

CHAPTER III EXPERIMENTAL

3.1 Materials

The Beta zeolite was provided by Institut Français du Pétrole (IFP), France. The γ -alumina was produced by Saint-Gobain Norpro, U.S. The granular activated carbon was supported by Right Solution Co., Ltd, Bangkok, Thailand. The properties of Beta zeolite, alumina and activated carbon as specified by the company are shown in Table 3.1. Metallic mercury (99.9995%) was purchased from Wendt-chemie, German. Copper (II) nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, 99.5%) was purchased from Italmar (Thailand) Co., Ltd. Ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$, 99%) was purchased from Ajax Finechem, Australia. Dimethyldisulfide (DMDS, $\geq 99\%$) was purchased from S.M. Chemical Supplies Co., Ltd, Thailand. Nitric acid (HNO_3 , 65%) was provided by Merck KGaA, German. Acetone (99.96%) was supplied by Fisher Scientific UK Limited, UK. *p*-Xylene (99.97%) was supported by Aromatics (Thailand) Public Company Limited (ATC).

Table 3.1 Physical properties of the supports

Support	Si/Al	Pore diameter (Å)	Surface area (m^2/g)
Beta zeolite	10.5	-	636
Alumina	-	104	274
Activated carbon	-	-	1150-1250

3.2 Equipment

3.2.1 Thermogravimetric Analyzer (TGA)

Thermo gravimetric analyzer (Du Pont TAG 2950, France) was used to determine the phase transfer of adsorbents. The specimen was heated up from room temperature to 900°C with the rate of 10°C/min under N_2 atmosphere (30 ml/min). The mass changes during temperature increase were monitored and recorded automatically by the instrument.

3.2.2 Atomic Absorption Spectroscopy (AAS)

The actual content of copper in the prepared CuS adsorbents was determined using atomic absorption spectroscopy, VARIAN Model 300/400. Firstly, a known weight of adsorbent was dissolved in a mixture of HF and HNO₃ solution at 70-80°C for 30 min. The solution was diluted to the measuring range. The concentration of copper was obtained by comparing its absorbance with the calibration curve of the standard solution.

3.2.3 X-Ray Diffraction (XRD) Spectrometer

The chemical composition of adsorbents was analyzed by using X-ray Diffraction Spectrometer (Ringaku, RINT-2200, Japan) equipped with graphite monochromator and a Cu tube for generating CuK α radiation ($\lambda = 1.5406 \text{ \AA}$) at a generator voltage of 40 kV and a generator current of 30 mA. Nickel filter is used as the K α filter. The goniometer parameters are 2°(2 θ) divergence slit, 2°(2 θ) scattering slit and 0.3 mm receiving slit. Samples were ground and packed into flat specimen holders and were examined between 10-80°(2 θ) with the scan step of 0.02°(2 θ)/minute. The digital output of proportional X-ray diffractor and the goniometer angle measurements are sent to microcomputer to record the data and subsequent analysis.

3.2.4 Surface Area Analyzer

Surface areas of adsorbents were determined by BET surface area analyzer (Sorptomatic 1990, Italy). The surface areas of alumina, activated carbon, Beta zeolite, CuS impregnated alumina, activated carbon and Beta zeolite were analyzed by using nitrogen gas adsorption. To eliminate adsorbed volatile compounds from micropore, adsorbents were dried and evacuated by turbo pump at 300°C for at least 15 h.

3.2.5 Mercury Analyzer

The mercury analyzer NIC (SP-3D) with gold as trapping medium was used for the direct determination of mercury contamination. The analyzer

consists of three units: (1) a mercury atomizer (MA), (2) a controller (MA-1) and (3) a mercury detector (MD-1). The sample is decomposed by heating in the instrument and mercury vapor is collected by the mercury collector as gold amalgam. The temperature of the mercury collector is kept at 150°C to prevent the adsorption of combustion products on the collector. After collection, the amalgam is heated and the mercury is re-amalgamation on a second collector. Upon completion of the two-step gold amalgamation process, the mercury is liberated by heating the collector to 700°C. The vaporized mercury is carried to an absorption cell with a pure carrier gas and detected by the cold vapor atomic absorption technique. Finally, the mercury concentration is calculated automatically by the instrument. The operating conditions of the instrument are shown in Table 3.2.

Table 3.2 Operating conditions of mercury analyzer (NIC SP-3D)

Temperature of sample heating furnace	950°C
Temperature of decomposition furnace element	850°C
Pre-heating temperature of mercury collector	150°C
Mercury collector temperature	700°C
Carrier gas	Dry purified room air
Carrier gas pressure	0.4 kg/cm ² (39 kPa)
Combustion system flow rate	0.5 L/min
Measuring system flow rate (AAS)	0.5 L/min
Recorder chart speed	5 mm/min
Recorder full scale	1 V
Analysis time	20 min

3.3 Methodology

3.3.1 Preparation of Supports

Before use, all supports were preheated in order to remove moisture presenting on the surface and pore of the supports. The alumina and the Beta zeolite were preheated at 350°C while the activated carbon was preheated at 200°C for 10 h.

3.3.2 Adsorbent Preparation

Impregnation Method

The copper oxide impregnated adsorbents were prepared by incipient wetness impregnation of the supports including alumina, activated carbon and Beta zeolite with aqueous solutions of copper nitrate ($\text{Cu}(\text{NO}_3)_2$), followed by drying at 120°C for 12 h and calcination at 500°C for 5 h. The two different loading amounts of copper were examined.

Sulphidation Method

The copper oxide adsorbent was reduced to copper impregnated adsorbent by flowing H_2 (100 ml/min/g of adsorbent) and heating at 300°C for 30 min. The sulfidation was carried out in a 1 L autoclave reactor. Twenty grams of copper impregnated adsorbent were sprayed with ten grams of sulfiding agent, dimethyldisulfide (DMDS), at room temperature. Prior to heating the reactor, the reactor was pressurized to 3.4 MPa. The copper impregnated adsorbent was sulfided in situ at 320°C for 2 h and 360°C for another 2 h. The resulting adsorbent was copper sulfide impregnated adsorbent.

3.3.3 Preparation of Stock Solution

All glasswares used in this experiment were thoroughly cleaned (according to UOP Method 938-00) by washing with 1:1 nitric acid, rinsed with water and acetone, followed by blow-drying with nitrogen or oil-free clean air. The stock solution of mercury was prepared by dropping the metallic mercury in treated heavy naphtha (75 g of Hg° per 1 L of treated heavy naphtha), a real feed after mercury removal unit (MRU) from Aromatics (Thailand) Public Company Limited (ATC), followed by vigorous mixing at least 12 h. Then the solution was filtered and kept in a refrigerator for 4 h and filtered again. The maximum solubility (1200 ppb at room temperature) was achieved and determined by mercury analyzer. The obtained mercury stock solution was diluted with treated heavy naphtha to prepare a stock solution of 500 ppb.

3.3.4 Blank Test

Blank test was conducted to study the stability of metallic mercury. Twenty milliliters of 500 ppb metallic mercury solution of 500 ppb was placed into a 20 ml glass vial without adding an adsorbent. An experiment was done at temperature of $50\pm 1^\circ\text{C}$. Small sample volumes ($40\ \mu\text{l}$) were taken through a syringe and placed separately into 2 ml glass vials containing $360\ \mu\text{l}$ of *p*-xylene, which was used for dilution, at time intervals of 0, 2, 4, 6 and 8 h and then analyzed for the mercury concentration by mercury analyzer NIC SP-3D.

3.3.5 Appropriate Quantity of Adsorbent

To determine the appropriate amount of adsorbent that used to continue a batch experiment, the 500 ppb of metallic mercury solution was used. The different quantities of adsorbent (0.001, 0.01, 0.05 and 0.1 g) were mixed with a solution separately. Temperature was also the same as a batch studies at $50\pm 1^\circ\text{C}$. Then the solution was sampled at 6 h and analyzed by NIC.

3.3.6 Kinetics of Adsorption of Metallic Mercury in Heavy Naphtha

The experiment was studied by using metallic mercury solution at 500 ppb. 20 ml of a solution was taken from a stock solution and placed into a 20 ml glass vial and put in a beaker containing water. Temperature was controlled at $50\pm 1^\circ\text{C}$. Then 0.001 g of adsorbent was added in a vial. Schematic of batch operation shows in Figure 3.1. The solution was then withdrawn at time intervals of 0, 5, 20, 50, 110, 200, 300 and 400 min and then analyzed by NIC. The concentration change of the remaining solution in 20 ml glass vial was assumed to be negligible as a small amount of a solution ($20\ \mu\text{l}$) was taken from a vial.

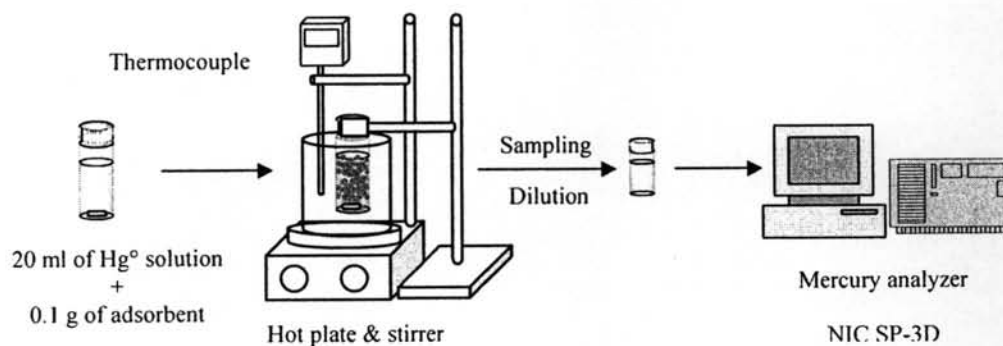


Figure 3.1 Schematic of batch operation.

3.3.7 Adsorption Isotherms of Metallic Mercury in Heavy Naphtha

The adsorption isotherms were constructed using the batch system to determine the Hg⁰ adsorption on adsorbents at various mercury concentrations. The metallic mercury solution in the range of 200 to 900 ppb (200, 300, 500, 700, 900 ppb by weight) were mixed separately with 0.001 g of adsorbents in 20 ml screw cap glass bottles and were shaken for 6 h at $50 \pm 1^\circ\text{C}$. The solution was then withdrawn for the analysis of the remaining mercury by NIC.

3.3.8 Pilot Operation

The breakthrough curve for metallic mercury removal was studied in pilot plant U844 (Figure 3.2) by using CuS on Beta zeolite and CuS on alumina. The reactor has I.D. of 9 mm and a height of 32.6 mm with the up flow configuration. The adsorbent was loaded into a reactor in the ratio of the adsorbent to silicon carbide (SiC) equaled to 0.5:2 ml. The experiments were operated at 50°C by using heated circulating oil, 7 bar and 2 ml/min of the feed flow rate.

The adsorbent was pretreated inside the reactor by heating to 80°C with passing N₂ gas in order to remove moisture, air and oil for at least 8 h. Then, the reactor was allowed to cool to 50°C before injecting the feed. The effluent after passing through the reactor was collected from the sample collecting drum and the effluent was sent to the waste disposal tank.

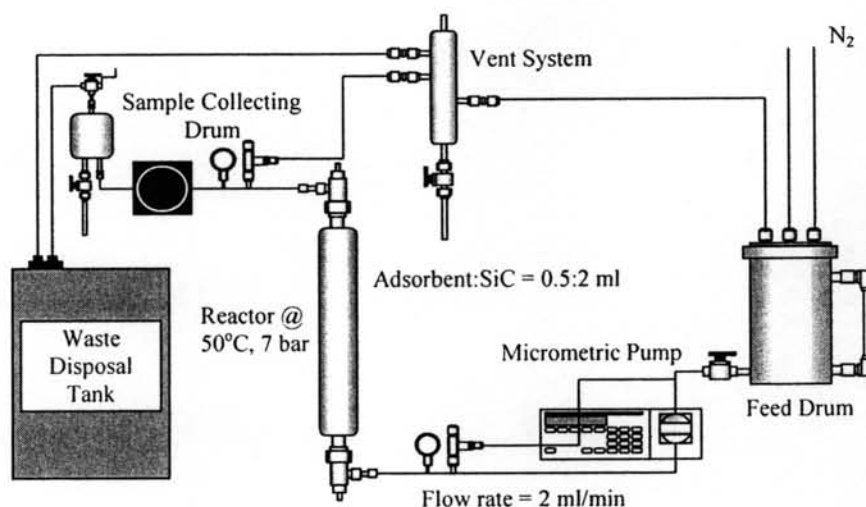


Figure 3.2 Schematic of pilot plant U844, Lyon, France.

3.3.9 Sample Analysis

Before mercury analysis, the sample boat, additive B and additive M were pretreated at 750°C in muffle furnace for at least 2 h and then placed in the sample vessel and allowed them to cool. After that, a 100 µl of sample was withdrawn through a syringe and then injected into the sample boat containing approximately 1 g of additive B. The sample was covered with additional additive B, approximately 1 g follow by approximately 3.5 g of additive M (see Figure 3.3). The sample boat was then placed into the combustion tube of the mercury analyzer and the analysis was started by pressing Mode 3 position. The buzzer would sound when the analysis was complete. And then the final reading was printed out by an online printer. The analysis time per sample was around 20 min (Reference: Method UOP 938-00).

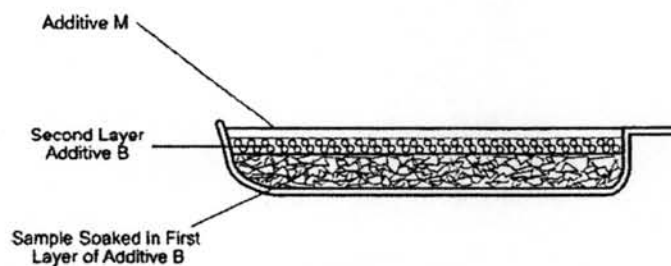


Figure 3.3 Sample boat with additive B and M and sample for analysis.