



## CHAPTER II

### LITERATURE REVIEWS

#### 2.1 Volatile Organic Carbons

Volatile organic compounds (VOCs) are a class of substances in which organic carbon is bonded to hydrogen or to other elements. As an approximate rule, VOCs may be defined as organic liquids or solids whose room temperature vapor pressures are greater than about 0.01 psia (0.0007 atm, 70 pa) and whose atmospheric boiling point are up to about 500 °F (260 °C, 533 K). There are two main classes of VOCs: hydrocarbons and compounds as shown in Table 2.1

Table 2.1 Classes of Volatile Organic Compounds

Hydrocarbons	Examples	Compounds	Examples
Paraffins	Propane, butane, octane	Alcohols	Methanol, ethanol
Olefins	Ethylene, butadiene	Aldehydes	Formaldehyde
Acetylenes	Acetylene	Ketones	Methyl ethylketone
Aromatics	Toluene, benzopyrene	Acids	Formic acid
		Hydroperoxides	Peroxyacetylnitrite
		Halides	(PAN)
		S compounds	Vinyl chloride,
		N compounds	bromobenzene
			Dimethyl sulfide
			Trimethyl amine

Source: Hunter, P. and Oyama, S.T., 2000

##### 2.1.1 Introduction to benzene, toluene and xylene

Benzene is an organic chemical compound with the formula  $C_6H_6$  as shown in Figure 2.1. Benzene is a colorless and flammable liquid with a sweet smell and relatively high melting point. It is carcinogenic and its use as additive in gasoline is now limited, but it is an important industrial solvent and precursor in the production of drugs, plastics, synthetic rubber, and dyes. Benzene is a natural constituent of crude oil, but it

is usually synthesized from other compounds present in petroleum. The properties are illustrated in Table 2.2

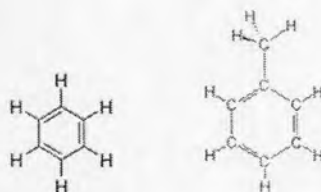


Figure 2.1 Molecular structures of benzene and toluene

Source: available from <http://en.wikipedia.org/wiki/Toluene>,

<http://en.wikipedia.org/wiki/Benzene>,

Table 2.2 Properties of benzene, toluene, and xylene

	Benzene	Toluene	o-xylene	m-xylene	p-xylene
Molecular formula	$C_6H_6$	$C_7H_8$	$C_8H_{10}$	$C_8H_{10}$	$C_8H_{10}$
Molar mass	78.1121 g/mol	92.14 g/mol	106.16 g/mol	106.16 g/mol	106.16 g/mol
Density	0.8786 g/cm <sup>3</sup>	0.8669 g/cm <sup>3</sup>	0.88 g/cm <sup>3</sup>	0.86 g/cm <sup>3</sup>	0.86 g/cm <sup>3</sup>
Melting Point	5.5 °C (278.6 K)	-93 °C (180 K)/ (-135.4°F)	-25 °C (248 K)	-48 °C (225 K)	13 °C (286 K)
Boiling Point	80.1 °C (353.2 K)	110.6 °C (383.8 K)/ 231.08°F	144 °C (417 K)	139 °C (412 K)	138 °C (411 K)

Source: available from <http://en.wikipedia.org/wiki/Toluene>,

<http://en.wikipedia.org/wiki/Benzene>, <http://en.wikipedia.org/wiki/Xylene>

Toluene, also known as methylbenzene or phenylmethane is a clear, water-insoluble liquid with the typical smell of paint thinners, redolent of the sweet smell of the related compound benzene. The properties are shown in Table 2.2

The term xylenes refers to a group of 3 benzene derivatives which encompasses *ortho*-, *meta*-, and *para*- isomers of dimethyl benzene. The *o*-, *m*- and *p*- isomers specify to which carbon atoms (of the main benzene ring) the two methyl groups are attached. Figure 2.2 shows the molecular structure of xylene.

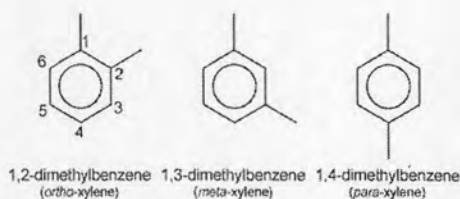


Figure 2.2 Xylene molecular structures

Source: available from <http://en.wikipedia.org/wiki/Xylene>

### 2.1.1.1 Uses

#### 1) Benzene

Today benzene is mainly used as an intermediate to make other chemicals. Its most widely-produced derivatives include styrene, which is used to make polymers and plastics, phenol for resins and adhesives (via cumene), and cyclohexane, which is used in the manufacture of nylon. Smaller amounts of benzene are used to make some types of rubbers, lubricants, dyes, detergents, drugs, explosives and pesticides. (Available from <http://en.wikipedia.org/wiki/Benzene>)

#### 2) Toluene

Toluene is a common solvent, able to dissolve: paints, paint thinners, many chemical reactants, rubber, printing ink, adhesives (glues), lacquers, leather tanners, and disinfectants. It can also be used as a fullerene indicator, and is a raw material for toluene diisocyanate (used in the manufacture of polyurethane foam), phenol and TNT. Toluene can be used as an octane booster in gasoline fuels used in internal combustion engines. Toluene at 84% by volume, fueled all the turbo Formula 1 teams in the 1980s. Small 1.5L turbo engines were known to operate at 5 bar (73 psi) boost in qualifying and 4 bars (59 psi) while racing. More than 1500bhp from 1.5L engines was possible. For proper atomization, the Toluene fuel blend was preheated. Industrial uses of toluene include dealkylation to benzene and disproportionation to a mixture of benzene and

xylene. Toluene can be used to break open red blood cells in order to extract haemoglobin in biochemistry experiments. (from <http://en.wikipedia.org/wiki/Toluene>)

### 3) Xylene

Xylene is used as a solvent and in the printing, rubber, and leather industries. *p*-Xylene is used as a feedstock in the production of terephthalic acid, which is a monomer used in the production of polymers. It is also used as a cleaning agent for steel, a pesticide, a thinner for paint, and in paints and varnishes. It is found in small amounts in airplane fuel and gasoline. With oxidizing agents, such as potassium permanganate ( $\text{KMnO}_4$ ), the methyl group can be oxidized to a carboxylic acid. (Available from <http://en.wikipedia.org/wiki/Xylene>)

#### 2.1.1.2 Toxicity

Aromatic hydrocarbons are a common class of solvents consisting of benzene and substituted benzene derivatives. Most of these solvent are readily absorbed by skin and lungs. The primary toxicological target is the CNS, although toxicity of the liver, kidneys, heart, and skin can occur. Acute exposure to high concentrations of these solvents can produce dizziness, euphoria, respiratory irritation, cardiac dysrhythmias, syncope, and coma. Chronic exposures have resulted in central neurotoxicity manifested by neurophysiologic dysfunction and cerebellar dysfunction.

Toluene demonstrates stereotypical toxicity for this class. The acute and chronic CNS effects described above are observed for toluene. Cardiotoxicity, hematotoxicity, and hepatotoxicity are rare. Toluene is not considered to be carcinogenic. Renal toxicity does occur resulting in a Type I renal tubular acidosis. This occurs almost exclusively in solvent abusers that inhale concentrations above 1000 ppm and has not been demonstrated in industrial exposures within the range of 100 ppm.

Xylene produces upper airway irritation and a typical picture of CNS depression following acute exposure to high concentrations. Exposures of several hundred ppm have produced dizziness, fatigue, headache, and nausea. In studies of levels above 300 ppm, short-term memory and reaction times have been affected. Gastrointestinal upset

with xylene exposure is common. Xylenes produce a synergistic effect with ethanol in producing hepatic toxicity.

However, the Occupational Safety and Health Administration establishes and enforces permissible exposure limits (PEL) for chemicals in the workplace. These are based on recommendations from the National Institute of Occupational Safety and Health (NIOSH) and American Conference of Government Industrial Hygienist (ACGIH). The ACGIH established time-weighted average-threshold limit values (TWA-TLV), which are average concentrations of workplace chemicals that should not be exceeded over an 8-h work day. The recommended value is shown in Table 2.3.

Table 2.3 Comparison of solvent concentrations in indoor air with workplace exposure standards

Solvent class	Chemical	Concentrations in indoor air (mg/m <sup>3</sup> )	8-h	Exposure limits
			OSHA-PEL (mg/m <sup>3</sup> )	ACGIH-TLV (mg/m <sup>3</sup> )
Aldehydes	Formaldehyde	0-0.48	1	1.5
Aliphatic hydrocarbons	n-Hexane	0-0.07	1800	1450
	n-Octane	0-0.003	2350	None
Aromatic hydrocarbons	Benzene	0.002-0.05	0.3	32
	Toluene	0.007-0.6	375	188
	Xylene	0.002-0.7	100	434
	Styrene	0-0.04	215	215
Chlorinated hydrocarbons	Chloroform	0-1.2	240	49
	Carbon tetrachloride	0-0.01	12	31
	Tetrachloroethylene	0-0.25	170	335
	1,1,1-Trichloroethane	0-0.2	1900	1910
	Dichlorobenzene	0-1.2	450	60

Source: Emil J., Bardana, J. and Montonaro, A., 1997

### 2.1.2 Methods of VOC control

A number of options are available for the elimination of VOCs. These are summarized in Table 2.4.

Table 2.4 Method of VOC Abatement

Methods
Condensation
Adsorption
Absorption/scrubbing
Thermal incineration
Catalytic incineration
Flaring
Biological treatment
Odor modification
Air dilution
Membrane separation
Ultraviolet treatment
Ozone catalytic oxidation

Source: Hunter, P. and Oyama, S.T. 2000

### 2.1.3 Ventilation system

Ventilation is an important method of reducing exposure to airborne contaminants. It also serves other purpose, such as preventing the accumulation of flammable or explosive concentrations of gases, vapors, or dusts in workplace. Local exhaust system captures at their source before they escape into the workroom environment. A typical system consists of ducts, hoods, and air cleaner if needed and a fan as Figure 2.3. (McDermott, H.J.,1985)

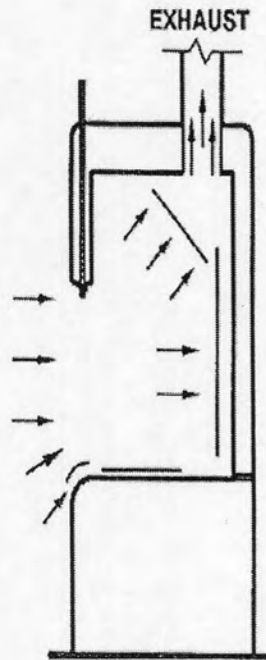


Figure 2.3 Local exhaust system

Therefore, VOC can be removed from workplace by ventilation system and abatement with adsorption technique. In terms of ventilation control, VOC is defined as a respiratory hazard substance. The particle sizes of each particulate including VOCs are defined in order to design the criteria for the exhaust system as listed in Table 2.5

Additionally, the importance design parameter for enclosures is inward air velocity through cracks, doors, and other openings. When the velocity is measured in the plane of the opening, it is called face velocity. The face velocity must be high enough to keep contaminants from escaping despite random room air currents, workers, walking past the openings, and other disruption forces. Typical recommendations are listed in Table 2.6.

Table 2.5 Types of air contaminants

Airborne Material	Size Range, $\mu\text{m}$	Characteristics
Dust	0.1-30.0	Generated by pulverization or crushing of solids. Typical examples are rock, metal, wood, and coal dust. Particles may be up to 300-400 $\mu\text{m}$ but those above 20-30 $\mu\text{m}$ usually do not remain airborne.
Fumes	0.001-1.0	Small solids particles created by condensation from vapor state, especially volatilized metals as in welding. Fumes tend to coalesce into larger particles as the small fume particles collide.
Mists	0.01-1.0	Suspended liquid particles formed by condensation from gaseous state or by dispersion of liquids. Mists occur above open surface electroplating tanks.
Smokes	0.01-1.0	Aerosol mixture from incomplete combustion of organic matter. This size range does not include fly ash.
Vapors	0.005	Gaseous forms of materials that are liquids or solids at room temperature. Many solvents generate vapors.
Gases	0.0005	Materials that do not usually exist as solids or liquids at room temperature, such as carbon monoxide and ammonia. Under sufficient pressure and/or low temperature they can be changed into liquids or solids.

Source: McDermott, H.J., 1985



Table 2.6 Face velocity guideline for enclosures

Operation	Face Velocity, ft/min
Welding booth	150
Paint spray booth	100-200
Laboratory hood	100-150
Belt conveyor	150-200
Mixer	100-200
Melting Furnace	150-250

Source: Nimmon, 2005

## 2.2 Adsorption

### 2.2.1 Adsorption process

The adsorption process occurs at solid-solid, gas-solid, gas-liquid, liquid-liquid, or liquid-solid interfaces. There are two methods of adsorption: physisorption and chemisorption. Physisorption occurs when, as a result of energy differences and/or electrical attractive forces (weak van der Waals forces), the adsorbate molecules become physically fastened to the adsorbent molecules. This type of adsorption is multilayered; that is, each molecular layer forms on top of the previous layer with the number of layers being proportional to the contaminant concentration. When a chemical compound is produced by the reaction between the adsorbed molecule and the adsorbent, chemisorption occurs. Unlike physisorption, this process is one molecule thick and irreversible because energy is required to form the new chemical compound at the surface of the adsorbent, and energy would be necessary to reverse the process. The reversibility of physisorption is dependent on the strength of attractive forces between adsorbate and adsorbent. Table 2.7 summarizes the characteristics of physisorption and chemisorption.

Table 2.7 Summary of types of adsorption

	Physisorption	Chemisorption
Adsorbent	All solids	Some solids
Adsorbate	All gases below critical point	Some gases that are chemically reactive
Temperature range		Generally high temperature
Heat of adsorption	Low temperature	High, 10-100 kcal/g-mol
Rate	Low, 1-15 kcal/g-mol	
Activation energy	Very rapid Low	Ranges from low for nonactivated adsorption to high for activated adsorption
Coverage	Multiple layers	Monolayer or less
Reversibility	Reversible	Frequently not reversible
Uses	Determination of pore sizes and surface area	Determination of surface concentration, estimates of active center area, and adsorption/desorption rates

Source: Hunter, P. and Oyama, S.T., 2000

Factors affecting adsorption include: (Cheremisinoff, N.P. and Cheremisinoff, P.N., 1993)

- The physical and chemical characteristics of the adsorbent, that is, surface area, pore size, chemical adsorption, and so on.
- The physical and chemical characteristics of the adsorbate, that is, molecular size, molecular polarity, chemical composition, and so on; the concentration of the adsorbate in the liquid phase (solution).
- The characteristics of the liquid phase, that is, pH and temperature.
- The residence time of the system.

### 2.2.2 Classification of pore sizes

According to the International Union of Pure and Applied Chemistry, IUPAC, classification of pores as listed in Table 2.8, the size ranges are micropores (<2 nm), mesopores (2-50 nm), and macropores (>50nm).

Table 2.8 Classification of pores according to their width

Type of Pores	Width
Micropores	Less than $\sim 20 \text{ \AA}$ (2 nm)
Mesopores	Between $\sim 20$ and $\sim 500 \text{ \AA}$ (2 and 50 nm)
Macropores	More than $\sim 500 \text{ \AA}$ (50 nm)

Sources; Gregg, S.G. and Sing, K.S.W., 1982

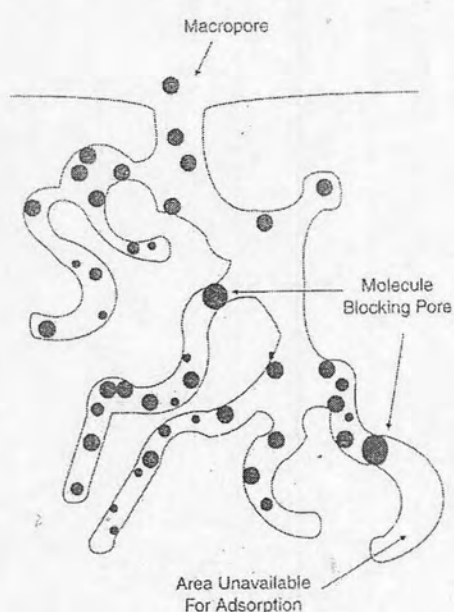


Figure 2.4 Pore structure

Source: Hunter, P. and Oyama, S.T., 2000

As shown in Figure 2.4, for micropores, adsorbed molecules can actually block access to internal surfaces. Diffusion and mass transfer rates govern the movement of the pollutant from the air stream to the exterior surface of the solid and then from the exterior into pore structure.

### 2.2.3 Classification of adsorption isotherms

The majority of physisorption isotherms may be grouped into six types shown in Figure 2.5. Type I isotherm is given by a microporous solid (e.g. molecular sieve, zeolite, or activated carbon) having a relatively small external surface. In contrast, the Type II isotherm represents unrestricted monolayer-multilayer adsorption on a non-porous or macroporous adsorbent. The characteristic features of the Type IV isotherm are its hysteresis loop and the limiting uptake at high  $p/p^0$ : these features are associated with capillary condensation taking place in mesopores. The remaining isotherms are less common: Type VI represents stepwise multilayer adsorption on a uniform non-porous surface, whereas Types III and V are associated with weak adsorbent-adsorbate interactions.

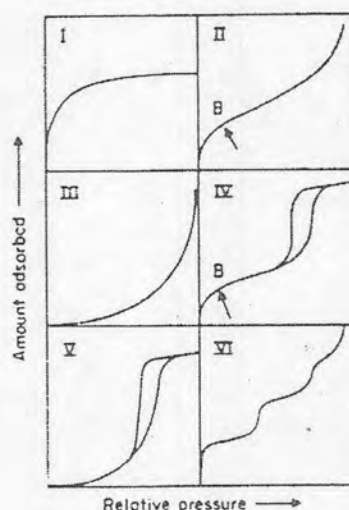


Figure 2.5 Type of physisorption isotherms

Source: Rodrigues, A., LeVan, M. D., and Tondeur, D. 1989

### 2.2.4 Gas-phase adsorption and air pollution control

Adsorption for gas purification comes under the category of dynamic adsorption. Where high separation efficiency is required, the adsorption would be stopped when the breakthrough point is reached. The relationship between adsorbate concentration in the

gas steam and the solid may be determined experimentally and plotted in the form of isotherms. These are usually determined under static equilibrium conditions but dynamic adsorption conditions operating in gas purification bear little relationship to these results. Isotherms indicate the affinity of the adsorbent for the adsorbate but do not relate the contact time or the amount of adsorbent required to reduce the adsorbate from one concentration to another.

Factors which influence the service time of an adsorbent bed include the following: (Cheremisinoff, N.P. and Cheremisinoff, P.N., 1993)

- Grain size of the adsorbent.
- Depth of adsorbent bed.
- Gas velocity.
- Temperature of gas and adsorbent.
- Pressure of the gas stream.
- Concentration of the adsorbates.
- Concentration of other gas constituents which may be adsorbed at the same time.
- Moisture content of the gas and adsorbent.
- Concentration of substances which may polymerize or react with the adsorbent.
- Adsorptive capacity of the adsorbent for the adsorbate over the concentration range applicable over the filter or carbon bed.
- Efficiency of adsorbate removal required.

Once the pollutant (or adsorbate) is adsorbed onto the surface of the solid (or adsorbent), the pollutant is held in place by van der Waals forces or by capillary condensation. Eventually, the pores are full or entry of additional molecules is blocked, and the solid is unable to adsorb any more pollutant. At this point, the solid is said to be "saturated" and it removed from service. It may be discarded or sent back to the manufacturer to be cleaned out, or it may be regenerated in place. Regeneration or desorption is the process of using heat or lower pressure to reverse the adsorption process as shown in Figure 2.6. Direct steam injection is the most widely used method

of providing heat for regeneration. A technique called pressure swing adsorption may also be used, in which the adsorption cycle is under high pressure and the desorption is accomplished by operating the adsorber at a lower pressure. (Hunter, P. and Oyama, S. T., 2000)

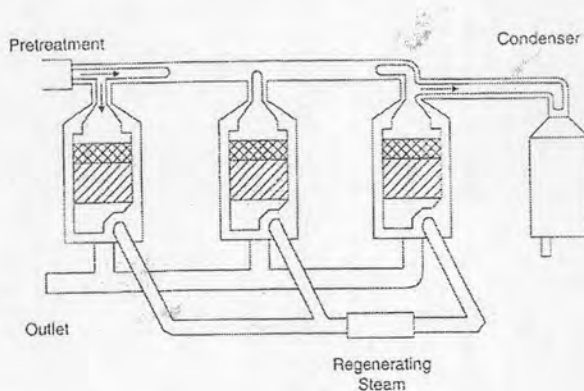


Figure 2.6 Typical process flow diagram of an adsorption system

Source: Hunter, P. and Oyama, S.T., 2000

### 2.2.5 Fixed-bed adsorbers

Enclosures for simple fixed-bed adsorbers may be vertical or horizontal, cylindrical or conical shells. Where multiple fixed-beds are needed, the usual configuration is a vertical cylindrical shell. The type of enclosure used is normally dependent on the gas volume handled and the permissible pressure drop. For continuous operation of fixed-bed adsorbers, it is desirable to have two or three units. With two adsorber units one unit adsorbs while the other regenerates or desorbs. The required times for regeneration and cooling of the adsorbent are the factors determining the cycle time. Under most situations, two adsorbing units are sufficient if the regeneration and cooling of the second bed can be complete prior to the breakthrough of the first unit. (Cheremisinoff, N.P. and Cheremisinoff, P.N., 1993)

About fluid velocities in air pollution control devices, almost all industrial-sized flows of air or gases are turbulent. The velocity in most air conditioning and other gases-flow ducts is about 40-60 ft/s (~ 12 to 18 m/s), for economic reasons. (Nevers, N D., 2000)

## 2.3 Adsorbents

### 2.3.1 Activated carbon

Activated carbon is the most widely used sorbent. It has an affinity for organics and its use for organic contaminant removal from gaseous streams and wastewaters is widespread. The effectiveness of activated carbon for the removal of organic compounds from fluids by adsorption is enhanced by its large surface area, a critical factor in the adsorption process. The surface area of activated carbon typically can range from 450-1,800 m<sup>2</sup>/g. Some activated carbon examples are shown in Table 2.9.

Table 2.9 Surface areas of typically available activated carbons

Origin	Surface area (m <sup>2</sup> /g)
Bituminous coal	1,200-1,400
Bituminous coal	800-1,000
Coconut shell	1,100-1,150
Pulp mill residue	550-650
Pulp mill residue	1,050-1,100
Wood	700-1,400

Source: Cheremisinoff, N.P. and Cheremisinoff, P.N., 1993

#### 2.3.1.1 Activated carbon characteristics

Activated carbons are characterized by a large surface area between 300-2,500 m<sup>2</sup>/g, as measured by BET method, which is the largest among all sorbents. The molecular discrimination effect of carbon is shown in Figure 2.7 and Table 2.10 presents the properties of several commercially available granulated carbons.

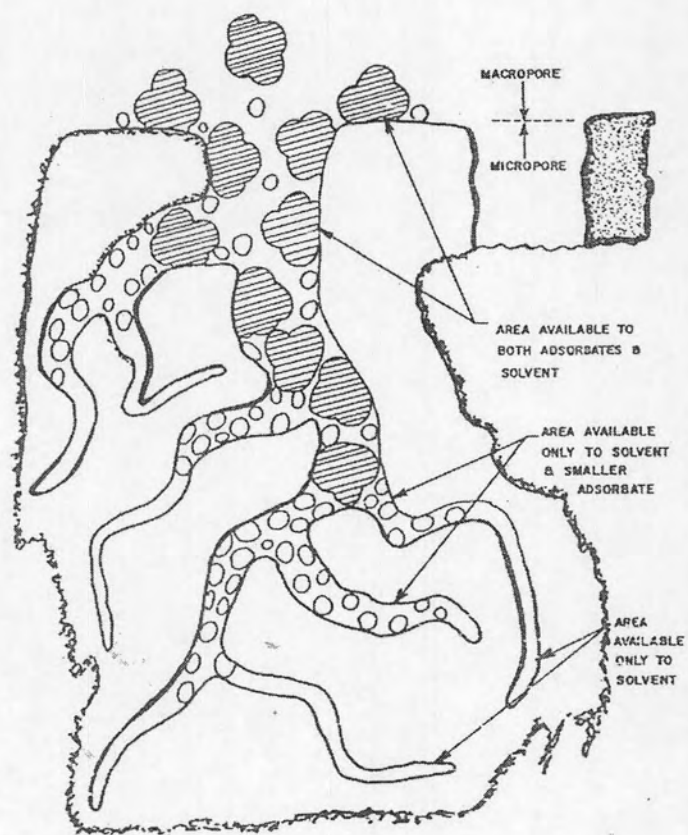


Figure 2.7 Conception of molecular discrimination effects of carbon

Source: Cheremisinoff, N.P. and Cheremisinoff, P.N., 1993



Table 2.10 Properties of several commercially available granulated carbon

Properties	ICI America Hydrodarco 3000	Calgon Filtrisorb 300 (8x30)	Westvaco Nuchar W-L (8x30)	Witco 517 (12X30)
Physical Properties				
Surface Area, m <sup>2</sup> /gm (BET)	600-650	950-1,050	1,000	1,050
Apparent Density, g/cc	0.43	0.48	0.48	0.48
Density, Backwashed and Drained, lb/ft <sup>3</sup>	22	26	26	30
Real Density, g/cc	2.0	2.1	2.1	2.1
Particle Density, g/cc	1.4-1.5	1.3-1.4	1.4	0.92
Effective Size, mm	0.8-0.9	0.8-0.9	0.85-1.05	0.89
Uniformity Coefficient	1.7	≤ 1.9	≤ 1.8	1.44
Pore volume, cc/g	0.95	0.85	0.85	0.60
Mean Particle Diameter, mm	1.6	1.5-1.7	1.5-1.7	1.2
Specifications				
Sieve Size ( U.S. standard series)				
Larger than No. 8, max. %	8	8	8	<sup>b</sup>
Larger than No. 12, max. %	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	5
Smaller than No. 30, max. %	5	5	5	5
Smaller than No. 40, max. %	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>	<sup>b</sup>
Iodine No.	650	900	950	1,000
Abrasion No., minimum	<sup>c</sup>	70	70	85
Ash, %	<sup>c</sup>	8	7.5	0.5
Moisture as packed, max. %	<sup>c</sup>	2	2	1

<sup>a</sup> Other sizes of carbon are available on request from the manufacturers.

<sup>b</sup> Not applicable to the size carbon.

<sup>c</sup> No available data from the manufacturer.

Source: Cheremisinoff, N.P. and Cheremisinoff, P.N., 1993

### 2.3.1.2 Formation and manufacturing of activated carbon

The modern manufacturing processes basically involve the following steps; raw material preparation, low-temperature carbonization, and activation. The conditions are carefully controlled to achieve the desired pore structure and mechanical strength. The raw materials for activated carbon are carbonaceous matters such as wood, peat, coals, petroleum coke, bones, coconut shell, and fruit nuts, illustrated in Table 2.11. Anthracite and bituminous coals have been the major sources. Starting with the initial pores present in the raw material, more pores, with desired size distributions, are created by the so-called activation process. After initial treatment and palletizing, one activation process involves carbonization at 400-500 °C to eliminate the bulk of the volatile matter, then partial gasification at 800-1,000 °C to develop the porosity and surface area. A mild oxidizing gas such as CO<sub>2</sub>, steam, or flue gas is used in the gasification step. The activated carbon created by this activation process is used primarily for gas and vapor adsorption processes. The other activation process depends on the action of inorganic additives to degrade and dehydrate the cellulosic materials and, simultaneously, to prevent shrinkage during carbonization. The activators used are phosphoric acid, zinc chloride, potassium sulfide, or potassium cyanate. (Yang, R.T., 1987)

Table 2.11 Source materials that have been studied for the production of activated carbon

Sources	Sources
Bagasse	Kelp and seaweed
Beet-sugar sludge	Lampblack
Blood	Leather waste
Bones	Lignin
Carbohydrates	Lignite
Cereals	Molasses
Coal	Nut shells
Coconut shells	Oil shale
Coffee beans	Peat
Corn cobs and corn stalks	Petroleum acid sludge
Cottonseed hulls	Petroleum coke
Distillery waste	Potassium ferrocyanide residue
Fish	Pulp-mill waste
Flue dust	Rice hulls
Fruit pits	Rubber waste
Graphite	Wood

Source: Hassler, J.W., 1974

### 2.3.2 Other adsorbents

Generic sorbents have dominated the commercial use of adsorption: activated carbon, zeolites, silica gel, and activated alumina. Table 2.12 Shows examples of commercial applications of these sorbents.

Table 2.12 Examples of commercial adsorption processes and sorbents used

Separation	Adsorbents
<u>Gas Bulk Separation</u>	
Normal paraffins/isoparaffins, aromatics	Zeolite
N <sub>2</sub> /O <sub>2</sub>	Zeolite
O <sub>2</sub> /N <sub>2</sub>	Carbon molecular sieve
CO, CH <sub>4</sub> , CO <sub>2</sub> , N <sub>2</sub> , Ar, NH <sub>3</sub> /H <sub>2</sub>	Activated carbon followed by zeolite (in layer beds)
Hydrocarbons/ vent streams	Activated carbon
H <sub>2</sub> O/ethanol	Zeolite (3A)
Chromatographic analytical separations	Wide range of inorganic and polymer resin agents
<u>Gas Purification</u>	
H <sub>2</sub> O/olefin-containing cracked gas, natural gas, air, synthesis gas, etc.	Silica, alumina, zeolite (3A)
CO <sub>2</sub> / C <sub>2</sub> H <sub>4</sub> , natural gas, etc.	Zeolite, carbon molecular sieve
Hydrocarbons, halogenated organics, solvent/ vent streams	Activated carbon, silicate, others
Sulfur compounds/natural gas, hydrogen, liquefied petroleum gas (LPG), etc.	Zeolite, activated alumina
SO <sub>2</sub> / vent streams	Zeolite, activated carbon
Odors/air	Silicate, others
Indoor air pollutions-VOCs	Activated carbon, silicalite, resins
Tank-vent emissions/ air or nitrogen	Activated carbon, silicalite
Hg/ chlor-alkali cell gas effluent	Zeolite
<u>Liquid Bulk Separation</u>	
Normal paraffins/isoparaffins, aromatics	Zeolite
<i>p</i> -xylene/ <i>o</i> -xylene, <i>m</i> -xylene	Zeolite
Detergent-range olefins/paraffins	Zeolite
<i>p</i> -Diethyl benzene/isomer mixture	Zeolite
Fructose/glucose	Zeolite
Chromatographic analytical separations	Wide range of inorganic, polymer, and affinity agents
<u>Liquid Purifications</u>	
H <sub>2</sub> / organics, oxygenated organics, halogenated organics, etc. dehydration	Silica, alumina, zeolite, com grits
Organics, halogenated organics, oxygenated organics, etc./ H <sub>2</sub> O- water purification	Activated carbon, silicalite, resins
Organics, etc./ H <sub>2</sub> O- water purification	Activated carbon
Inorganics (As, Cd, Cr, Cu, Se, Pb, F, Cl, radionuclides, etc.)/ H <sub>2</sub> O- water purification	Activated carbon
Odor and taste bodies/ H <sub>2</sub> O	Zeolite, alumina, others
Sulfur compounds/ organics	Activated carbon
Decolorizing petroleum fractions, syrups, vegetable oils, etc.	Activated carbon, affinity agents
Various fermentation products/ fermentor effluent	Activated carbon
Drug detoxification in the body	Activated carbon

Source: Yang, R.T., 2003

### 2.3.2.1 Zeolites

Zeolites are the aluminosilicate members of the family of microporous solids known as "molecular sieves". The term molecular sieve refers to a particular property of these materials, i.e. the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the diameters of the tunnels. These are conventionally defined by the ring size of the aperture, where, for example, the term "8ring" refers to a closed loop that is built from 8 tetrahedrally coordinated silicon (or aluminium) atoms and 8 oxygen atoms. These rings are not always perfectly flat and symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pore openings for all rings of one size are not identical. (Available from: <http://en.wikipedia.org/wiki/Zeolite>)

Zeolites are widely used as ion-exchange beds in domestic and commercial water purification, softening, and other applications. In chemistry, zeolites are used to separate molecules (only molecules of certain sizes and shapes can pass through), as traps for molecules so they can be analyzed. Zeolites have the potential of providing precise and specific separation of gases including the removal of H<sub>2</sub>O, CO<sub>2</sub> and SO<sub>2</sub> from low-grade natural gas streams. Other separations include: noble gases, N<sub>2</sub>, freon and formaldehyde. However at present, the true potential to improve the handling of such gases in this manner remains unknown.

### 2.3.2.2 Silica gel

Silica gel is the most widely used desiccant because of its large capacity for water (~40% by weight) and ease in regeneration (~150 °C). Commercial silica gel sorbents are mesoporous, that is, with pores mostly larger than 20 Å. Silica gel can be formed by two routes: (1) polymerization of silicic acid, and (2) aggregation of particles of colloidal silica. Silicic acid, Si(OH)<sub>4</sub>, has strong tendency to polymerize form a network of siloxane (Si-O-Si), leaving a minimum number of uncondensed Si-O-H groups. The

second route involves coagulation of silica sols of rather uniform sizes. These submicrometer particles can coagulate by van der Waals forces or by cations bridging as coagulants. Commercially, silica is prepared through the first route by mixing a sodium silicate solution with a mineral acid, such as sulfuric acid or hydrochloric acid. The reaction produces a concentrated dispersion of finely divided particles of hydrated SiO<sub>2</sub>, known as silica hydrosol or silicic acid: (Yang, R.T., 2003)



### 2.3.2.3 Activated alumina

Activated alumina is one of the solids having the greatest affinity for water. An important industrial application for activated alumina continues to be the drying of gases and liquids, because of its hydrophilic property and large surface area. The term *activated alumina* refers to dehydrated or partially dehydrated alumina hydrates, both crystalline and amorphous, with high surface areas. It has been prepared by a variety of procedures. The major use of activated alumina as a sorbent is in drying. It has been especially important in drying of hydrocarbons produced by the thermal cracking of petroleum fractions.

## 2.4 Clay

Clays are mostly colloidal in size and thus remain suspended in water and have large surface areas (unit mass basis). There are a large and varied number of clays that differ in terms of both the arrangement of their components and in the components they contain (Table 2.13). These clays can be grouped into two classes: (1) clays composed of layers of alumina octahedral sheets and silica tetrahedral sheets as shown in Figure 2.8 and (2) the amorphous clays.

Many different classifications have been suggested. Thus, a committee on nomenclature of the Clay Minerals Group of Mineralogical Society of Great Britain suggested that the crystalline clay minerals be divided into chain and layer structures

and that the layer structures are divided into 2:1 and 1:1 families, with the names triphormic and diphormic applied to these families. (Grim, R.E. 1968)

**Table 2.13 Classification of the clay minerals**

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I. Amorphous
Allophane group
II. Crystalline
A. Two-layer type (sheet structures composed of units of one layer of silica tetrahedrons and one layer of alumina octahedrons)
1. Equidimensional
Kaolinite group
Kaolinite, nacrite, etc.
2. Elongate
Halloysite group
B. Three-layer types (sheet structures composed of two layers of silica tetrahedrons and one central dioctahedral layer)
1. Expanding lattice
a. Equidimensional
Montmorillonite group
Montmorillonite, sauconite, etc.
Vermiculite
b. Elongate
Montmorillonite group
Nontronite, saponite, hectorite
2. Nonexpanding lattice
Illite group
C. Regular mixed-layer types (ordered stacking of alternative layers of different types)
Chlorite group
D. Chain-structure types (hornblende-like chains of silica tetrahedrons linked together by octahedral groups of oxygens and hydroxyls containing Al and Mg atoms)
Attapulgite
Sepiolite
Palygorskite

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Source: Grim, R.E., 1968

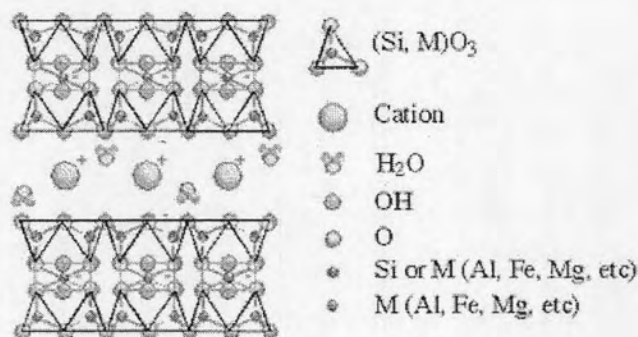


Figure 2.8 Basic structure of a natural clay mineral

## 2.4.1 Clay properties

### 2.4.1.1 CEC

Cation exchange capacity, CEC, is the capacity of a soil for ion exchange of positively charged ions between the soil and the soil solution. A positively-charged ion, which has fewer electrons than protons, is known as a cation due to its attraction to cathodes. Cation exchange capacity is used as a measure of fertility, nutrient retention capacity, and the capacity to protect groundwater from cation contamination. Cation exchange capacity of clay minerals is given in Table 2.14

Table 2.14 Cation exchange capacity of clay minerals, in milliequivalents per 100 g

Kaolinite	3-15
Hallosite $2H_2O$	5-10
Hallosite $4H_2O$	40-50
Smectite	80-150
Illite	10-40
Vermiculite	100-150
Chlorite	10-40
Sepiolite-attapulgite-palygorskite	3-15

Source: Grim, R. E., 1968



### 2.4.2 Organo clay

The interactions between organic matter and clay minerals are among the most widespread reactions in nature.

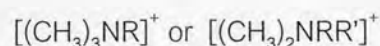
The interactions include cation exchange and adsorption of polar and nonpolar molecules. In these interactions, adsorption, in which physical or chemical bonds are formed between the mineral and the organic matter, is the primary process. In most adsorption reactions the clay minerals serve as the substrates and the organic entities are the adsorbed species. This is true for clay particles with sizes larger than those of the organic entities. However, in the case of huge polymers with very high molecular weight, such as cellulose, the clay particles may be located in the organic web.

Secondary processes may follow the primary adsorption reactions:

1. The colloidal properties of the clay particles and the colloidal state of the system can be changed as a result of adsorption. Depending on the type of the organic compound and organic matter /clay ratio, the particles may either peptize or flocculate or may form a gel or a paste.
2. Adsorption properties of clay minerals may be altered after primary adsorption. In their natural form clay minerals appear with inorganic exchangeable cations, which contribute to their hydrophilicity. As a result of replacement of inorganic cations by organic cations, the clay hydrophilicity decreases and its organophilicity increases. Thus, primary adsorption of organic cations may be followed by secondary adsorption of nonpolar organic compounds. In other words, adsorbability of organic molecules by clay minerals is improved by exchanging the metallic cations with organic cations.
3. Activation energies of different reactions, in which the adsorbed organic compounds are involved, are altered as a result of adsorption on clay surfaces.
4. The reactivity of molecules adsorbed onto the interlayers of TOT clay minerals may be influenced by the limitations that the interlayer space impose on the orientation and packing arrangement of the molecules.

### 1) Clay-organic interactions

The exchange cations can also be replaced with different organic cations by simple ion exchange. A variety of organic cations may be used in this regard to form organoclays that, unlike natural clay, are effective adsorbents for removing organic contaminants from water. One class of organic cations that have been widely used to synthesize organoclays are quaternary ammonium cations (QUATs) of the general form:



Where R and R' are aromatic or alkyl hydrocarbon species. Substituting such organic cations for native metal cations drastically alters the surface properties of the clay, which change from hydrophilic to organophilic.

This occurs because the heat of hydration of the organic cations is very low so that 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.

### 2) Nature of organocation

The interaction of quaternary alkylammonium cations (QACs) with clay is affected by the size and structure of the R group, the clay type, solution conditions and the nature of the exchange cation. In general, the interactions between clays and QACs are strong.

The synthesis of organoclays using short-chain QACs is relatively straightforward. This is because short-chain length organocations have high solubilities in water and are sorbed on the clay exclusively by cation exchange. For QACs with large hydrophobic moieties, there are two complicating factors (i) they have a very low solubility in water so that solvents may be needed to dissolve the organic modifiers and (ii) both a cation exchange and non-exchange mechanism may contribute to the overall adsorption of such organocations by clays. The non-exchange adsorption of QACs is

due to non-electrostatic interactions between the alkyl moieties (tails) of QACs that have bound to the clay surface by cation exchange and the alkyl tails of QACs that have not undergone ion exchange. Depending on the size of the organic cations and the layer charge of the mineral, the alkyl chain of organic cations may form flat lying monolayer, bilayer, pseudotrimolecular layer, or paraffin complexes.

Quaternary alkylammonium ions are preferentially adsorbed on to the cation exchange sites of montmorillonites. Thus solvents do not significantly displace the organocation from the clay, and the structure is stable in the presence of high concentrations of metal cations.

### 3) Ion-dipole and coordination

Many polar molecules can be adsorbed on clay minerals. Depending on the nature of the saturating cation, it serves as an adsorption site by ion-dipole or as a coordination type of intercalation. The greater the affinity that the exchangeable cations have for electrons, the greater will be the energy of interaction with polar groups of organic molecules capable of donating electrons. Hence, transition metal cations on the exchange complex having unfilled *d* orbitals will interact strongly with electron supplying groups.

### 4) Hydrogen bonding

This is an extremely important bonding process in many clay-organic complexes. It becomes very significant, particularly in large molecules where additive bonds of this type coupled with large molecular weight may produce a relatively stable complex. Three classes of hydrogen bonds are distinguished;

- Water bridge: It involves the linking of a polar organic molecule to an exchangeable metal cation through a water molecule in the primary hydration shell.
- Organic-organic hydrogen bonding: This phenomenon appears when the exchangeable cation on the clay is an organic cation, where the possibility of interaction with another species of organic compound through hydrogen bonding exists.
- Clay mineral oxygens and hydroxyls: It requires the interaction of molecules capable of hydrogen bonding with oxygens or hydroxyls of the clay mineral surface.

### 5) Van der Waals forces

Van der Waals or physical forces are interactions operating between all atoms, ions, or molecules, but are relatively weak. They result from attractions between oscillating dipoles in the adjacent molecules. They decrease very rapidly with an increasing distance between the interacting species. They are quite significant in clay-organic complexes, particularly for organic compounds of high molecular weight.

### 6) Adsorption behavior

If certain organic cations are placed on the exchange complex by ion exchange, however, the surface becomes hydrophobic and, in turn, organophilic. Organic cations possessing long-chain alkyl groups are particularly able to impart the hydrophobic quality to the mineral surface. Such organoclay complexes are able to sorb molecules which themselves are hydrophobic by what has been called hydrophobic bonding (Figure 2.9). This process is essentially a non-polar interaction between the organic phase of the clay organic complex and the hydrophobic organic molecule. (Yariv, S. , 2002)

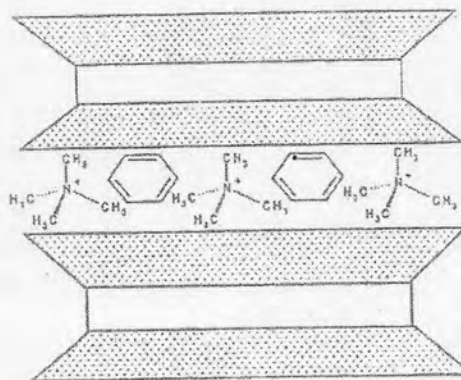


Figure 2.9 Schematic representation of the adsorption of benzene over organoclay

Source; Wypych, F. and Satyanarayana, K.G., 2004

### 2.4.3 Pillared clay

Pillared interlayered clays (PILC), or pillared clays, are a class of porous, high surface area, two-dimensional materials as catalysts and as sorbents for gas separations. PILCs are relatively hydrophobic when compared with zeolites, silica gel, and activated alumina. Synthetic clays are already produced commercially. The availability of inexpensive clays of controlled quality is ensured by the availability of the synthetic clays. For further investigation, PILCs is possible sorbents for gas purification and purification is warranted.

#### 2.4.3.1 Synthesis of PILCs

Pillared clays are prepared by exchanging the charge compensating cations between the clay layers with larger inorganic hydroxyl cations, which are polymeric or oligomeric hydroxyl metal cations formed by hydrolysis of metal salts. Upon heating, the metal hydroxyl cations undergo dehydration and dehydroxylation, forming stable metal oxide clusters which act as pillars keeping the clay layers separated and creating interlayer spacing (gallery) of molecular dimension. Any metal oxide or salt that forms polynuclear species upon hydrolysis can be inserted as pillars, and all layered clays of the abundant phyllosilicate family as well as other layered clays can be used as the hosts. (Yang, R.T., 2003) The steps for PILC synthesis are depicted in Figure 2.10.

In the scheme for PILC synthesis, the first step is to replace the charge-compensating cations in the clay by large polynuclear cations. The polynuclear cations are formed by hydrolysis of salts that contain these cations. After pillaring, the clay containing polynuclear cation is calcined. Thus, the original CEC is now taken up by the protons. Some or most of these protons migrate, at the calcination temperature, into the octahedral sheet of the clay. The migration of the cations into the octahedral layer is basically responsible for the CEC loss of the calcined product because these protons are no longer accessible for ion exchange.

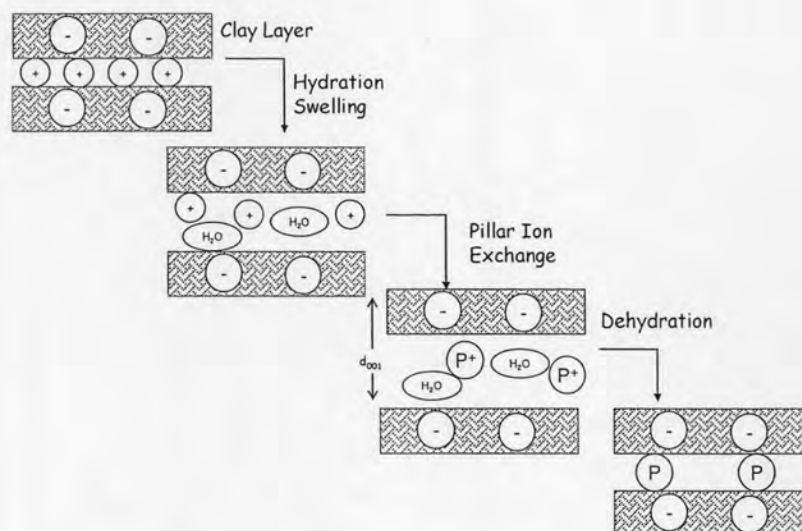


Figure 2.10 General scheme for synthetic pillared clays

Source: Yang, R.T., 2003

#### 2.4.3.2 CEC of PILCs

The cation exchange capacity (CEC) is important for two reasons. First, like zeolites, by placing proper cations in the PILC, its adsorption properties can be tailored. Its pore structure can also be altered by ion exchange. Second, PILC can be used as a stable, economical ion exchanger. It has been considered as a sorbent for the removal of heavy metal ions from aqueous media. (Yang, R.T., 2003) The CEC of the precursor clay is equal to the total amount of the charge compensating cations. Upon PILC synthesis, most of the CEC is lost; only about 10-20% remains.

#### 2.5 Related papers

Lee (1990) studied on adsorption of benzene, toluene, and xylene by two tetramethylammonium-smectites having different charge densities and prepared homoionic tetramethylammonium (TMT)-clay complex from a high-charge smectite from Arizona and a low-charge smectite from Wyoming. Found that the adsorption of the organic vapors by the dry TMA-smectite samples was strong and apparently consisted of interactions with both the aluminosilicate mineral surface and TMA exchange ions in the interlayers. The low charge Wyoming TMA-smectite was a highly effective adsorbent

for removing benzene from water and may be useful for purifying benzene-contaminated water.

Molinard and Vansant (1995) intercalated montmorillonite with particles of titania, zirconia, alumina, iron oxide and mixed lanthnia/alumina to produce several types of microporous pillared clays (PILC). The gas adsorption experiments indicated that the adsorption properties of these PILCs depend on the pillars.

Gitipour, Browsers and Bodocsi (1997) investigated the clay-aromatic interactions with a view to the use of bentonite clay for binding benzene, toluene, ethylbenzene, and o-xylene (BTEX compounds) in contaminated soils. The modified (organophillic) bentonites are prepared by replacing the exchangeable inorganic cations present in bentonite particles with a quaternary ammonium salt. The findings of this study reveal that organophillic bentonite can act as a successful adsorbent for removing the aromatic organics from contaminated soil.

Hutson, Hoekstra and Yang (1999) showed that clays prepared from an oligomeric solution with an  $\text{OH}^-/\text{Al}$  of 2.2 and calcined at  $400^\circ\text{C}$  yielded the highest overall surface area and the largest micropore volume. The high CEC resulted in a higher pillar density and consequently a larger ultramicroporosity (with 0.4 nm pores).

Chiang, Chiang and Huang (2001) investigated the pore structure of three activated carbons and determine the temperature dependence of the adsorption of VOCs onto activated carbon. The adsorption of VOCs showed that only  $\text{C}_6\text{H}_6$  exhibited the activated entry effect. Also, benzene adsorption was the most preferable compared to other three VOCs because of higher heats of adsorption and lower entropy change. Result indicates physical adsorption played a critical role during adsorption process.

Shin, Oh and Ha (2003) studied on the Korean montmorillonite intercalated with Al-hydroxypolycation solution and aged for 1, 4 and 7 days and then calcined at  $400^\circ\text{C}$ ,  $600^\circ\text{C}$  and  $760^\circ\text{C}$ , respectively. The basal spacing formed by intercalation appeared

at about 17 Å and decreased with the heating temperature for the sample aged for 1 day. The total surface area and pore volume also increased with the aging time of Al-solution, in which micropore area increased more rapidly.

Kongsuebchat (2003) investigated the factors of preparation baked clay adsorbent from clay and sawdust and also the properties and capacity in treating wastewater containing cadmium compared with activated carbon. The results demonstrated that the weight ration of clay to sawdust 10:90 and pyrolysis temperature 600 °C for 30 minutes with increasing rate 3 °C/minute was suitable condition for making baked clay adsorbent. The efficiency of bake clay for cadmium removal was 83.95% or 23.05% more than of activated carbon.

Jiang and Cooper (2003) prepared modified clay adsorbents for the removal of humic acid in wastewater and found that Al/Fe-modified montmorillonites are potential efficient adsorbent for treating color-causing natural organic matter.

Gill and Ganda (2003) characterized the microporous structure of a alumina intercalated clay that calcined at temperature between 473 and 873 K. It has been found that the ultramicropores generated by the pillaring process were the most deteriorated at the highest calcinations temperatures.

Sergio (2006) studied the aluminium-pillaring of a montmorillonitic clay on the textural properties as a function of the starting mineral particle size. He found that in all cases microporous solids were obtained, with specific surface areas over 350 m<sup>2</sup>/g and specific total pore volume about 0.250 ml/g. The sample calcined at 750 °C produces high specific surface area.

Mahboub (2006) revealed that the prepared materials were mainly mesoporous solids in consequence of their delaminated nature, when the amine pre-adsorption was used before the pillaring, microporosity was also formed.



Changchaivong (2006) studied on the adsorption of polycyclic aromatic hydrocarbons, PAHs, from synthetic wastewater by organoclays. The sorption capacities of PAHs increased with the amount of dodecylpyridinium chloride, DPC, by increasing from 0.25-1.25 times CEC. When the amount of DPC increased from 1.25 to 2.00 times the CEC, the sorption capacities were not different.