



CHAPTER III EXPERIMENTAL

3.1 Materials

Activated carbon and alumina used to be impregnated with metal ions were provided from Institut Français du Pétrole (IFP, France).

Nickel (II) chloride (NiCl_2 , 98%) and Copper (II) chloride (CuCl_2 , 97%) used to be impregnated with activated carbon and alumina were purchased from Alfa Aesar and Carlo Erba respectively.

Ethanol ($\text{C}_2\text{H}_5\text{OH}$) used to be as solvent was purchased from Carlo Erba.

Acetonitrile (CH_3CN , 99%) used to be as solvent was purchase from Aldrich.

Dodecane ($\text{C}_{12}\text{H}_{26}$, 99%) and Paradiethylbenzene (C_8H_{10}), which represented as composition in simulated diesel fuel, were supplied by VWR and IFP respectively.

Dibenzothiophene ($\text{C}_{12}\text{H}_8\text{S}$, 98%), and 4,6-dimethyldibenzothiophene ($\text{C}_{14}\text{H}_{12}\text{S}$, 95%), which represented sulfur compounds in simulated diesel fuel, were purchased from Alfa Aesar and Acros Organics respectively. Their relevant properties are shown in Table 3.1.

Naphthalene (C_{10}H_8 , 99%) and Phenanthrene ($\text{C}_{14}\text{H}_{10}$, 98%), which represented polyaromatic compounds in simulated diesel fuel, were purchased from Aldrich.

Carbazole ($\text{C}_{12}\text{H}_9\text{N}$, 96%) and Acridine ($\text{C}_{13}\text{H}_9\text{N}$, 97%), which represented nitrogen compounds in simulated diesel fuel, were purchased from Aldrich and Sigma-Aldrich respectively.

Table 3.1 Physical properties of sulfur compounds and simulated diesel fuel

Material	Molecular weight	Boiling point (°C)	Density (g/cm ³)
Dodecane	170.34	216.2	0.75
Paradiethylbenzene	106.17	136.0	0.87
Dibenzothiophene	184.26	332-333 @ 760 mmHg	-
4,6-dimethyldibenzothiophene	212.31	-	-
Naphthalene	128.17	218	1.14
Phenanthrene	178.23	340	1.06
Acridine	179.22	346	1.01
Carbazole	167.21	354.7	1.10

3.2 Equipments

1. Gas Chromatography (HP 5890 Series2) with FID detector and HP-5 column (30 m x 0.32mm x 0.25mm film thickness)
2. Surface Area Analyzer (SAA) (Thermo Finnigan, Sorptomatic model)
3. Atomic Absorption Spectrometer (AAS) (Varian, SpectrAA 300 model)
4. Vial 1.8 cm³
5. Magnetic stirrer
6. Stirring plate
7. Calcined equipment
8. Fixed bed column
9. Rotary evaporation
10. Collector
11. Glassware

3.3 Methodology

3.3.1 Adsorbents Preparation

3.3.1.1 *Preparation of Cu Impregnated on Activated Alumina by Using CuCl₂ in Deionized Water*

Impregnated activated alumina was prepared by the incipient wetness method. The activated alumina, is dried in an oven at 250°C. A known amount of CuCl₂ (11.78 and 9.28 g for mesoporous and macroporous alumina, respectively) was magnetically stirred in 25 cm³ deionized water (CuCl₂ monolayer calculation was in an appendices A). A volume of the solution equal to the total pore volume of the substrate was brought into contact with the activated alumina drop by drop. After the activated alumina had imbibed the solution containing the salt into its pore structure, the sample was dried by using a rotary evaporator at 40°C and 72 mbar (Takahashi *et al.*, 2000).

3.3.1.2 *Preparation of Cu Impregnated on Activated Carbon by Using CuCl₂ in Ethanol*

Impregnated activated carbon (AC) adsorbent was prepared by the incipient wetness method. The activated carbon is dried in an oven at 200°C. A known amount of CuCl₂ (25 g) was magnetically stirred in 100 cm³ ethanol. A volume of the solution equal to the total pore volume of the adsorbent was brought into contact with the activated carbon drop by drop. The impregnation was done 8 times to obtain monolayer coverage. After the activated carbon had imbibed the solution containing the salt into its pore structure, the sample was dried by using rotary evaporator at 40°C and 175 mbar (Han *et al.*, 2003).

3.3.1.3 *Preparation of Cu Impregnated on Mesoporous Alumina by Using CuCl in 75% Acetonitrile-25% Deionized Water*

Impregnated activated alumina was prepared by the incipient wetness method. 25 g of CuCl and 100 cm³ of 75% of acetonitrile and 25% of deionized water were first prepared. The synthesis process was handled with special care to avoid transformation of Cu⁺ to Cu²⁺ due to the oxidation. A volume of the solution equal to the total pore volume of the substrate was brought into contact with the adsorbents drop by drop under N₂ atmosphere. The impregnation was done 6

times to obtain a monolayer coverage. After the activated alumina had imbibed the solution containing the salt into its pore structure, the sample was dried by using a rotary evaporator at 40°C and 72 mbar (Hirai *et al.*, 1985).

3.3.1.4 Preparation of Ni Impregnated on Activated Alumina by Using NiCl₂ in Deionized Water

Impregnated activated alumina was prepared by the incipient wetness method. A known amount of NiCl₂ (5.28 and 4.16 g for mesoporous and macroporous alumina, respectively) was magnetically stirred in 25 cm³ deionized water. A volume of the solution equal to the total pore volume of the substrate was brought into contact with the activated alumina drop by drop. After the activated alumina had imbibed the solution containing the salt into its pore structure, the sample was dried by using rotary evaporator at 40°C and 72 mbar (Takahashi *et al.*, 2000).

3.3.2 Reduction

The CuCl₂ impregnated on activated carbon and aluminas were reduced to Cu⁺ by using reduction gas (He or H₂). This procedure was necessary because stable Cu⁺ salt were not water-soluble. The TPR conditions will be explained shortly.

3.3.3 Characterization of Adsorbents

Surface area and pore volume was determined by BET surface area analyzer – SAA (Themo Finnigan, Sorptomatic model) and analyzed by using nitrogen gas adsorption and desorption. To eliminate adsorbed volatile compounds from the pores, before being analyzed, adsorbents are dried and evacuated at 300°C for at least 3 hours

The amount of metal loading was obtained by using an Atomic Absorption Spectrometer – AAS (Varian, SpectrAA 300 model). All the adsorbent samples were dissolved in a hydrogenfluoric (HF) solution. Then the samples were mixed with aqua regia to dissolve the metal ions completely.

The temperature of reduction Cu²⁺ to Cu⁺ was obtained by using Temperature-Programmed Reduction – TPR. The amount of adsorbent used was 0.5 g and it was held in place by glass wool plugs. The gas mixture used was 10% H₂ in Ar at flow rate of 37 cm³/min, and the heating rate was 5°C/min.

3.3.4 Preparation of Simulated Diesel

In this study, the simulated diesel used was dodecane and paradiethylbenzene (PDEB) as a model. The sulfur compounds used were dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). The samples were prepared in binary system (by mixing organic sulfur compounds) and in tertiary system (by mixing organic sulfur compounds and polyaromatic compounds or nitrogen compounds).

3.3.5 Adsorption of Sulfur Compounds from Simulated Diesel by Fixed Bed Adsorption

Experiments were done in laboratory plant unit 179 at Institut Français du Pétrole (IFP), Lyon, France. The schematic of continuous system is shown in Figure 3.1.

All dynamic adsorption or breakthrough experiments were performed in a stainless steel column. For CuCl_2 impregnated on the adsorbents, initially about 7 g of adsorbent was loaded inside the column, and reduced to CuCl using reduction gas at flow rate $37 \text{ cm}^3/\text{min}$, heated up to 300°C and kept at this temperature for about 1 h (Rouco, 1994). After reduction, the temperature of the adsorbent bed was reduced to ambient temperature for the subsequent adsorption experiment.

For NiCl_2 impregnated on the adsorbents, initially about 7 g of the adsorbent was loaded inside the column, and activated using N_2 at 200°C and kept at this temperature for 1 h (Yang *et al.*, 1996). After activation, the temperature of the adsorbent bed was reduced to ambient temperature.

The adsorbent bed was then washed with a sulfur-free hydrocarbon (n-dodecane) at flow rate $2 \text{ cm}^3/\text{min}$ to remove any entrapped gas. After allowing the liquid hydrocarbon to disappear, the simulated diesel fuel was allowed to contact the bed at varied flow rate and temperature. Effluent samples were collected in small vials by collector equipment shown Figure 3.2 at regular time intervals until saturation of the adsorbent was achieved. This could be observed when total sulfur concentration is similar in the feed and at the outlet of the column. All the samples collected during the breakthrough experiments were analyzed by using gas chromatography.

Breakthrough adsorption curves were generated by plotting the transient total sulfur concentration normalized by the feed total sulfur concentration versus cumulative fuel volume.

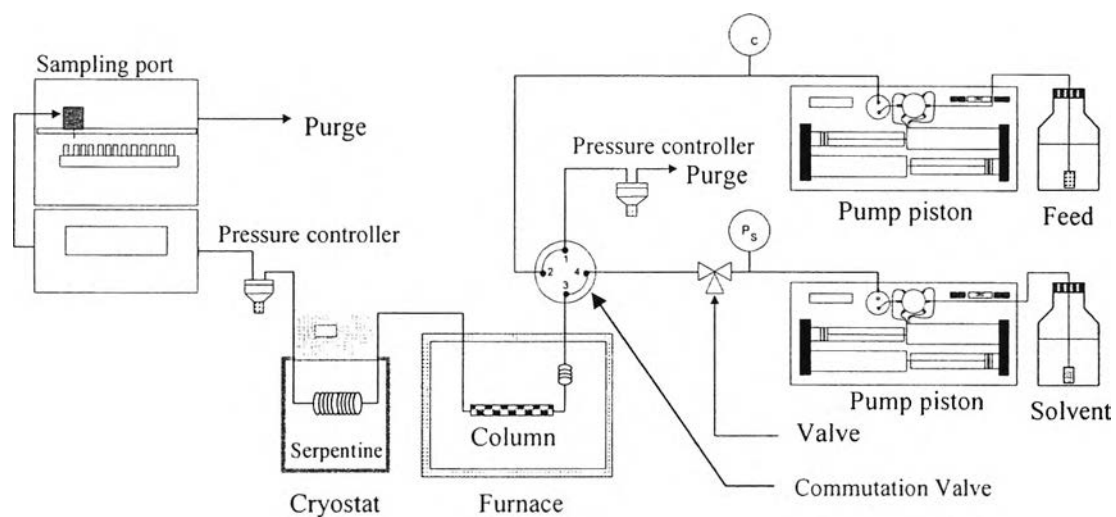


Figure 3.1 Schematic of the fixed bed adsorption breakthrough (Unit 179, IFP-Lyon, France).

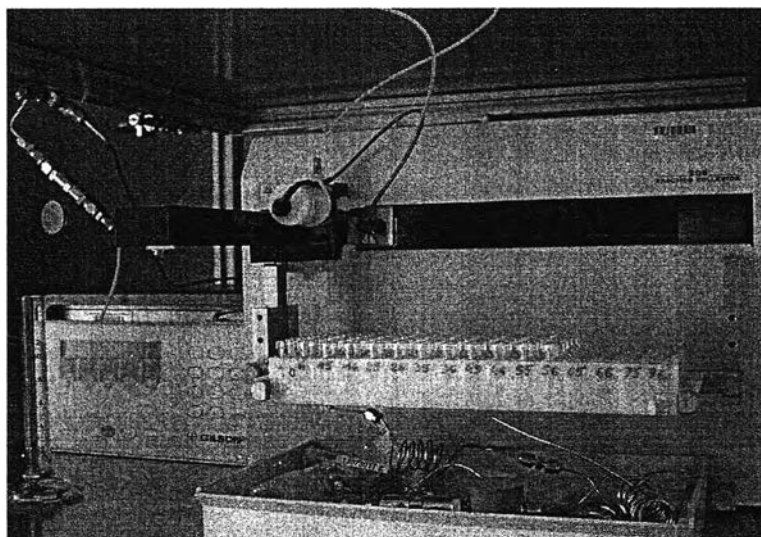


Figure 3.2 Collector in the fixed bed adsorption model.

3.3.6 Sulfur Compounds Analysis

Sulfur compounds are analyzed by using gas chromatography (HP 5890 Series2) with a FID detector and HP-5 column. Concentration of the sulfur compound in the liquid phase is determined. Then the breakthrough curve can be constructed to evaluate the adsorption capacity and selectivity of the adsorbent. The conditions of gas chromatography used in this experiment are summarized in Table 3.2.

Table 3.2 GC conditions for the analysis

Setting	Condition
Injection temperature	250°C
Oven temperature	50°C/5min, 10°C/min to 250°C, hold for 1 min
Detector temperature	280°C
Carrier gas	Helium 99.99% purity
Injection volume	1 μ l

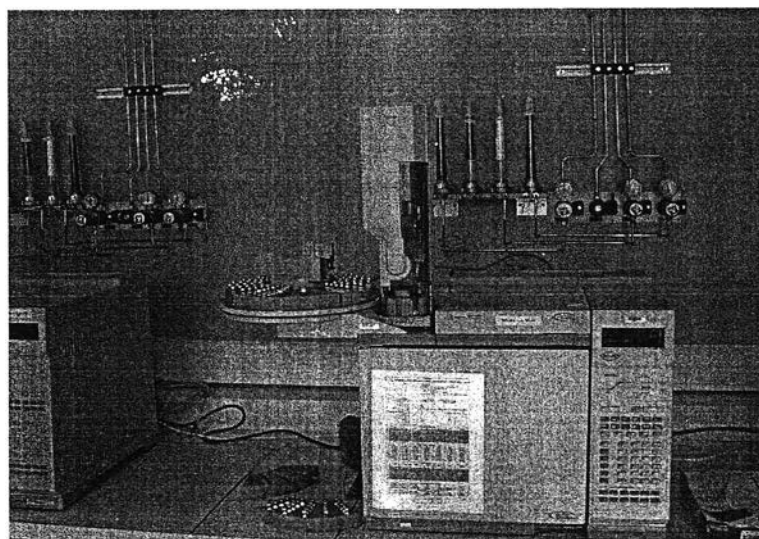


Figure 3.3 Gas chromatography.

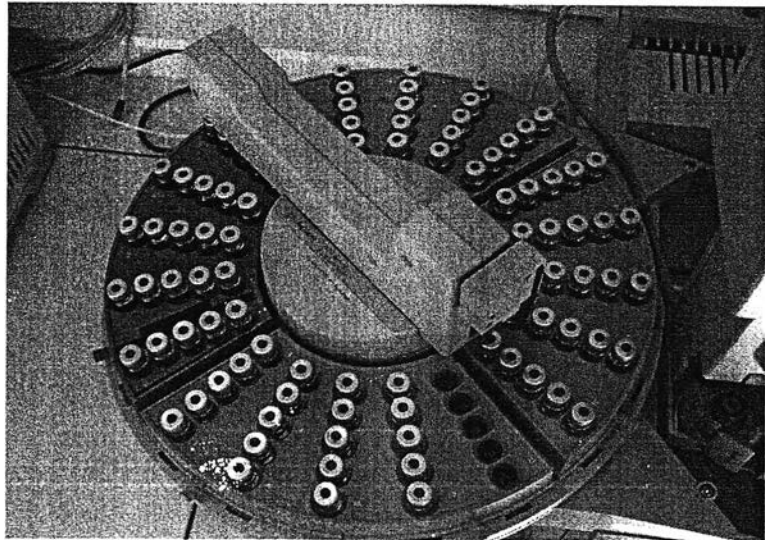


Figure 3.4 Support of vials in gas chromatography.

3.3.7 Calculation Method of Breakthrough Curve

The adsorber geometry is schematically depicted in Figure 3.5. Simulated diesel is fed to the fixed bed adsorber packed with adsorbents having a biporous structure. The void between the crystals creates macropores. These pores act as conduit for transportation of the sulfur compound molecules from bulk phase to the interior of the crystal. Once the sulfur compounds molecules are inside the particle, they are adsorbed at the pore mouth of the micropores and hence, the adsorbed specific diffuse into the interior of the crystal through micropores of the crystal. The diffusion process in the macropores and mesopores follows the molecular diffusion mechanisms while that inside the crystal follows an intra crystalline diffusion mechanism. Thus, in case of former, adsorption is usually controlled by intra crystalline diffusion.

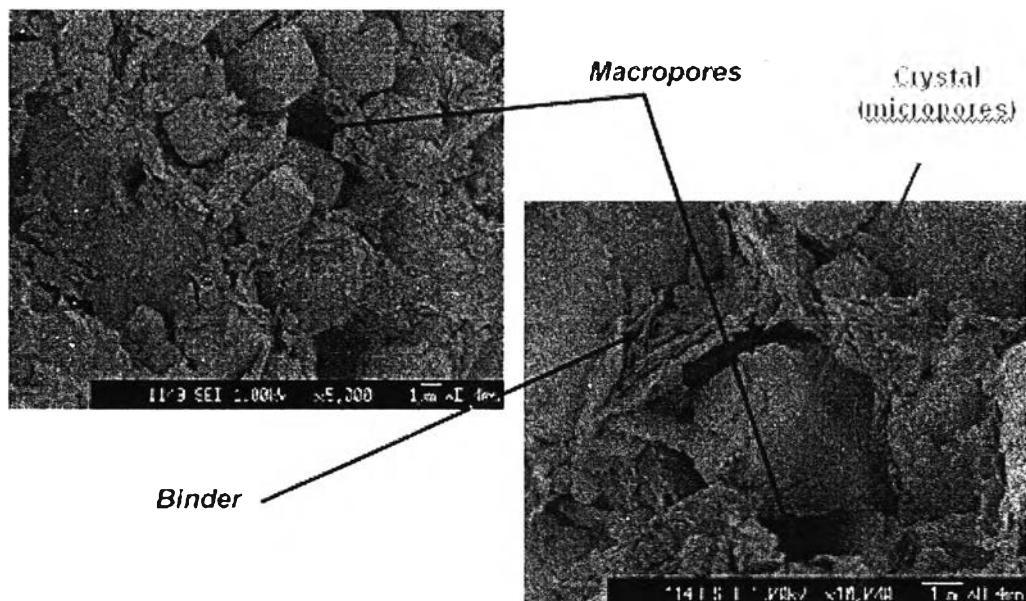
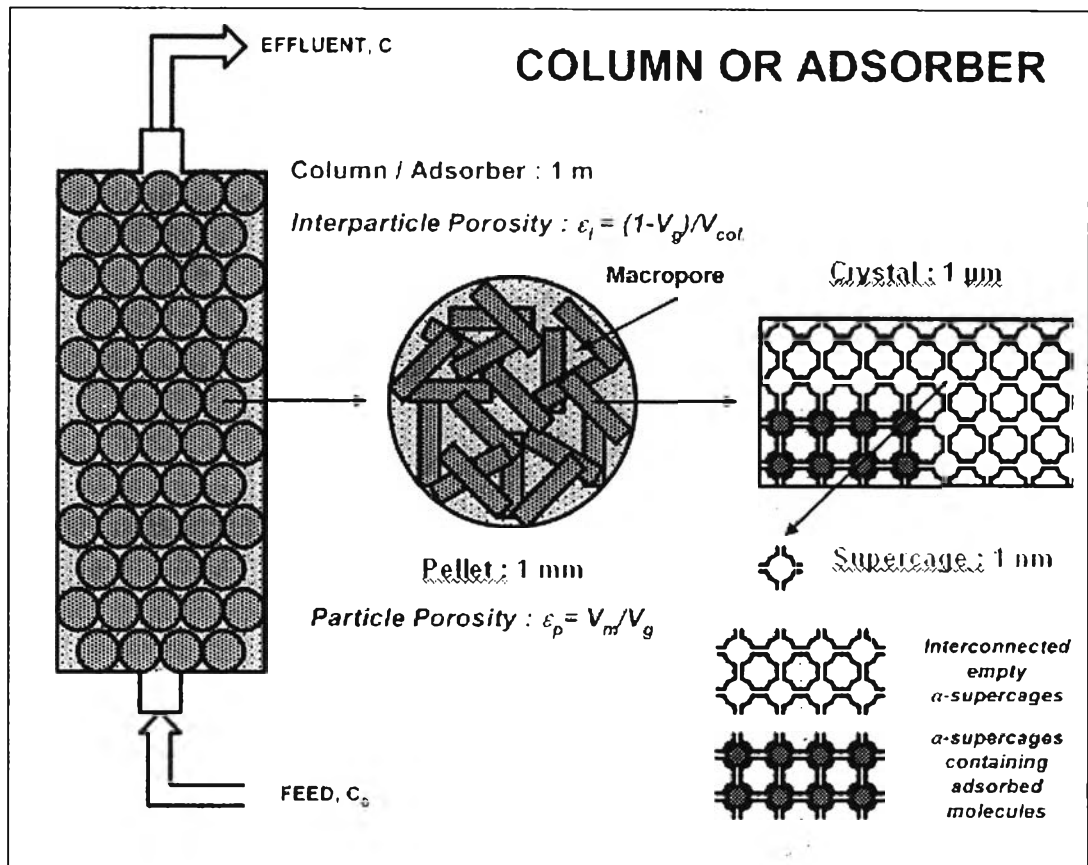


Figure 3.5 The adsorber geometry.

3.3.7.1 Definitions of the Different Volumes in the Column

The total volume of the column:

- The total volume of the column: V_C
- The total inter-particle volume = The void volume between the particles: V_I
- The total volume of the adsorbent particles: V_P

➤ Volume balance:

$$V_C = V_I + V_P \quad (3.1)$$

The total adsorbent particle volume can be divided into:

- The macro porous volume (Void between the crystals within the particle): V_M
- The micro porous volume (α -cages = calculated from "Dubinin Volume" form N_2 at 77K adsorption): V_μ
- The volume of the solid (Si, Al, O, C, Ni, Cu, cations, binder, etc.): V_S

➤ Volume balance:

$$V_P = V_M + V_\mu + V_S \quad (3.2)$$

3.3.7.2 Porosity Levels in the Column

- Inter-particle porosity: ε_I = Void between the particles (beads, extrudates) of adsorbent
- Particle porosity: ε_P = Macro porous void in the particles (beads, extrudates) of adsorbent
- Total Bed porosity: ε_B = Void between particle + macro porous void in the particles = volume occupied by the fluid (liquid) phase

$$\varepsilon_I = \frac{V_I}{V_C} \quad (3.3)$$

$$\varepsilon_P = \frac{V_M}{V_P} \quad (3.4)$$

$$\varepsilon_B = \frac{V_I + V_M}{V_C} = \frac{V_I}{V_C} + \frac{V_M}{V_P} \frac{V_P}{V_C} = \frac{V_I}{V_C} + \frac{V_M}{V_P} \frac{(V_C - V_I)}{V_C} = \varepsilon_I + (1 - \varepsilon_I) \varepsilon_P \quad (3.5)$$

Determination of ε_I and ε_P : by "density measurements"

- Bulk density: $\rho_B = \text{Mass of solid } (M_S) / \text{Bulk volume occupied } (V_C)$
- Particle density: $\rho_P = \text{Mass of solid } (M_S) / \text{Volume of Particles (from Hg porosimetry at low pressure) } (V_P)$
- Structural density: $\rho_S = \text{Mass of solid } (M_S) / \text{Volume of Particles, macro porosity excluded (from Hg porosimetry at high pressure) } (V_S + V_\mu)$
- Macroporous volume: $V_M = \text{Macroporous volume per gram of solid (Hg porosimetry at "high" pressure)}$

$$\rho_B = \frac{M_S}{V_C} \quad (3.6)$$

$$\rho_P = \frac{M_S}{V_P} \quad (3.7)$$

$$\rho_S = \frac{M_S}{V_S + V_\mu} \quad (3.8)$$

$$\varepsilon_I = \frac{V_I}{V_C} = \frac{V_C - V_P}{V_C} = 1 - \frac{V_P}{V_C} \frac{M_S}{M_S} = 1 - \frac{\rho_B}{\rho_P} \quad (3.9)$$

$$\varepsilon_P = \frac{V_M}{V_P} = \frac{V_P - (V_S + V_\mu)}{V_P} = 1 - \frac{(V_S + V_\mu) M_S}{M_S V_P} = 1 - \frac{\rho_P}{\rho_S} \quad (3.10)$$

$$\varepsilon_P = \frac{V_M}{V_P} = (v_M M_S) \frac{\rho_P}{M_S} = v_M \rho_P \quad (3.11)$$

3.3.7.3 First Moment of the Breakthrough Curve (μ)

The breakthrough curve can be defined as the "S" shaped curve that typically results when the effluent adsorbate concentration is plotted against time or volume (as seen in Figure 3.6). Breakthrough curves can be

constructed for full scale, dynamic, or pilot testing. The breakthrough point is the point on the breakthrough curve where the effluent adsorbate concentration reaches its maximum allowable concentration, which often corresponds to the treatment goal. The treatment goal is usually based on regulatory or risk based numbers. The main aim when sizing adsorptive columns is the ability to predict the service time (or total effluent volume) until the column effluent exceeds breakpoint concentration.

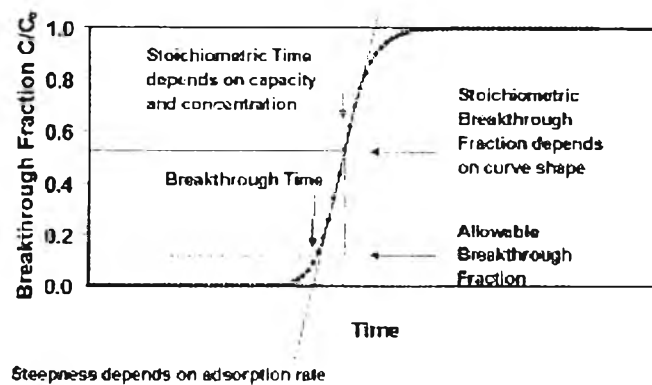


Figure 3.6 Characteristics of a typical adsorption breakthrough curve.

A breakthrough curve is defined by three characteristics: geometric midpoint (stoichiometric time and corresponding relative concentration), steepness, and shape. The midpoint is determined by the flow rate, the concentration, and the capacity of the adsorbent bed and temperature. The steepness of a breakthrough curve is related to the rate (speed) at which the sulfur compounds are removed from the simulated fuels as it flows through the bed. In the simplest case, steepness is described by an overall mass-transfer (adsorption) rate coefficient, which is larger for larger adsorption rates. If this rate coefficient is constant throughout the breakthrough process, the shape of the breakthrough curve will be symmetrical. However, it has often been observed that breakthrough curves are skewed (asymmetrical), usually steeper at the beginning of breakthrough than at the end.

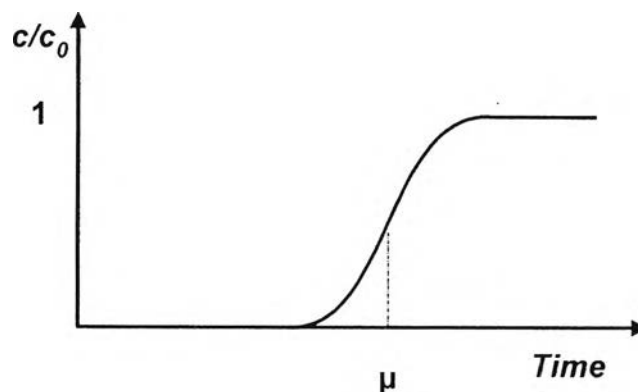


Figure 3.7 The first moment of the breakthrough curve (μ).

In order to apply moment analysis to a pulse response curve to estimate linear adsorption constants and mass transfer parameters, the following assumptions are made:

- ❖ The mobile phase is a dilute solution.
- ❖ Velocity is constant throughout column cross-section. This assumption is valid due to the fact change in concentration of adsorbing species is occurred at trace level which does not contribute to a significant change in local velocity inside the bed.
- ❖ No chemical reactions occur.
- ❖ Temperature is uniform throughout the bed and the pellet.
- ❖ Intra-particle diffusion is described by pore diffusion. For a linear isotherm system, the flux due to surface diffusion, if important, can be lumped together with the pore diffusion flux.
- ❖ External mass transfer from the bulk liquid to the pores is described by film mass transfer.
- ❖ Axial dispersion effects are considered.

First Moment of the Breakthrough Curve (μ) (Figure 3.7):

$$\mu_1 = \mu = \int_0^{\infty} (1-y) dt \quad y = \frac{c(t)}{c_0} \quad (3.12)$$

For a given adsorbed component (sulfur compounds), at $t = \mu$, all the sulfur compounds introduced in the column is in the column. So, the total amount of sulfur compounds in the column:

$$Q^{TOT} = \mu FC = \mu S_c uC = \mu \frac{V_c}{L_c} uC \quad (3.13)$$

Where Q^{TOT} = total amount of sulfur compounds in the column (mole or g)
 μ = mean breakthrough time (experimental determination or calculation)
 C = concentration of sulfur compounds in the feed (mole or g)
 F = feed flow rate (cm^3/min)
 V_c, S_c, L_c = volume, section and length of the column (adsorbent bed)
 u = superficial liquid velocity in empty column (cm/min)
 ϵ = ratio flow rate / column section

Sulfur compounds in the column is partially adsorbed in $V\mu$, and partially adsorbed in solution (at feed concentration) in $V_I + V_M$. So:

$$Q^{TOT} = \epsilon_i V_c C + (1 - \epsilon_i) V_c Q \quad (3.14)$$

Where Q = total amount of sulfur compounds in the particle (in $V_M + V_\mu$)

By comparing the two expressions (1) and (2) for Q^{TOT} , we have:

$$Q^{\text{TOT}} = \mu \frac{V_c}{L_c} u C = \varepsilon_l V_c C + (1 - \varepsilon_l) V_c Q \quad (3.15)$$

$$\mu = \frac{L_c}{u} \left[\varepsilon_l + (1 - \varepsilon_l) \frac{Q}{C} \right] = \frac{L_c}{v} \left[1 + \frac{(1 - \varepsilon_l) Q}{\varepsilon_l C} \right] \quad (3.16)$$

Where v = real liquid velocity ($v = \frac{u}{\varepsilon_l}$)

We have also:

$$Q = \varepsilon_p C + (1 - \varepsilon_p) q \quad \text{or} \quad \frac{Q}{C} = \varepsilon_p + (1 - \varepsilon_p) \frac{q}{C} = \varepsilon_p + (1 - \varepsilon_p) K \quad (3.17)$$

Where q = amount of sulfur compounds adsorbed in the micropores only

K = the equilibrium adsorption constant