

## CHAPTER IV

### EXPERIMENTAL PROCEDURE

#### 4.1 Preparation of Raw Materials

##### 4.1.1 Vulcanized waste tires

Used tires were cut, crushed, ground, and centrifuged in order to remove the steel wires and fabric cords included in them. The particle size of the rubber sample obtained through this process was smaller than 0.595 mm. The results of elemental analysis of vulcanized waste tires are summarized in Table 4.1.

##### 4.1.2 Decrosslinked waste tires

The decrosslinked waste tires were supplied from Union Commercial Development, Thailand, and the detailed procedure of preparation can not be opened. Before using, this sample was cut in size 5×5 mm, and its elemental analysis results are also presented in Table 4.1.

Table 4.1 Elemental analysis of vulcanized and decrosslinked waste tires

	Vulcanized waste tires	Decrosslinked waste tires
C (wt%)	84.2	83.6
H (wt%)	12.0	7.7
N (wt%)	1.1	0.8
S (wt%)	2.1	2.3
Other (wt%)	0.6	5.6

## 4.2 Preparation of Activated Carbons

### 4.2.1 Conventional process

Activated carbons were produced from waste tires through the process of carbonization followed by steam activation. In the carbonization step, about 3 g of waste tire rubber was put in a quartz tube reactor. This reactor was electrically heated in  $N_2$  atmosphere from room temperature to carbonization temperature varied in the range of 500-850°C at a constant heating rate of 0.5, 5, or 20°C/min, then held at the carbonization temperature for 1 hour, and finally left to naturally cool down. In the activation step, 0.3-0.5 g of the carbonized sample was activated with steam in a quartz tube reactor by heating the reactor to activation temperature varied in the range of 750-950°C at a heating rate of 20°C/min. The steam used for activation was generated from a heating pot at a constant rate of 0.5 g/min, and was introduced to the reactor with a 200 cm<sup>3</sup>/min flow of  $N_2$ . Therefore, the partial pressure of water vapor was around 0.46 and the activation time was varied in the range of 1-4 hours. Figure 4.2.1 presents the quartz tube reactor which can be used for both carbonization and steam activation.

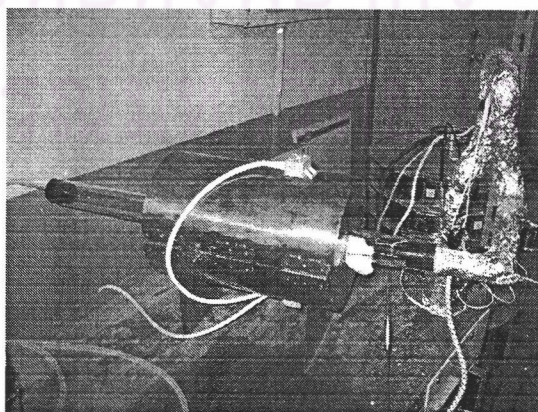


Figure 4.2.1 Quartz tube reactor

#### 4.2.2 Acid treatment prior to steam activation

Before steam activation, around 3 g of char obtained through carbonization step was immersed in 100 cm<sup>3</sup> of 1 M HCl or HNO<sub>3</sub> at room temperature. After 1 day, the acid-treated char was thoroughly rinsed with distilled water and dried in an oven at 110°C.

#### 4.2.3 Chemical pre-treatment

The raw materials were mixed with one of the following metal compounds; Ca(OH)<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, and KNO<sub>3</sub>, before carbonization at 500°C. Then, the carbonized sample was treated with HCl as mentioned above prior to steam activation at 850°C.

### 4.3 Characterization of Porous Properties

The BET surface area  $S_{\text{BET}}$ , mesopore volume  $V_{\text{meso}}$ , micropore volume  $V_{\text{micro}}$ , and pore size distribution, of each samples were determined from N<sub>2</sub> adsorption-desorption isotherms measured at 77 K using the adsorption apparatus (BELSORP 28, BEL Japan Inc., Japan or AUTOSORB-1-C, Quantachrome, USA). Pore size distribution and  $V_{\text{meso}}$  were evaluated by applying the Dollimore-Heal method to the desorption isotherm, whereas the t-plot method was used to estimate  $V_{\text{micro}}$ .

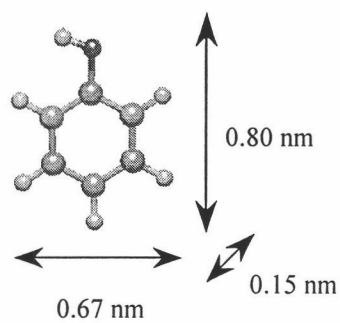
### 4.4 Liquid-Phase Adsorption-Desorption Characteristics

The activated carbon prepared with HCl prior to steam activation, AC HCl, was used as the representative adsorbent in the liquid-phase adsorption-desorption experiments, and for comparison a commercial activated carbon, CAL (Calgon Co., Ltd., USA), was also characterized. Phenol (Wako Pure

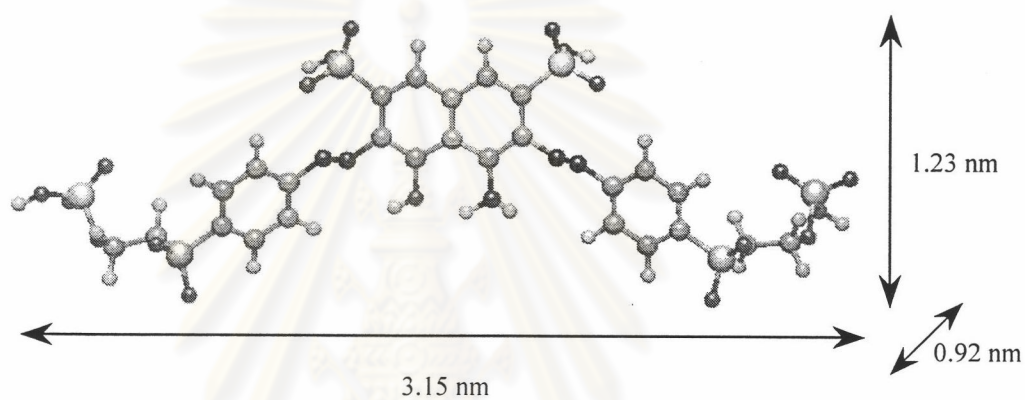
Chemical Industries Inc., Japan and Fisher Scientific Ltd., UK) and two reactive dyes, Black 5 and Red 31 (Asia Dyestuff Industries, Thailand), were used as adsorbates. Their molecular sizes and structures, which were estimated using the WINMOPAC program, are shown in Figure 4.4.1.



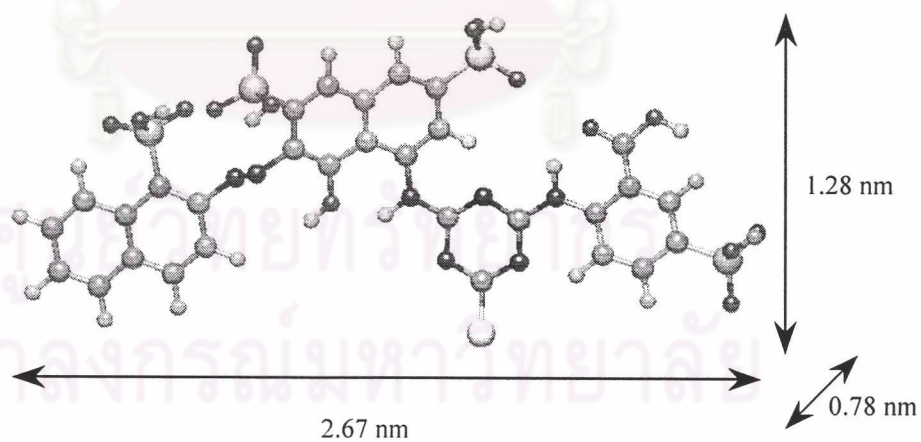
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a) Phenol [ $C_6H_5OH$ ] (MW: 94)



b) Black 5 [ $C_{26}H_{21}N_5O_{19}Na_4S_6$ ] (MW: 993)



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

Figure 4.4.1 Molecular sizes and structures of adsorbates

Aqueous solutions of various initial concentrations were prepared by diluting the adsorbates with distilled water. 20-100 mg 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, 14, 15 days for phenol, Black 5, 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-2200, Shimadzu Corporation, Japan or UV-6405, Jenway, England) at the maximum wavelengths ( $\lambda_{\max}$ ) of 270, 595, and 540 nm for phenol, Black 5, 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.

#### **4.5 Regeneration of Spent Activated Carbon by Ethanol**

To determine the adsorption capacity of activated carbon regenerated by ethanol, after reaching equilibrium, the saturated activated carbon was filtered and contacted with 200 cm<sup>3</sup> of ethanol at 30°C for the same times as adsorption. After the ethanol was removed, the activated carbon was dried by nitrogen at 110°C for 1 hour. Then the regenerated activated carbon was used for adsorption of the same compound again.