CHAPTER IV

EXPERIMENTAL PROCEDURE

4.1 Preparation of Raw Material

Waste anthracite powder received from V. S. Coal Company Limited was sieved to classify the size of the powder. The anthracite powder size in range 0.60 – 0.710 mm was selected as raw material. The anthracite powder was sent to analyze proximate and ultimate analysis. The results of these two analyses were summarized in tables below.

Table 4.1.1 Ultimate analysis of anthracite powder (on a Dry Basis)

Elemental	%wt
Carbon	82.35
Hydrogen	2.13
Nitrogen	1.59
Oxygen	7.84

Table 4.1.2 Proximate analysis of anthracite powder (as received)

Proximate analysis	%wt
Fixed carbon	80.2
Moisture content	0.8
Volatile matter content	8.5
Ash content	10.5

4.2 Preparation of Activated Anthracite

Activated anthracites were prepared from anthracite powder by steam activation directly without carbonization because the anthracite powder already have high fixed carbon content. About 0.75 g of the anthracite powder was put in the ceramic boat and placed in a quartz tube reactor. This reactor was electrically heated in N_2 atmosphere from room temperature and to the desired temperature, which we varied in the range of 750–950°C at a constant heating rate of 20 °C /min. The steam used for activation was generated from a heating pot at a constant rate of 0.25 or 0.5 g/min, and was introduced to the reactor together with a 200 cm^3/min flow of N_2. Therefore, the mole fraction of water vapor was around 0.23 or 0.46, respectively and the activation time was varied to obtain 30-75% burn-off of the activated anthracite. Figure 4.2.1 present the quartz tube reactor which is used for steam activation.

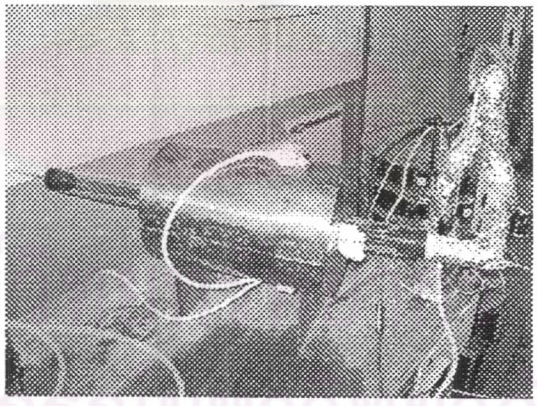


Figure 4.2.1 Quartz tube reactor

4.3 Characterization of Porous Properties

The BET surface area S_{BET}, mesopore volume V_{meso}, micropore volume V_{micro}, and pore size distribution, of each samples were determined from N_2 adsorption-desorption

isotherms measured at 77 K using the adsorption apparatus (ASAP 2000 V3.03, Micromeritics Instrument corporation or AUTOSORB-1-C, Quantachrome Corporation, USA). Pore size distribution (range of pore radii = 1.0-20 nm) and V_{meso} were evaluated by applying the Dollimore-Heal method to the desorption isotherm, whereas the t-plot method was used to estimate V_{micro}.

4.4 Supercritical Water Treated Anthracite

Supercritical water treatment is a treatment that conducts above critical condition of water (374.5 °C and 220.2 bar). About 1 g. of anthracite powder and calculated amount of water were added into ¾ " stainless steel tube reactor. This reactor was electrically heated in the furnace with a constant heating rate of 5 °C/min from room temperature to 400 °C and held at this temperature for 15min – 2 hr. At this condition the liquid water inside the reactor will vaporize and increase the pressure inside the reactor to 360 bar, which is supercritical water condition (374.5 °C, 220.2 bar). The reactor was left to naturally cool down. The sample inside was filtered and dried at 110°C before measure the weight of anthracite powder after treatment. In some case hydrogen peroxide solution (30% by volume) was used instead of distilled water to observe the effect of supercritical water oxidation on anthracite powder.

4.5 Supercritical Water Treated Activated Carbon

In this case, activated carbon was used instead of anthracite powder to observe the change of porous properties change after treatment. About 1 g of CAL carbon, activated anthracite (≈60% burn-off) and activated carbon from waste tires (≈60% burn-off) were

mixed with calculated amount of water or hydrogen peroxide solution inside ¼" stainless steel tube reactor. This reactor was electrically heated in the furnace with a constant heating rate 5 °C/min from room temperature to 400 °C and held at this temperature for 15min. At this condition the water inside the reactor will vaporize and increase the pressure inside the reactor to 360 bar, which is supercritical water condition (374.5 °C, 220.2 bar). The reactor was left to naturally cool down. The sample inside was filtered and dried at 110°C before measure the weight of activated carbon after treatment.

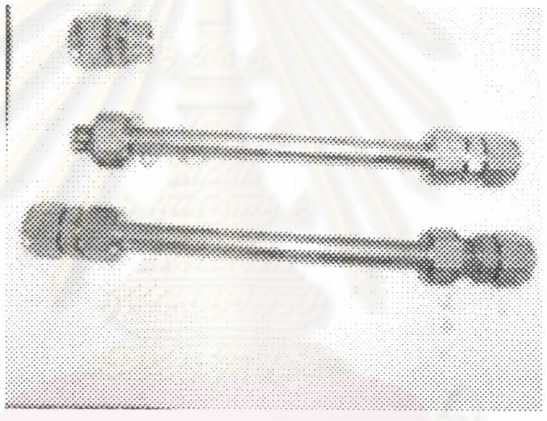
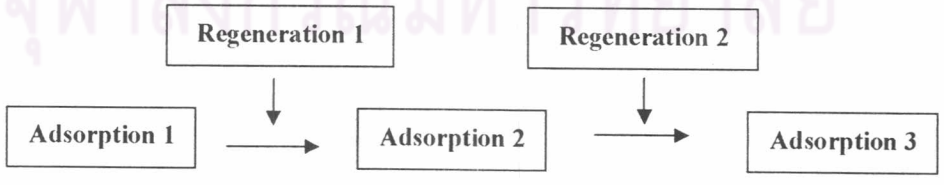


Figure 4.5.1 Stainless steal tube reactor for supercritical water treatment

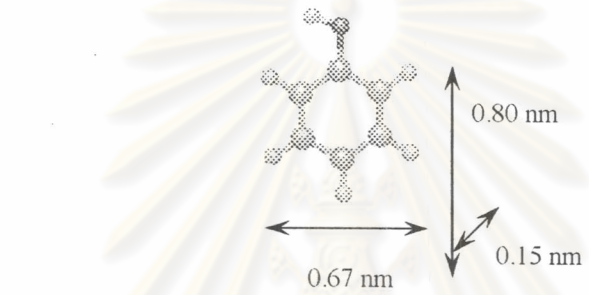
4.6 Liquid-Phase Adsorption-Desorption Characteristics

In this research the adsorption was studied in 3 cycles.

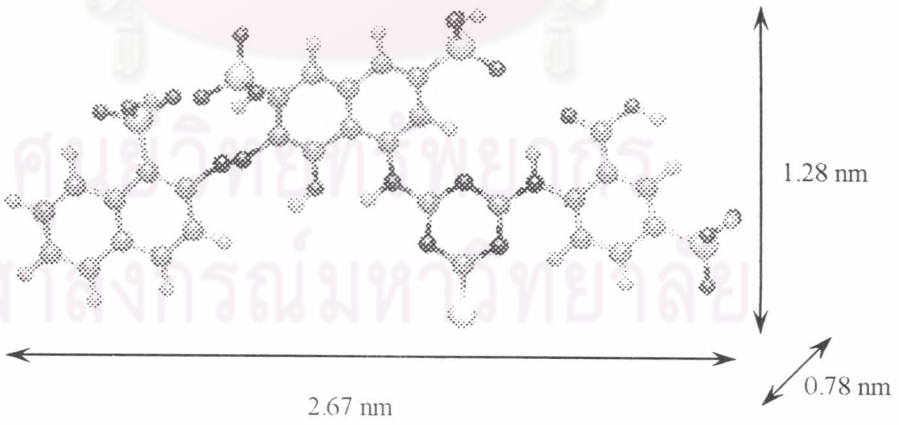


The activated anthracite prepared at 850°C and the steam concentration was 0.005 g/cm^3 was used as the representative adsorbent in the liquid-phase adsorption-desorption

USA), was also characterized. Phenol (Fisher Scientific Ltd., UK) and a reactive dye, Red 31 (Asia Dyestuff Industries, Thailand), were used as adsorbates. Their molecular sizes and structures, which were estimated using the WINMOPAC program, are shown in Figure 4.6.1.



a) Phenol [C_6H_5OH] (MW: 94)



b) Red 31 [$C_{30}H_{15}N_7O_{15}Na_5Cl$] (MW: 864)

Figure 4.6.1 Molecular sizes and structures of adsorbates

Aqueous solutions of various initial concentrations were prepared by diluting the adsorbates with distilled water. 0.5 – 2.0 g of activated carbons were contacted with the prepared solutions. To maintain well-mixed conditions, these mixtures were put in a gyratory air bath or a shaking water bath, which were kept at 30°C. After equilibrium was achieved, which normally took 10 and 15 days for phenol and Red 31, respectively, the solutions were filtered and their residual concentrations were measured. The concentration of solution was determined using the UV-visible spectrophotometer (UV-6405, Jenway, England) at the maximum wavelengths (λ_{max}) of 270 and 540 nm for phenol and Red 31 solutions, respectively. The amounts adsorbed on the activated carbons were calculated from the measured concentrations, and the adsorption isotherms were obtained. To determine the desorption isotherms, after filtration, the spent activated carbons were put in distilled water and left for the same times used in adsorption step. The desorption isotherms were obtained by calculating from the amounts adsorbed and finally measured concentrations.

4.7 Regeneration of Spent Activated Carbon by Supercritical Water

To determine the adsorption capacity of activated carbon regenerated by supercritical water, after reaching equilibrium, the saturated activated carbon was filtered and mixed with calculated amount of water (3.71 ml) of water inside stainless tube reactor. Then stainless tube reactor was placed and heated in a furnace at a constant heating rate 5 °C/min from room temperature to 400 °C and held at this temperature for 1 hr, at this condition the pressure inside the reactor is 250 bar. After the reactor was cooled

down, the activated carbon was filtered and dried by nitrogen at 110°C for 1 hour. Then the regenerated activated carbon was used for adsorption of the same compound again.