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APPENDICES

APPENDIX A Calculation of Sample Preparation

A1 Amount of Metal Chemical for Sample Preparation

Example: Amount of $CuCl_2$ chemical for impregnation of macroporous alumina (Concentration of metal is corresponded to monolayer of $CuCl_2$ on macroporous alumina surface)

From

Monolayer of CuCl on alumina surface $= 0.095$ g CuCl/100 m^2 of alumina

Surface area of macroporous alumina $= 194\ m^2/g$

Monolayer of CuCl on alumina surface $= \dfrac{0.095 \times 194}{100}$

$= 0.184$ g CuCl/1 g of alumina

$= \dfrac{0.184}{98.999}$

$= 0.00186$ mole CuCl/1 g of alumina

Starting chemical: $CuCl_2$

To obtain monolayer on macroporous alumina, $CuCl_2$ is used as the same molar concentration of CuCl.

Monolayer of $CuCl_2$ on macroporous alumina surface

$= 0.00186$ mole $CuCl_2$ /1 g of alumina

$= 0.00186 \times 134.45$

$= 0.250$ g $CuCl_2$ /1 g of alumina

From

Pore volume of macro porous alumina $= 0.674\ cm^3/g$ of alumina

Amount of $CuCl_2$ used $= \dfrac{0.250}{0.674}$

So, amount of $CuCl_2$ used $= 0.371$ g $CuCl_2/cm^3$

A2 <u>Simulated Diesel Fuel Preparation</u>

Example: Preparation of 1000 cm^3 simulated diesel (80%wt. Dodecane, 20%wt. of Paradiethylbenzene and 150 ppmw of Dibenzothiophene)

From

Density of Dodecane = 0.75 g/cm^3

Density of Paradiethylbenzene = 0.87 g/cm^3

Molecular weight of Dibenzothiophene (DBT) = 184.26

Density of simulated diesel $= \left(\frac{80 \times 0.75}{100}\right) + \left(\frac{20 \times 0.87}{100}\right)$

So, density of simulated diesel = 0.774 g/cm^3

Weight of simulated diesel $= 0.774 \times 1000$

So, weight of simulated diesel = 774.00 g

Amount of Dodecane $= \left(\frac{80}{100}\right) \times 774 = 619.20$ g

Amount of Paradiethylbenzene $= \left(\frac{20}{100}\right) \times 774 = 154.80$ g

Dibenzothiophene concentration = 150 ppmw

$= \frac{150}{10^6}$

= 0.00015 g of S/g of simulated diesel

$= \frac{0.00015}{32}$

$= 4.69 \times 10^{-6}$ mole of S/g of simulated diesel

$= (4.69 \times 10^{-6}) \times 184.26$

$= 8.64 \times 10^{-4}$ g of DBT/g of simulated diesel

Amount of Dibenzothiophene $= (8.64 \times 10^{-4}) \times 774.00$

So, amount of Dibenzothiophene = 0.6685 g

APPENDIX B Calculations of Amount of Metal Loading on Adsorbents

B1 Amount of Metal Loading on Adsorbent

From

$$C_{i;1} = C_{i;2} \times T$$

$$M = C_{i,2} \times V_0 \times 10^{-6}$$

$$\%wt = \frac{M}{A_0} \times 100\,\% \qquad (A1.1.1)$$

Where,

$C_{i,1}$ = Concentration before dilution (μg/ml)

$C_{i,2}$ = Concentration after dilution of metal solution (μg/ml)

T = Times of dilution

M = Amount of metal loading on adsorbent (g)

V_o = Initial volume of metal solution (ml)

%wt = Weight percent (%)

A_o = Weight of initial adsorbent (g)

Example: Amount of Ni^{2+} loading on macroporous alumina

Result data from AAS ($C_{Ni,2}$) = 2.30 μg/ml

Times of dilution (T) = 5

Therefore, concentration before dilution ($C_{Ni,1}$)

$= 2.30 \times 5$

$= 11.50$ μg/ml

Initial volume of metal solution (V_o) = 100 ml

So, amount of metal loading on macroporous alumina

$= 11.50 \times 100 \times 10^{-6}$

= 0.001150 g

Weight of initial adsorbent (A_o) = 0.0263 g

Weight percent (%wt) $= \dfrac{0.001150}{0.0263} \times 100$

$= 2.04\ \%$

APPENDIX C Calculation of Amount of Adsorption of Sulfur Compounds in Dynamic Adsorption Experiment

C1 Death-Volume of Fixed Bed Reactor

To find out the death-volume of fixed bed reactor, the breakthrough curve of simulated diesel fuel (80% dodecane, 20% paradiethylbenzene and 150 dibenzothhiophene) without adsorbent was performed in this study. By applying first moment of the breakthrough curve (μ), we can determine the death-volume:

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

Where μ: mean breakthrough volume

C: concentration of sulfur compounds in the feed (mole or g)

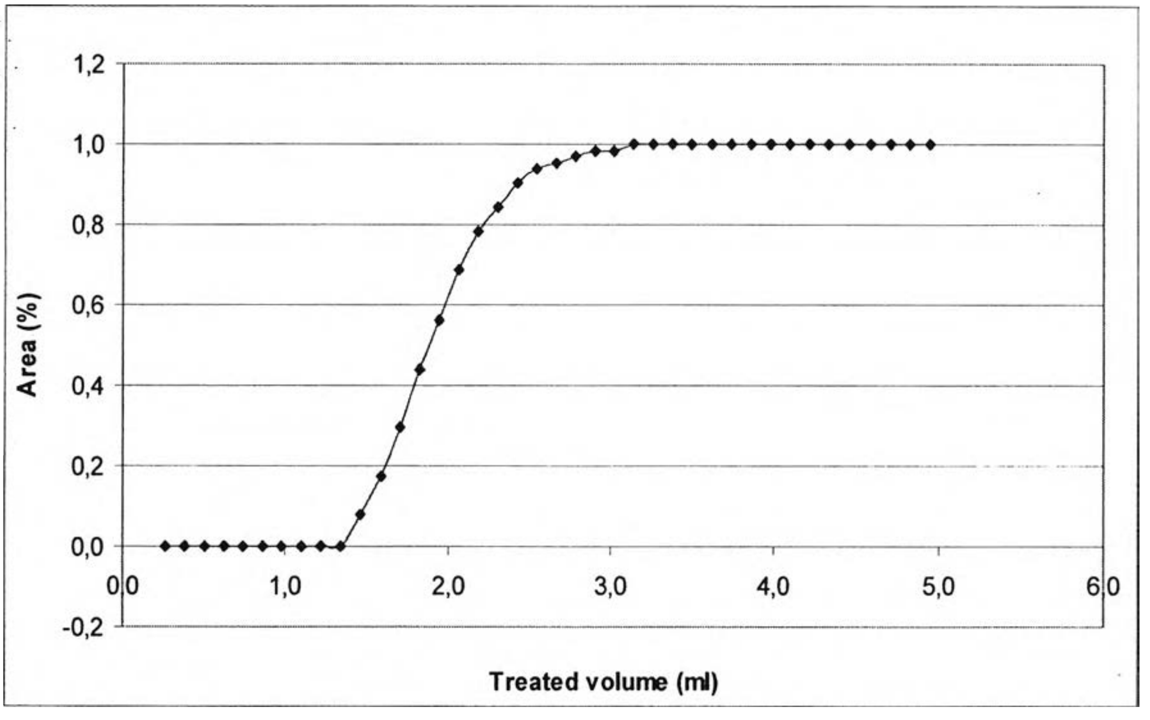

Figure C1. Breakthrough curve without adsorbent.

Hence, Death-volume = μ = 1.932 ml

C2 <u>Amount of Adsorption of Sulfur Compounds in Dynamic Adsorption</u> Experiment

Example: Adsorption of dibenzothiophene in simulated diesel fuel (72.6% dodecane, 20% paradiethylbenzene, 7% naphthalene, 0.4% phenanthrene, 150 ppmw sulfur content) on Ni^{2+} impregnated on mesoporous alumina

Setting parameter of breakthrough adsorption experiment:

Number of the collected vials	= 80
Collected time	= 4.50 min
Waste time	= 4.83 min
Wait time	= 5.94 min
Flow rate (F)	= 0.4 cm^3/min
Death-volume	= 1.932 cm^3
Diameter of grain	= 0.25 mm
Structural density (ρ_S)	= 2.739 g/cm^3
Macroporous volume (V_M)	= 0.009 cm^3/g
Mesoporous volume (V_m)	= 0.654 cm^3/g
Microporous volume (V_μ)	= 0.000 cm^3/g
Mass of adsorbent	= 5.93 g
Density of simulated diesel fuel (d)	= 0.774 g/cm^3
Particle density (ρ_P)	= 0.575 g/cm^3
Bulk density (ρ_B)	= 0.675 g/cm^3
C_0 (DBT)	= 150 ppm

T_a = Waste time + Wait time/2

= 7.800 min

T_p = Total time / Numbers of vials

= 10.440 min

u (superficial liquid velocity in empty column, cm/min)

= flow rate / column section

= 0.509 cm/min

Particle porosity (ε_P) = Partical density × V_M

= 0.005

Interparticle porosity (ε_I) = $1-\left(\frac{\rho_B}{\rho_P}\right)$

= 0.000

Total Macroporous volume = V_M × Mass of adsorbent

= 0.053 cm^3

Total Microporous volume = V_μ × Mass of adsorbent

= 0.000 cm^3

Total Macroporous and Microporous volume

= 0.053 cm^3

Total Bed porosity (ε_B) = Total Macroporous and Microporous volume/ Volume of column

= 0.006

At the Collected vials number i:

Average time = $T_a + \left(i-\frac{1}{2}\right) \times T_P$

Average volume of fuel = $(T_a \times F) + \left(i-\frac{1}{2}\right) \times T_P \times F$

Amount of treated volume = Average volume of fuel – Death volume

Hence, Cumulative effluent volume of DBT

= μ_{DBT}

= 6.984 cm^3

= 6.984 / mass of adsorbent

= 1.178 cm^3g-adsorbent

Mass of cumulative effluent volume of DBT

= $\mu_{DBT} \times d_{DBT}$

= 0.946 g

Amount of DBT in the column (M_{DBT})

$$= \mu_{DBT} \times d_{DBT} \times C_0$$

= 0.062 g

Amount of DBT adsorbed = $M_{DBT} \times (1 - \varepsilon_B)$

= 0.062 g

= 0.062 × 1000/mass of adsorbent

= 62 mg/g-adsorbent

= 62 / molecular weight of DBT

= 0.336 mmole/g-adsorbent

Cumulative effluent volume of Naphthalene

$$= \mu_N$$

= 6.825 cm^3

= 6.825 / mass of adsorbent

= 1.151 cm^3/g-adsorbent

Mass of Cumulative effluent volume of Naphthalene

$$= \mu_N \times d_N$$

= 0.925 g

Amount of Naphthalene in the column (M_N)

$$= \mu_N \times d_N \times C_0$$

= 7.057 g

Amount of Naphthalene adsorbed

= $M_N \times (1 - \varepsilon_B)$

= 7.015 g

= 7.015 × 1000/mass of adsorbent

= 7015 mg/g-adsorbent

= 7015 / molecular weight of Toluene

= 54.732 mmole/g-adsorbent

Cumulative effluent volume of Phenanthrene

$= \mu_P$

$= 10.336\ cm^3$

$= 10.336$ / mass of adsorbent

$= 1.743\ cm^3/g$-adsorbent

Mass of Cumulative effluent volume of Phenanthrene

$= \mu_P \times d_P$

$= 1.340$ g

Amount of Phenanthrene in the column (M_P)

$= \mu_P \times d_P \times C_0$

$= 0.570$ g

Amount of Phenanthrene adsorbed

$= M_P \times (1 - \varepsilon_B)$

$= 0.567$ g

$= 0.567 \times 1000$/mass of adsorbent

$= 567$ mg/g-adsorbent

$= 567$ / molecular weight of Toluene

$= 3.181$ mmole/g-adsorbent

Selectivity of DBT over Naphthalene

$= \alpha_{Sul/Nap}$

$= \dfrac{q_{sul}/C_{sul}}{q_{Nap}/C_{Nap}}$

$= 2.275$

Selectivity of Phenanthrene over Naphthalene

$= \alpha_{Phe/Nap}$

$= \dfrac{q_{Phe}/C_{Phe}}{q_{Nap}/C_{Nap}}$

$= 2.275$

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1. Prateepamornkul, S.; Malakul, P.; and Michel, T. (2009, April 22) Adsorptive removal of sulfur compounds from diesel using activated carbon and alumina modified with Cu(I) and Ni(II). The 15th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.