

CHAPTER II

LITURATURE REVIEWS

2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are a group of chemicals that are formed during the incomplete burning of coal, oil, gas, wood, garbage, or other organic substances, such as tobacco and charbroiled meat. There are more than 100 different PAHs. PAHs generally occur as complex mixture (for example, as part of combustion products such as soot), not as single compounds. PAHs usually occur naturally, but they can be manufactured as individual compounds for research purposes; however, not as the mixtures found in combustion products. As pure chemical, PAHs generally exist as colorless, white or pale yellow-green solids. They can have a faint, pleasant odor (U. S. Department of Health and Human Services, 1995).

According to the formation mechanisms, PAHs can be classified as pyrolytic and petrogenic PAHs. Pyrolytic PAHs are formed as a consequence of incomplete combustion, such as industrial operations and power plants using fossil fuels, smelting, waste incinerations, exhaust from vehicles powered by gasoline or diesel fuel and forest fires. Petrogenic PAHs are mainly derived from crude oil and petroleum products. Petroleum products include kerosene, gasoline, diesel fuel, lubricating oil, and asphalt (Doong and Lin, 2004).

The U.S. Environmental Protection Agency has indentified 16 unsubstituted PAHs as priority pollutants. They are including naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(a)anthrecene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene. Molecular structure of 16 PAHs is shown in Figure 2.1.

PAHs can enter body through drinking water and swallowing food, soil, or dust particles that contain PAHs. PAHs can be harmful to health under some circumstances. Several of the

PAHs, including benzo[a]anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, and indeno(1,2,3-cd)pyrene have caused tumors in laboratory animals when they breathed these substances in the air, when they ate them, or when they had long periods of skin contact with them. Studies of people show that individuals exposed by breathing or skin contact for long periods to mixtures that contain PAHs and other compounds can also develop cancer (U. S. Department of Health and Human Services, 1995).

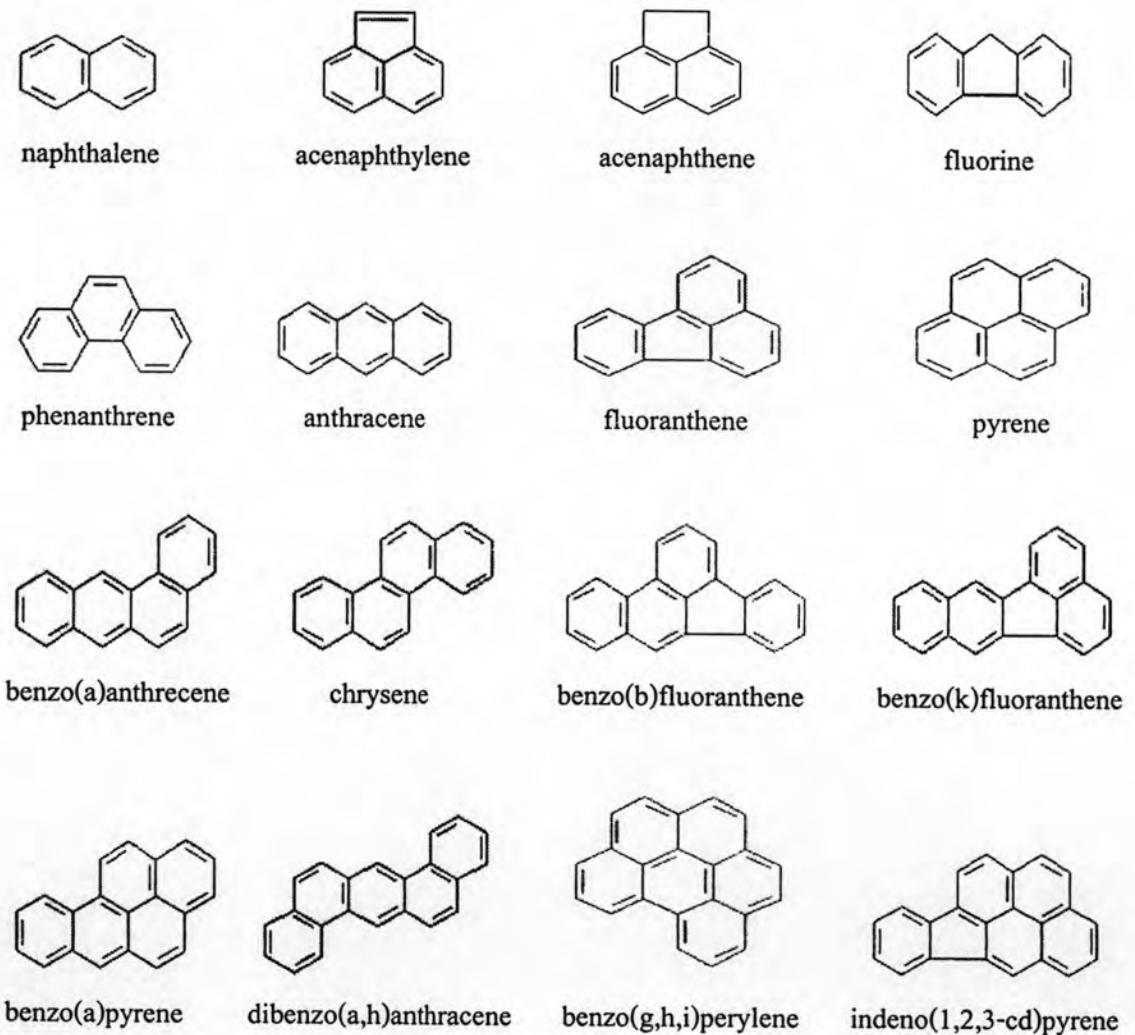


Figure 2.1 Molecular structures of 16 PAHs as priority pollutants

2.1.1 Physical and chemical properties

PAHs are made up of two or more fused benzene rings in linear, angular, or cluster arrangements and contain only C and H. Individual PAHs differ substantially in their physical and chemical properties. In general, the low molecular weight PAHs is more volatile, more water soluble and less lipophilic than their high molecular weight relatives. These physical and chemical properties largely determine the environmental behaviour of PAHs and indicate that transfer and turnover of low molecular weight PAHs will be more rapid than other group members (Wild and Jones, 1995). Physical and chemical properties of PAHs as priority pollutant are shown in Table 2.1.

Table 2.1 Physical and chemical properties of PAHs

PAHs	Molecular weight (g/mol)	Melting point (°C)	Boiling point (°C)	Water solubility (mg/L)	Log K _{ow}
naphthalene	128.16	80.2	217.9	30.0	3.30
acenaphthylene	152.20	92-93	265-275	3.93	3.70
acenaphthene	154.21	95	96.2	3.42	4.00
fluorine	166.22	116-117	295	1.69	4.18
phenanthrene	178.24	100	340	1.00	4.46
anthracene	178.24	218	342	4.50x10 ⁻²	4.45
fluoranthene	202.26	11	375	2.06x10 ⁻¹	4.90
pyrene	202.26	156	393	1.30x10 ⁻¹	4.88
benzo(a)anthracene	228.30	158-159	400	5.70x10 ⁻³	5.60
chrysene	228.30	255-256	448	1.80x10 ⁻³	5.61
benzo(b)fluoranthene	252.32	168.3	-	1.40x10 ⁻²	6.06
benzo(k)fluoranthene	252.32	215.7	480	4.30x10 ⁻³	6.06
benzo(a)pyrene	252.32	179-179.3	310-312	3.80x10 ⁻³	6.06
dibenzo(a,h)anthracene	278.36	262	-	5.00x10 ⁻⁴	6.80
benzo(g,h,i)perylene	276.34	273	550	2.60x10 ⁻⁴	6.51
indeno(1,2,3-cd)pyrene	276.34	163.6	530	5.30x10 ⁻⁴	6.50

Sources: U. S. Department of Health and Human Services, 1995; Chaipuriwong, 2001;

LaGrega et al., 2001

2.1.2 Source and distribution of PAHs in surface water

PAHs, as semivolatile organic compounds, exist in both the gaseous and the particulate phase in air, and are subject to both vapor and particle washout from the atmosphere during precipitation (Manoli and Samara, 1999). Atmospheric deposition is considered to be an important input of PAHs to surface waters. The occurrence of PAHs found in surface water and rainwater samples of Lake Maggiore, a subalpine lake in Northern Italy, followed a distribution dominated by the low molecular weight compounds (e.g., phenanthrene, fluoranthene, pyrene) being preferentially found in dissolved phase. The comparison of PAHs signatures in rainwater and surface waters indicated that wet deposition ($2.5\text{--}44.5 \mu\text{g m}^{-2} \text{ month}^{-1}$) was the main source of PAHs contamination into surface waters of Lake Maggiore (Olivella, 2005). The concentrations of PAHs in surface waters of Northern Greece were in general lower than those in bulk precipitation, and among the lowest reported for European rivers excepting naphthalene and phenanthrene (Manoli et al., 2000).

A significant amount of PAHs carried to surface waters by sewers derives from urban runoff. Urban runoff consists of stormwater from impervious area, such as road motorways, roofs, sidewalks, etc., and pervious areas (for example, gardens construction sites, etc.). As a consequence, urban runoff contains PAHs deposited on surface, as well as mobile-related PAHs from gasoline and oil drips or spills, exhaust products, tire particles, and bitumen from road surfaces (Bomboi and Hernandez, 1991). Total PAHs concentrations in stormwater were highest during the early periods of precipitation and runoff (e.g. during the first or second flushes) and typically decreased at later times (Hoffman et al., 1984). Smith et al. (2000) collected stormwater samples from four sampling sites in Virginia, USA and analyzed for 16 PAHs. The results showed that the gas station site produced the highest total PAHs loading (2.24 g/yr/m^2), followed by the high traffic volume parking lot ($5.56 \times 10^{-2} \text{ g/yr/m}^2$), the highway off-ramp ($5.20 \times 10^{-2} \text{ g/yr/m}^2$), and the low traffic volume parking lot ($3.23 \times 10^{-2} \text{ g/yr/m}^2$).

Zakaria et al. (2002) indicated that used crankcase oil was the major source of sedimentary PAHs in Malaysia urban areas. These PAHs reach aquatic environment by two main routes: (1) indiscriminate dumping and poor management in service stations and garages, and (2) leakages from poorly maintained vehicles to road surfaces, followed by incorporation into

street dust, and subsequent wash-out as stormwater runoff to streams and rivers. In generally, the PAHs content of new motor oil is relatively low, but increases with motor operating time. In this way, the PAHs content of used motor oil is higher than that of new motor oil. Used oils can contain 670 times more PAHs than new motor oils. This increase varies according to engine type. For example, the PAHs content of used crankcase oil from the diesel motors of lorries can be three times higher than that of new oil; for diesel buses it can be 6 times higher than that of new oil; and for diesel cars it can be 30 times higher than that of new oil. The PAHs content of used motor oil from petrol motors can be 180 times higher than that of new crankcase oil (Table 2.2) (Vazquez-Duhalt, 1989).

Table 2.2 PAHs content of different motor oils

Polycyclic aromatic hydrocarbons	Concentration ($\mu\text{g g}^{-1}$)				
	New motor oil	Used motor oil from Petro vehicles	Used motor oil from Diesel vehicles	Used motor oil from Diesel lorries	Used motor oil from Diesel buses
Anthracene	0.002-0.030	1.6-10.8	0.5-4.4	0.02-0.12	0.03-0.16
Benzo[a]pyrene	0.008-0.266	5.2-35.1	0.7-11.9	0.13-0.060	0.07-0.55
Benzo[e]pyrene	0.030-0.402	6.4-48.9	1.3-10.7	0.23-1.10	0.29-1.04
Benzo[ghi]perylene	0.010-0.139	4.4-85.2	2.1-16.0	0.20-0.78	0.26-0.65
Benzo[b]naphtha[2,1-d]thohene	0.097-9.430	ND	0.7-4.3	0.78-6.20	1.60-4.80
Benzofluoranethenes[b+k+k]	0.013-0.234	5.7-44.3	1.8-16.8	0.26-1.30	0.37-1.20
Chrysene+triphenylene	0.182-11.900	8.7-74.0	5.1-42.8	1.60-6.10	1.90-8.00
Coronene	0.001-0.016	2.8-29.4	0.1-6.4	0.10-0.13	0.00-0.08
Fluoranthene	0.008-2.750	3.4-109.0	1.3-58.9	0.18-2.90	0.40-2.70
Indeno[1,2,3-cd]pyrene	0.001-0.020	2.1-12.5	0.8-9.0	0.06-0.28	0.07-0.25
perylene	0.007-0.224	1.9-10.0	0.4-2.7	0.11-0.35	0.04-0.29
pyrene	0.039-6.530	5.7-326.0	1.4-78.0	0.33-6.40	0.90-4.90

Source: Vazquez-Duhalt, 1989

Another source of PAHs to surface water is industrial effluents. Doong and Lin (2004) reported that concentrations of 16 PAHs in water samples collected near industrial area than those from nonindustrial locations in Gao-ping River, Taiwan. Naphthalene was abundant in water samples, whereas phenanthrene and anthracene were the most frequently detected PAHs in water samples. The authors indicated that petrochemical industrial parks located in the vicinity of Gao-ping River might be the possible source for PAHs input. Another similar study in Tianjin, China showed that the dominant PAHs in reclaimed waters and surface waters were low molecular weight (two- and three-ring) PAHs including naphthalene, acenaphthylene, acenaphthene, fluorine, phenanthrene, and anthracene. Oil spill and leakage from boats and ships, vehicular exhaust emission, discharge from municipal and industrial wastewater and runoff were important sources of PAHs in Tianjin (Cao et al., 2005).

To assess the status of PAHs contamination in coastal and riverine environments in Thailand, Boonyatumanond et al. (2006) collected 42 surface sediment samples from canals, a river, an estuary, and coastal areas in Thailand in 2003 and analyzed them for PAHs with 3-7 benzene rings. The results showed that total concentration of PAHs ranged from 6 to 8399 ng/g dry weight. Much higher concentrations of PAHs were found in the reach near Bangkok (estuarine and riverine locations) than at other sites. The authors concluded that street dust was one of the major sources of petrogenic PAHs in the urban area. These street dust particles having high concentrations of PAHs could wash out from the road selectively and cause the high concentrations of PAHs in the aquatic sediments in Bangkok. While Chaipuriwong (2001) indicated that primary sources of accumulated PAHs in sediments from Tha Chin estuary were mostly of pyrolytic origin, namely automobile exhaust, industrial pollution and discharge of used lubricating oil directly into the river. Secondary sources were of petrogenic origin. Dominant PAHs in sediments from Tha Chin estuary were naphthalene, biphenyl, acenaphthene, fluorine, phenanthrene, chrysene, perylene, benzo(a)anthracene, anthracene, fluoranthene and pyrene.

2.1.3 Removal of PAHs from contaminated water

Chlorination

Several PAHs in surface water are degraded by addition of chlorine (Cl_2) or chlorine dioxide (ClO_2). Rav-Acha and Blits (1985) found that fluoranthene and benzo(e)pyrene reacted with Cl_2 faster than with ClO_2 , the opposite was found for benzo(a)pyrene, benzo(a)anthracene and anthracene that reacted much faster with ClO_2 . However, chlorination of PAHs polluted water may lead to formation of a wide range of oxygenated and chlorinated PAHs, a several of these products are know as carcinogenic and mutagenic. Johnsen et al. (1989) found that some chlorinated PAHs were potential mutagens even though their parent PAHs did not show any mutagen activity. Further, chlorinated PAHs had higher $\log K_{ow}$ values than their corresponding parent PAHs, and their theoretically determined bioconcentration factor values were extremely high. In addition, the production of chlorinated and oxygenated PAHs was dependent on the chlorine dose, the initial concentrations of PAHs, and the reaction pH (Mori et al., 1991).

Oxidation

Beltran et al. (1995a,b and 1996a,b) studied the suitability of advanced oxidation processes for the removal of PAHs from water. Four advanced oxidation processes were 1. ozonation 2. ozone combined with UV radiation 3. UV radiation combined with hydrogen peroxide 4. ozone combined with hydrogen peroxide. The results showed that advanced oxidation of PAHs yielded numerous potentially hazardous compounds. However, most of these compounds destroyed as oxidation time were increased. The authors indicated that ozone combined with UV radiation allowed the highest oxidation rates, although differences with respect to ozonation alone were so small that in a practical case it was likely that the cost associated with the use of UV radiation made ozonation alone the most convenient technology to remove PAHs from water.

Ultrasonic irradiation

Low frequency ultrasonic irradiation proved to be a viable tool for the effective degradation of PAHs in aqueous solutions. The extent of degradation was a function of sonication time and operating conditions such as ultrasound intensity and frequency, temperature and initial concentration (Psillakis et al., 2004). However, the utility of sonochemical treatment for the degradation of aqueous PAHs was limited by the presence of dissolved matrix compounds (Taylor et al., 1999). Laughrey et al. (2001) found that organic compounds, including humic acid, benzoic acid, and sodium decyl sulfate, decreased PAHs degradation rate constants by scavenging oxygen derived reactive transients.

Sorption

There are several studies using various sorbents for removal of PAHs from water. For example, Walters and Luthy (1984) studied adsorption of PAHs from water onto filtrisorb 400 activated carbon at 25 °C by batch shake testing and compared to adsorption of PAHs onto other adsorbents. They found that the adsorption of PAHs onto activated carbon was greater than adsorption of PAHs onto soil, sediments, and suspended organic matter and greater than the adsorption of other classes of hydrophobic organics onto activated carbon. Gunasekara et al. (2000) found that ground discarded tire rubber was an attractive and inexpensive medium for the sorption of naphthalene and other organic contaminants from water. Chang et al. (2004) investigated the feasibility of using hydrophobic zeolites to remove naphthalene from a water-butanol solution which serves as a surfactant-enriched scrubbing liquid. The results showed that butanol did not possess competitive adsorption on zeolite from the water-butanol solution containing naphthalene. Boving and Zhang (2004) indicated that aspen wood had the potential to become an effective remedial agent of PAHs in stormwater runoff or their PAHs contaminated water. In addition, they found that removal efficiency of aspen wood increased with the molecular weight and hydrophobicity of the PAHs. Therefore, physical and chemical characteristics, such as the BET surface area, porosity and hydrophobicity, of sorbent relate to sorption capacity of PAHs (Ahn et al., 2005).

2.2 Clay Minerals

Soils consist of a complex mixture of solids, liquids and gases. The solid fraction of soils is made up of organic and inorganic components. Most inorganic soil components are crystalline compounds of definite structure called minerals. The inorganic component includes both primary and secondary minerals. Clay minerals, layered aluminosilicates, are the most important secondary minerals in the clay fraction of soils. Clay minerals play a very important role in the chemical reaction which take place in soil and influence the movement and retention of contaminants, metals, and nutrients in the soil.

2.2.1 Layer structure of clay minerals

Clay minerals are the dominant inorganic colloids in most all soils, especially those of temperate areas. The most important properties are their layerlike, crystalline structures and their negative charges. There are two basic building blocks viz. tetrahedral and octahedral layer, which are common to clay minerals.

The basic building block for the silica-dominated sheet is a unit composed of one silicon atom surrounded by four oxygen atoms. It is called the silica tetrahedron because of its four-sided configuration (Figure 2.2 (a)). An interlocking array of a series of these silica tetrahedral tied together horizontally by shared oxygen anions gives a tetrahedral sheet (Figure 2.2 (b)). Aluminum and/or magnesium ions are the key cations in the second type of sheet. An aluminum (or magnesium) ion surrounded by six oxygen atoms or hydroxyl groups gives an eight-sided building block termed octahedron (Figure 2.2 (c)). Numerous octahedral linked together horizontally comprise the octahedral sheet (Figure 2.2 (d)).

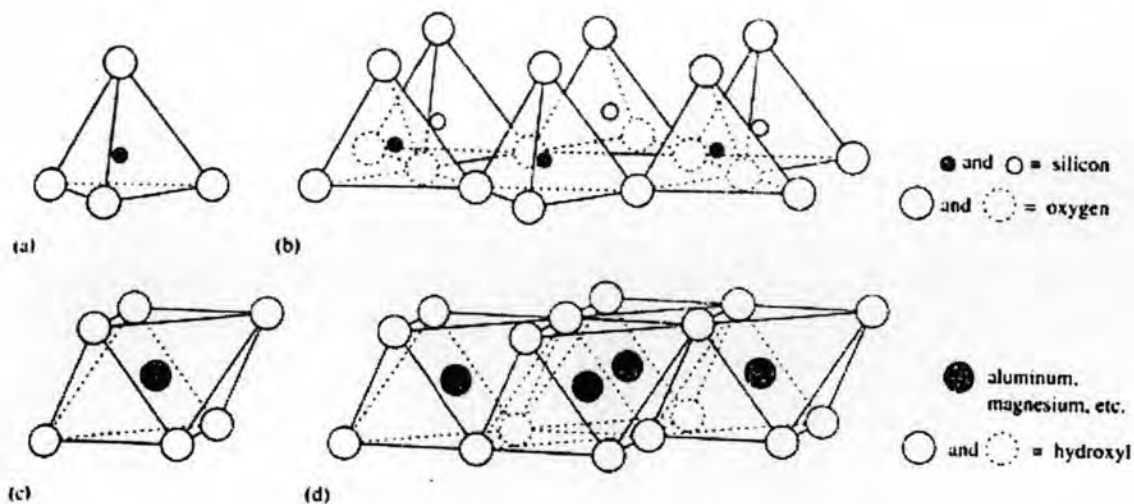


Figure 2.2 Basic molecular and structural components of silicate clays.

Top diagram is a single silica tetrahedron (a) and sheet structure of tetrahedral units (b). Lower diagram shows a single alumina octahedron (c) and sheet structure of octahedral units (d).

The tetrahedral and octahedral sheets are the fundamental structural units of clay minerals. They, in turn, are bound together within the crystals by shared oxygen atoms into different layers. The specific nature and combination of sheets in these layers vary from one type of clay to another and largely control the physical and chemical properties of each clays (Brady and Weil, 2002). Thus, clay minerals are differentiated by (1) the number and sequence of tetrahedral and octahedral sheets, (2) the layer charge per unit cell, (3) the type of interlayer bond and interlayer cations, (4) the cations in the octahedral sheet, and (5) the type of stacking along the basal dimension (Bohn et al., 2001).

2.2.2 Smectites

Smectites are the swelling, or expanding-lattice clays. Montmorillonite is the most prominent member of this group in soils, although beidellite, nontronite, and saponite also are found. While, bentonite is an impure deposit of montmorillonite or other swelling clay. The crystal units (layers) of smectites are characterized by an octahedral sheet sandwiched between two tetrahedral sheets, as shown in Figure 2.3. In turn, these layers are loosely held together by very weak oxygen-to-oxygen and cation-to-oxygen linkages. Exchangeable cations and associated water molecules are attracted between layers (the interlamellar space), causing expansion of the crystal lattice. The internal surface thus exposed by far exceeds the external surface area of these

minerals. The smectites commonly show a high cation exchange capacity, range from 80 to 120 meq/100 g. Smectites also are noted for their high plasticity and cohesion and their marked swelling when wet and shrinkage on drying (Brady and Weil, 2002). The basal spacing (interlayer spacing) of smectite varies with the exchangeable cation and the degree of interlayer solvation. Complete drying yields a spacing of 0.95 to 1.0 nm, and full hydration can swell the layers up to tens of nanometers (Bohn et al., 2001).

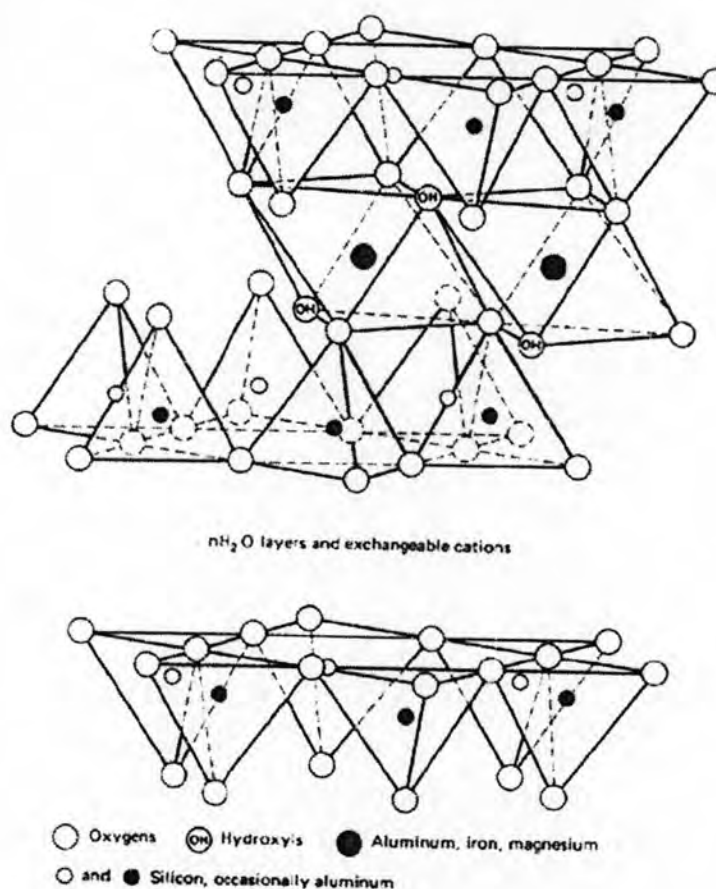


Figure 2.3 Crystal units (layers) of smectites

2.2.3 Cation exchange capacity (CEC)

Clays have a net negative charge, which will attract and hold positively charged ions (cations). A small amount of the negative charge comes from ionizable hydrogen ions, but most is from isomorphous substitution. Ionizable hydrogen ions are hydrogens from hydroxyl ions on clay surfaces. The $-\text{Al}-\text{OH}$ or $-\text{Si}-\text{OH}$ portion of the clay surface ionizes the H and leaves

an unneutralized negative charge on the oxygen ($-Al-O^-$ or $-Si-O^-$). The extent of ionized hydrogen depends on soil pH (Miller and Gardiner, 1998).

Isomorphous substitution, the second source of charge on clay particles, is the substitution during clay genesis of one cation for another of similar size and usually with lower positive valence. In clay structures (having ionic bonds), cations can substitute for coordinating cations in either the tetrahedral or the octahedral sheets. If a cation of lower valence substitutes for one of higher valence, such as Mg^{2+} for Al^{3+} or Al^{3+} for Si^{4+} , the negative charge of O^{2-} and OH^- ions in the mineral structure is left unsatisfied, yielding a net negative charge (Bohn et al., 2001).

The excess negative charge from isomorphous substitution and ionized hydrogens create electron excess sites that attract cations from the surrounding solution, but these cations do not become a part of the clay structure; they are held somewhat loosely. The negatively charged locations are called cation exchange sites. Other cations in solution can compete with and often replace originally adsorbed cations. The total amount of the negative sites is referred to as the soil's cation exchange capacity (CEC). Besides the charge deficit that causes cation exchange, the amount of cation exchange also depends on the surface of the colloid exposed to the soil solution. Ionic attraction for cations is effective only at distances of a few oxygens' thicknesses. Clays whose layers are spread apart to allow the soil solution to pass between clay layers have accessible exchange sites also along this internal surface (Miller and Gardiner, 1998).

2.3 Organoclays

In expanding clay minerals, smectites are widely used in a range of applications because of their high cation exchange capacity, swelling capacity, high surface area, and resulting strong adsorption/absorption capacities (Dentel et al., 1995; Breen et al., 1997). Because of the hydration of inorganic cations on the exchange sites, the clay mineral surfaces are hydrophilic in nature. Thus, the natural clays are ineffective sorbents for organic compounds. The exchange inorganic cations of clay can be replaced with different organic cations by simple ion exchange reactions (Xu and Boyd, 1995). Substituting such organic cations for inorganic cations alters the surface

properties of the clay, which change from hydrophilic to organophilic (Pal and Vanjara, 2001). These modified clays are commonly referred to as organoclays. Clay-organic cation interactions occur because the heat of hydration of the organic cations is very low so that they do not attract water molecules, and because of the substantial amount of organic carbon associated with the clay surface and interlayers. Additionally, the intercalated organic cations act as pillars to prop open the aluminosilicate sheets resulting in greater interlayer spacing that do not change substantially in the presence of water (Wypych and Satyanarayana, 2004).

The exchanged organic cations used to form organoclays affect the sorptive behavior of clay in some manner that appeared to be related to the size and molecular arrangement of the exchanged cations in the interlamellar space. When large organic cations such as hexadecyltrimethylammonium (HDTMA) or dodecyltrimethylammonium (DDTMA) are fixed on the clay surface, an organic phase forms that is derived from the alkyl hydrocarbon moieties. This organic phase functions as a partition medium for organic compounds and is highly effective in removing such compounds from water (Kowalska et al., 1994). In contrast, when small organic cations such as tetramethylammonium (TMA) or benzyltrimethylammonium (BTMA) are used as exchanged cations onto clay, these smaller exchanged cations exist as discrete entities on the clay layers. The surfaces of these clays can be viewed as containing isolated organic cations that are separated by free (uncovered) planar aluminosilicate mineral surfaces. Therefore, both the siloxane surfaces and organic cations in the interlamellar space are potential sites for organic compounds adsorption (Lee et al., 1990; Jaynes and Boyd, 1991).

At present, there are several studies of organoclays as sorbents in pollution prevention and environmental remediation. For example, Lo et al. (2001) found that organoclays can be added as a component of soil liners to enhance organic removal capability and to maintain hydraulic conductivity for earthen liners at waste disposal facilities. Smith et al. (2003) indicated that the use of organoclays as liners for underground gasoline storage tanks reduced the risk of subsurface contamination. In addition, Undabeytia et al. (2000) and El-Nahhal et al. (2001) showed that organoclays prepared from suitable organic cations formed a basis for ecologically acceptable formulations of herbicides with reduced leaching, ground water contamination and enhanced weed control efficacy.

2.3.1 Sorption of organic compounds from aqueous solution by organoclays

The magnitude and mechanism of organic compounds sorption from aqueous solution are functions of the molecular structure of exchanged organic cation, the amount of exchanged organic cation, the chemical properties of organic compounds, the molecular structure of organic compounds, the CEC of clay, and pH of aqueous solution.

The molecular structure of exchanged organic cation

The molecular structure of the organic cations used to modify clay affects both the magnitude and mechanism of nonionic solute sorption. Smith et al. (1990) and Smith and Galan (1995) demonstrated that tetrachloromethane sorption to bentonites modified by small organic cations (e.g., quaternary ammonium cations (QACs) with methyl, ethyl, or benzyl functional groups) was characterized by nonlinear isotherms, strong solute uptake, and competitive sorption. In contrast, tetrachloromethane sorption to bentonites modified by relatively large organic cations (e.g., QACs with dodecyl, tetradecyl, or hexadecyl functional groups) was characterized by linear isotherms, relatively weak solute uptake, and noncompetitive sorption. These authors concluded that the observed difference between the two groups of sorbents was attributable to different sorption mechanisms (adsorption for bentonite modified with QACs with small functional groups and partition for bentonite modified with QACs with relatively large functional groups).

The removal percentages for organoclays to treat the organic pollutants were relative to the length of alkyl chains of organic cations exchanged on the clay. Zhu et al. (1997) indicated that the higher removal percentage for organobentonites prepared from organic cations with the longer alkyl chains to treat the organic compounds was observed. They found that when organobentonites synthesized by adding the same amount of organic cations were applied to treat the organic pollutants in water, the order of the removal percentages was following: octadecyltrimethylammonium (C_{18})-bentonite > cetyltrimethylammonium (C_{16})-bentonite > dodecyltrimethylammonium (C_{12})-bentonite. Accordingly Pal and Vanjara (2001), the removal efficiency of organoclay to treat malathion was in the order of cetylpyridinium (C_{16})-montmorillonite > tetradecyltrimethylammonium (C_{14})-montmorillonite > dodecyltrimethylammonium (C_{12})-montmorillonite.

The amount of exchanged organic cation

For hexadecyltrimethylammonium (HDTMA)-clay, in which partitioning was the dominant sorptive medium, it was determined that as the amount of organic cation adsorbed onto the surface of clay was increased, the sorption capacity of this organoclay increased. When more of the HDTMA cation was loaded onto the internal and external surfaces of the clay, the alkyl chains might become more densely packed, resulting in a more effective partition medium for organic compounds. In contrast, the sorption capacity of benzyltriethylammonium (BTEA)-clay decreased as the amount of organic cation adsorbed onto the surface of the clay was increased. Because sorption to BTEA-clay occurred by adsorption mechanism that was directly dependent on the surface area available for interaction between the solid phase and the organic sorbate. As the surface area decreased with increasing BTEA cation loading on the surface of clay, thus the sorption capacity for organic compounds was decreased (Redding et al., 2002; Bartelt-Hunt et al., 2003; Upson and Burns, 2005).

Zhao et al. (1996) found that the different sorption capacities for dicamba and the resulting interlayer spacing expansion of organoclays could be related both to the amount and the arrangement of organic cations in the interlamellar space. Several studies showed that when organic cations with long alkyl chains were used to prepare organoclays, the interlayer spacing of clay increased stepwise with organic cation loading and that the adsorbed organic cations in the interlamellar space formed many arrangements such as monolayer, bilayer, pseudotrimolecular, or paraffin-type arrangements (Bonczek et al., 2002; Xi et al., 2004; Chen et al., 2005). Bonczek et al. (2002) found that below 70% exchanged hexadecyltrimethylammonium (HDTMA) existed predominantly in monolayer. At greater levels of HDTMA exchanged (up to 100% of the CEC), HDTMA assumed a predominantly bilayer arrangement. For octadecyltrimethylammonium (ODTMA)-montmorillonite, up to 40% of the CEC, ODTMA monolayer was formed between the aluminosilicate layers; up to 80% of the CEC, lateral-bilayer arrangement was formed; and above 150% of the CEC, pseudotrimolecular layer was formed (Xi et al., 2004).

The chemical properties of organic compounds

Zhu et al. (1998) indicated that the sorption characteristics of organic compounds from water on organobentonite were closely related to the chemical properties of organic compounds, such as polarity and octanol-water partition coefficient (K_{ow}). For weakly polar organic compounds, the higher the K_{ow} is, the stronger was the partitioning of the solute in the organic phase composed of the long alkyl chains on organobentonites. For relatively polar organic compounds, the lower the K_{ow} is, the stronger was the solute adsorption by organobentonites prepared from small organic cations. According to Groisman et al. (2004) studied the sorption of six compounds with a range of $\log K_{ow}$ values from 2.5 to 6.0 on tetramethylammonium (TMA)- and octadecyltrimethylammonium (ODTMA)-bentonite, representing short- and long-chain organoclay, respectively. The results showed that the less hydrophobic compounds ($\log K_{ow}$ 2.5-3.8) were sorbed considerably stronger by the TMA-bentonite than by the ODTMA-bentonite. The more hydrophobic compounds ($\log K_{ow}$ 5.2-6.1) were sorbed more strongly on the ODTMA-bentonite.

The partition process is dependent on the solute's aqueous solubility. It is generally believed that solutes having a high aqueous solubility will not be sorbed as strongly as solutes with comparatively low aqueous solubility (Bartelt-Hunt et al., 2003). Rawajfih and Nsour (2006) compared the sorption of phenol, p-chlorophenol, and 2,4-dichlorophenol onto hexadecyltrimethylammonium (HDTMA)-bentonite. The water solubility of phenol, p-chlorophenol, and 2,4-dichlorophenol is 77.5, 27.1, and 4.5 g/L, respectively. The results showed that the sorption capacities for three solutes onto organoclays increased in the order of phenol < p-chlorophenol < 2,4-dichlorophenol, which corresponds to the order of increasing hydrophobicity.

The molecular structure of organic compounds

Sheng et al. (1997) studied the adsorption of aromatic hydrocarbons of various molecular sizes on trimethylphenylammonium (TMPA)-clays in aqueous solution. Results of adsorption isotherms indicated that benzene showed the highest uptake by the TMPA-clays; progressively lower uptake occurred for larger moleculars in the order of benzene > toluene >

p-xylene \approx ethylbenzene $>$ *n*-propylbenzene. They concluded that the adsorption of aromatic hydrocarbons by TMPA-clays was dependent on the molecular size of adsorbates. Lawrence et al. (1998) studied the adsorption of phenol and 2-, 3-, and 4-chlorophenol from water by TMPA-smectite. Results from study showed that the adsorption was not strongly dependent on the water solubility of the molecule, but rather on molecular size and shape. It appeared that placement of the Cl substituent opposite to the phenolic OH did not create a steric limitation to the adsorption. However, Cl substituents in *ortho* or *meta* positions would increase the width of the molecule (compared to phenol) and this apparently caused steric exclusion. Therefore phenol and 4-chlorophenol were effectively adsorbed by TMPA-smectite, whereas 2- and 3- chlorophenol were not adsorbed.

Bartelt-Hunt et al (2003) found that the sorption of benzene and trichloroethene (TCE) by hexadecyltrimethylammonium (HDTMA)-bentonite were not dependent on the aqueous solubility of the solutes, but dependent on molecular shape of solutes. Results of the sorption tests indicated that benzene was sorbed more strongly than TCE. They explained that benzene, being a planar molecule, would be able to access the interlamella spaces of the HDTMA-bentonite, resulting in a higher sorptive capacity for benzene than TCE. Deitsch et al. (1998) studied the rates of 1,2-dichlorobenzene (1,2-DCB) and carbontetrachloride (CCl_4) sorption to organobentonites. The results showed that the rates of 1,2-DCB sorption to the tetradecyltrimethylammonium (TDTMA)- and octadecyltrimethylammonium (ODTMA)-clays were significantly slower than the rate of CCl_4 sorption. It was reasonable that 1,2-DCB diffusion through the long alkyl chains may be more restricted than CCl_4 diffusion through the same alkyl chains because of 1,2-DCB's larger molecular size.

The CEC of clay

The adsorption capacity of organic cations onto clay was mainly dependent on the CEC of each clay type. The higher CEC of clay would be the more exchange of organic cation and resulting clay surface would be more hydrophobic. Pal and Vanjara (2001) found that when the CEC of clays increased in the order of bentonite $>$ montmorillonite $>$ kaolinite, the removal efficiency of organoclays to remove pesticide increased in the order of tetradecyltrimethylammonium (TTA)-bentonite $>$ TTA-montmorillonite $>$ TTA-kaolinite.

According to Koh and Dixon (2001) studied the potential of organo-modified minerals for sorbents of nonionic organic contaminants (NOCs) such as benzene, phenol, and toluene from petroleum refineries. The results showed that the adsorption capacity of organic cations onto minerals was in the order of montmorillonite > zeolite > sericite, which was mainly dependent on the CEC of each mineral. The results from the sorption capacity of NOCs onto the organo-minerals showed in the order of organo-montmorillonite > organo-zeolite > organo-sericite.

Shen (2004) studied the effect of charge characteristics of clay on the mechanistic function of the organoclay in phenol sorption. Organoclays were synthesized by placing benzyltrimethylammonium (BTMA) ion and hexadecyltrimethylammonium (HDTMA) ion on two smectites. The CEC of two smectites, low-charge smectite (LCS) and high-charge smectite (HCS) were 71 meq/100 g and 107 meq/100 g, respectively. The results showed that HDTMA-HCS retained more phenol than HDTMA-LCS with the same number of HDTMA cations exchanged onto each smectite. In contrast, uptake of phenol by BTMA-LCS was considerably higher than that by BTMA-HCS. The author suggested that HCS should be used for preparing organoclay intercalated with organic cations with long alkyl chain; whereas, LCS should be used for preparing organoclay intercalated with organic cations with short alkyl chain.

pH of aqueous solution

pH is one of the important parameters controlling the sorption process. Solution pH significantly affected the sorption of ionizable organic compounds by organoclays. Zhao et al. (1996) examined the effect of solution pH on the sorption of dicamba on hexadecyltrimethylammonium (HDTMA)- and dioctadecyldimethylammonium (DODMA)-clays. They found that at $\text{pH} < \text{pK}_a$ where dicamba exists largely in neutral form, both HDTMA- and DODMA-clays could sorbed nearly twice as much dicamba as compared to $\text{pH} > \text{pK}_a$. Hsu et al. (2000) found that the amount of 2,4-dichlorophenoxy propionic acid (2,4-DP) sorbed on HDTMA-clay decreased continuously with pH increased from 3 to 8, and it reduced markedly as the pH decreased from 3 to 1.5. The maximum 2,4-DP sorption occurred at a pH level of approximately 3 corresponding to $\text{pK}_a = 3$ of 2,4-DP.

Yildiz et al. (2005) studied the sorption capacities of benzoic acid and hydroquinone by octadecyltrimethylammonium (ODTMA)- and hexadecyltrimethylammonium (HDTMA)-bentonites at different pH. Experimental results showed that the sorption capacities increased with decreasing pH value. They explained that a lower sorption at higher pH may be due to the abundance of OH⁻ ions and consequently the ionic repulsion between the negatively charged surface and the ionic organic compounds. The increased sorption at low pH suggested that the sorption of the less ionic species of benzoic acid and hydroquinone were higher than the more ionic species. Similar behaviour has been reported by Abate et al. (2006) for fulvic acid onto HDTMA-vermiculite, and by Yaron-Marcovich et al. (2004) for fluridone on benzyltrimethylammonium (BTMA)-, benzyltriethylammonium (BTEA)-, and HDTMA-montmorillonite.

2.3.2 Study of naphthalene and other organic compounds sorption by organoclays

Nzungu et al. (1996) studied the sorption of naphthalene and diuron from methanol-water mixtures by Na-montmorillonite clay exchanged with four kinds of organic cations and compared the organoclays in terms of their sorption capacities for naphthalene and diuron, respectively. Four organoclays were tetramethylammonium (TMA)-, trimethylphenylammonium (TMPA)-, hexadecyltrimethylammonium (HDTMA)-, and benzyldimethyltetradecylammonium (BDTDA)-clay. The fraction of CEC occupied by TMA, TMPA, HDTMA, and BDTDA were 80, 76, 102, and 87%, respectively. The results indicated that TMPA-clay showed the greatest sorptive capacity of naphthalene, while BDTDA-clay was the most effective sorbent for diuron. The sorption mechanism of each sorbate-sorbent combination was related to the arrangement of organic cations in the exchanged clay and the volume fraction of methanol in solution.

Borisover et al. (2001) demonstrated the potential of dye-clays for removing non-ionic organic compounds from aqueous solutions. Na-montmorillonite (CEC = 90 meq/100g), crystal violet, rhodamine-B were used for preparation of dye-clay complexes. Sorption on dye-clay complexes was tested for atrazine, phenol, and naphthalene representing different classes of organic compounds. Sorption isotherms were found to be non-linear. This indicated that the rigid nature of the dye-clay organic coverage provided a finite surface for adsorption. High values of

organic-carbon-normalized distribution coefficients reached 46800 L/kg for naphthalene on crystal violet-montmorillonite, 8150 L/kg for atrazine on rhodamin-B-montmorillonite, and 970 L/kg for phenol on crystal violet-montmorillonite.

Lee and Kim (2002b) studied the adsorption characteristics of organic cation (hexadecyltrimethylammonium, HDTMA) on kaolinite and halloysite and examined the partitioning of naphthalene on the HDTMA-kaolinite and HDTMA-halloysite. Fourier transformed infrared (FTIR) spectroscopic studies revealed a change of organic cation arrangement with solution conditions. The results showed that the adsorption isotherms for naphthalene were nearly linear. At high surface coverage (e.g., >60% of CEC), the bilayer HDTMA structure formed on kaolinite adsorbed large amounts of naphthalene. On halloysite, HDTMA formed clusters, and no prominent increase of naphthalene adsorption even at high HDTMA loading was observed. The author concluded that the clay mineral structure and morphology had a considerable influence on the organic cation arrangement responsible for partitioning naphthalene.

Chen et al. (2005) studied the relation of the phenol and naphthalene sorption to the configurations of the sorbed Myristylpyridinium (MP^+) within the basal spacing of bentonite. Organoclays were produced from bentonite and MP^+ with loading level 0.2-4.0 times the CEC. The results showed that at low loading level (i.e., <CEC), MP^+ formed flat-layer and when MP^+ loading 0.8 times the CEC, the sorption coefficient (K_{sr}) values of phenol and naphthalene on organoclay were high to 340 mL/g and 15000 mL/g, respectively. When the MP^+ loading exceed the CEC, MP^+ formed paraffin-type structures and the K_{sr} values decreased sharply and leveled off.