 4 and 5.5, respectively so at pH 3 both charge of silica and SWNTs were positively and we used anionic surfactant then it removed both particles but if we consider in the foam stability when we adjust the pH solution by hydrochloric acid, the counterion- $H^+$  come to balance the charge between the head of surfactant. Consequently foam ability was high and foam stability was low because it reduced the repulsive force between foams, Figure 4.12. From this reason, the large particle-silica-was hard to remove to the top of the column so the percentage of carbon purity is higher than another pH solution. Furthermore at pH 5 the charge of SWNTs was positively and silica was negatively so the anionic surfactant can remove only SWNTs but from Figure 4.12 the foam stability at pH 5 was higher so the silica particle was removed to the top of the column, too then the percentage of carbon purity decreased. Finally, at pH 7 the charge of SWNTs and silica are negatively so the anionic surfactant did not removed both particles. But the result of foam stability, Figure 4.12, was high then the foam was able to remove both particles and made the percentage of carbon purity decrease.

4.3.4 Scanning Electro Microscope Results (SEM)

(a)



(b)



**Figure 4.13** Scanning electron microscopy (a) Raw SWNT, (b) SWNTs after dissolved catalyst particles, (c) SWNTs after dissolved catalyst particles and froth flotation process.

From Figure 4.13 showed the SEM image of SWNTs before and after treated by HCl acid. As can be seen the image, Figure 4.13 (c), after froth flotation process the SWNT still rap the silica molecule then the percentage of carbon purity was not high. So in the next section the dissolving silica molecule was necessary.

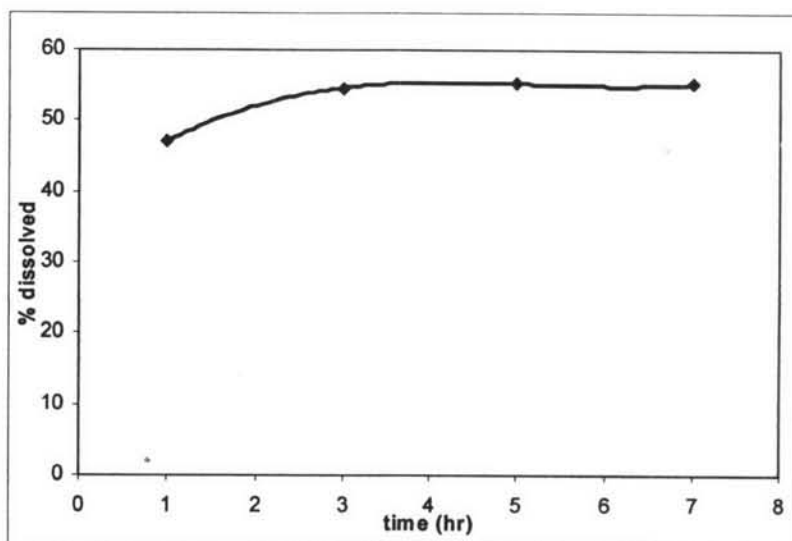
#### 4.4 Silica Dissolution Results

The SWNTs which used in this section were dissolved catalyst particles with the optimum condition in part 4.2.

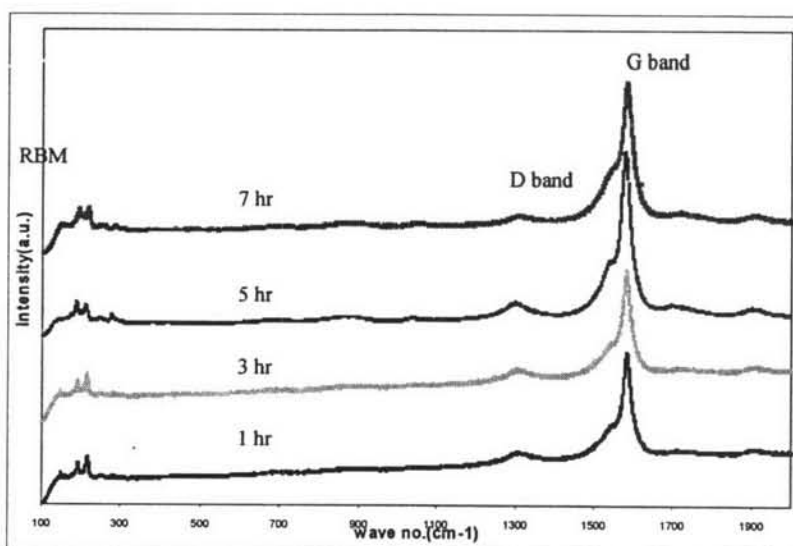
##### 4.4.1 Effect of Sonication Time

The SWNTs 0.1 g were future dissolved silica by sodium hydroxide (NaOH), which a concentration at 10 M about 30 ml and placed into the sonication bath at 70°C. An atomic analysis spectroscopy (AAS) was used to determine the concentration of dissolved silica particle. Figure 4.14 summarizes the result of percentage of silica dissolved at different sonication time.





**Figure 4.14** The effect of sonication time to dissolve silica particle.



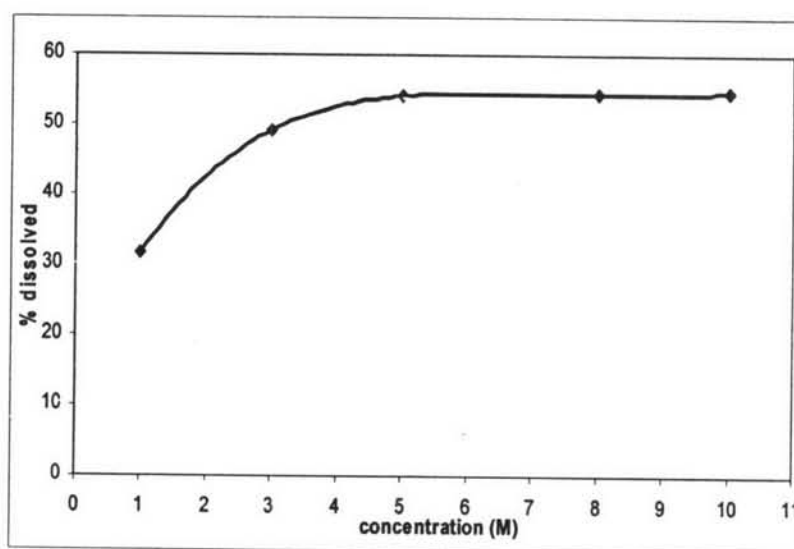
**Figure 4.15** Raman spectra of SWNT treated by NaOH with different sonication time at 70°C.

From Figure 4.14, the percentage of silica dissolved was increased when increased the sonication. From the Raman spectra in Figure 4.15, all peaks of G-band, D-band and RBM were found in all samples indicated the carbon structure

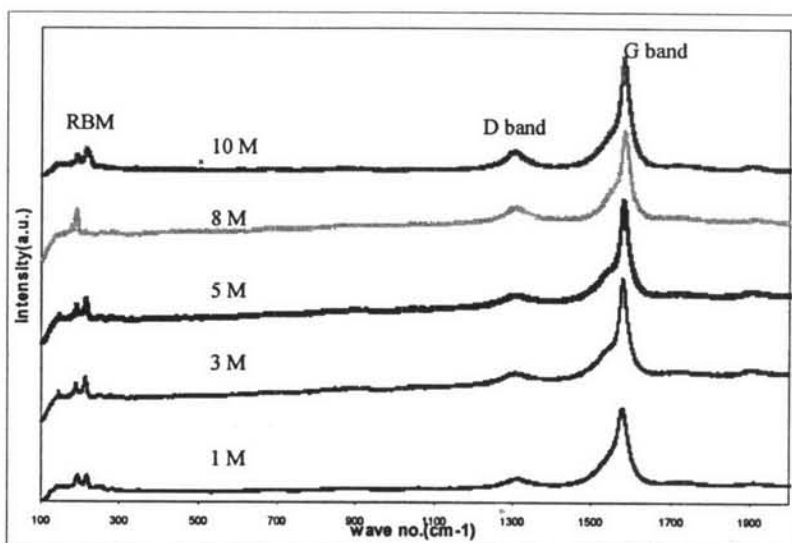
was not destroyed by the NaOH. Then, in the next part, the experiment was operated at 3 hour of sonication to make sure the highest silica were dissolved

#### 4.4.2 Effect of Sodium Hydroxide Concentration

In this part was sonicated at 3 hr and operated at 70°C. The same procedure as mentioned above was done. We also used AAS to determine the dissolved silica particle and the result was shown in Figure 4.16.



**Figure 4.16** The effect of NaOH concentration to dissolve silica particle.

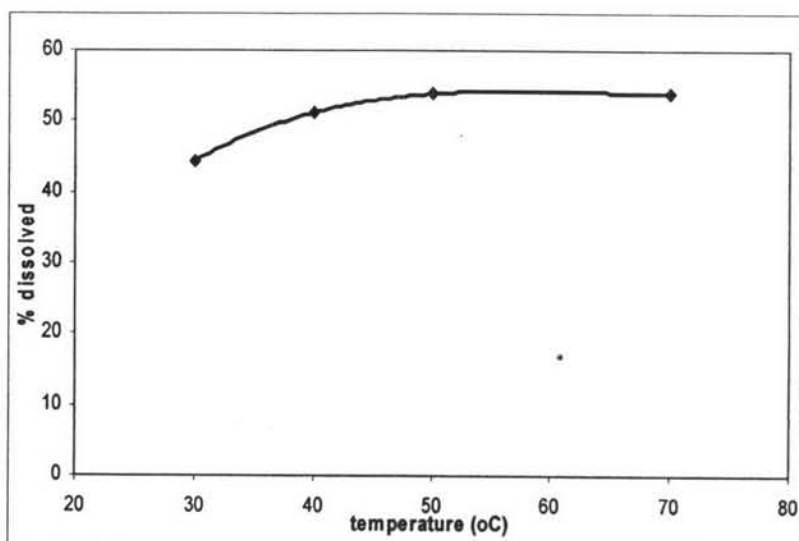


**Figure 4.17** Raman spectra of SWNTs treated by NaOH with different concentration at 70°C.

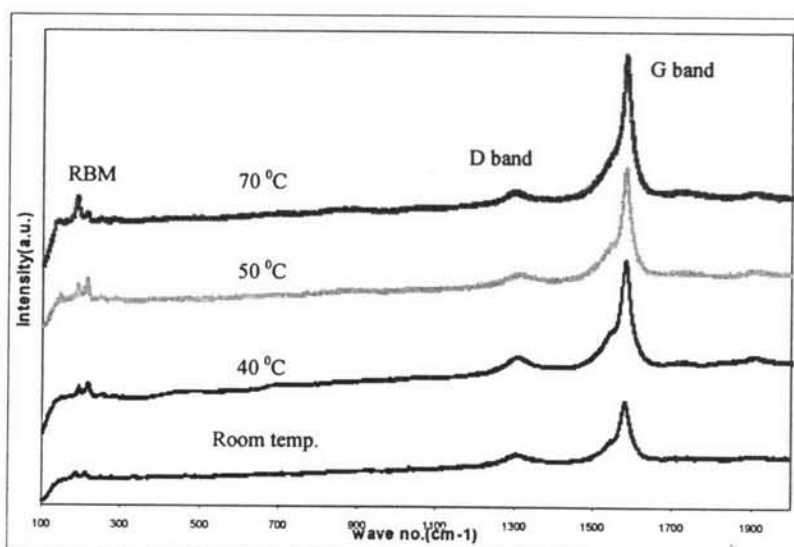
From Figure 4.16 showed the effect of NaOH concentration, when the concentration increased the percentage of silica dissolved was increased too. The Raman results (Figure 4.17) suggest that NaOH did not changed the carbon structure of the SWNTs. Hence, the optimum NaOH concentration, 5M, was used in next experiments.

#### 4.4.3 Effect of Reaction Temperature

The experiment procedure was same as above but this part was done in the different reaction temperature. In this section was operated at 5 M of NaOH and sonicate for 3 hour. The AAS result of metal dissolved was shown in Figure 4.18.



**Figure 4.18** The effect of reaction temperature for dissolve silica particle.



**Figure 4.19** Raman spectra of SWNT treated by NaOH with different temperature.

The effect of reaction temperature was expressed in Figure 4.18. As we can see, when the temperature increased the percentage of silica dissolved was increased too. After 50°C the percentage was changed a little so the optimum

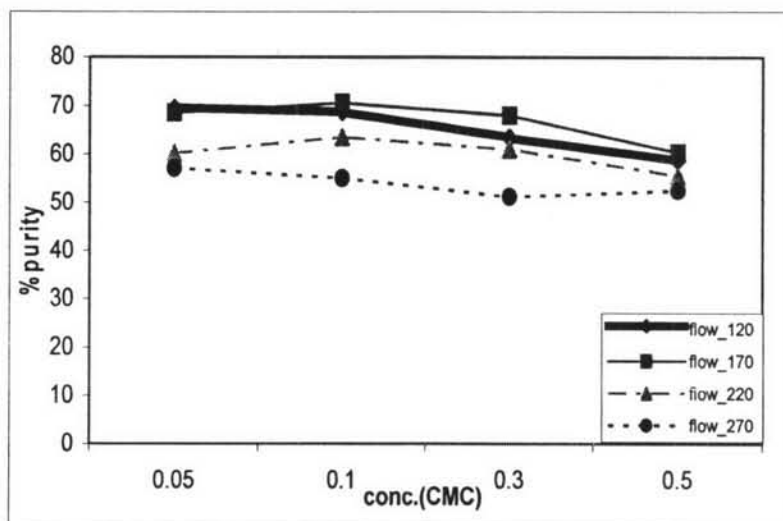
temperature was 50°C. From the Raman spectra in Figure 4.19 illustrated the temperature was not destroyed the structure of SWNTs.

#### 4.5 Froth Flotation Results (After dissolved catalyst and silica particles)

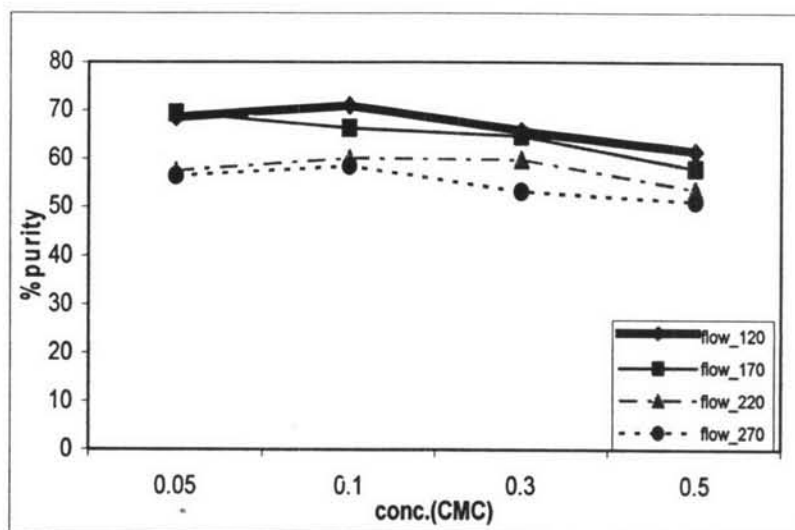
The SWNTs which used in this section were dissolved catalyst and silica particles, with the optimum condition in part 4.2 and 4.4, respectively. The froth flotation was further used to and silica particle for the carbon nanotubes characterization, Temperature Programmed Oxidation (TPO) technique was employed to determine the quantity of the samples after the froth flotation.

##### 4.5.1 Effect of Surfactant Concentration

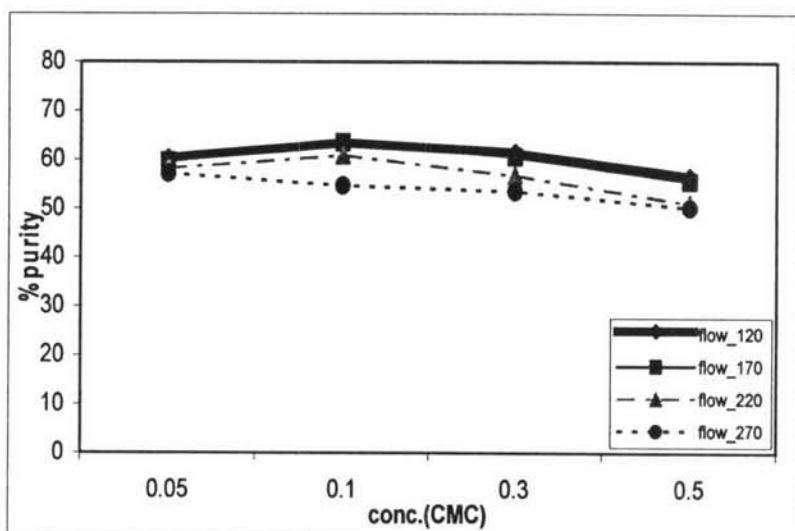
After dissolve metal and silica particle with HCl and NaOH, respectively. The froth flotation process was applied to concentrate the SWNTs. In this study we also used an anionic surfactant, sodium dodecylbenzensulfonate. Figure 4.20 showed the results in terms of carbon purity of SWNTs at different surfactant concentration.



(a)



(b)



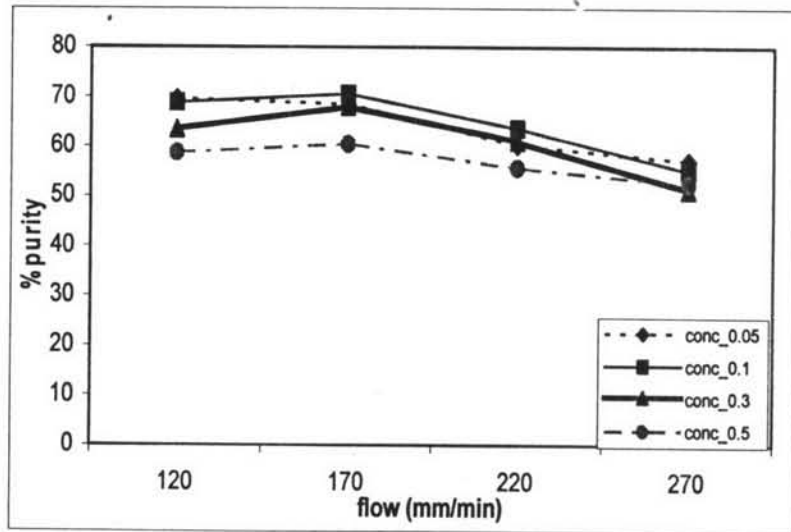
(c)

**Figure 4.20** Effect of surfactant concentration (a) pH 3, (b) pH 5, (c) pH 7.

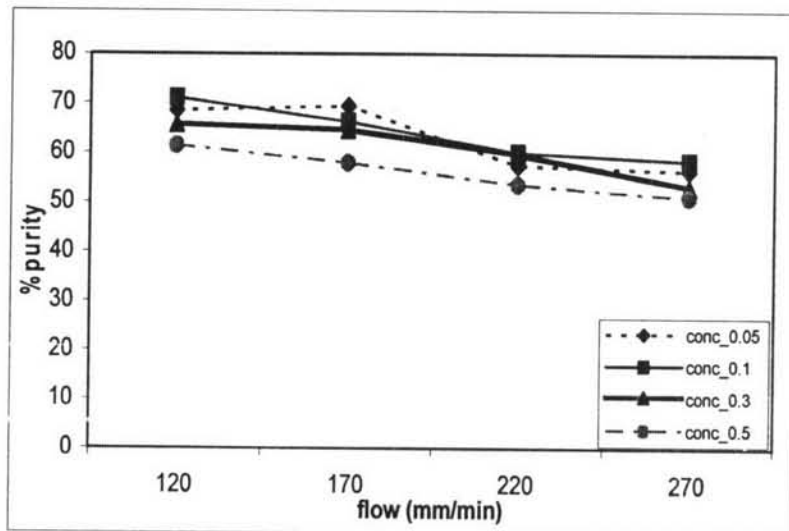
As can be seen in Figure 4.20 the percentage of carbon purity decreased with increasing surfactant concentration. The deterioration of carbon purity was due to the ability of surfactant to remove the particle in the solution. The higher surfactant concentration, the higher particle can remove. So at high concentration both SWNTs and impurity particles were removed to the top of the column then the carbon purity was decreased.

#### 4.5.2 Effect of Air Flow Rate

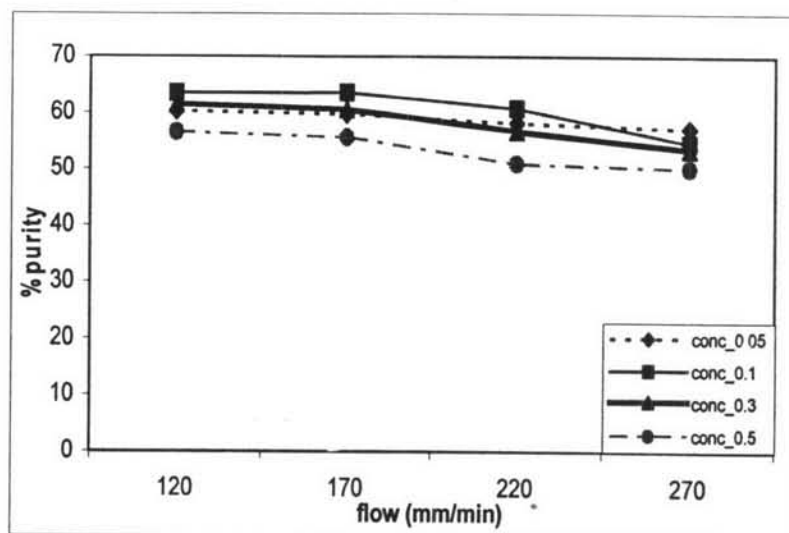
The air flow rate is the key of separation. This factor was corresponded with the foam generation and the ability of particle removed. This section was studied in the different flow rate, 120 ml/min, 170 ml/min, 220 ml/min and 270ml/min.



(a)



(b)



(c)

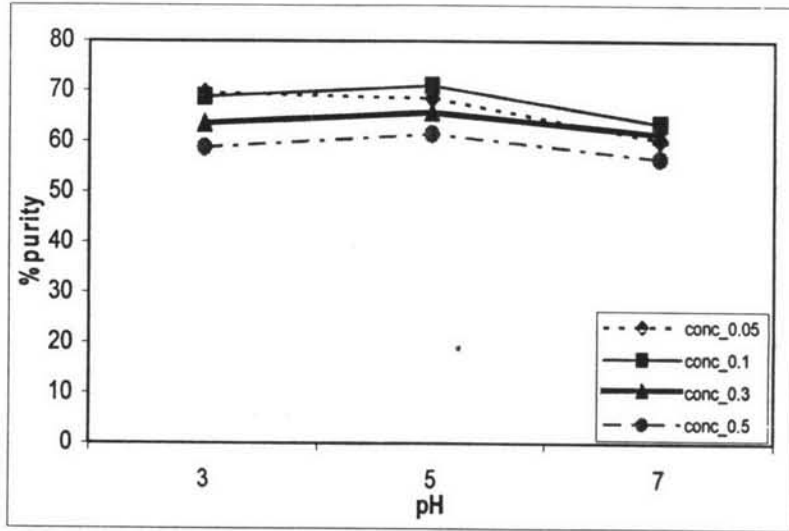
**Figure 4.21** Effect of air flow rate (a) pH 3, (b) pH 5, (c) pH 7.

The Figure 4.21 expressed the effect of air flow rate with different pH solution. The air flow rate relate to the power of the air to remove the particle, at low flow rate, 120 ml/min, the SWNTs was removed and gave a high carbon purity but if we consider in the higher flow rate the carbon purity was decreased because the impurity was removed to the top of the column too. So the optimum flow rate was 120 ml/min.

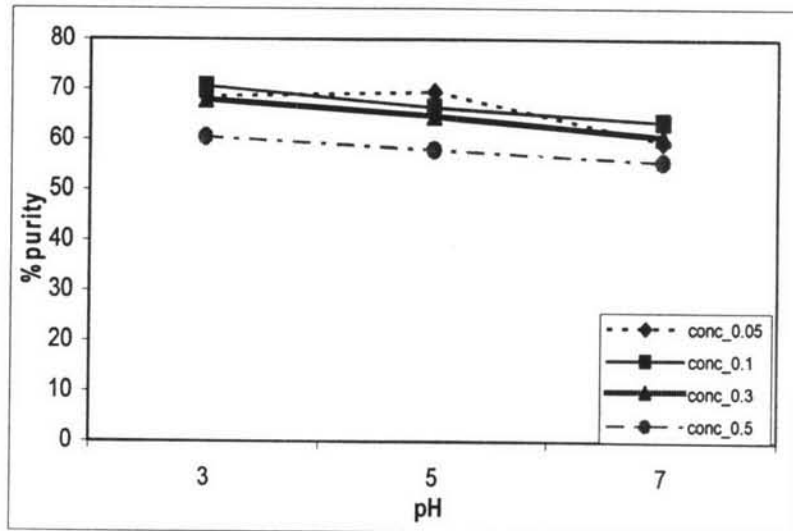
#### 4.5.3 Effect of pH Solution

The pH solution can change the charge of particle. Since the point of zero charge (PZC) of silica and SWNTs was different so in this part use the pH solution as the key of separation.

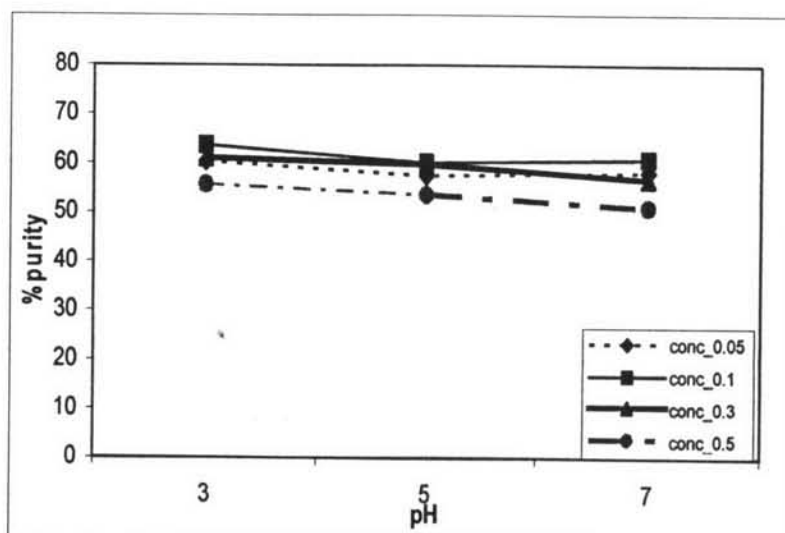




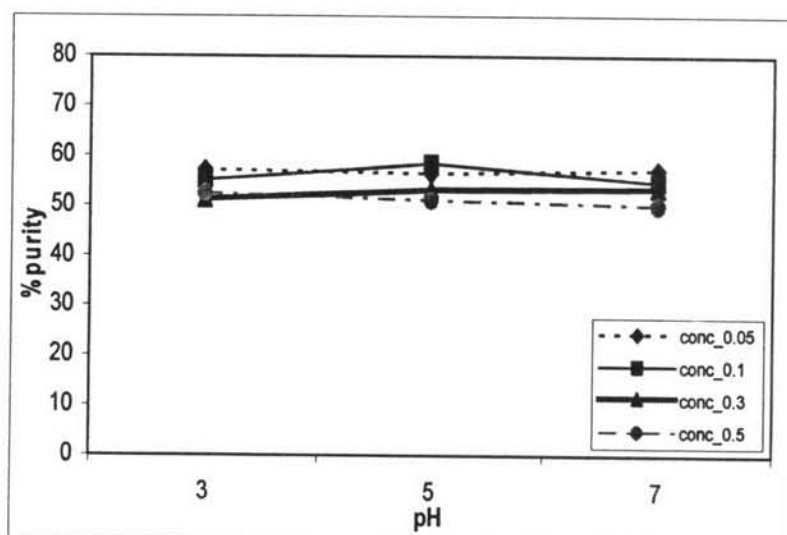
(a)



(b)



(c)

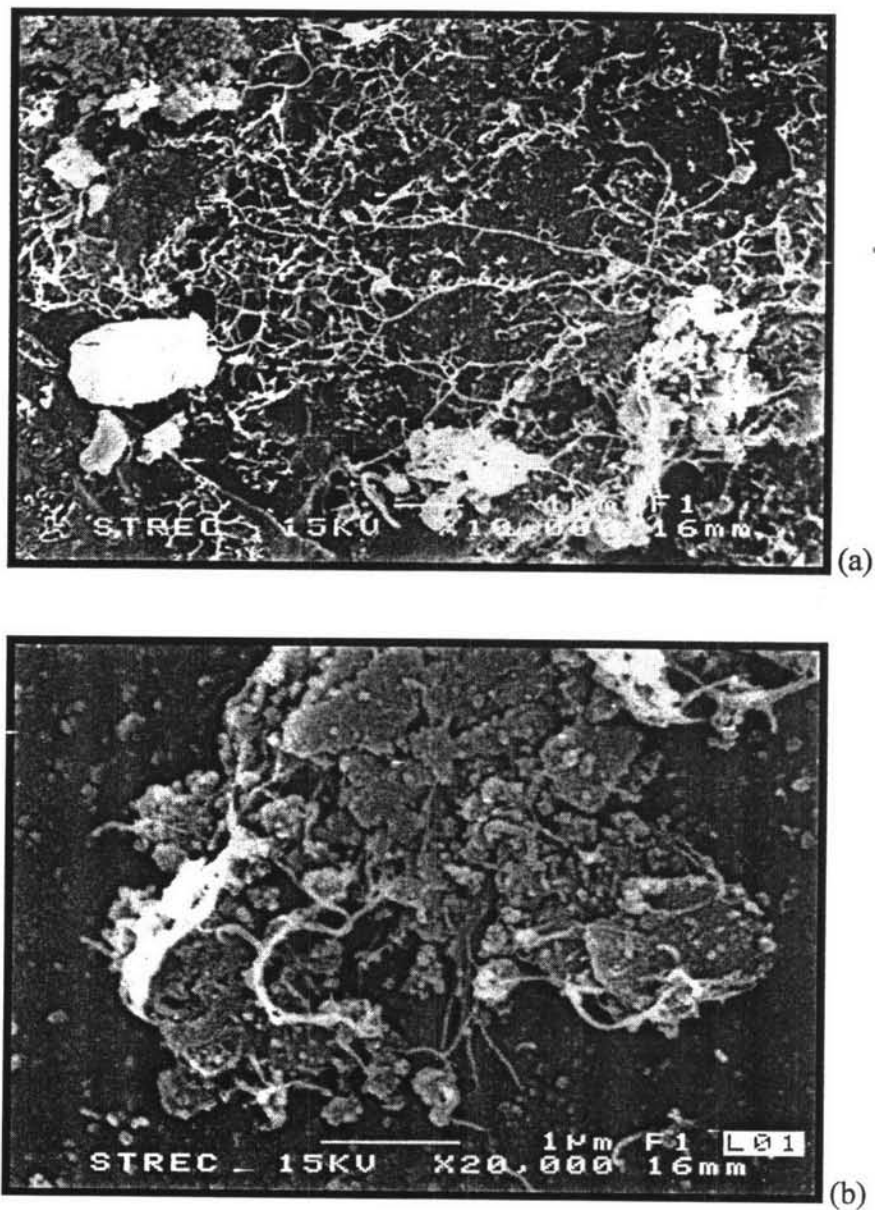


(d)

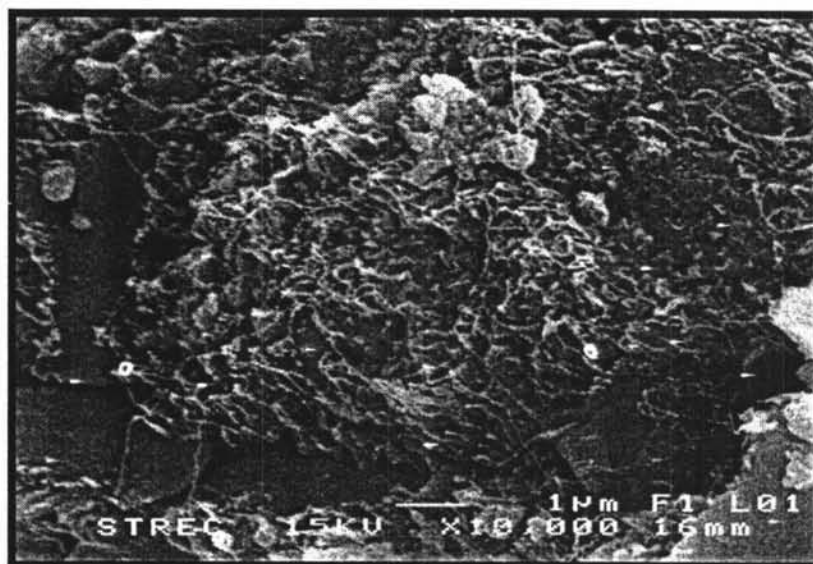
**Figure 4.22** Effect of pH solution (a) air flow rate 120 mm/min, (b) air flow rate 170 mm/min, (c) air flow rate 220 mm/min, (d) air flow rate 270 mm/min.

From Figure 4.22, at pH 3 gave the highest percentage carbon purity and decreased a little in pH 5 and pH 7. This result was due to the effect of the counterion- $H^+$  as we described in part 4.3.

## 4.5.4 Scanning Electro Microscope Results (SEM)



**Figure 4.23** Scanning electron microscopy of SWNTs after dissolved catalyst and silica particles (a) x 10,000 (b) x 20,000



**Figure 4.24** Scanning electron microscopy of SWNTs after dissolved catalyst and silica and froth flotation process.

From Figure 4.23 showed the SEM image of SWNTs after dissolved catalyst and silica as we can see the particle had less silica if compared with Figure 4.21 and the Figure 4.24 was illustrated the SWNTs after froth flotation and it showed that the particle had high carbon nanotubes and small other impurities.