CHAPTER IV

EXPERIMENTAL

Procedures of experiment and analysis techniques are described in this chapter. This research emphasizes on removal of dye in aqueous solutions with CNPs adsorbent as a batch operation which are explained in 4.3 and 4.4. The analysis instruments necessary for characterization all relevant substance and methods are also shown in 4.5.

Before adsorption experiment, synthesizing of CNPs with magnetic characteristics are conducted with available equipment. The experimental apparatus for synthesizing CNPs are represented in 4.1 and the experimental procedures for synthesizing CNPs are also described in 4.2 as follows.

4.1 Experimental setup for synthesizing of CNPs

The preliminary part of this work is to use a tubular quartz reactor for synthesizing of carbon nanoparticles. There are many researches which use a similar reactor with single and dual tube furnace reactor for pyrolysis of various carbon sources. For this work, a single tube furnace reactor is applied from Charinpanitkul's research [7]. The advantage of the single tube furnace is the continuity of temperature profile in the tube is better than that of the dual furnace although it has a problem in controlling the vaporization temperature of the raw materials used in the process. The schematic diagram of experimental apparatus has shown in Figure 4.1.

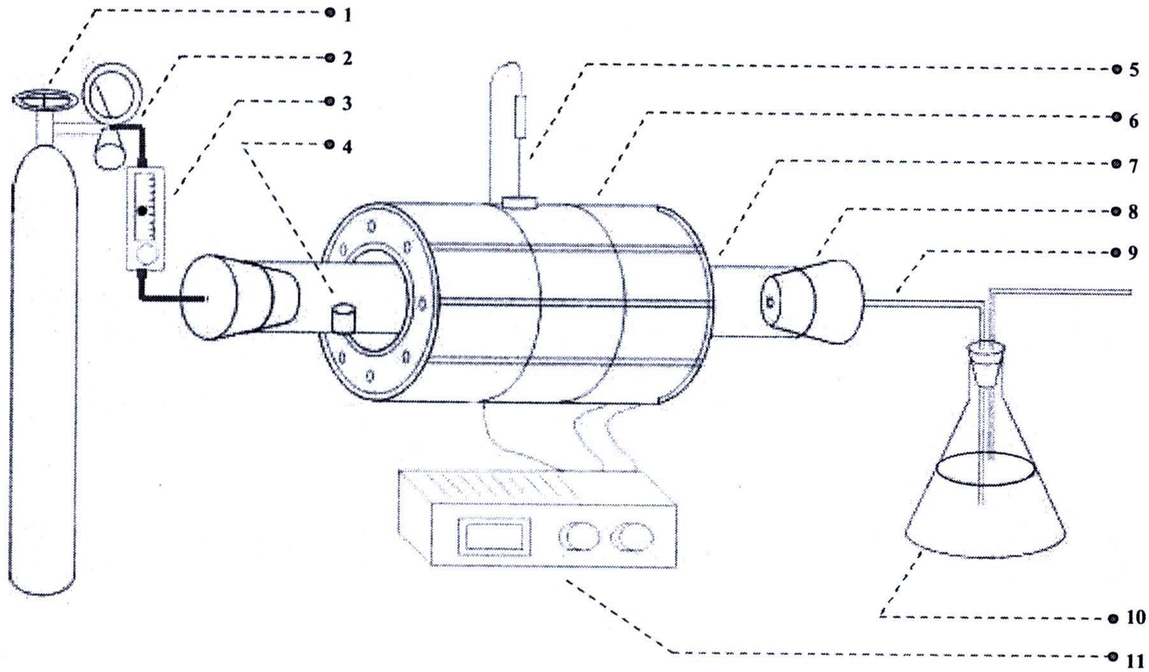

Figure 4.1 Schematic diagrams of experimental apparatus for thermal co-pyrolysis
1) Nitrogen storage tank 2) Regulator 3) Flow meter 4) Ceramic boat
5) Thermocouple 6) Electrical furnace 7) Tubular quartz reactor 8) Silicone plugs
9) Rubber tube 10) Water trapping 11) Temperature controller

It is consisted of tube furnace reactor (Figure 4.2) equipped with temperature controller (Figure 4.3) for controlling the pyrolysis temperature at 900 °C. Quartz tube with 4.1 cm inner diameter and 60 cm length (Figure 4.4) is used for co-pyrolyzing the mixture of precursors. The gas supplier will provide carrier gas during the pyrolysis process and silicone plug (Figure 4.5) has been used for preventing the process from other gas. The gas from the process will be removed by trapping with water before purging to outside.

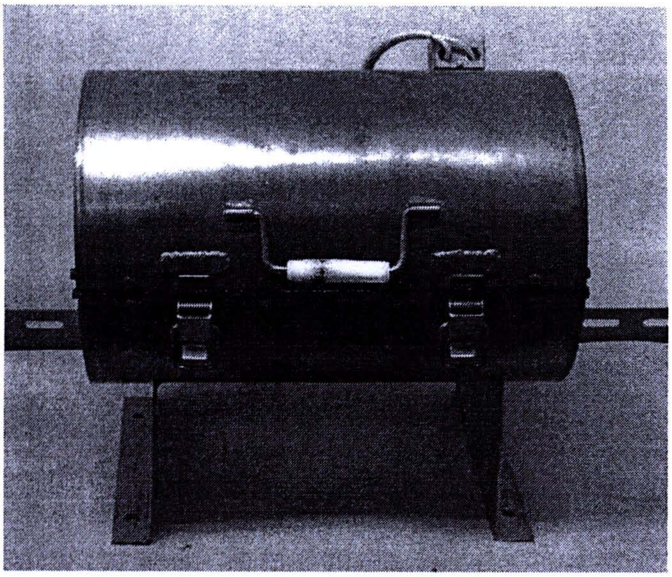

Figure 4.2 Electrical furnace

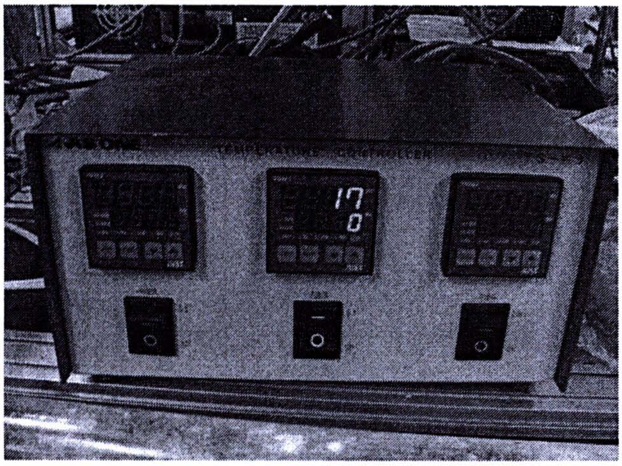

Figure 4.3 Temperature controller

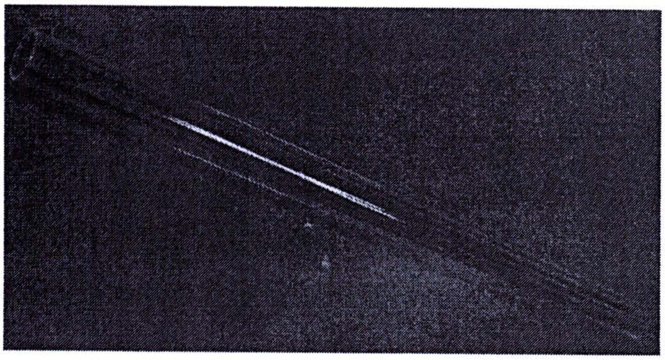

Figure 4.4 Quartz tube with inner diameter of 41 mm.

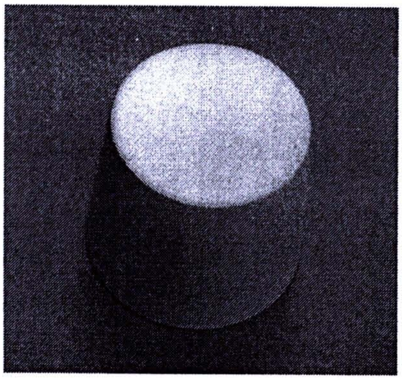

Figure 4.5 Silicone Plug for controlling leakage of gas

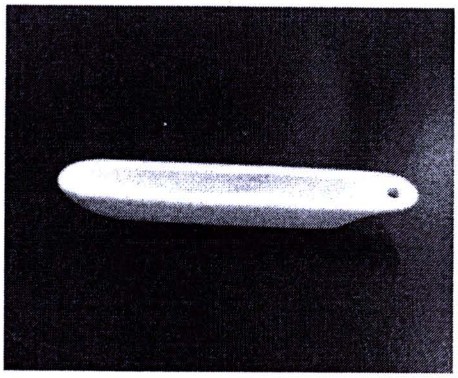

Figure 4.6 Ceramic boat for situating raw materials

4.2 Experimental procedures for synthesizing CNPs by co-pyrolysis

The tubular quartz reactor set within the temperature controlled furnace shown in figure 4.1 is employed for co-pyrolyzing mixture of ferrocene and glycerol to synthesize carbon nanoparticles. The apparatus consists of a single-stage furnace equipped with temperature controller and quartz tube (inner diameter, 41 mm). The nitrogen gas (nitrogen 99.99%) which used as carrier gas is fed continuously through a flow meter at desired flow rate. The experimental procedures are shown as follows;

a) The furnace temperature will be set a designated set point of 900 °C by using temperature controller.

b) Ferrocene (Sigma-Aldrich, ≥98% Fe, b.p. = 249 °C) and glycerol (Ajax Chemicals, b.p. = 290 °C) are mixed to adjust a specific molar ratio of 1:5 of ferrocene to glycerol and then are loaded into a ceramic boat (Figure 4.6) which is placed at the entrance of the quartz tube reactor where the temperature is kept above the vaporization temperature of the mixture.

c) The decomposition of the mixture occurred at about 400□C, resulting in free carbon and iron vapor which are carried over by the carrier gas at 100 ml/min through the tube into the hot zone where self-assembling and catalytic growth reactions took place.

d) Large quantities of the as-grown deposit films as in Figure 4.6 can be found as accumulation along the inner surface of the quartz tube after reaction complete (30 min). The detailed experimental parameters are represented in Table 4.1.

Table 4.1 The condition for co-pyrolysis work studied

F[a]:G[b] molar ratio	1:5
Amount of F/G (g)	2.3022/0.9300
Amount of Fe/C (g)	55.845/636.5671
Carrier gas	N_2
Operation temperature (□C)	900

[a]Ferrocene, [b]Glycerol

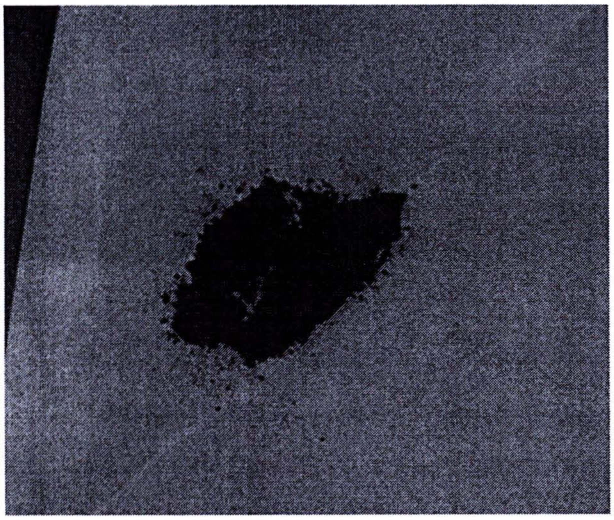

Figure 4.7 As-grown carbon nanoparticles obtained from co-pyrolysis process

4.3 Experimental setup for dye pollutant removal

4.3.1 Preparation of dye solution

Synthetic dye solution of B5, R31 and MB are prepared by dissolving the dyes powder in distilled water at desire initial concentration. The model structure of all dyes in this study is shown in figure 4.8. The wavelength of maximum absorbance (λ_{max}) was analyzed with a spectrophotometer by scanning in the visible range of 400 to 800 nm, as shown in Table 4.2.

Table 4.2 Properties of dyes in this study

Name in Color Index	Commercial Name	MW.	λ_{max} (nm)	Molecular Formular
C.I. Reactive Black 5 (B5)	Benefix Black B	991.82	595	$C_{26}H_{21}N_5O_{19}Na_4S_6$
C.I. Reactive Red 31 (R31)	Benecion Red P8B	864	545	$C_{30}H_{15}N_7O_{15}Na_5Cl$
C.I. Basic Blue 9 (MB)	Methylene Blue	319.85	664	$C_{16}H_{18}N_3SCl$

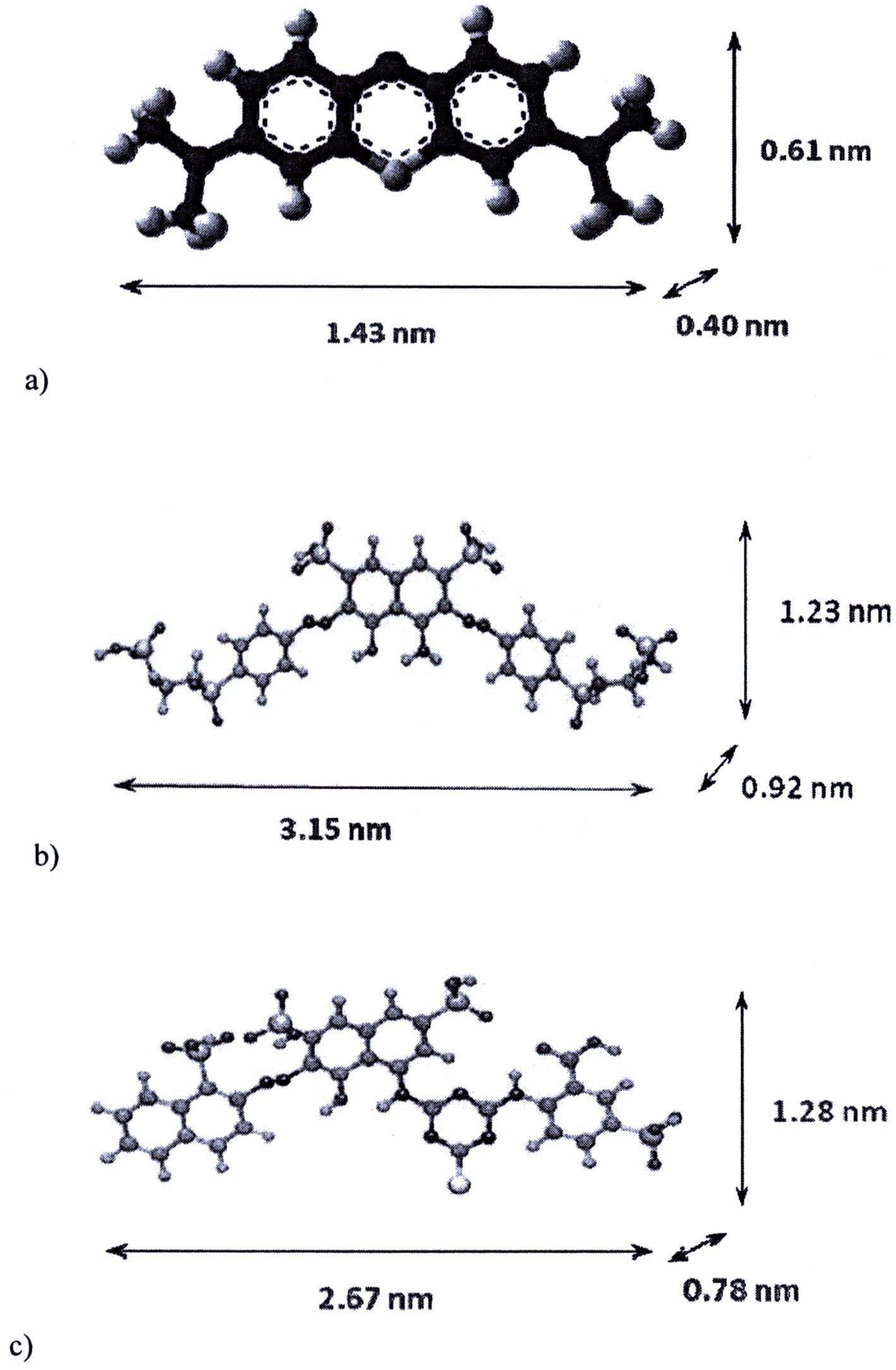

Figure 4.8 Molecular model of adsorbates: a) Methylene Blue, b) Reactive Black 5 and c) Reactive Red 31

4.3.2 Batch experimental

Batch system is used in sorption experiment with a shaker bath as shown in figure 4.9. All batch experiments are conducted at designated initial dye concentration, pH solution and dose of adsorbents by shaking 100 ml dye solution in 250-ml flask, using a speed of 100 rpm with a temperature of 25 ± 2°C in water tank.

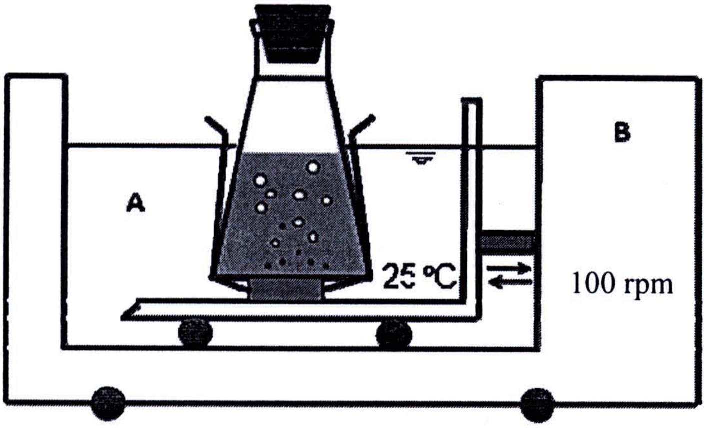

Figure 4.9 Schematic diagram of batch system for adsorption experiment (A) dye solution in 250-ml flask; (B) horizontal shaker bath with controlled temperature of 25 °C.

4.4 Experimental procedures for dye sorption onto synthesized CNPs

The adsorption and desorption of the synthetic dye on synthesized MWCNTs are investigated. All experiments are conducted in batch system. The experimental are carried out in 250 ml glass bottle at 25 ± 2°C, and 100 ml of dye solution of known initial concentration which are prepared in distilled water. NaOH and HCl 0.01 mM are used to adjust the initial pH value of solution. CNPs as adsorbent are added into glass bottle with desired quantity. Then, CNPs are dispersed in solution with ultrasonic for 10 minutes and shaking by shaker bath at a speed of 100 rpm. The concentration of dyes in effluent solution is measured by UV-visible spectrophotometer (UV-1700PC, Shimadzu, Japan). Three repeated experiments were conducted, leading to a summarized result. Table 4.3 showed variables of this study. The adsorption procedures are described below.

a) Condition of contact time study is the initial dye concentration of 40 mg/L, 0.5 g/L adsorbent and initial pH value of 6. Take sample until the adsorption reach equilibrium to determine the minimum time require.

b) Effect of the initial dye concentration is investigated to determine the maximum adsorption capacity and compare with the adsorption isotherm model. The experiments are performed in the range of 10 to 100 mg/L, 300 minutes of contact time, 0.5 g/L adsorbent and initial pH value of 6.

c) Effect of CNPs loading are performed in the range of 0.3 to 0.9 g/L, initial concentration of 60 mg/L, 300 minutes of contact time and initial pH value of 6.

d) Effect of initial pH value is performed in the range of 3 to 11.

Table 4.3 Variables of the adsorption experiments.

Study	Variables			
	Initial dye concentration (mg/L)	Initial pH value	Dose of adsorbents (g/L)	Temp. and Contact time (°C and min)
Effect of contact time	40	6	0.5	25 ± 2, 300
Effect of initial dye concentration	10 - 100	6	0.5	25 ± 2, 300
Effect of CNPs loading	60	6	0.3 - 0.9	25 ± 2, 300
Effect of initial pH values	100	3 - 11	0.5	25 ± 2, 300

The condition of desorption experiment are initial dye concentration of 100 mg/l, 0.5 g/L adsorbent and 24 hours of adsorption time at 25 °C and the initial pH value of 6. After adsorption, adsorbents were seperated from the solution by an external permanent magnetic and oven-dried at 80 °C to a constant mass. The solution was measured the concentration with UV-spectrophotometer.

Exhausted CNPs were suspended in distillated water which was adjusted the pH value. In this study, the range of initial pH value of the solution is 3-11. Re-adsorption experiment following the procedure described above for 3 cycles.

4.5 Analytical Instruments

The morphology of the as-grown samples was first analyzed by Scanning electron microscope (SEM, JEOL: JSM-5410LV, Japan). The structure and crystallinity of the as-grown samples were investigated by Transmission Electron Microscope (TEM, JEOL: JEOL-2010, Japan). The crystallinity of CNPs was evaluated by X-ray Diffraction analysis. While dynamic light scattering (DLS; MALVERN, ZETASIZER 300HSA) is employed for determining particles size distribution and zeta potential of the obtained products.

4.5.1 Scanning Electron Microscopy (SEM)

The microstructure of the carbon nanoparticles were studied by using Scanning Electron Microscopy (SEM), JSM-5410LV (Figure 4.10). The specimen used for SEM analysis was either obtained from the as-grown film or scratched (Figure 4.7). The sample was prepared by grinding using a granite mortar and then appropriate amount of the prepared samples were mounted on carbon tape. The specimens were loaded into the sample chamber and then the observation was conducted immediately with using image catcher scanner for taking the photos.

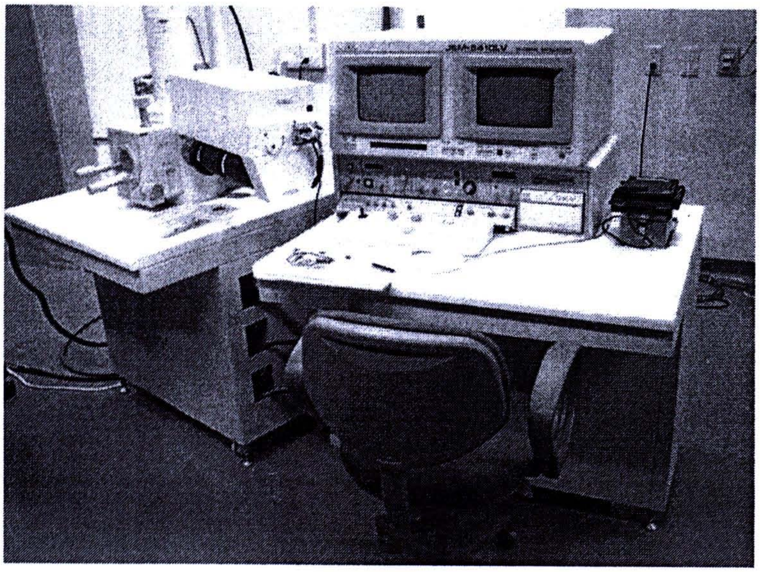

Figure 4.10 Scanning Electron Microscope (SEM, JEOL: JSM-5410LV, Japan)

4.5.2 Energy Dispersive X-ray Spectroscopy (EDX)

Energy dispersive X-ray spectroscopy is a relatively simple technique used to identify the elemental composition of a cubic micron of material. The equipment is attached to the SEM to allow for elemental information to be gathered about the specimen under investigation. The technique is non-destructive and has a sensitivity of >0.1% for elements heavier than C.

EDX works by detecting X-rays that are produced by a sample placed in an electron beam. The electron beam excites the atoms in the sample that subsequently produce X-rays to discharge the excess energy. The energy of the X-rays is characteristic of the atoms that produced them, forming peaks in the spectrum. The individual elements may have more than one peak associated with them and some peaks from different elements may overlap to a certain degree.

The samples were analyzed by energy-dispersive X-ray spectra (EDX) to show elemental component in the obtained particles after co-pyrolysis process. The elemental analysis by EDX is achieved by monitoring and analyzing X-rays emitted by matter when bombarded with charged particles. The JEOL JSM-5410LV SEM is equipped with an Oxford Link Isis - Energy Dispersive X-ray Spectrometer (EDX), which serves as an elemental analyzer. The solid state Si(Li) detector, permits the detection of X-rays and identification of the elements responsible for the emission in a microscopic location.

4.5.2 Transmission Electron Microscopy (TEM)

TEM analysis used in this work is JEOL-2010 as shown in Figure 4.11. The specimen for analyzing was elaborately prepared by grinding as-grown particles deposit (Figure 4.7) by a granite mortar. The appropriate amounts of carbon nanoparticles were suspended in toluene before ultrasonic treatment with the sufficient time for ensuring its uniform dispersion. A few drop of clear solution was poured onto a microgrid covered with a carbon thin film (Figure 4.12). The specimen was loaded into the sample chamber and waiting for the vaccum condition and steady state inside the chamber for 30 min.

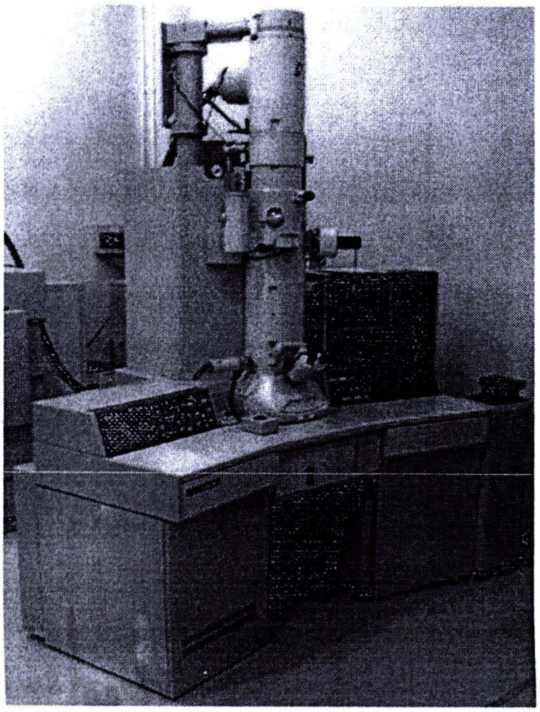

Figure 4.11 Transmission Electron Microscopy (TEM JEOL: JEOL-2010, Japan)

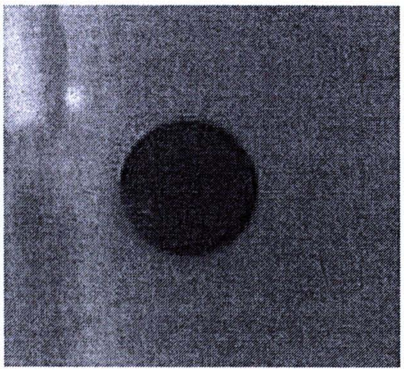

Figure 4.12 Copper grid coated with carbon films for Transmission Electron Microscopy

4.5.3 Dynamic Light Scattering (DLS)

For particle size distribution analysis, Dynamic Light Scattering (DLS) using ZETASIZER 300HSA as shown in Figure 4.13 was employed. It should be noted that DLS is based on the measurement of the dispersion of light scattering by particles motion in a static solvent such as toluene, water, acetone or ethanol, the measured particle size should correspond to hydrodynamic diameter but not to the real diameters of the particles with complex structures. However, DLS results were expected to give at least the qualitative trend in particle sizes distribution. Moreover, zeta potential of sample can be obtained by this measurement. For preparation of the sample, DLS specimens were also prepared by grinding as-grown particles (Figure 4.7) by the granite mortar and then suspended in toluene before ultrasonic treatment with the sufficient time for ensuring its uniform dispersion. Afterwards, the specimen was diluted by toluene again until they became transparent and ultrasonicated again for 15 min before loading to the sample cell for analysis.

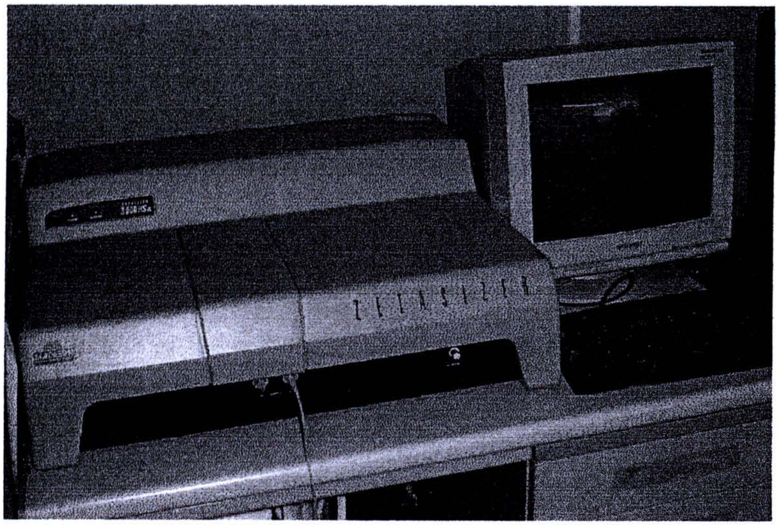

Figure 4.13 Dynamic Light Scattering (DLS: ZETASIZER 300HSA)

4.5.4 Porosity analysis

Porous structure of the obtained CNPs (see figure 4.7) by co-pyrolysis process was characterized by nitrogen adsorption – desorption at 77 K with a BET analyzer (*BEL: BELSORP-mini, Japan*) as shown in Figure 4.14. The CNPs sample about 0.8 grams was pretreated at 150°C under vacuum for 3 hours in order to remove moisture and gaseous residual. Brunauer–Emmett–Teller (BET) surface area (S_{BET}) and total pore volume (V_{tot}) were determined by BET equation and mesopore volume (V_{mes}) was determined by BJH (Barrett-Joyner-Halenda) plot method. Moreover, average pore diameter of synthesized CNPs was also determined.

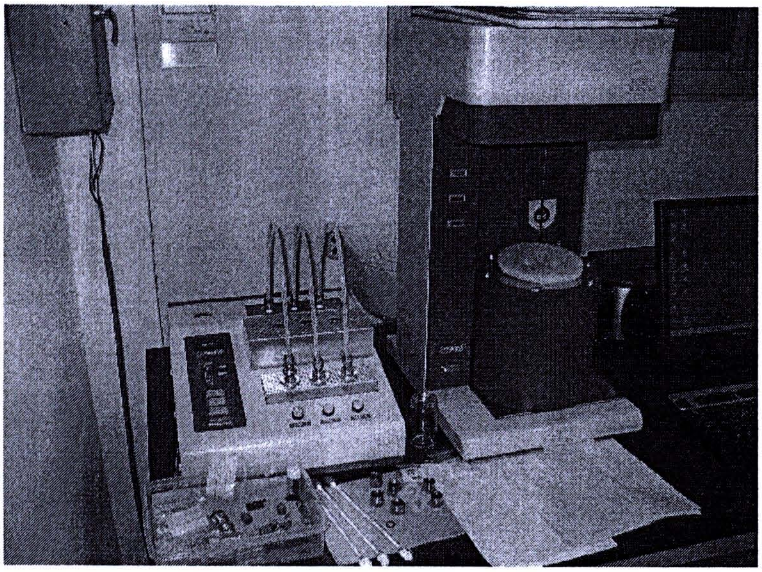

Figure 4.14 N_2 adsorption – desorption analyzer (*BEL: BELSORP-mini, Japan*)

4.5.5 X-ray diffraction (XRD)

Structure and crystallinity of CNPs particles was determined by X-ray diffraction analysis. The as-grown CNPs samples (see Figure 4.7) were characterized by X-ray powder diffraction (*XRD, SIEMENS D 5000, Japan*) as shown in Figure 4.15 using CuKα radiation with Ni filter in the 2q range of 20-80 degrees resolution 0.04°. The crystallite size was calculated from Scherrer's equation.

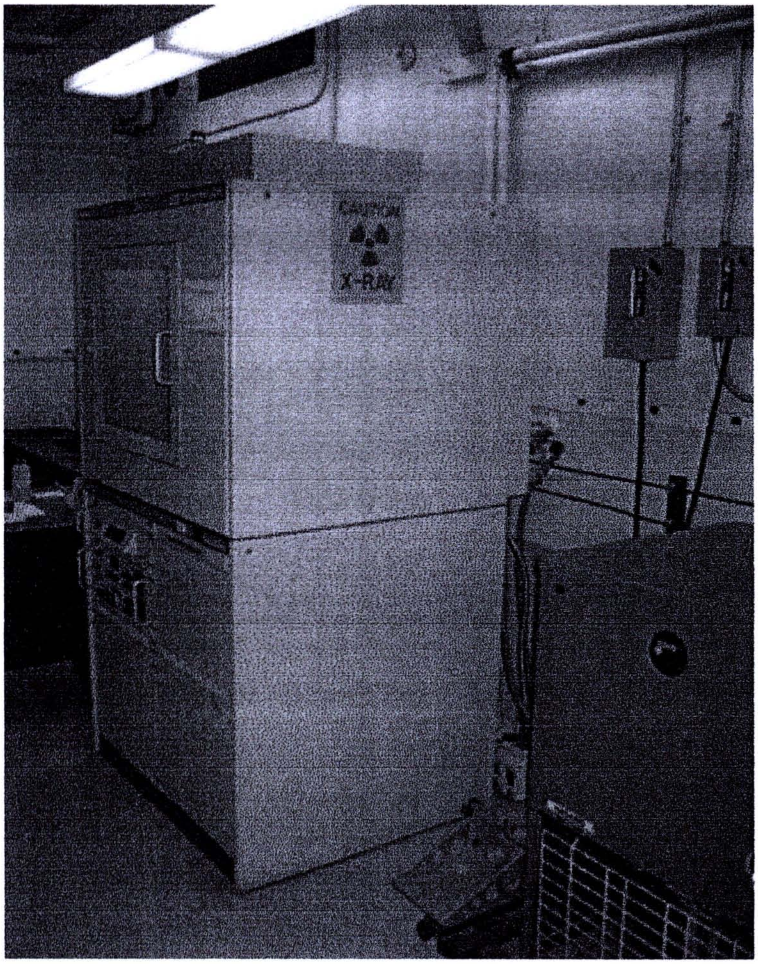

Figure 4.15 X-ray diffraction analyzer (*XRD, SIEMENS D 5000, Japan*)

4.5.6 UV-Visible spectrophotometer

For measure the concentration change, Ultraviolet and visible spectrophotometer as shown in figure 4.16 was employed. The UV-Visible spectrophotometer uses two light sources, a deuterium (D_2) lamp for ultraviolet light and a tungsten (W) lamp for visible light. After bouncing off a mirror, the light beam passes through a slit and hits a diffraction grating. The grating can be rotated allowing for a specific wavelength to be selected. At any specific orientation of the grating, only single wavelength successfully passes through a slit. A filter is used to remove unwanted higher orders of diffraction. The light beam hits a second mirror before it gets split by a half mirror (half of the light is reflected, the other half passes through). One of the beams is allowed to pass through a reference cuvette (which contains the solvent only), the other passes through the sample cuvette. The intensities of the light beams are then measured at the end.

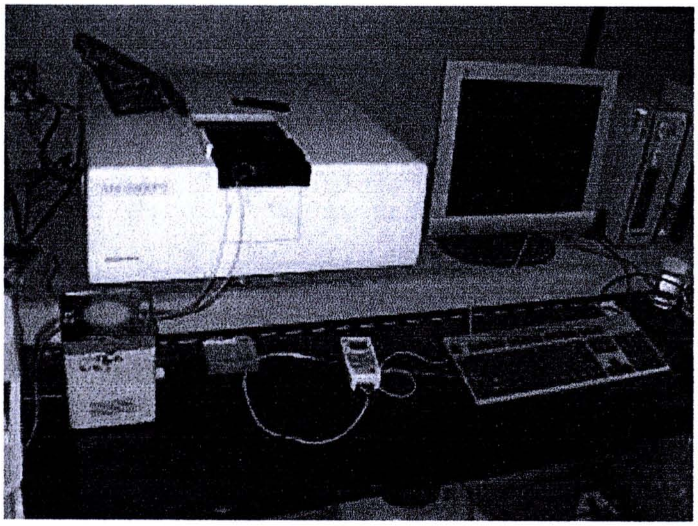

Figure 4.16 UV-vis spectrophotometer (Shimatsu: UV-1700PC, Japan)