CHAPTER IV

RESULTS AND DISCUSSION

This chapter is categorized into three parts:

Part 4.1 Adsorption of DPC onto clay

This part describes experimental results and discusses mechanism of adsorption of DPC onto clay.

Part 4.2 Characteristics of clay and organoclays

Results from accelerated surface area and porosimetry system and X-ray diffraction (XRD) are described for BET surface area and interlayer spacing of clay and organoclays. FTIR spectra are described for structure of clay and structural features of organoclays. In addition, the effect of the amount of organic cations on the characteristics of organoclays is discussed.

Part 4.3 Sorption of PAHs onto clay and organoclays

In this part, experimental results of naphthalene and phenanthrene sorption onto clay and organoclays are described. The sorption capacities of eight organoclays for PAHs from synthetic wastewater were compared. And then sorption mechanism for PAHs by organoclays and effect of the amount of organic cations on PAHs sorption by organoclays are discussed.
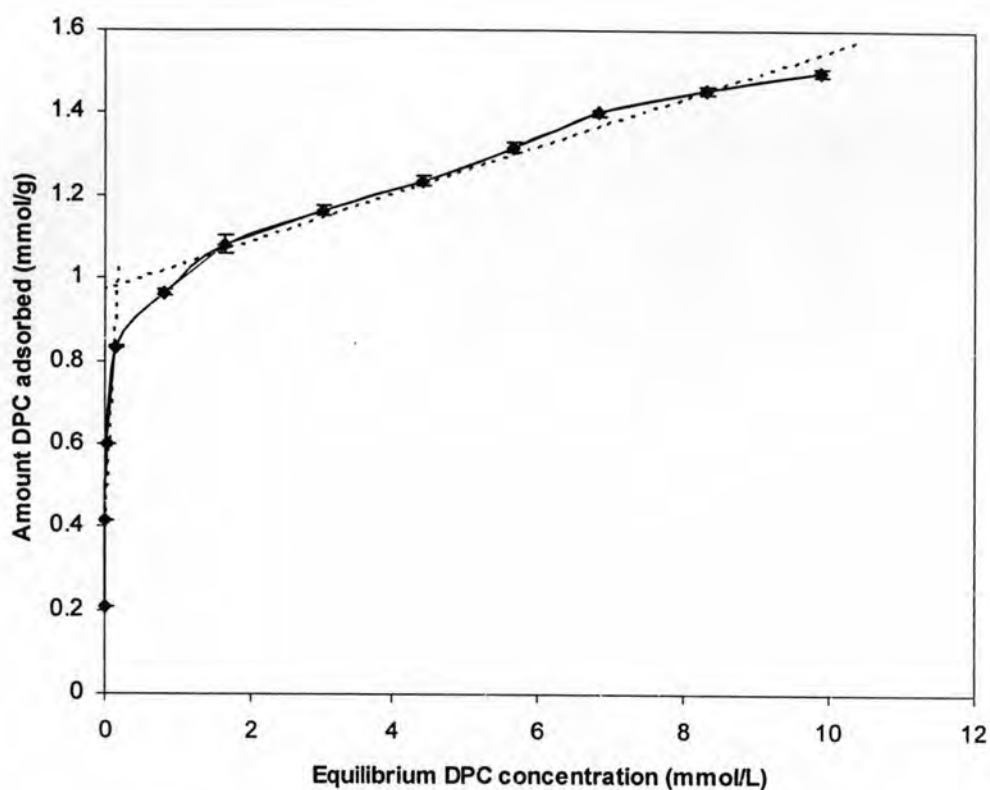
4.1 Adsorption of DPC onto Clay

Figure 4.1 Adsorption isotherm of DPC onto clay

The CEC of clay in this study were 82 meq/100 g. Initial concentrations of DPC were calculated to be equivalent to 0.25-3.00 times the CEC of clay. Figure 4.1 shows the adsorption isotherm of DPC onto clay. From the isotherm, it is obvious that there are two regions on the adsorption isotherm. The first region, from 0.208 to 0.832 mmol/g of the amount DPC adsorbed, corresponding to 0.25 to 1.00 time the CEC, is characterized by nearly vertical line. At the higher adsorbed DPC concentrations, up to 1.00 times the CEC, the slope of the adsorption isotherm decrease gradually. This isotherm suggests that DPC can adsorb onto clay in excess of the CEC of clay. This behavior is similar to the adsorption on montmorillonite of dodecyldimethylbenzylammonium bromide (Kwolek et al., 2003). Koh et al. (2005) studied the adsorb behaviour of cetylpyridinium (hexadecylpyridinium) on smectite (CEC = 115 meq/100 g). The results showed that cetylpyridinium continued to be adsorbed on smectite in proportion to the add amounts until amount equivalent to 2.00 times the CEC, and then the slope of the curve decreased irregularly from 2.00 to 4.20 times the CEC.

Generally, there are two important mechanisms of the organic cation adsorption onto clay: cation exchange and hydrophobic interaction (Xu and Boyd, 1995; Kwolek et al., 2003). At loading levels of organic cations was less than 1.00 time the CEC, cation exchange was apparently the primary mechanism (Chen et al., 2005). The reaction may be expressed as:

$$\text{Clay--M}^+ + \text{OC}^+ = \text{Clay--OC}^+ + \text{M}^+$$

Where M^+ was inorganic cation saturating the structural negative charge on the silicate layers of clay and OC^+ was organic cation (Kowalska et al., 1994). When loading levels of organic cations was more than 1.00 times the CEC, hydrophobic interaction was the main mechanism (Lee and Kim, 2002a). The degree to which organic cations were adsorbed with the hydrophobic interaction was directly related to the length of the alkyl chains of organic cations. It appeared that the interaction involving the alkyl chains was not strong enough to contribute to the adsorption until a critical length of 12 carbons was reached (Zhang et al., 1993). Therefore, the adsorption capacity of organic cations onto clay was influenced by the CEC of clay and molecular structure of organic cations (Shen, 2004).

4.2 Characteristics of Clay and Organoclays
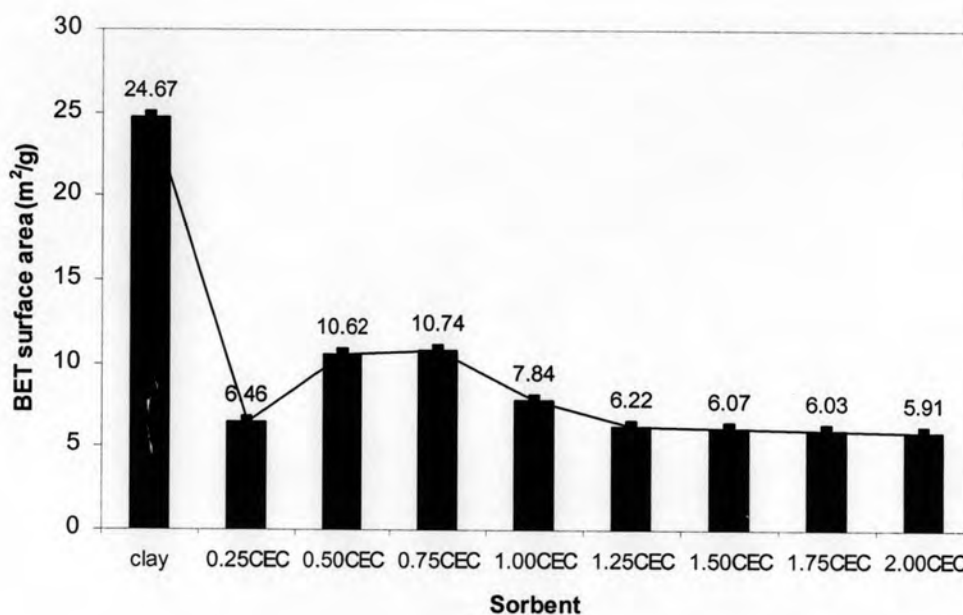
4.2.1 BET Surface area

Figure 4.2 BET surface area of clay and organoclays

Figure 4.2 shows the BET surface area of clay and organoclays. The BET surface areas of the base clay are 24.67 m^2/g. The BET surface areas of eight organoclays are lower than the base clay. It is well known that smectite has the capability of interlayer expansion and large organic cations are exchanged into the interlamellar space. These large organic cations may be subject to compact packing in the interlamellar space and result in more serious pore blocking which inhibits the passage of nitrogen molecules (Lee et al., 1999; Wang et al., 2004). Thus, the BET surface areas of organoclay are smaller than that of the base clay.

The BET surface areas of organoclays, as amount of DPC increased from 0.25 to 0.75 times the CEC, increase from 6.46 to 10.74 m^2/g. When added amount of DPC increased from 1.00 to 2.00 times the CEC, the BET surface areas of organoclay decrease from 7.84 to 5.91 m^2/g. This result are in agreement with Bartelt-Hunt et al. (2003), who determined the BET surface area of bentonite prepared using several hexadecyltrimethylammonium (HDTMA) ratios, The result showed that at lower ratio of HDTMA, the BET surface area of organobentonites increased. At higher ratio of HDTMA, the BET surface area of organobentonites decreased. The difference in the BET surface areas of organoclays that can increase or decrease depend on the arrangement and the packing of organic cations in the interlamellar space (Lee et al., 1999; Wang et al., 2004; Cruz-Guzman et al., 2004).
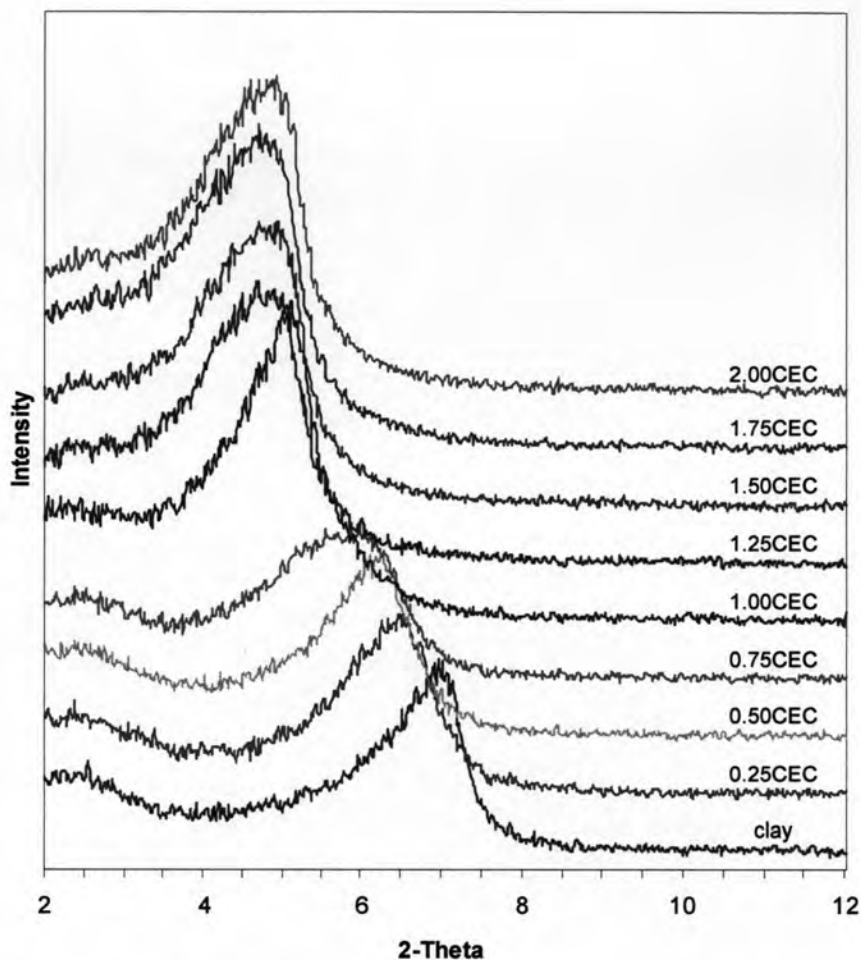
4.2.2 Interlayer spacing

Figure 4.3 XRD patterns of clay and organoclays

The cation exchange of the inorganic cation for the organic cation can expand of the clay layer. This expansion is readily measured by X-ray diffraction (XRD). Figure 4.3 shows the XRD patterns of clay and organoclays recorded between 2 and 12° (2θ). The XRD peaks of organoclays were moving toward a lower 2θ angle relative to the clay. This indicates that the distance between silicate layers, the interlayer spacing, was expanded due to the intercalated DPC molecules.
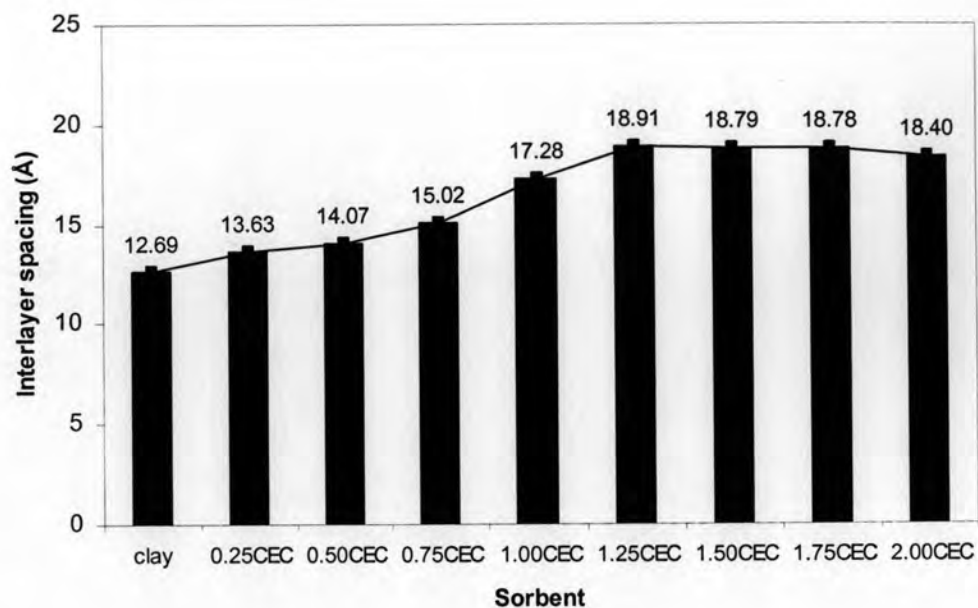
Figure 4.4 Interlayer spacing of clay and organoclays

Figure 4.4 shows the interlayer spacing of clay and organoclays. The interlayer spacings increase from 12.69 to 18.91Å for clay and 1.25CEC. When the amount of DPC is more than 1.25 times the CEC of clay, the interlayer spacing of organoclays decreases slightly. Xi et al. (2004) found that the interlayer spacing of octadecyltrimethylammonium (ODTMA)-montmorillonite (CEC = 76.4 meq/ 100 g) increased from 11.69 to 20.10 Å as concentration of ODTMA increased from montmorillonite to 1.5 times the CEC. Above 1.5 times the CEC, the interlayer spacing only increased slightly. According to Hsu et al. (2000), the interlayer spacing of hexadecyltrimethylammonium (HDTMA)-montmorillomite (CEC = 80.5 meq/ 100 g) reached a constant value when HDTMA added to 1.5 times the CEC. While, Zhou et al. (2007) found that the interlayer spacing of HDTMA-montmorillonite (CEC = 90.8 meq/ 100 g) increased from 12.4 Å to 38.4 Å with concentration of HDTMA increased from montmorillonite to 2.5 times the CEC. A number of previous studies have demonstrated that the interlayer spacing of organoclays depend on the CEC of clay, amount of organic cations, the length and number of alkyl chains, arrangement and packing density of organic cations within the interlayer of clay (Koh and Dixon, 2001; Osman et al., 2004; Shen, 2004; Xi et al., 2004; He et al., 2006; Onal and Sarikaya, 2007; Xi et al., 2007).
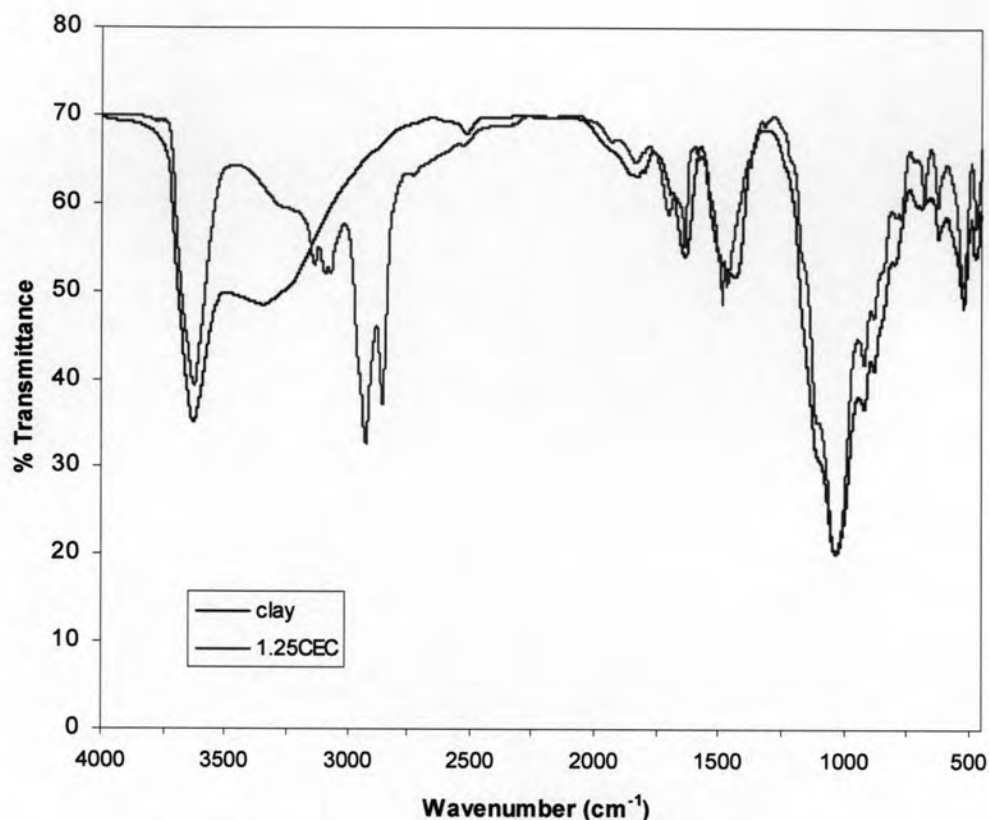
4.2.3 FTIR spectra

Figure 4.5 FTIR spectra of clay and organoclay (1.25CEC)

Figure 4.5 shows the FTIR spectra between 4000 and 450 cm^{-1} for clay and 1.25CEC. From the results, the clay shows specifically characteristic bands at 3629.01, 3347.59, 1636.82, and 1034.76 cm^{-1} which are assigned to O-H stretching vibration of the structural O-H groups, O-H stretching vibration of H-bonded water, H-O-H bending vibration of water molecules adsorbed on clay, and Si-O stretching vibration, respectively (Madejova, 2003). For organoclays, the additional bands at ~2920 and ~2850 cm^{-1} and between 1520 and 1440 cm^{-1}, which are absent in base clay, correspond to the CH$_2$ asymmetric stretching, $\nu_{as}(CH_2)$, and symmetric stretching, $\nu_s(CH_2)$, vibration and the CH$_2$ bending vibration, $\delta(CH_2)$ of alkyl chains, respectively (Vaia et al., 1994; Xi et al., 2005). In addition, the intensity of the band at 3347.59 cm^{-1} decreases. This observation clearly indicates that the surface property of clay is modified, i.e. the hydrophilic surface of clay has been changed to organophilic.

The frequency and bandwidth of $\delta(CH_2)$ is sensitive to interaction between the alkyl chains and packing arrangement of intercalated organic cations (Vaia et al., 1994; Ding et al., 2006). Lower frequency, broadening band, and decreasing intensity of $\delta(CH_2)$ indicated the decrease in interaction between the alkyl chains (Vaia et al., 1994). While, the frequency and bandwidth of $\delta(CH_2)$ that were close to the frequency and bandwidth of the pure organic cation indicated strong interaction between the alkyl chains and the increase of packing density of intercalated organic cations (Zhu et al., 2005; Yu, 2007).

Figure 4.6 shows FTIR spectra between 1800 and 1200 cm^{-1} of organoclays and DPC. The results indicate that the frequency and bandwidth of $\delta(CH_2)$ of intercalated DP cation strongly depend on the DPC loading. For organoclays with higher DPC loading, the bandwidth of $\delta(CH_2)$ decreases and is relatively constant. These observations suggest that, going from low to high DPC loading, the interaction between the alkyl chains and packing density of intercalated DP cation increase. Zhu et al. (2007) indicated that the packing density difference of the adsorbed organic cations on clay could be deduced from organic cation adsorption mechanism and the CEC of clay.
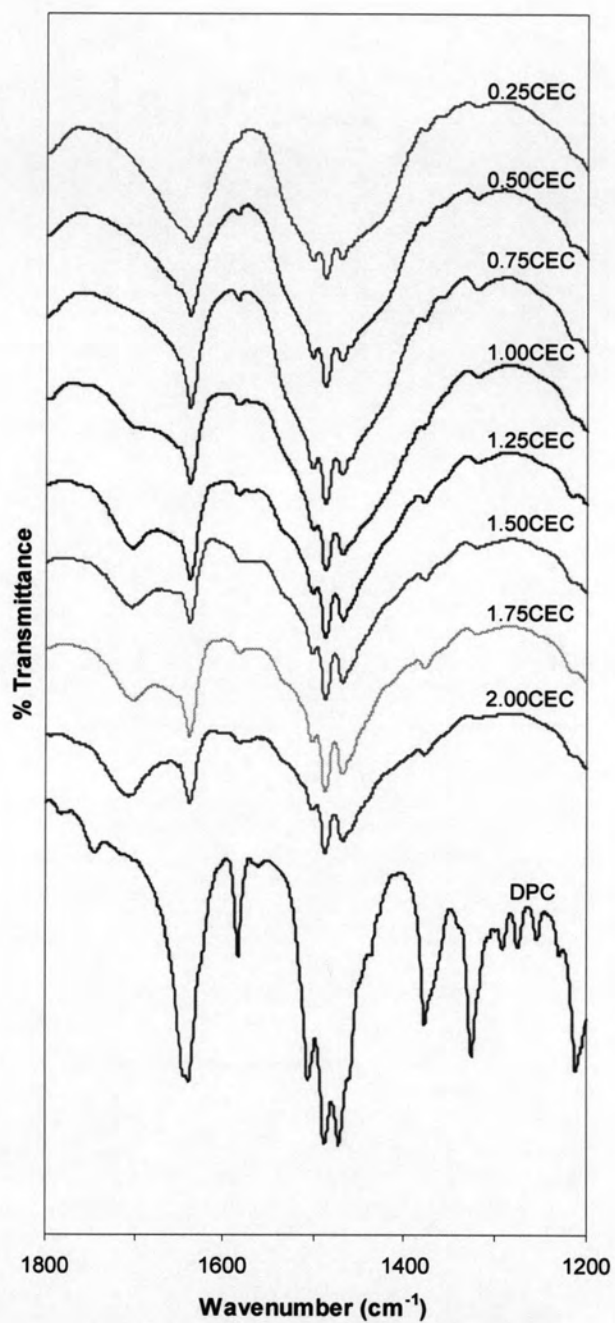
Figure 4.6 FTIR spectra between 1800 and 1200 cm^{-1} of organoclays and DPC

4.2.4 Effect of the amount of organic cations on the characteristics of organoclays

Results in this section indicate that the characteristics of organoclays depend on the amount of DPC. The BET surface areas of organoclays increase with the amount of DPC increased from 0.25 to 0.75 times the CEC. At higher DPC loading, the BET surface areas decrease. The interlayer spacing of organoclays increases gradually with the amount of DPC increased from 0.25 to 1.25 times the CEC. When the amount of DPC is more than 1.25 times the CEC, the interlayer spacing of organoclays decreases slightly. In addition, the results from FTIR spectra indicate that the interaction between the alkyl chains and packing density of intercalated DP cation increase as the amount of DPC increased.

After organic cations enter into the interlamellar space, the strong electrostatic interaction between negatively charged clay surface and the positively charged headgroup of organic cation will hold the headgroup of organic cation close to the clay surface (Zeng et al., 2003). On the other hand, since the silicate surface of clay is hydrophilic whereas the alkyl chain of organic cation is hydrophobic, the silicate surface-alkyl chain interaction is of a repulsive nature (He et al., 2006). At lower organic cations loading, organic cations are individually separated and the alkyl chains are parallel to the silicate surface (Li and Ishida, 2003). In this case, the repulsive force between the silicate surface-alkyl chain is dominant whereas the interaction among the alkyl chains is very weak (He et al., 2006). The repulsive force from the silicate surface will increase the mobility of alkyl chains but this force is limited by the distance of clay layer (Li and Ishida, 2003).

With the increase of organic cations loading, the alkyl chains of organic cations begin to radiate away from the silicate surface, thus the interlayer spacing increases quickly (Yu, 2006). Accordingly, when alkyl chains radiate away from the silicate surface, the interaction among the alkyl chains is relatively strong while that between the silicate suface-alkyl chain is very weak (He et al., 2006). At higher organic cations loading, strong hydrophobic interaction among the alkyl chains may have reduced the interlayer spacing of organoclays (Peker et al., 1995), and leads to higher packing density of organic cations (Li and Ishida, 2003).

4.3 Sorption of PAHs onto Clay and Organoclays

Batch experiment was used to determine the sorption of naphthalene and phenanthrene onto clay and organoclays, at room temperature. Sorption experiments of naphthalene and phenanthrene were performed in triplicate. Sorption isotherms and removal efficiencies of naphthalene and phenanthrene are shown in term of the average of triplicate.

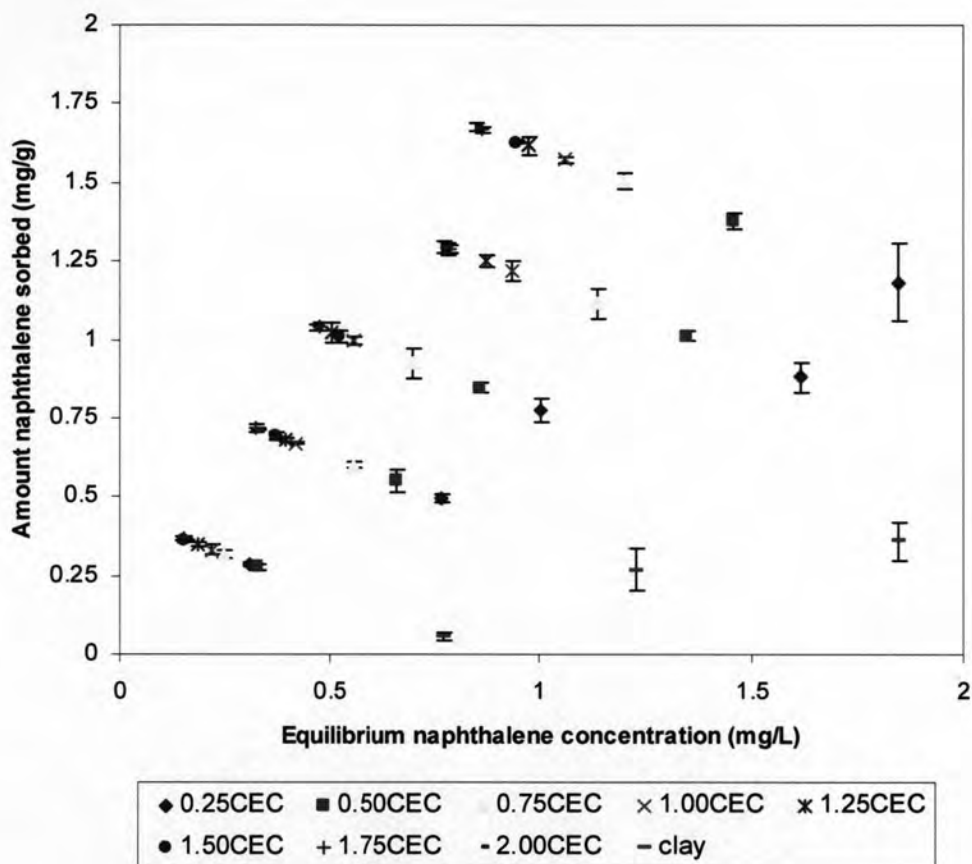### 4.3.1 Sorption of naphthalene onto clay and organoclays

Figure 4.7 Sorption isotherms of naphthalene onto clay and organoclays

The initial concentration of naphthalene ranged from 1.520 to 7.161 mg/L, equivalent to 5 to 25% of the aqueous solubility. Figure 4.7 shows the sorption isotherms of naphthalene onto clay and organoclays. The results indicate that sorption of naphthalene onto organoclays is higher than that of clay and is increased with the amount of DPC increased from 0.25 to 1.25 times the CEC. However, as the amount of DPC increased from 1.25 to 2.00 times the CEC, only small increases in the sorption capacity are observed.

All sorption isotherms of naphthalene fit well both linear and freundlich model (Table B1). From the properties of sorbent and PAHs and from literature reviews, the sorption of PAHs onto organoclays occurs primarily by partitioning between the aqueous solution and the organic phase created by the alkyl chains of organic cations. For partition equilibria, the isotherm should be linear over a wide range of C_e values relative to the aqueous solubility of the solute (Smith et al., 1990). Therefore, in this research only the linear model is closed for description the sorption of PAHs onto clay and organoclays. The linear model has the following equation:

$$q_e = K_d C_e$$

where q_e is the amount of solute sorbed per mass unit of sorbent, C_e is the equilibrium concentration of solute, and K_d is the distribution coefficient derived from the slope of sorption isotherm. Nzengung et al. (1996) found that isotherms for naphthalene sorption on hexadecyltrimethylammonium (HDTMA) and benzyldimethyltetradecylammonium (BDTDA)-clay were linear. The long alkyl chain of HDTMA and BDTDA (C_{16} and C_{14}, respectively) led to the formation of a predominantly partition phase for naphthalene sorption. The authors indicated that the degree of naphthalene uptake depended not only on the amount but also on the arrangement of organic cations into the interlamellar space. Previous study reported that partitioning of naphthalene into HDTMA-montmorillonite appeared to decline at HDTMA in amounts equal to less than 80% and more than 150% of the CEC (Bonczek et al., 2002).
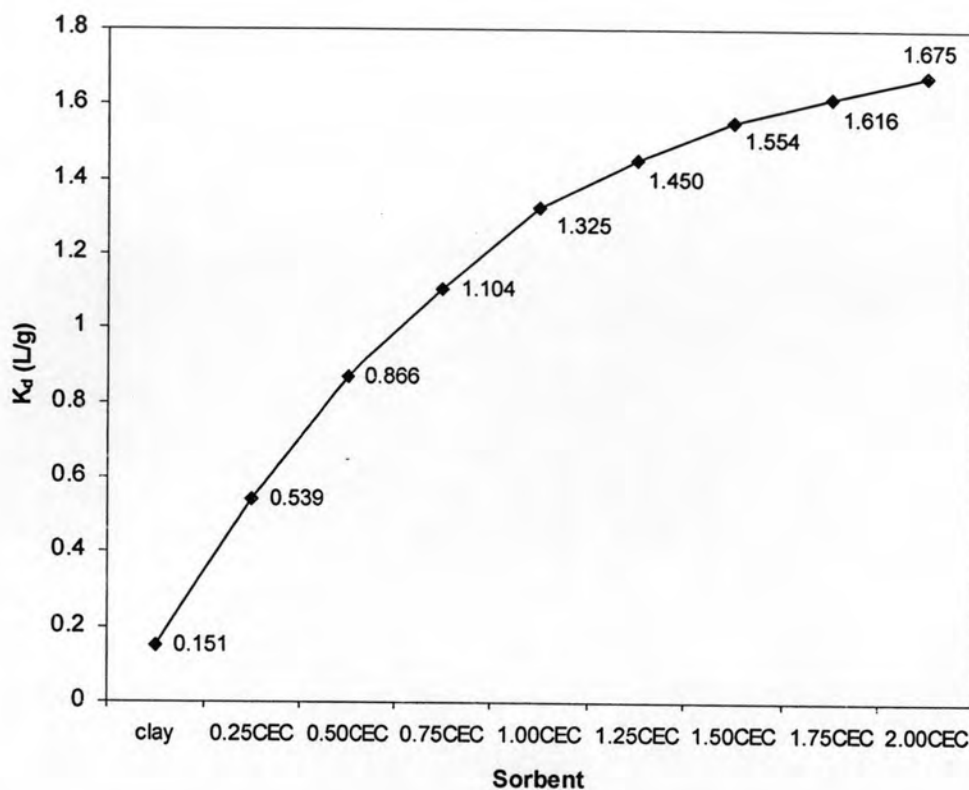
Figure 4.8 Relationship between sorbent and the distribution coefficient (K_d) of naphthalene

Figure 4.8 shows the relationship between sorbent (clay and organoclays) and the distribution coefficient (K_d) of naphthalene. The result shows that K_d values of naphthalene increase from 0.151 to 1.675 L/g with the amount of DPC increased from clay to 2.00 times the CEC. This result agrees with Lee and Kim (2002b), who examined the partitioning of naphthalene onto the hexadecyltrimethylammonium (HDTMA)-kaolinite. The results showed that when the HDTMA coverage on kaolinite was 42% of CEC, K_d values of naphthalene increased from 0.9 to 109 L/kg. As the HDTMA coverage increased to 150% of CEC, K_d values further increased to 256 L/kg.

Table 4.1 Removal efficiency (%) of organoclays for naphthalene

Sorbent	Initial concentration (mg/L)				
	1.520	3.057	4.628	5.640	7.162
0.25CEC	64.755±1.781[e]	56.617±1.367[e]	60.771±3.089[d]	52.375±2.705[e]	56.376±5.973[e]
0.50CEC	62.636±2.424[e]	62.566±4.009[d]	66.367±1.347[c]	60.207±0.949[d]	65.495±1.215[d]
0.75CEC	71.875±2.553[d]	68.380±0.800[c]	72.569±3.724[b]	66.466±2.857[c]	71.585±1.210[c]
1.00CEC	75.371±2.959[c]	76.167±0.535[b]	78.220±0.936[a]	72.285±2.065[b]	74.946±0.480[b]
1.25CEC	78.791±1.640[b]	77.468±0.624[b]	80.200±2.499[a]	74.202±0.883[ab]	76.902±1.350[ab]
1.50CEC	82.588±1.725[a]	78.955±1.406[ab]	79.494±1.617[a]	76.787±1.268[a]	77.662±0.305[ab]
1.75CEC	83.010±0.412[a]	81.691±1.349[a]	81.351±0.857[a]	76.683±0.898[a]	79.478±0.422[a]
2.00CEC	83.326±0.510[a]	81.378±0.772[a]	81.639±0.458[a]	77.152±1.156[a]	79.882±0.422[a]

Note: The alphabet on the right corner means there is significant difference at 95% confidence

Table 4.1 summarizes the removal efficiencies of eight organoclays for naphthalene from synthetic wastewater. Results indicate that the removal efficiencies of eight organoclays increase as the amount of DPC increased. From statistical analysis, it is shown that there is significant different of the removal efficiencies for naphthalene from synthetic wastewater between 0.25CEC, 0.50CEC, 0.75CEC, and 1.00CEC (p. <0.05). However, there is not significant different of the removal efficiencies for naphthalene from synthetic wastewater between 1.25CEC, 1.50CEC, 1.75CEC, and 2.00CEC (p. <0.05).

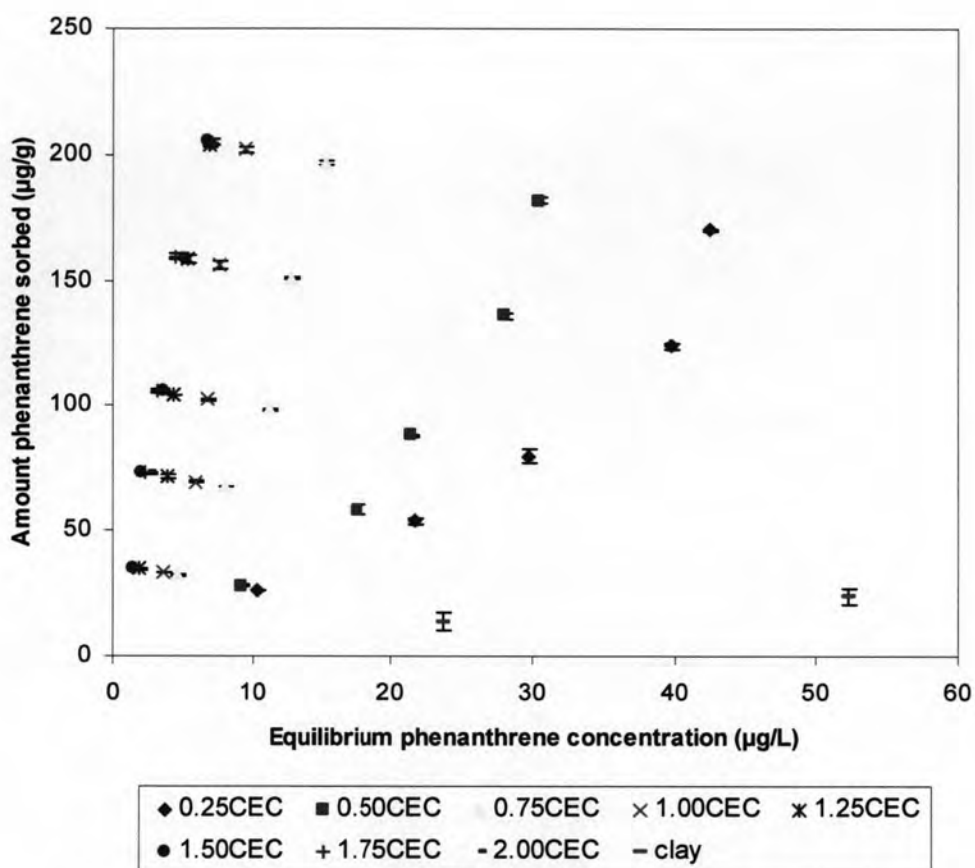**4.3.2 Sorption of phenanthrene onto clay and organoclays**

Figure 4.9 Sorption isotherms of phenanthrene onto clay and organoclays

The initial concentration of phenanthrene ranged from 49.644 to 275.039 µg/L, equivalent to 5 to 25% of the solubility. Figure 4.9 shows the sorption isotherms of phenanthrene onto clay and organoclays. The results indicate that sorption of phenanthrene onto organoclays is higher than that of clay and is increased with the amount of DPC increased from 0.25 to 1.25 times the CEC. However, as the amount of DPC increased from 1.25 to 2.00 times the CEC, no additional increase in sorption capacity is observed. Previous study found that the magnitude of aromatic compound, such as benzene sorption to HDTMA-bentonites increased as the organic cation loading increased from 25 to 100 % of the CEC. However, the magnitude of sorption was not increased as the cation loading onto the bentonite increased from 100 to 125 % of the CEC (Smith et al., 2003).
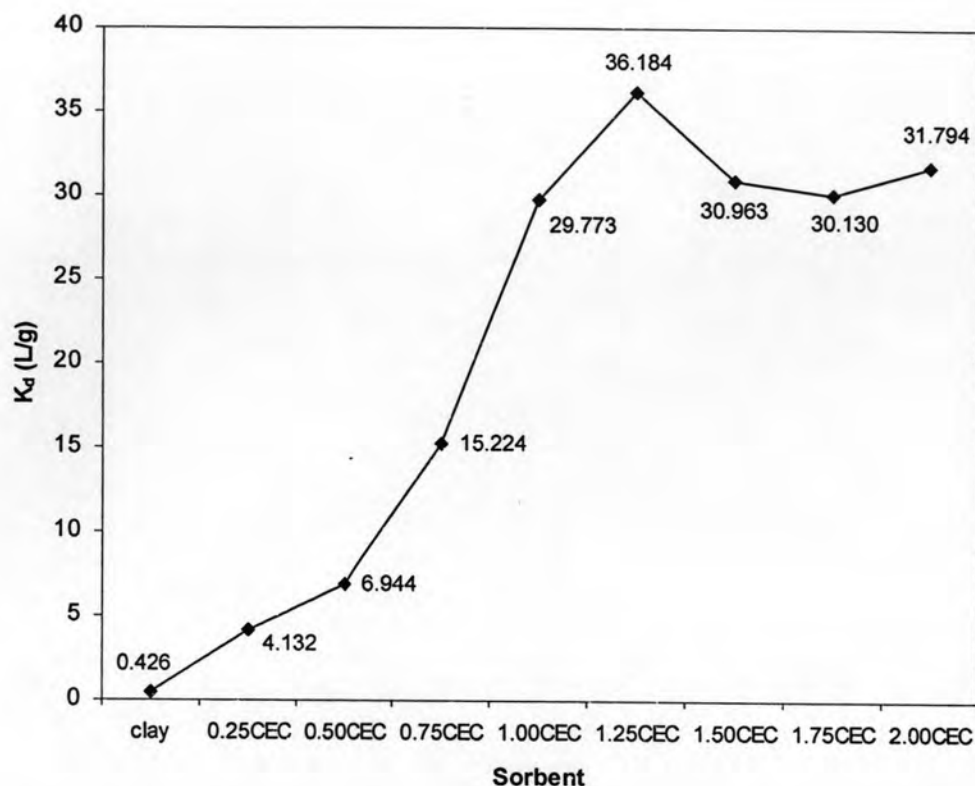
Figure 4.10 Relationship between sorbent and the distribution coefficient (K_d) of phenanthrene

All sorption isotherms of phenanthrene fit well both linear and freundlich model (Table B2). The linear model is closed for description the sorption of phenanthrene onto clay and organoclays similar to naphthalene. Figure 4.10 shows the relationship between sorbent (clay and organoclays) and the distribution coefficient (K_d) of phenanthrene. The result shows that when the amount of DPC increased from clay to 1.25 times the CEC, K_d values rise quickly from 0.426 to 36.184 L/g. Thereafter, K_d values of phenanthrene decrease slightly. Decrease of K_d values for highly surfactant concentrations noticed by Ko et al. (1998). The authors examined the partitioning of naphthalene and phenanthrene to the adsorbed surfactant; sodium dodecyl sulphate (SDS) and Tween 80 to kaolinite. The results showed that K_d values of naphthalene and phenanthrene increased initially with increasing surfactant concentrations before decreased at higher doses.

Table 4.2 Removal efficiency (%) of organoclays for phenanthrene

Sorbent	Initial concentration (μg/L)				
	49.644	98.142	144.022	214.761	267.962
0.25CEC	72.284±0.420[f]	71.722±1.331[f]	73.247±2.835[e]	76.005±0.598[e]	80.222±0.368[e]
0.50CEC	75.496±0.976[e]	77.122±2.312[e]	80.796±0.700[d]	83.069±0.618[d]	85.788±0.305[d]
0.75CEC	87.911±0.693[d]	89.600±0.080[d]	89.971±0.254[c]	92.331±0.133[c]	92.874±0.216[c]
1.00CEC	90.448±0.431[c]	92.263±0.342[c]	93.866±0.207[b]	95.402±0.356[b]	95.557±0.080[b]
1.25CEC	94.886±1.368[b]	94.877±0.598[b]	96.164±0.088[a]	96.782±0.445[a]	96.811±0.453[a]
1.50CEC	96.009±0.117[ab]	97.409±0.451[a]	96.759±0.190[a]	96.910±0.136[a]	96.884±0.003[a]
1.75CEC	96.129±0.753[ab]	97.100±0.540[a]	97.150±0.447[a]	97.351±0.068[a]	96.715±0.059[a]
2.00CEC	96.275±0.097[a]	96.564±0.425[ab]	96.931±0.298[a]	97.165±0.130[a]	96.799±0.079[a]

Note: The alphabet on the right corner means there is significant difference at 95% confidence

Table 4.2 summarizes the removal efficiencies of eight organoclays for phenanthrene from synthetic wastewater. Results indicate that the removal efficiencies of phenanthrene from synthetic wastewater increase as the amount of DPC increased from 0.25 to 1.25 CEC. When amount of DPC increased from 1.25 to 2.00 times the CEC, the removal efficiencies are comparatively constant. From statistical analysis, it is shown that there is significant different of the removal efficiencies for from synthetic wastewater between 0.25CEC, 0.50CEC, 0.75CEC, 1.00CEC, and 1.25CEC ($p. < 0.05$). However, there is not significant different of the removal efficiencies for phenanthrene from synthetic wastewater between 1.25CEC, 1.50CEC, 1.75CEC, and 2.00CEC ($p. < 0.05$).

4.3.3 Sorption mechanism for PAHs by organoclays

For naphthalene and phenanthrene sorption to each of organoclays (Figure 4.6 and 4.8), the isotherms are linear with $R^2 > 0.9$. This result indicates that sorption is caused by partition process between the aqueous solution and the organic phase formed by conglomeration of organic cations with long alkyl chains into the interlamellar space (Smith and Jaffe, 1991; Smith and Galan, 1995). These organic cations pack tightly on the clay surfaces, forming a well structured organic phase that is available for uptake of organic compounds (Upson and Burns, 2005). The partition process appears similar to the dissolution of organic compounds in a bulk organic solvent phase such as hexane or octanol, except that here the organic partition phase is fixed on the clay surfaces analogous to the partition behavior of natural soil organic matter (Lee et al., 1989; Gullick and Weber, 2001).

The lower isotherm describes the sorption of naphthalene and phenanthrene onto clay that has not been modified with DPC. For the reason, the hydrated mineral surface of clay prevented organic compound sorption and low organic carbon content of clay resulted in negligible solute uptake by partitioning (Smith et al., 1990). By contrast, the addition of a relatively small amount of DPC (0.25 times the CEC) causes a dramatic increase in the uptake of naphthalene and phenanthrene relative to clay. The relatively high affinity between naphthalene and phenanthrene and DPC-clay is probably the result of the naphthalene and phenanthrene molecules interacting favorably with pyridinium ring in DPC through π-π interactions (Huang et al., 2005)

The distribution coefficient (K_d) of naphthalene range from 0.151 to 1.675 L/g and phenanthrene from 0.426 to 36.184 L/g. Since the partition process is depended on the aqueous solubility of organic compounds, it is generally believed that organic compounds having a high aqueous solubility will not be sorbed as strongly as organic compounds with comparatively low aqueous solubility (Bartelt-Hunt et al., 2003), The aqueous solubility of phenanthrene (1.0 mg/L) is 30 times lower than naphthalene (30.0 mg/L). Therefore, K_d values of phenanthrene are much larger than naphthalene.

4.3.4 Effect of the amount of organic cations on PAHs sorption by organoclays

Results in this section prove that the amount of DPC has an important effect on the magnitude of naphthalene and phenanthrene sorption from synthetic wastewater by organoclays. The sorption capacities and K_d values of naphthalene and phenanthrene increase with the amount of DPC increased from 0.25 to 1.25 times the CEC. When the amount of DPC increased from 1.25 to 2.00 times the CEC, K_d values of naphthalene increase; on the contrary, K_d values of phenanthrene decrease. However, the sorption capacities of organoclays for naphthalene and phenanthrene at high loading level of DPC are not different.

For organoclays with lower organic cation loading, the headgroups of organic cations in the interlamellar space were anchored on the charge sites of clay surface by strong electrostatic interaction (Yu, 2007). In this case, water and inorganic cations presented in close proximity to the organic phase (Bonczek, 2002). As a result, the hydrophobic affinity of adsorbed organic cations toward organic sorbates was low, resulting in small sorption capacity. When increased organic cations loading, not only more hydrophobic interaction of the alkyl chains in the interlamellar space decreased interference of water competing on the charge sites, but also increased interlayer spacing promoted solute partitioning into the organic phase (Sheng et al., 1996; Chen et al., 2005). Therefore, the magnitude of organic sorbates uptake increased.

At higher organic cation loading, most of the interlamellar spaces of organoclays were filled with adsorbed organic cations. In the confined interlayer spacing, the available free space to accommodate the organic sorbates reduced greatly. As a result, the organic sorbates could not penetrate into packing density of organic phase easily (Zhu et al., 2007). In addition, polar or charged groups on organic cations which were adsorbed beyond the CEC and were unbalanced by charges on clay surface may have diminished the hydrophobic character of the interlayer and thus limited the uptake of organic sorbates (Bonczek, 2002). Hence, it is reasonable for the observed decrease of K_d values of phenanthrene in high DPC loading level. In contrast, when higher organic cations were loaded onto clay surfaces, the alkyl chains densely packed in the interlamellar space may result in more effective partition medium for organic sorbates (Bartelt-Hunt et al., 2003) Thus, K_d values of naphthalene increased with the amount of DPC increased.