

## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

Diphenylmercury ( $C_{12}H_{10}Hg$  99%, DPM) was supplied by ACROS ORGANICS, New Jersey (USA).

Mercury standard stock solution ( $1000 \pm 3 \mu\text{g/ml}$  in 2%  $HNO_3$ ) was provided by VARIAN, Australia.

Nitric acid ( $HNO_3$  70% A.R. grade), hydrochloric ( $HCl$  37% A.R. grade), and n-heptane ( $CH_3(CH_2)_5CH_3$  99% A.R. grade) were supplied by Lab-Scan Analytical Sciences, Thailand.

Potassium dichromate ( $K_2Cr_2O_7$ ) and sodium borohydride ( $NaBH_4$ ) were supplied by CARLO ERBA REAGENTI, Italy.

Sodium hydroxide ( $NaOH$  A.R. grade, 1.000 M solution) was supplied by APS Ajax Finechem, Australia.

Adsorbents (3A, 4A, 5A, NaX and NaY zeolites) were obtained from Institut Français du Pétrole (IFP) in France, and activated carbon, granular activated coconut shell based carbon (grade PHO 8x30) was obtained from Carbokarn (Thailand) Co., Ltd.

#### 3.2 Experimental

##### 3.2.1 Surface Area Analysis

Surface areas of adsorbents were determined by BET surface area analyzer (Sorptomatic 1990, Italy). The surface areas of NaX, NaY, and 5A zeolites were analyzed by using nitrogen gas adsorption while 3A and 4A zeolites were analyzed by using argon gas instead because the kinetic selectivity restrict to nitrogen adsorption. Surface area datum of activated carbon was reported by the company. To eliminate adsorbed volatile compounds from micropore, adsorbents were dried and evacuated by turbo pump at  $300\text{ }^\circ\text{C}$  for at least 15 h.

### 3.2.2 X-Ray Diffraction (XRD) Analysis

The chemical composition of adsorbents was analyzed by using X-ray diffraction (Ringaku, RINT-2200, Japan) equipped with graphite monochromator and a Cu tube for generating CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at a generator voltage of 40 kV and a generator current of 30 mA. Nickel filter was used as the K $\alpha$  filter. The goniometer parameters were  $2^\circ(2\theta)$  divergence slit,  $2^\circ(2\theta)$  scattering slit, and 0.3 mm receiving slit. Samples were ground and packed into flat specimen holders and were examined between  $1.2 - 50^\circ(2\theta)$  with the scan step of  $0.02^\circ(2\theta)/\text{minute}$ . The digital output of proportional x-ray diffractor and the goniometer angle measurements were sent to microcomputer to record the data and subsequent analysis.

### 3.2.3 Thermo Gravimetric Analysis

Thermo gravimetric analyzer (Du Pont TGA 2950, France) was used to determine the phase transfer of adsorbents. The specimen was heated up from  $30^\circ\text{C}$  to  $800^\circ\text{C}$  with the rate of  $10^\circ\text{C}/\text{min}$  for zeolite adsorbents except the activated carbon which it was heated up from  $30^\circ\text{C}$  to  $150^\circ\text{C}$  at the same heating rate. The change of mass during temperature increase were monitored and recorded automatically by the instrument.

### 3.2.4 Cold Vapor Atomic Absorption Spectrometric Analysis

Analysis of mercury was performed using 2 analyzers: cold vapor AAS (Varian) and mercury-gold amalgam analyzer (NIC SP-3D). Both are a physical method based on the adsorption of wavelength at 253.7 nm by mercury vapor. For the cold vapor atomic absorption spectrometric analysis (CVAAS) technique, each sample was measured by using atomic absorption spectrometer (Varian model 300/400, Australia) equipped with a 10-cm-long path quartz cell and a mercury source lamp. The mercury was reduced to the elemental state by the cold vapor process and aerated from the solution. All of the mercury in the sample solutions placed in the reaction capillary column was chemically atomized and transported to the sample cell for atomic absorption measurement by collecting and integrating data over a 60-s time

window while background correction was on. The mercury vapor passed through a cell positioned in the light path of an atomic absorption spectrophotometer. Absorbance (peak height) was measured as a function of mercury concentration.

For the mercury analyzer NIC SP-3D (Nippon Instruments Corporation, Japan), all operations from the sample decomposing process to the mercury detection after feeding a sample are automatically carried out with the mercury controller. The fed sample is decomposed by heating. Only mercury vapor in the gaseous products is collected in the mercury collector (chromosorb coated with gold) as gold amalgam. Mercury is set free as atomic mercury by heating the mercury collector and is detected at the absorption cell by the cold vapor atomic absorption. The mercury collector can be used again after setting the mercury free and being cooled. To eliminate the bad influence of gaseous products other than mercury on the atomic absorption analysis, temperature biased two steps collecting process is adopted. As the result, the mercury vapor is refined and only pure mercury vapor passes through the absorption cell.

### 3.2.5 Mercury Standard Solutions for Cold Vapor Atomic Absorption Spectrometric Analysis

All glassware and plastic containers were thoroughly cleaned by washing with 1:1 (v/v) nitric acid, rinsed with distilled water, and followed by drying in an oven at 80 °C according to UOP method 938-00.

According to the operation manual of Varian instrument, mercury standard solution 1 mg/l was prepared by dilution of the mercury standard stock solution (1000 mg/l). Add 5 ml of the mercury standard stock solution into a 50 ml volumetric flask and dilute to the mark with water. Then, pipet 5 ml into a 50 ml volumetric flask and add 5.0 mg (0.01% w/v) of  $K_2Cr_2O_7$  for enhanced stability of  $Hg^{2+}$  (3.60 ml (7.2% v/v) of concentrated  $HNO_3$  and dilute to 50 ml with water) in order to prevent the loss of mercury through volatilization by preventing the formation of  $Hg^0$  (Anderson, 2000). Finally, pipet 10 ml of previous solution into 100 ml volumetric flask and

dilute to the mark with water to obtain 1 mg/l of mercury standard solution. The sample was transferred into an acid cleaned 100 ml plastic bottle and kept refrigerated at 4°C for using only one week.

Mercury standard solutions for calibration curve (5.0, 10.0, 20.0, 50.0, and 70.0 µg/l) were prepared from dilution of the 1 mg/l mercury standard solution. For 10.0 µg/l, pipet 1 ml of the mercury standard solution into a 100 ml volumetric flask and add 10.0 mg (0.01% w/v) of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, 7.2 ml (7.2% v/v) of concentrated HNO<sub>3</sub> and dilute to 100 ml with water. Finally, transfer the standard solution into an acid cleaned 100 ml plastic bottle. The standard was prepared daily for an experiment.

### 3.2.6 Preparation of Diphenylmercury in n-Heptane

According to UOP 938-00 standard, the concentration of diphenylmercury (DPM) contaminated in n-heptane was calculated into three significant figures by the following equation.

$$Hg, mg/l = \frac{10^3(0.565)M}{0.500} \quad (3.1)$$

Where:

M = weight of DPM, g

0.500 = volume of volumetric flask, liter

0.565 = molecular mass of mercury (200.59) divided by the molecular mass of DPM (354.81)

10<sup>3</sup> = factor to convert g to mg

Low DPM of 2.0 mg/l in heptane solution was prepared by weighing 0.0018 g of DPM to the nearest 0.1 mg and then transferred quantitatively with n-heptane into a 500 ml volumetric flask. Cap and invert several times to mix thoroughly. Finally, the solution was transferred into a plastic bottle and kept refrigerated at 4°C for using within one week.

High DPM of 5.0 mg/l in heptane solution was prepared by weighing 0.0045 g of DPM to the nearest 0.1 mg and then followed the previous description.

### 3.2.7 Preparation of Other Reagents for Cold Vapor Atomic Absorption Spectrometric Analysis

According to the operation manual of Varian instrument, sodium borohydride reducing solution (0.3% NaBH<sub>4</sub> in 0.5% NaOH) was prepared by weighing 0.75 g of NaBH<sub>4</sub> and transferred quantitatively with water into 250 ml volumetric flask. Pipet 31.25 ml of NaOH (12.5% v/v) and add slowly to the mixture and then dilute to 250 ml with water. Cap and invert several times to mix thoroughly. The reducing solution was freshly prepared for daily use.

Hydrochloric acid (HCl) 5 M was prepared by transferring 250 ml of 37% HCl into a 500 ml volumetric flask and diluted to a mark with water.

### 3.2.8 Adsorption of Diphenylmercury on Plastic Containers (HDPE)

Each of 2.0 mg/l and 5.0 mg/l DPM concentrations was pipetted into separated HDPE plastic containers and stored at 4°C up to one week. In each day, the remaining of DPM was analyzed by CVAAS.

### 3.2.9 Kinetic Studies of Diphenylmercury Removal

The kinetics of mercury removal using 3A, 4A, 5A, NaX, NaY and activated carbon were obtained from batch adsorption data for both 2.0 mg/l and 5.0 mg/l DPM concentrations. A 0.1000 g of adsorbent was mixed with 15 ml of a DPM in n-heptane solution and stored in a 15 ml screw-cap HDPE plastic container. The HDPE plastic containers were shaken at the speed of 100 rpm at 25°C. Time was varied from 10 minutes to 900 minutes for the study.

### 3.2.10 Effect of Pore Size on Diphenylmercury Adsorption

The effect of pore sizes on DPM adsorption were performed with 3A, 4A, 5A, NaX and NaY zeolites, with opening pore diameters of 2.9, 3.8, 4.4, 7.4 and 7.4 Å respectively. The procedures were performed the same manner as described in 3.2.9.

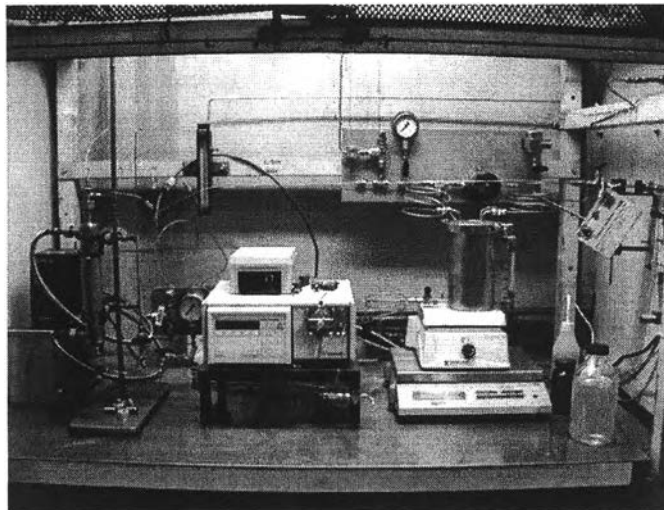
### 3.2.11 Adsorption Isotherms of Diphenylmercury on Adsorbents

Adsorption isotherms were constructed from the batch adsorption data to determine the DPM sorption on the adsorbents at various DPM concentrations. The concentration of DPM in n-heptane solution varied from 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 5.0 mg/l. A 0.1000 g of adsorbent was mixed with 15 ml of a DPM in n-heptane solution in a 15 ml screw-cap plastic and was shaken for 12 h at 25°C. The solution was then withdrawn for the analysis of mercury by CVAAS.

### 3.2.12 Pilot Operations

For the demonstration of the overall operating performance of the zeolites: NaX and NaY, the n-heptane solution containing 2100 ppb of diphenylmercury was tested in the small pilot scale of unit number U844 at IFP Lyon, France, as shown in Figure 3.1.

In general, these tests were performed using one reactor (I.D 9 mm, height 32.6 cm) in the up-flow configuration which contained 1.5 ml of the trapping mass solids and operated at 80°C by using heated circulating oil while the pressure of the unit was optional. Only the feedstock needed to be pressurized under a light nitrogen pressure for pushing the solution throughout the process line. The feed flow rate was set at 60 ml/h. The adsorbent was packed between two inert packing materials of SiC. Prior to the actual testing, the adsorbent or trapping mass solid was pretreated by loading the adsorbent inside the reactor and was heated up to 200°C with passing N<sub>2</sub> in order to remove moisture, air and oil for at least 12 hours. Then, the unit was cooled down to 80°C and stopped the passing of N<sub>2</sub> before injecting the feed for the experiment. The effluents were collected every hour by stocking in HDPE plastic (60 ml, Nalgene) and then they were analyzed by mercury analyzer model NIC SP-3D (Nippon Instruments Corporation, Japan).



**Figure 3.1** Small pilot plant unit number U844, IFP Lyon, France.