

CHAPTER III EXPERIMENTAL

3.1 Materials

The commercial zeolites NaX, NaY, and CMG 273 were provided by Institut Français du Pétrole (IFP), France. The zeolite L (K-LTL) was produced by Tosoh Co. while zeolite Beta (NaH-BEA) and zeolite Omega (H-MAZ) was produced by Zeolyst International, USA. The properties of Zeolites and commercial adsorbent CMG273 are shown in Table 3.1. Metallic Mercury (99.8%) was purchased from HiMedia Laboratories Pvt. Ltd., Mumbai, India. n-Heptane (99.9%) was purchased from Lab Scan, Thailand. Additive B was supplied by NIC, Cat. No. 2754-02.

Table 3.1 Physical properties of zeolites and commercial adsorbent CMG273

Adsorbent	Si/Al	Pore(Å)	Area (m ² /g)
Zeolite X	1.3	7.4	680
Zeolite Y	2.8	7.4	650
Omega	2.4	7.4	-
Beta	8.3	7.4	660
L	2.8	7.1	300
CuS/Al ₂ O ₃ (CMG273)	-	-	142

3.2 Experimental Equipments

3.2.1 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was used to determine the phase transfer of the adsorbents. The thermogravimetric analyzer (Du Pont TAG 2950, France) was programmed to heat from room temperature to 900 °C at a rate of 10°C/min for Zeolites. The mass changes during temperature increase were monitored and recorded using the TA instrument thermal analyst system.

3.2.2 Mercury Analyzer

The mercury analyzer NIC (SP-3D) with gold as trapping medium was used for the direct determination of mercury contamination. The operating conditions of the instrument are shown in Table 3.1.

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 Stock Solution

Before starting the experiment, all the glassware was thoroughly cleaned (according to UOP method 938-00) by washing with 1:1 nitric acid, rinsed with water, rinsed with acetone, followed by blow-drying with nitrogen or oil-free clean air. Then, a stock solution of mercury was prepared by dropping a small drop of metallic mercury in n- heptane into a previously cleaned 1L volumetric flask, followed by medium to vigorous mixing for 24 hrs. The maximum solubility (1200 ppb at room temperature) was achieved and determined by mercury analyzer. The contaminated mercury stock solution, thus obtained, was diluted with pure n heptane to prepare two stock solutions of 500 ppb and 1000 ppb as low and high concentrations of mercury, respectively.

3.3.2 Adsorption of Metallic Mercury on Container Wall

Seven concentrations (in the proximity of 200, 400, 500, 600, 800, 1000 ppb) used in the experimental work were kept in 10 ml glass vials with no head space, in order to prevent evaporation losses. These concentrations were prepared according to the procedure explained above and were stored for 3 days. The concentrations were determined at the end of each day.

3.3.3 Adsorption Kinetics of Hg⁰ in n-Heptane Substitute Condensate

The adsorption kinetics was studied in an experiment using concentrations of 500 ppb and 1000 ppb. 10 ml of Hg⁰ spiked contaminated n-heptane was taken from a stock solution of 500ppb/1000ppb and placed into a 10 ml glass vial and mixed with 0.1 g adsorbent. Small sample volumes (10 µl) were taken through a syringe and analyzed at time intervals of 0, 10, 20, 40, 60, 90, 120, 180, 240, 360 and 480 mins. The concentration change of the remaining solution in the glass vial was negligible as only a small amount (a total of 0.1 ml) was taken from the vial. All experiments were done at temperatures of 30°C, 40°C, and 50°C with triplications. A similar procedure was done for the kinetics study of evaporation, for this purpose a blank experiment was run at temperatures of 30°C, 40°C and 50°C.

3.3.4 Adsorption of Hg⁰ in n-Heptane Substitute Condensate

The adsorption isotherms were constructed using the batch system to determine the Hg⁰ sorption on adsorbents at various mercury concentrations. The mercury concentrations in the n-heptane solution in the range of 200 to 1200 ppb (200, 400, 500, 600, 800, 1000, 1100 ppb by weight) were mixed with 0.1000 g of adsorbents in 10 ml screw cap glass bottles and were shaken for 8 hours at 30, 40 and 50 °C. The solutions were then withdrawn for the analysis of mercury by NIC.

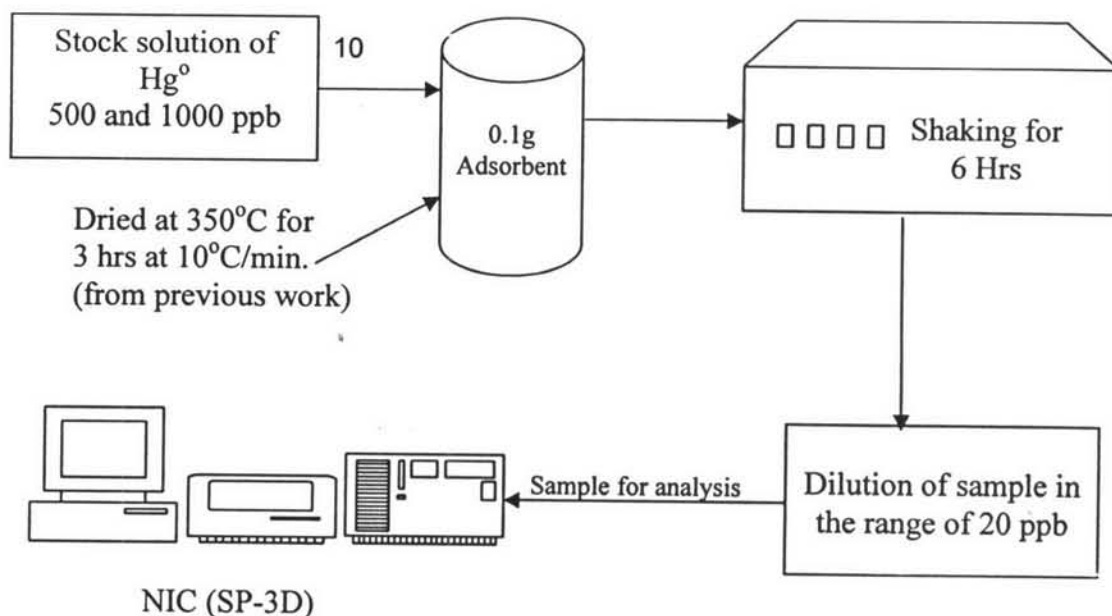


Figure 3.1 Schematic of batch operation.

3.3.5 Sample Analysis

All samples were collected into 2 ml glass vials with an air tight cap. The sample boat and additive B used in the mercury analyzer were pretreated at 800°C for 2 hrs (recommended). A 100 µl of sample was then withdrawn through a syringe and was injected into the sample boat containing 5 gram of additive B. The sample boat was then placed into the combustion tube of the mercury analyzer and the analysis was started by pressing MODE 4 position. The automatic system allowed 5 min preheating, followed by the atomization of the mercury species, followed by heating, and finally the determination of mercury content in a cold vapor atomic absorption system. The analysis time per sample was around 20 mins and the final reading was printed out by an online printer (Reference: Method UOP 938-00).

3.3.6 Pilot Operation

For the demonstration of the overall operating performance of CMG273 for n-heptane solution containing 800-1000 ppb of metallic mercury were tested in a small pilot plant U844 at IFP Lyon, France, as shown in Figure 3.2

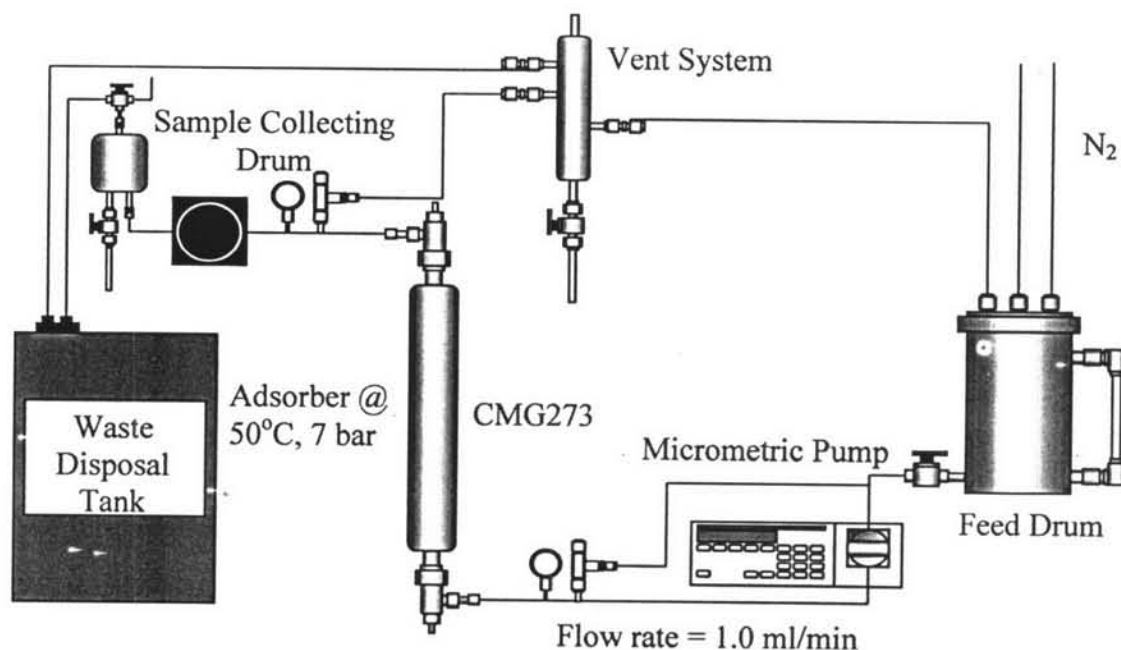


Figure 3.2 Schematic of pilot plant U844, IFP Lyon, France.

In general these tests were performed using one reactor (I.D. 9 mm, height 32.6 mm) in the up flow configuration, which contained 0.5 g of the trapping mass (CMG273) and was operated at 70°C by using heated circulating oil at 7 bar pressure condition in order to keep the feed in the liquid phase. The feed flow rate was set at 60 ml/hr. The adsorbent was packed between two inert packing materials of SiC, as shown in Figure 3.3.

Prior to the actual testing, the adsorbent or trapping mass was pretreated by loading the adsorbent inside the reactor and heating up to 80°C with passing N₂ in order to remove moisture, air and oil for at least 12 hrs. Then, the unit was allowed to cool to 50°C. The N₂ supply was stopped before injecting the feed for the experiment. The effluent was collected every hour by stocking in glass bottles (30 ml) and was analyzed by mercury analyzer NIC SP-3D (Nippon Instruments Corporation, Japan) as described in 3.3.5.

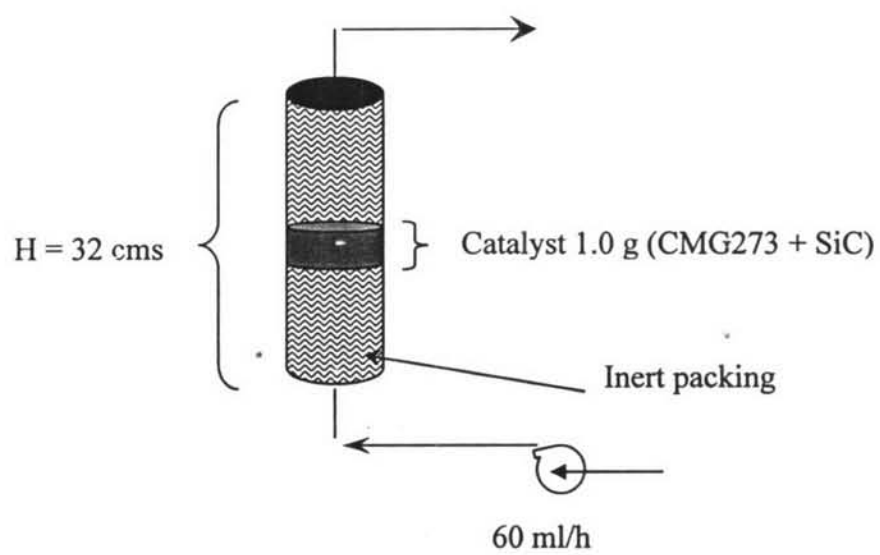


Figure 3.3 Loading diagram of CMG273.