CHAPTER III

METHODOLOGY

3.1 Experimental Approach

Eight organoclays were prepared by exchanging the inorganic cations on the surface of clay with organic cation (dodecylpyridinium chloride; DPC) at cation loading level of 0.25-2.00 times the CEC. Organoclays were characterized by Accelerated surface area and porosimetry system, X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). Eight organoclays were used for PAHs sorption studied. PAHs used to prepare synthetic wastewater were naphthalene and phenanthrene. The sorption experiments of PAHs onto clay and organoclays were determined by batch experiment. The sorption capacities and removal efficiencies of eight organoclays for PAHs from synthetic wastewater were compared. All samples were carried out in triplicate and each point on the isotherm is the average of the three samples.
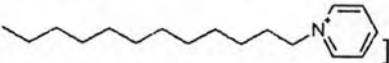
3.2 Materials and Chemicals

1. Clay used in this study was a Na-bentonite which was obtained from Thai Nippon Chemical Industrial Co. Ltd. The cation-exchange capacity (CEC), data from the supplier, was 82 meq/100 g. Dry particle size of clay was 75% passing 200 mesh. The chemical composition of clay is shown in Table 3.1.

Clay sample was washed with deionized water three times to remove soluble inorganic salts and any adhering materials. Then clay sample was separated from aqueous phase by centrifugation at 8000 rmp for 20 min. Clay sample was dried at 105 °C for 24 h and ground to pass a number 40 sieve for further use.

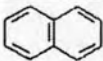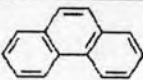**Table 3.1** Chemical composition (in wt.%) of clay

Constituents	Weight (%)
SiO_2	52.0-58.0
Al_2O_3	14.0-18.0
Fe_2O_3	6.0-9.0
Na_2O	2.5-3.5
MgO	2.5-3.2
CaO	2.0-2.5
K_2O	0.2-0.3
TiO_2	1.0-1.4

2. Organic cation used to prepared organoclays was dodecylpyridinium chloride [DPC; ～～～～～N⁺◯] obtained from Aldrich Chemical Company, Inc. Molecular weight is 283.90 g/mol.

3. PAHs used to prepare synthetic wastewater were naphthalene and phenanthrene obtained from Aldrich Chemical Company, Inc. The properties of naphthalene and phenanthrene are shown in Table 3.2.

Table 3.2 Physical and chemical properties of naphthalene and phenanthrene

PAHs	Structure	Molecular weight (g/mol)	Water solubility (mg/L)	Log K_{ow}
Naphthalene		128.16	30.0	3.30
Phenanthrene		178.24	1.0	4.46

Source: Chaipuriwong, 2001; LaGrega et al., 2001

3.3 Instruments

1. UV/visible spectrophotometer

   Helios-Alpha Model UVA 113731

2. CHNS/O analyzer

   Perkin Elmer PE2400 Series II

3. Accelerated Surface Area and Porosimetry System

   Micromeritics Model ASAP 2000

4. X-ray diffraction (XRD)

   Bruker AXS Model D8 Discover

5. Fourier transform infrared spectroscopy (FTIR)

   Perkin Elmer Model 1760x

6. High-pressure liquid chromatography

   Shimadzu, LC-10 AD VP

3.4 Experimental Procedure

3.4.1 Adsorption of DPC onto clay

The adsorption isotherm of DPC onto clay was determined by batch experiment. Clay samples of 250 mg were weighed in each of the centrifuge tube, and then the DPC solution was added with different amounts of DPC equivalent to 0.25-3.00 times the CEC of clay. The quantity of DPC added to clay was calculated by

$$f = \frac{M_{cation}}{CEC \times M_{clay} \times GMW_{cation} \times Z} \qquad 3.1$$

where f = fraction of CEC satisfied by organic cation, M_{cation} = mass of organic cation required to achieve the desired fraction of CEC (mass), M_{clay} = mass of the base clay (mass), GMW_{cation} = gram molecular weight of organic cation (mass/mol), Z = moles of charge per equivalent (mol/equivalent) (Bartelt-Hunt et al., 2003).

These DPC-clay suspensions were shaken at 150 rpm for 18 h under room temperature. The aqueous and solid phases were separated by centrifugation at 8000 rpm for 20 min. The supernatant were removed and analyzed for DPC concentration using UV/visible spectrophotometer at a wavelength of 260 nm (Brownawell et al., 1990). The amount of DPC adsorbed onto clay was calculated by mass balance equation:

$$q_e = \frac{(C_i - C_e)V}{M}$$

<div align="right">3.2</div>

where C_i and C_e were the initial and quilibrium concentrations of DPC, respectively. V was the volume of the solution, q_e was the amount of DPC adsorbed onto clay, and M was the mass of clay used. Adsorption isotherms were obtained by ploting the amount of DPC adsorbed (q_e = mmol/g clay) versus the equilibrium concentrations of DPC (C_e = mmol/L).

3.4.2 Preparation of organoclays

Eight organoclays were prepared by adding amount of DPC equivalent to 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, and 2.00 times the CEC of clay. The mass of DPC needed to achieve the desired fraction of the CEC was calculated using equation 3.1. The desired amount of DPC was dissolved in 100 mL of deionized water and 5 g of the base clay was added to the solution. The samples were shaken at 150 rpm for 18 h under room temperature. Organoclays were separated from aqueous phase by filtration through filter paper (No. 1). Organoclays were then washed with deionized water repeatedly until free of chloride ions as indicated by $AgNO_3$. Organoclays were air dried and ground to pass a number 40 sieve. Organoclays prepared at the amount of DPC equivalent to 0.25 times the CEC was named as 0.25CEC and the others were named in the same way.

3.4.3 Characteristics of clay and organoclays

The elemental analysis was carried out to determine percentages of C, H, and N elements in clay and 1.25CEC. Table 3.3 shows percentages of C, H, and N elements of clay and 1.25CEC.

Table 3.3 Percentages of CHN elements of clay and 1.25CEC

Sorbent	%C	%H	%N
clay	0.479	0.807	-
1.25CEC	16.290	2.832	1.044

These results confirmed that the intercalation of DPC molecules between the clay layers occurred, and were associated with results from Accelerated surface area and porosimetry system, X-ray diffraction (XRD), and Fourier transform infrared spectroscopy (FTIR). Accelerated surface area and porosimetry system and XRD were carried out to determine BET surface area and interlayer spacing of clay and organoclays. FTIR was carried out to study of structure of clay and structural features of organoclays.

3.4.4 Preparation of synthetic wastewater

Synthetic wastewater of each PAHs was prepared by dissolving the desired amount of PAHs in 10 mL methanol and adjusting volume to 1000 mL with deionized water. Concentration of methanol in synthetic wastewater is 1% by volume, a level at which methanol had no measurable effect on adsorption (Kibbey and Hayes, 1993). The initial concentrations of PAHs in synthetic wastewater were prepared at 5-25% of its aqueous solubility.

3.4.5 Sorption of PAHs onto clay and organoclays

Sorption of PAHs onto nine sorbents consisted of clay and eight organoclays were carried out by batch experiment. For sorption isotherm tests of naphthalene, 50 mg of sorbent were weighted into 30 ml glass bottles with caps that were then added with 25 mL synthetic wastewater of naphthalene with different concentrations ranged from 1.5 to 7.5 mg/L. For sorption isotherm tests of phenanthrene, 25 mg of sorbent were weighted into 30 ml glass bottles with caps that were then added with 25 mL synthetic wastewater of phenanthrene with different concentrations ranged from 50 to 250 µg/L. Parafilm was promptly placed on the cap to reduce evaporation. The samples were shaken at 150 rpm for 18 h under room temperature. The aqueous and solid phases were separated by centrifugation at 8000 rpm for 20 min.

The supernatant were removed and analyzed for PAHs concentration. The initial and final PAHs concentrations were determined according to APHA method 6440 (APHA, 1998) using high-pressure liquid chromatography (Shimadzu, LC-10 AD VP) equipped with reverse-phase column C18 and UV detector (254 nm) with isocratic operation (1 mL/min) of mobile phase (80/20 vol.% acetonitrile/water). The blank tests of synthetic wastewater alone were prepared and handled in parallel with the experiments discussed above. These blank tests were used to quantify naphthalene and phenanthrene losses caused by processes other than sorption to the sorbent (e.g., volatilization and sorption to the glassware). Recovery of naphthalene in blank samples ranged from 55 to 60% and phenanthrene from 75 to 80%. Thus, the amounts of PAHs sorbed onto sorbent were calculated as

$$q_e = \frac{(C_b - C_e)V}{M}$$ 3.3

where C_b and C_e were the blank and equilibrium concentrations of sorbate, respectively. V was the volume of the solution, q_e was the amount of sorbate sorbed onto sorbent, and M was the mass of sorbent used. Sorption isotherms of PAHs were obtained by ploting the amount of PAHs sorbed versus the equilibrium concentration of PAHs.

Removal efficiencies (R) of eight organoclays were calculated as percentage using the equation:

$$R = \frac{C_b - C_e}{C_b} \times 100$$ 3.4

where C_b was the blank concentration of sorbate and C_e was the equilibrium concentration of sorbate. Removal efficiencies of eight organoclays for PAHs from synthetic wastewater were tested by analysis of variance (one-way ANOVA) with confidential level of 95%.