CHAPTER III
EXPERIMENTAL

3.1 Materials

Macro- and mesoporous alumina and activated carbon used as adsorbents were provided from Institut Français du Pétrole (IFP, France) and VWR respectively.

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

Dodecane (C$_{12}$H$_{26}$, 99%) and Toluene (C$_7$H$_8$), which represented as composition in simulated diesel fuel, were purchased from VWR.

Dibenzothiophene (C$_{12}$H$_8$S, 98%) which represented sulfur compounds in simulated diesel fuel, were purchased from Alfa Aesar. Their relevant properties are shown in Table 3.1.

Table 3.1 Physical properties of sulfur compounds and simulated diesel fuel

Material	Molecular weight (g/mol)	Boiling point (°C)	Density (g/cm^3)
Dodecane	170.34	216.2	0.75
Toluene	92.14	110.6	0.8669
Dibenzothiophene	184.26	332-333 @ 760 mmHg	-

3.2 Equipments

1. Gas Chromatograph (HP 5890 Series2) with FID detector and HP-5 column (30 m*0.32mm*0.25mm film thickness)

2. N_2 adsorption/desorption analyzer (Micromeritics ASAP 2420)

3. Hg porosimeter (AutoPore IV 9500 series)

4. Temperature-Programmed Reduction analyzer (AutoChem 2920)

5. Scanning electron microscopy (ZEISS Supra 40)

6. Magnetic stirrer

7. Oven

8. Fixed bed column

9. Collector, vial 1.8 cm^3 and Inserter 0.1 cm^3

10. Glassware

3.3 Methodology

3.3.1 Adsorbents Preparation

3.3.1.1 Preparation of Cu^{2+} Impregnated on Activated Alumina by Using $CuCl_2$ in Deionized Water

Impregnated activated alumina adsorbent was prepared by the incipient wetness method. Firstly, activated alumina was dried in an oven at 250°C for 24 hours. $CuCl_2$ was used because it is very solutable in water but CuCl is very insolutable in water. A known amount of $CuCl_2$ was magnetically stirred in deionized water ($CuCl_2$ monolayer was calculated). 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 imbibed the solution containing the salt into its pore structure, the adsorbent was dried to remove the water in the oven at 110°C for 24 hours (Takahashi et al., 2000). The adsorbents were prepared with different metal loadings, from 100 % = theoretical amount corresponding to monolayer coverage, down 75% and 50%, respectively.

3.3.1.2 Preparation of Cu^{2+} Impregnated on Activated Carbon by Using $CuCl_2$ in HCl

Impregnated activated carbon (AC) adsorbent was prepared by impregnating activated carbon with $CuCl_2$. The activated carbon was dried in an oven at 250°C for 24 hours. The amount of $CuCl_2$ at concentration 43 wt % was magnetically stirred in 1M HCl aqueous solution by the volume of the solution equal to the total pore volume of AC then brought into contact with AC drop by drop. After 24 h, the sample was washed with deionized water until the pH of the water became around 5.0, and the sample was died in the oven at 110°C for 24 hours. (Wang and Yang, 2007).

3.3.1.3 Preparation of Ni^{2+} Impregnated on Activated Alumina by Using $NiCl_2$ in Deionized Water

Impregnated activated alumina was prepared by the incipient wetness method. A known amount of $NiCl_2$ was magnetically stirred in 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 imbibed the solution containing the salt into its pore structure, the adsorbent was dried to remove the water in the oven at 110°C for 24 hours (Takahashi *et al.*, 2000). The adsorbents were prepared with different metal loadings, from 100 % = theoretical amount corresponding to monolayer coverage, down 75% and 50%, respectively.

3.3.2 Reduction

The reduction condition was obtained from TPR characterization. $CuCl_2/Al_2O_3$ was reduced to Cu^+ under H_2 atmosphere at a flow rate of 74 cm^3/min/g, heated up to 290 °C at heating rate 6.5 °C/min then hold for 1 hour. Then the temperature was reduced to ambient temperature for subsequent adsorption experiment.

3.3.3 Characterization of Adsorbents

The temperature of reduction Cu^{2+} to Cu^+ was obtained by using Temperature-Programmed Reduction (TPR) using AutoChem 2920. 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% H_2 in Ar at flow rate of 74 cm^3/min/g and the heating rate was 5 °C/min.

BET surface area and pore volume of the adsorbents were measured by N_2 adsorption/desorption method at 77 K using Micromeritics ASAP 2420. To eliminate adsorbed volatile compounds from the pores, before being analyzed, adsorbents were dried and evacuated at 300 °C for at least 3 hours.

Particle density, structural density and pore volume were measured by Hg porosimeter, AutoPore IV 9500 series.

Scanning electron microscopy (SEM) images were obtained from Zeiss Supra 40. The analysis was done at a resolution of 8 mm at 15 kV under high vacuum and ambient temperature.

3.3.4 Preparation of Simulated Diesel

Dodecane and Toluene was used as a simulated diesel. DBT was used as the sulfur compounds at concentration of 150 ppm of S.

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 (the volume of the column around 8 cm^3). For $CuCl_2$ impregnated on the adsorbents, initially the adsorbent was loaded inside the column (5-6 g for alumina and 3 g for AC), then reduced from Cu^{2+} to Cu^+ by using H_2 at flow rate 37 cm^3/min, heated up to 290°C and hold temperature for 1 hour. 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 around 5-6 g (depend on the concentration of metal) of the adsorbent was loaded inside the column, and activated using N$_2$ at 200°C and hold temperature for 1 hour (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 the same flow rate of feed flow rate 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 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.
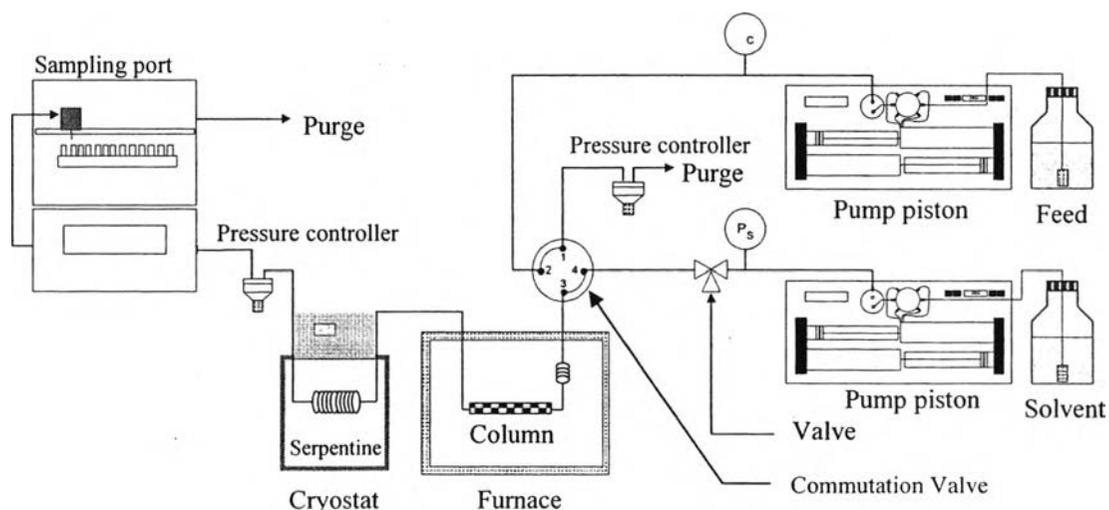
Figure 3.1 Schematic of the fixed bed adsorption breakthrough (Unit 179, IFP-Lyon, France).

3.3.6 Sulfur Concentration Analysis

All of the samples which collected during breakthrough experiments were 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 was 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 Gas chromatography 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 μl

3.3.7 Calculation Method of Breakthrough Curve

The adsorber geometry is schematically depicted in Figure 3.2. 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.
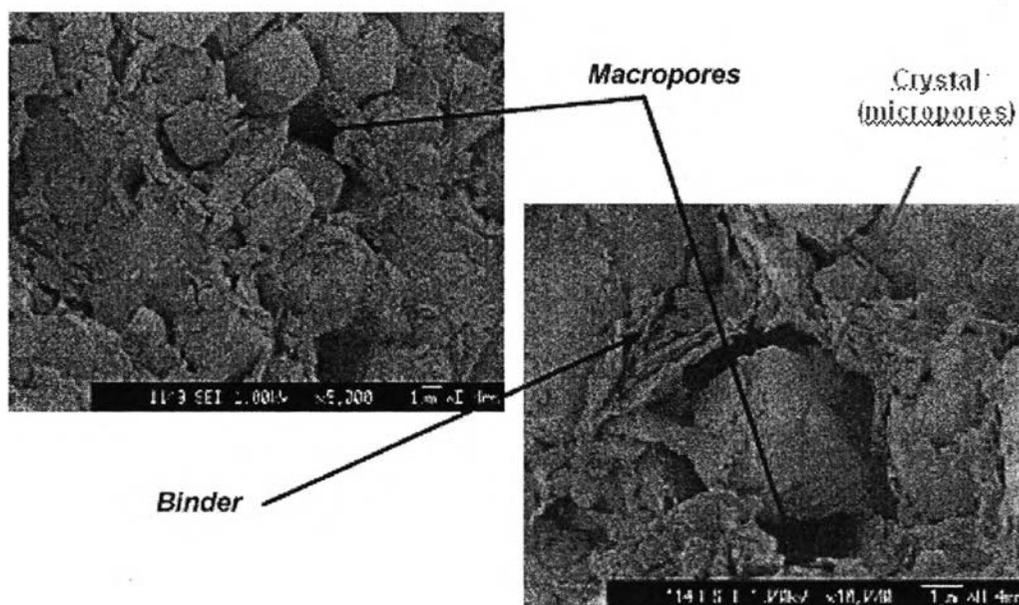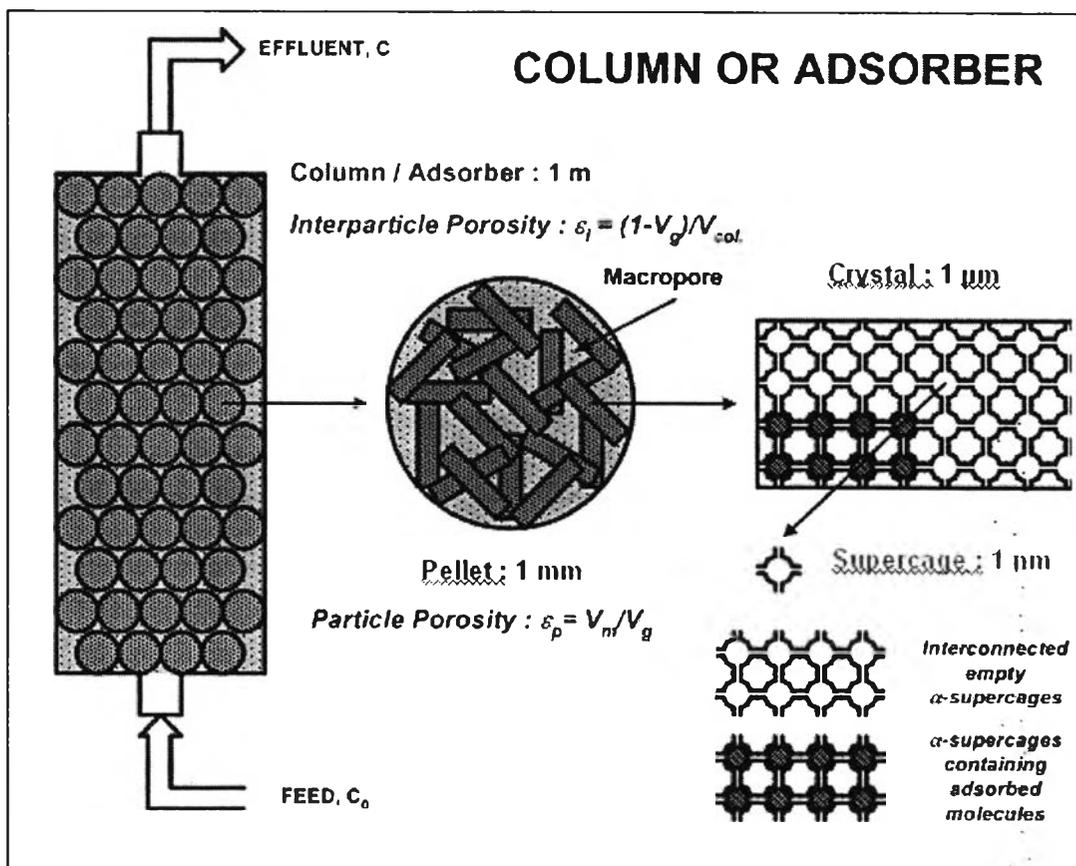
COLUMN OR ADSORBER

EFFLUENT, C

Column / Adsorber : 1 m

Interparticle Porosity : $\varepsilon_i = (1-V_g)/V_{col.}$

Macropore

Crystal : 1 μm

Pellet : 1 mm

Particle Porosity : $\varepsilon_p = V_n/V_g$

Supercage : 1 nm

Interconnected empty α-supercages

α-supercages containing adsorbed molecules

FEED, C₀

Macropores

Crystal (micropores)

Binder

Figure 3.2 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:

$$V_C = V_I + V_P \tag{3.1}$$

The total adsorbent particle volume can be divided into (case of microporous solids):

- 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): $V\mu$
- The volume of the solid (Si, Al, O, C, Ni, Cu, cations, binder, etc.): V_S

➢ Volume balance:

$$V_P = V_M + V_\mu + V_S \tag{3.2}$$

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

$$\varepsilon_I = \frac{V_I}{V_C} \tag{3.3}$$

$$\varepsilon_P = \frac{V_M}{V_P} \tag{3.4}$$

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

Determination of ε_I and ε_P : by "density measurements"

- Bulk density: ρ_B = Mass of solid (M_S) / Bulk volume occupied (V_C)
- Particle density: ρ_P = Mass of solid (M_S) / Volume of Particles (from Hg porosimetry at low pressure) (V_P)
- Structural density: ρ_S = Mass of solid (M_S) / Volume of Particles, macro porosity excluded (from Hg porosimetry at high pressure) ($V_S + V\mu$)
- Macroporous volume: V_M = Macroporous volume per gram of solid (Hg porosimetry at "high" pressure")

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

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

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

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

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

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

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.
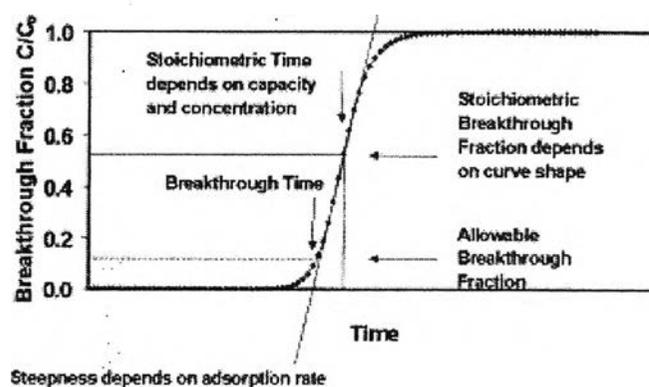
Figure 3.3 Characteristics of a typical adsorption breakthrough curve.

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.
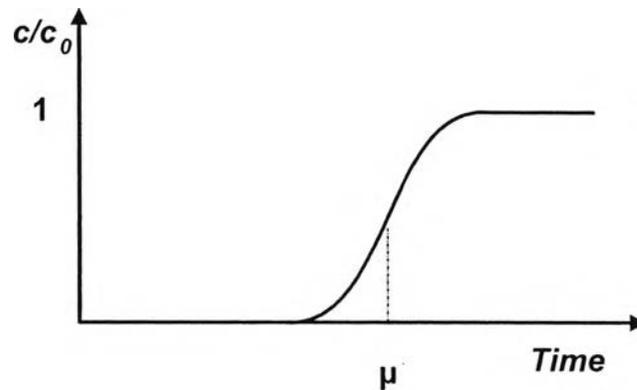
Figure 3.4 The first moment of the breakthrough curve (μ).

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):

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

(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:

$$Q^{TOT} = \mu FC = \mu S_c uC = \mu \frac{V_c}{L_c} uC$$

(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)

= 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:

$$Q^{TOT} = \varepsilon_I V_C C + (1-\varepsilon_I)V_C Q$$

(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:

$$Q^{TOT} = \mu \frac{V_C}{L_C} uC = \varepsilon_l V_C C + (1 - \varepsilon_l) V_C Q \tag{3.15}$$

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

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

We have also:

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

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

   K   = the equilibrium adsorption constant