

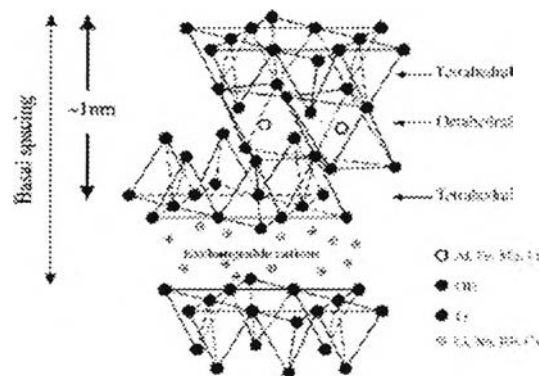


## CHAPTER II LITERATURE REVIEW

### 2.1 Clay Minerals

Clay minerals, or phyllosilicate, is a certain group of layered crystalline silicates mineral which consist of two types of sheets, octahedral and tetrahedral, which are held together by weak interaction forces between the layers. According to the differences in chemical composition and crystal structure, they are divided into four main groups which are smectite, vermiculite, illite, and kaolinite. The most commonly used layered silicates is a group of smectite clay.

Minerals of the smectite group (sometimes known as the montmorillonite group) is phyllosilicates or layered crystalline silicates belong to the structural family known as the 2:1 phyllosilicates. Their crystal lattice consists of two-dimensional layers where a central octahedral sheet of alumina or magnesium is fused to two external silica tetrahedral sheets so that the oxygen ions of the octahedral sheet also belong to the tetrahedral sheet. The layer thickness is around 1 nm and the lateral dimensions of these layers may vary from 300 Å to several micron or larger depending on the particular clay, their structure is given in Fig. 2.1. and their chemical formula and characteristic parameter are shown in Table 1. These layer organize themselves to form stacks with the regular van der Waals gap in between them called inter layer or gallery (Manias *et al.*, 2001).



**Figure 2.1** Structure of 2:1 phyllosilicates (Sinha Ray and Okamoto, 2003).

**Table 2.1** Chemical formula and characteristic parameter of commonly used 2:1 phyllosilicates (Sinha and Okamoto, 2003).

2:1 phyllosilicates	Chemical formular	CEC (meq/100g)	Particle length (nm)
Monmorillonite	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$	110	100-150
Hectorite	$M_x(Mg_{6-x}Li_x)Si_8O_{20}(OH)_4$	120	200-300
Saponite	$M_xMg_6(Si_{8-x}Al_x)Si_8O_{20}(OH)_4$	86.6	50-60

\*M: monovalent cation; x: degree of isomorphous substitution (between 0.5 and 1.3)

Both the octahedral and tetrahedral sheets can be substituted, which generates a charge imbalance in the 2:1 layer. The tetrahedral Si atom is isomorphically substituted by Al and the octahedral atoms (Al or Mg) is substituted by atom of lower oxidation number. The resulting charge deficiency is balanced by hydrated cations, mainly K, Na, Ca and Mg, which is located between the parallel clay layers. This type of clay is characterized by a moderate negative surface charge known as the cation exchange capacity, CEC, and expressed in meq/100g. The charge of the layer is not locally constant it varies from layer to layer and must be considered as an average value over the whole crystal (Manias *et al.*, 2001; Sinha and Okamoto, 2003).

Bentonite is a local clay minerals in Thailand that generally found in Lopburi, Sara-buri, and Prageenburi province. It is a clay minerals generated from the alteration of volcanic ash, comprising predominantly of smectite minerals, usually montmorillonite. These minerals may include quartz, feldspar, calcite and gypsum. The presence of these compounds can impact the industrial value of bentonite. Its chemical formula is  $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$  and the CEC values have been in the range of 70-100 meq/100g depending on source of bentonite.

There are two types of bentonite : (1) *sodium-bentonite or high-swelling type*, generated from volcanic ash that was deposited in marine environment; (2) *calcium-bentonite or low-swelling type*, which evolved from volcanic ash deposited in fresh-water environment.

Bentonite clay found in Thailand is the calcium-bentonite which contains a lot of impurity. To increase its value, it must be purified by removing the associated gangue minerals or treated with acids to produce acid-activated bentonite, moreover; activated with the addition of soda ash for changing calcium-bentonite to sodium-bentonite. The special properties of bentonite such as swelling, large chemically active surface area, high cation exchange capacity and high adsorption, make it a valuable material for a wide range of usage and application.

In 1999, Altin *et al.* determined surface area, pore volume distribution, and porosity of montmorillonite after being exposed to aqueous solutions with various pH values. For the pH-adjusted montmorillonite, the results demonstrated that the micropore and mesopore surface areas were greatly increased by increasing pH due to increasing pH creates a more porous structure, since the interlayer repulsive force become dominant.

Banat *et al.* (2000) studied the potential of bentonite to adsorb phenol from aqueous solution with various pH values, the results demonstrated that the adsorption capability bentonite was strongly depended on the pH of the solution. The adsorption capacity was increased with decrease in the pH and an increase in the initial phenol concentration. Moreover, they also investigated the possible regeneration of bentonite using difference solvent by studied the adsorption equilibrium isotherms of phenol in water, methanol and cyclohexane. The results showed that the phenol adsorption using methanol was the lowest of the three solvents so that methanol was used to extract the adsorbed phenol.

## 2.2 Porous Clay Heterostructure (PCH)

Porous silica is a class of materials that fulfils all the requirements. Silica is chemically inert but allows irreversible surface modification by reaction of the surface silanol groups. Mesoporous silica materials were first synthesized in 1992 by Beck *et al.* These material play a prominent role in materials chemistry due to the mesoporous materials have large surface area because of their numerous pore. There are various type of clays such as hectorite, vermiculite, synthetic saponite and montmorillonite can be used to synthesize the Porous Clay Heterostructure (PCH).

In 1995, Galarneau *et al.* reported the discovery of a new material known as porous clay heterostructure (PCH). The PCH was prepared from fluorohectorite which are 2:1 mica-type layered silicate. These intercalation compounds are formed through the surfactant micelle ordering of silicate species in the restricted two-dimensional intragallery region of host smectite clay. The obtained materials afford the materials with uniform pore diameters in the supermicropore to small mesopore range (1.5 – 3.0 nm).

Polverejan *et al.* (2000) prepared porous clay heterostructures through the surfactant-direct assembly of mesoporous silica within the galleries of synthetic saponite clays with targeted layer charge densities in the range  $x = 1.2-1.7 e^-$  units per  $Q^+_x[Mg_6](Si_{8-x}Al_x)O_{20}(OH)_4$  unit cell. The CEC value proportionally increases with the aluminum content of the clays. All three saponites were used to assemble porous clay heterostructures that were denoted SAP1.2-, SAP1.5-, and SAP1.7-PCH, respectively. The intragallery mixture of neutral alkylamine and quaternary ammonium ion surfactant ( $Q^+$ ) was removed by calcination. The resulting PCH exhibited basal spacings of 33-35 Å. The BET specific surface areas progressively decreased with increasing aluminum loading from 921 to 797 m<sup>2</sup>/g and the framework pore volumes decreased from 0.44 to 0.37 cm<sup>3</sup>/g. Moreover, these materials exhibited the framework pore sizes were in the supermicropore to small mesopore region 15-23 Å.

In 2002, they have further studied the functionalization of PCH derived from synthetic saponite through postsynthesis grafting reactions using AlCl<sub>3</sub> and NaAlO<sub>2</sub> as alumination agents (Polverejan *et al.*, 2002). The amount of tetrahedral aluminum incorporated into the saponite gallery structure is correlated with the concentration of aluminum in the grafting solution. However, some loss of gallery mesostructure occurred at higher aluminum loadings (e.g., Si/Al = 5) with sodium aluminate. Depending on the choice of aluminum reagent (AlCl<sub>3</sub> or NaAlO<sub>2</sub>), the Al-SAP/PCH derivatives exhibited basal spacings of 32-34.8 Å, BET surface areas of 623-906 m<sup>2</sup>/g, pore volumes of 0.32-0.45 cm<sup>3</sup>/g, and pore sizes in the large micropore to small mesopore range (14-25 Å).

Benjelloun *et al.* (2002) studied the cationic exchange capacities (CECs) of two porous clay heterostructures (PCHs), derived from natural montmorillonite

(PMH) and synthetic saponite (PSH). Three methods for the formation of  $\text{NH}_4^+$ -exchanged PCH forms are described and evaluated: (1) adsorption of ammonia under a gas flow on calcined and extracted PCHs in acidified methanol; (2) direct exchange in  $\text{NH}_4\text{Cl}$  solutions; (3) solvent extraction with  $\text{NH}_4\text{Ac}/\text{EtOH}/\text{H}_2\text{O}$ . When comparing gas flow proves the adsorption under  $\text{NH}_3$ , the different methods for exchange PCH to be the best method. The resulting extracted materials had a higher specific surface area and porosity and even a slightly narrower pore size distribution than the calcined ones with maxima of  $997 \text{ m}^2/\text{g}$  and  $0.76 \text{ cm}^3/\text{g}$  for PMH and  $1118 \text{ m}^2/\text{g}$  and  $0.97 \text{ cm}^3/\text{g}$  for PSH.

The next year, Benjelloun *et al.* (2002) further synthesized the two different porous clay heterostructures PMH and PSH. The templates were removed either by calcination at  $550^\circ\text{C}$  or by solvent extraction and both materials were compared. Acidified methanol extraction resulted in the successful removal more than 90% of the organics from the PCH precursors, without an additional calcination step. The extracted materials had a high surface area ( $896 \text{ m}^2/\text{g}$  for PMH and  $1122 \text{ m}^2/\text{g}$  for PSH) and pore volume ( $0.84 \text{ cm}^3/\text{g}$  for PMH and  $1.13 \text{ cm}^3 \text{ g}^{-1}$  for PSH). The silanol numbers of the extracted and calcined PMH and PSH have been determined and compared. The results demonstrated that the calcined samples contained slightly less  $\text{OH nm}^{-2}$  than the extracted samples, while all silanol numbers are situated between  $0.96$  and  $1.17 \text{ OH nm}^{-2}$ . These high OH numbers after extraction are a great advantage for subsequent post modifications to catalytically activate the PCH surface.

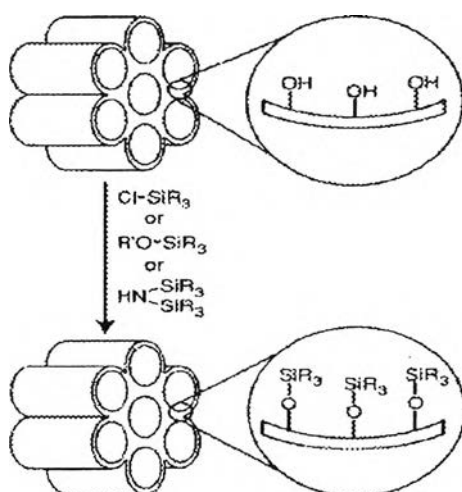
### 2.3 Functionalization of Porous Clay Heterostructure

The important way of modifying the physical and chemical properties of mesoporous silicates has been the incorporation of organic components, either on the silicate surface or trapped within the channels. The inorganic components can provide mechanical, thermal or structural stability, whereas the organic features can introduce flexibility into the framework. Through the development of hybrid inorganic-organic mesoporous solids, much progress has been made in the last few years towards applications of mesoporous solids in a variety of fields. Mesoporous solids

have been functionalized at specific sites, and were demonstrated to exhibit improved activity, selectivity, and stability in a large number of catalytic reactions and sorption processes.

Surface modified mesoporous silica via covalent bonding of organic molecules can be achieved by using two general strategies which are post-synthesis modification also called grafting method and co-condensation reaction also called one-pot synthesis (Stein *et al.*, 2000; Sayari and Hamoudi, 2001).

1) *Post-synthesis modification*, this approach refers to direct grafting of a mesoporous support by attachment of functional molecules to the surface of mesoporous, usually after surfactant removal as shown in Fig 2.2.

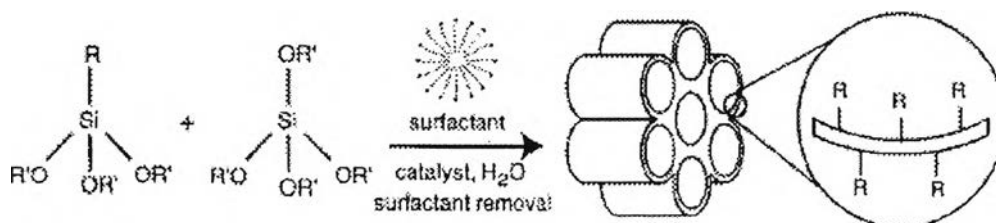


**Figure 2.2** Functionalization of mesoporous silicates by grafting( Stein *et al.*, 2000).

Mesoporous silicates possess surface silanol (Si-OH) groups that can be present in high concentration and act as anchoring points for organic functionalization. Surface modification with organic groups is most commonly carried out by silylation with a suitable organosilane reagent.

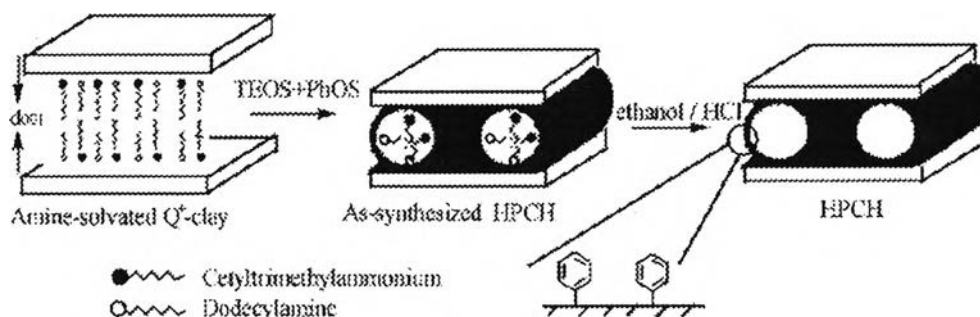
2) *Co-condensation reaction*. This method refers to co-condensation of tetraalkoxysilane and one or more organosilane precursors via sol-gel technique to produce organic functionalized mesoporous silicates. Such co-condensation reactions have also been applied to surfactant templated synthesis (Fig. 2.3). In this method,

the organic moieties are covalently linked via a non-hydrolyzable Si-C bonds to a siloxane species, which hydrolyzes to form a silica network.



**Figure 2.3** Preparation of hybrid mesoporous silicates by co-condensation) Stein *et al.*, 2000)

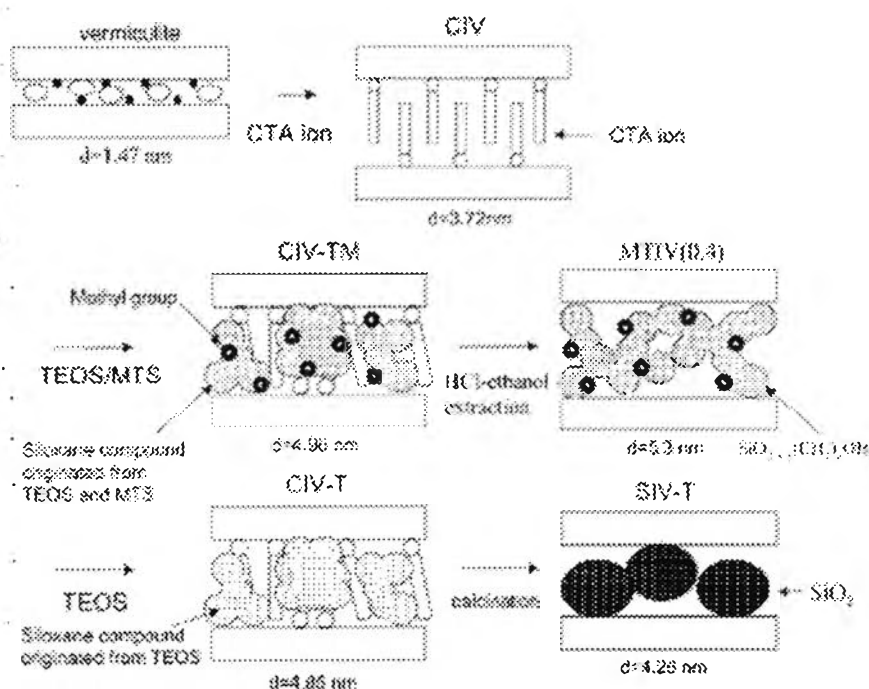
Wei *et al.* (2004) prepared a new class of organic-inorganic hybrid porous clay heterostructures (HPCHs) through the surfactant-directed assembly of organosilica in the galleries of montmorillonite by using co-condensation method. The reaction involved hydrolysis and condensation of phenyltriethoxysilane and tetraethoxysilane in the presence of dodecylamine and cetyltrimethylammonium ion as the surfactant templates, which were removed by solvent-extraction. The mechanism for the formation of hybrid porous clay heterostructure (HPCH) has shown in Fig. 2.4. The products were characterized by XRD,  $\text{N}_2$  adsorption, NMR and FTIR. Depending on the loading of phenyl groups, HPCHs had BET surface areas of 390-771  $\text{m}^2/\text{g}$ , pore volumes of 0.3-0.59  $\text{cm}^3/\text{g}$ , and the framework pore sizes in the supermicropore to small mesopore range which are 1.2-2.6 nm.



**Figure 2.4** Schematic illustration of mechanism for formation of hybrid porous clay heterostructure (HPCH) through surfactant-directed assembly of organosilica in the

galleries of clay (Wei *et al.*, 2004).

In 2004, Nakatsuji *et al.* reported the synthesis of porous vermiculite (AV-I) pillared with methyl incorporated polysiloxane using ethanol/HCl extraction. The formation of stable precursors of the pillars containing methyl groups was investigated using intercalation of methyltriethoxysilane (MTS) and tetraethoxysilane (TEOS) into the cetyltrimethylammonium ion (CTA)-exchanged vermiculite, as shown in Fig 2.5.



**Figure 2.5** Schematic representation of the formation of the pillars in vermiculite (Nakatsuji *et al.*, 2004).

The results demonstrated that the BET surface areas increase to above  $500 \text{ m}^2/\text{g}$  with an increase the HCl concentration to  $0.4 \text{ mol}/\text{dm}^3$  which nearly the calcined product obtained by the conventional method. However, the pore size of ethanol/HCl treated materials were narrower than the calcined products. The porosity and adsorptivity of the modified porous vermiculite was also evaluated, the results revealed that the product treated with a TEOS/MTS mixture had a hydrophobic surface as a result of the successful incorporation of methyl groups.



Ishii *et al.* (2005) synthesized highly porous silica nanocomposites from a clay minerals by a new approach using a pillaring method combined with a selective leaching method. The preparation was conducted by applying an the extraction HCl/ethanol after intercalation and condensation of tetraethoxysilane (TEOS) and/or methytriethoxysilane (MTS) into cetyltrimethylammonium ion-exchanged vermiculite. The products were investigated by N<sub>2</sub> adsorption isotherms the results revealed that the products had high porosity with 1205–715 m<sup>2</sup>g<sup>-1</sup> of BET surface area, owing to the multiple pore formations in and between the silicate layers.

Prakobna *et al.* (2006) synthesized Porous clay heterostructures (PCHs) and hybrid organic-inorganic PCHs (HPCHs) from Na-bentonite clay by surfactant directed assembly of silica species within the clay galleries. Before the modification, clay was adjusted pH to four conditions, including pH 9, 7, 5, and 3. HPCHs have been functionalized with the methyl group through co-condensation reaction to improve the hydrophobicity on the porous structures for finding a new application of these porous clays utilizing as ethylene scavenger in active packaging. According to N<sub>2</sub> adsorption-desorption data, the results show that PCHs have surface areas of 501–668 m<sup>2</sup>/g, an average pore diameter in the supermicropore to small mesopore range of 3.01–3.85 nm, and a pore volume of 0.43–0.64 cc/g, while HPCHs have a result of 469–582 m<sup>2</sup>/g, 3.19–3.88 nm, and 0.33–0.49 cc/g, respectively. The ethylene adsorption capacity of these porous clays is investigated using gas chromatography. The results demonstrate that the enhancement of the hydrophobicity on HPCHs play an important role in ethylene adsorption. After these PCHs and HPCHs were obtained, the PCHs and HPCHs nanocomposites of PP have been fabricated. The dispersion of the 1 wt% porous clays in PP matrix is improved by incorporating 2 wt% of surlyn ionomer. According to ethylene permeability test, both PCHs and HPCHs significantly affect on the ethylene barrier property of the nanocomposite films.

#### **2.4 Strategies for PCH Applicable in Wastewater Treatment**

The contamination of water by toxic heavy metals and organic chemicals through the discharge of industrial wastewater is a worldwide environmental problem (Ajmal *et al.*, 2003). Their presence in streams and lakes has been responsible

for several health problem with animals, plants, and human beings. In the last few years, adsorption technologies has been shown to be an alternative method for removing these toxic substance from liquid wastes (Bayat ,2002)

PCH are interesting materials for using in wastewater treatment due to their large surface area and unique combined micro- and mesoporosity. One outstanding feature of PCH is the large amount of silanol groups (Si-OH) present on the PCH surface, generated by the synthesis, which gives the opportunity for further modification of the substrate for wastewater treatment.

#### Organic pollutant removal

Many organic chemicals such as benzene, chloroform, carbon tetrachloride, pentachlorophenol, naphthalene, phenanthrene, etc. are one of the most common pollutants emitted by the chemical process industries. Several techniques for removing these organic compounds have been investigated such as thermal incineration, catalytic oxidation, condensation, bio-filtration, and membrane separation. Organic compounds are often removed by using adsorption process. By specific surface functionalization, mesoporous silicates can increase the hydrophobicity making suitable for sorption of organics. This process can be used to separate liquids of different polarity.

Pires, *et al.*, 2004 prepared porous materials from clay by the gallery templated synthesis using a quaternary ammonium cation (CTAB) and neutral amines with different chain length (octalamine and decylamine). The materials prepared in this work, after calcinations at 650 °c, had BET surface area values in the range of 600-700 m<sup>2</sup>/g and micropore volume near 0.3 cm<sup>3</sup>/g. The possibility of using such materials as adsorbents of organic compounds was studied by the adsorption of ethanol and methyl ethyl ketone. The results showed that, particularly one sample were decylamine was used in the synthesis, has interesting properties regarding the adsorption of these organocompounds.

In 2005, Sayari *et al.* developed a novel two-step methodology consisting of (1) synthesis of MCM-41 at relatively low temperature, typically 70-100 ° c, and (2) post-synthesis hydrothermal treatment of the as-synthesized silica mesophase in an aqueous emulsion of *N,N*-dimethylalkylamine at 120-130 ° c. They investigated the adsorption properties of obtained materials toward metal cations and organic pollut-

ants. In the adsorption of metallic cations ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Co}^{2+}$ ), the pore-expanded amine containing mesoporous silica MCM-41 were found to be fast and high capacity for numerous metallic cations. For the adsorption of organic pollutants (4-chloroguaiacol, and 2,6-dinitrophenol) by the pore-expanded meso-porous silica MCM-41 which achieved through post-synthesis hydrothermal treatment results revealed that the adsorption capacity was quite high for both substances. Moreover, in both case the adsorbents can be easily regenerate through acid or solvent washing.

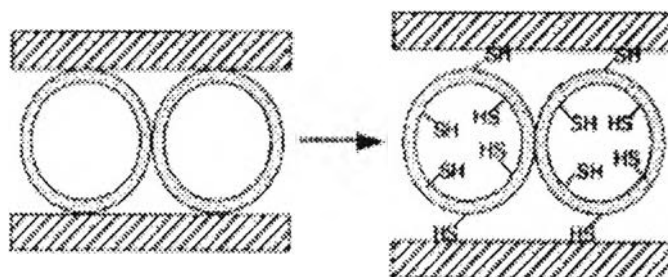
#### *Heavy metal ions removal*

Heavy metals refer to high density metallic elements such as mercury, cobalt, copper, chromium(III), iron, manganese, zinc, etc. Some of these are essential to human, animal and plant life. On the contrary, excessive levels of some of them may be toxic. There are others, which are harmful to health even in low concentration such as mercury, lead, cadmium, chromium(VI), arsenic, and antimony.

Thus, there is an increasing interest around the world in cleaning up polluted rivers and lakes, and implementing system that regulate the disposal of waste that contains metals. These may be carried out through various techniques including, chemical precipitation, ultra-filtration, ionic exchange, reverse osmosis, adsorption, etc. Different natural substances especially the preparation of modified clays and design of new adsorbent materials have been studied as a way to improving environmental conditions.

Mesoporous sieve of interest for the removal of toxic heavy metals, such as mercury, cadmium, and lead, are based mostly on mesoporous silicates functionalized with mercaptopropyl surface groups. The thiol functionalities, which exhibit a high affinity for these metals, have been incorporated either by grafting or by co-condensation techniques (Stein et al., 2000).

Mercier and Pinnavaia (1998) demonstrated the first potential environmental application of a porous clay heterostructure. A heavy metal ion adsorbent that bind  $\text{Hg}^{2+}$  ions was prepared by grafting 3-mercaptopropyltrimethoxysilane to the intragallery framework walls of a porous fluorohectorite clay heterostructure (PCH) as illustrated in Fig. 2.6.



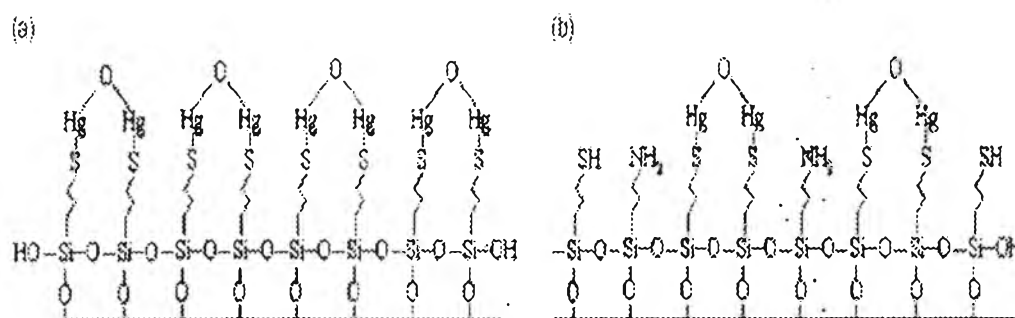
**Figure 2.6** Grafting of mercaptopropylsilane groups to the inner and outer walls of mesostructural silica intercalated in smectite clay (Mercier and Pinnavaia, 1998).

The results showed that the BET surface area of MP-PCH ( $175 \text{ m}^2/\text{g}$ ) was significantly lower than PCH ( $550 \text{ m}^2/\text{g}$ ). Moreover, a pore size of 2.1 nm was observed in PCH but no mesoporosity is discernible for MP-PCH. Thus, the grafting process results in constriction of the pore channel. Although there was a considerable reduction in the size of the PCH pore channels, the thiol sites should still be accessible for metal ion binding, because the MP-PCH retained an appreciable surface area and pore volume. For the  $\text{Hg}^{2+}$  adsorption experiment the results revealed that up to 67% of the immobilized thiol groups were accessible for  $\text{Hg}^{2+}$  trapping.

In 2000, thiol- and amino- functionalized SBA-15 silica with uniform mesoporosities were prepared and employed for removing heavy metal ions from wastewater by Liu *et al.* SBA-15 functionalized with 3-mercaptopropyl and 3-aminopropyl groups were obtained through the treatment with chloroform solution of 3-mercaptopropyltriethoxysilane and 3-aminopropyltriethoxysilane, respectively. It was found that, upon functionalization, the surface area, total pore volume, and pore size decreased significantly, revealing that the surface modification indeed occurred inside the primary mesoporous of the SBA-15. The thiolated SBA-15 adsorbent exhibited a higher affinity for  $\text{Hg}^{2+}$ , while the other metal ions ( $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$ ) showed higher binding ability with its aminated analogue. In addition, both adsorbents remained effective even after extended regeneration and reuse cycle, the BET surface area and pore volume only slightly decreased, while the pore size essentially remained unchanged.

Lee *et al.* (2001) synthesized bi-functional porous silica via the introduction

of 3-aminopropyltriethoxysilane (APTES) and 3-mercaptopropyltrimethoxysilane (MPTMS) by co-condensation process. Dodecylamine was used as a template, and tetraethoxysilane (TEOS) as a silica precursor. In order to investigate the adsorption capacity of metal ions and the properties of adsorbents, the fraction of amino and mercapto groups were changed. The results demonstrated that as the mercaptopropyl concentration in the adsorbents increased, the adsorption capacities for heavy metal ions also increased because the number of active sites of mercapto groups which are capable of adsorbing mercury ions increased as shown in Fig. 2.7. and the amino ligands increased the surface hydrophobicity of the adsorbents.



**Figure 2.7** The form of combination between mercapto groups and mercury ions in (a) the mercapto-functionalized silica and (b) the mercapto- and amine- functionalized silica (Lee *et al.*, 2001).

Bois *et al.* (2003) prepared the heavy metal ion adsorbents by co-condensation of tetraethoxysilane and functionalized trialkoxysilane  $\text{RSi}(\text{OR}')_3$ . Functionalized porous silicas with aminopropyl ( $\text{H}_2\text{N}(\text{CH}_2)_3-$ ), [amino-ethylamino] propyl ( $\text{H}_2\text{N}(\text{CH}_2)_2\text{-NH}(\text{CH}_2)_3$ ), (2-aminoethylamino)-ethylamino]propyl ( $\text{H}_2\text{N}(\text{CH}_2)_2\text{-NH}(\text{CH}_2)_2\text{-NH}(\text{CH}_2)_3$ ), and mercaptopropyl ( $\text{HS}(\text{CH}_2)_3-$ ) groups were synthesized using dodecylamine as directing agent. These organo-silicas were tested for the removal of heavy metal ions from aqueous solutions by batch adsorption experiment. The results demonstrated that samples synthesized with [aminoethyl amino]propyl- and (2-aminoethylamino)ethylamino]propyl- functions show a high loading capacity for  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and the anion  $\text{Cr}(\text{VI})$ . The sample synthesized with a mercaptopropyl function has a high loading capacity for  $\text{Cd}^{2+}$ .

Recently, Quintanilla *et al.*, 2006 functionalized mesoporous silica (SBA-15 and MCM-41) by two different methods. Using the heterogeneous route the silylating agent, 3-chloropropyltriethoxysilane, was initially immobilized onto the mesoporous silica surface to give the chlorinated mesoporous silica Cl-SBA-15 or Cl-MCM-41. In a second reaction a multi-functionalized N, S donor compound (2-mercaptopyridine, MP) was incorporated to obtain the functionalized silica denoted as MP-SBA-15-Het or MP-MCM-41-Het. Using the homogeneous route, the functionalization was achieved via the one step reaction of the mesoporous silica with an organic ligand containing the chelating functions, to give the modified mesoporous silica denoted as MP-SBA-15-Hom or MP-MCM-41-Hom. When the functionalized mesoporous silicas were employed as adsorbents for the regeneration of aqueous solutions contaminated with Hg(II) the results showed that mercury adsorption was higher in the mesoporous silicas prepared by the homogeneous method. The modified mesoporous silica MP-SBA-15-Hom displayed the best mercury adsorption efficiency.

## 2.5 Applications of Mesoporous Clay in Adsorbent Materials

Because of unique properties of mesoporous materials such as large surface area, combined micro- and mesoporosity, and well-modified surface properties, they offer many application as adsorbents, catalyst, gas-separation devices, gas-storage materials, optical applications, and polymer nanocomposites.

### Adsorption

One of the most adsorption application of mesoporous clay is used as adsorbent. Beside the environmental applications that explained in above section, porous materials can be use in other applications such as adsorption of gaseous molecule.

Newalkar *et al.*, 2003 investigated equilibrium adsorption isotherms for light hydrocarbons such as ethane, ethylene, acetylene, propane, and propylene on hexagonal mesoporous silica (HMS)-type mesoporous silica. The adsorption capacity for C<sub>2</sub> and C<sub>3</sub> olefins are found to be higher than for corresponding alkanes. Further, up-

take of acetylene is observed to be more comparable to ethylene. The isosteric heats of adsorption for ethylene are marginally higher than ethane but those observed for propylene are found to be significantly higher than for propane. The isosteric heats observed for propylene are found to be comparable with those reported for p-complexation based systems. Such a trend has in turn suggested a higher affinity of HMS framework for propylene over propane.

### Catalyst

Mesoporous materials can improve the overall efficiency of the catalytic processes because: 1) it is easier to retain the solid catalyst in the reactor or to separate it from the liquid process stream by filtration; 2) often the catalyst can be regenerated and recycled; and 3) confinement of the catalyst within mesopores provides a means of introducing size and/or shape selectivity and thus greater specificity to a reaction (Stein *et al.*, 2000).

Shirai *et al.* (2003) prepared mesoporous smectite-type clays containing cobalt species in lattice (MST(Co)) by a hydrothermal method and examined for hydrodesulfurization (HDS) which is an important process for producing clean fuel. The results showed that the MST(Co) catalysts showed higher HDS activities than a commercial alumina-supported cobalt-molybdenum catalyst (Co-Mo/Al<sub>2</sub>O<sub>3</sub>). In situ XAFS and nitrogen adsorption techniques showed that surface cobalt species located at the edge of silicate fragments of MST(Co) were the active sites.

### Porous Clay Nanocomposites

Incorporation of layered silicates (i.e., clay minerals) into the polymer microstructures to improve the mechanical, thermal and barrier properties has been an attractive approach developed. Nanocomposites with different morphology, i.e., agglomerated, intercalated and exfoliated structures are accessible based on the processing conditions and interactions between the layered clays and polymer systems. A number of studies revealed the enhanced properties of clay/polymer nanocomposite systems.

Tanoglu *et al.* (2007) prepared PMMA based porous nanocomposites that contain clay (montmorillonite, MMT) platelets as reinforcements within the cell

walls of the porous structure. To render the clay layers organophilic, MMT was surface treated by an ion exchange reaction between interlayer cations of the clay and ammonium ions of a surfactant. Clay/PMMA based porous nanocomposites were prepared by polymerization of water-in-oil emulsions with and without clay addition. The microstructure and compressive mechanical behavior of the nanocomposites were investigated. The results of mechanical tests showed that the porous systems with the addition of 1 wt.% of organoclay (OMMT) exhibited a 90% and 50% increase of collapse stress and elastic modulus values, respectively, as compared to neat porous PMMA.

### Optical Applications

Suitable functionalized hybrid mesoporous silicates are promising candidates for optical applications, including lasers, light filters, sensors, solar cells, pigments, optical data storage, photocatalysis, and frequency doubling devices.

Recently, Tchinda *et al.*, 2007 prepared thiol-functionalized porous clay heterostructures (PCHs) by intragallery assembly of mesoporous organosilica in natural smectite clay. The mesoporous framework was formed by surfactant-directed co-condensation of tetraethoxysilane (TEOS) and 3-mercaptopropyltrimethoxysilane (MPTMS), at various MPTMS/TEOS ratios, in the interlayer region of the clay. After template removal, the resulting PCHs were characterized by large specific surface areas ( $400\text{--}800\text{m}^2/\text{g}$ ) and pore volumes ( $0.3\text{--}0.6\text{mL/g}$ ), with mesopore channels bearing a high number of accessible mercaptopropyl groups ( $0.4\text{--}3.0\text{mmol/g}$ ). These functionalized mesoporous layered materials were deposited as thin films onto the surface of glassy carbon electrodes and applied to the voltammetric detection of Hg(II) subsequent to open-circuit accumulation. They displayed attractive features as the regular mesostructure offered a favorable environment for fast diffusion rates, resulting in great sensitivity, while the layered morphology ensured good mechanical stability. Various parameters have been optimized to get the highest current responses, such as the film composition and thickness, accumulation time, detection conditions, and concentration of the sample. Linear calibration curves were obtained in the Hg(II) concentration ranges from 4 nM to 20 nM and 0.05  $\mu\text{M}$  to 0.8  $\mu\text{M}$ , respectively, for 20 min and 3 min accumulation. The detection limit calculated on the



basis of a signal-to-noise ratio of 3 was  $5 \times 10^{-10}$  M (20 min).

## 2.6 Characterizations of Heavy Metal Adsorbent

The heavy metal adsorbent can be characterized by two ways (1) *batch experiment*, which is the conventional experiment that used to test in small scale to study the suitable condition; and (2) *continuous column method*, which is the experiment that commonly used to study in the practical application and regeneration property of a solid adsorbent. Although batch experiment provide useful information of the adsorption property of the adsorbent, continuous column studies provide the most practical application. For industrial water treatment, operation in the column mode is more preferable. Therefore, experimental and theoretical data obtained from the continuous column method is desired from the industry point of view (Lv *et al.*, 2007). Goel *et al.*, 2005 studied the adsorption behavior of Pb(II) from aqueous systems onto activated carbon (AC) and treated activated carbon (AC-S) via static and column mode studies under various conditions. Both the adsorbents are subjected to static mode adsorption studies and then after a comparison based on isotherm analysis; more efficient adsorbent is screened for column mode adsorption studies. The Pb(II) removal increased for sample of treated carbon. The extent of Pb(II) removal was found to be higher in the treated activated carbon. The aim of carrying out the continuous-flow studies was to assess the effect of various process variables, bed height, hydraulic loading rate and initial feed concentration on breakthrough time and adsorption capacity. This has helped in ascertaining the practical applicability of the adsorbent. Breakthrough curves were plotted for the adsorption of lead on the adsorbent using continuous-flow column operation by varying different operating parameters like hydraulic loading rate ( $3.0\text{--}10.5 \text{ m}^3/(\text{hm}^2)$ ), bed height (0.3–0.5 m) and feed concentrations (2.0–6.0 mg/l). At the end, an attempt has also been made to model the data generated from column studies using the empirical relationship based on Bohart–Adams model. AC–S column regeneration using 0.5 and 1.0 M concentration of  $\text{HNO}_3$  has been investigated. It has shown a regeneration efficiency of 52.0% with 0.5 M  $\text{HNO}_3$ .

Figueiredo *et al.*, 2005 used the three natural waste materials containing chi-

tin, namely the Anodonta (*Anodonta cygnea*) shell, the Sepia (*Sepia officinalis*) and the Squid (*Loligo vulgaris*) pens, as adsorbents for textile dyestuffs. The selected dyestuffs were the Cibacron green T3G-E (CI reactive green 12), and the Solophenyl green BLE 155% (CI direct green 26), both from CIBA, commonly used in cellulosic fiber dyeing, the most used fiber in the textile industry. Batch equilibrium studies showed that the adsorption capacities of materials increase after a simple and inexpensive chemical treatment, which increases their porosity and chitin relative content. Kinetic studies suggested the existence of a high internal resistance in both systems. Fixed bed column experiments performed showed an improvement in behavior of adsorbents after chemical treatment. However, in the column experiments, the biodegradation was the main mechanism of dyestuff removal, allowing the bioregeneration of the materials. The adsorption was strongly reduced by the pore clogging effect of the biomass. The deproteinised Squid pen was the adsorbent with highest adsorption capacity (0.27 and 0.037 g/g, respectively, for the reactive and direct dyestuffs, at 20°C), followed by the demineralised Sepia pen and Anodonta shell, behaving like pure chitin in all experiments, but showing inferior performances than the granular activated carbon tested in the column experiments.

Recently, Vijayaraghavan *et al.*, 2006 reported biosorption of copper(II) ions onto *Sargassum wightii* biomass in batch and continuous mode of operation. Batch experiments were fundamentally aimed to determine the favorable pH for copper(II) biosorption. Langmuir model was used to describe the copper(II) biosorption isotherm and maximum uptake of 115 mg/g was obtained at pH 4.5. Continuous experiments in a packed column were performed to study the influence of bed height, flow rate and inlet solute concentration on copper(II) biosorption. The highest bed height (25 cm), lowest flow rate (5 ml/min) and highest inlet Cu(II) concentration (100 mg/l) resulted in highest copper(II) uptake of 52.6 mg/g, compared to other conditions examined. Column data obtained at different conditions were described using the Thomas, Yoon–Nelson and modified dose–response models. All three models were able to predict breakthrough curves; in particular, the breakthrough curve prediction by the Thomas and Yoon–Nelson models were found to be very satisfactory. Also, the well-established design model, the Bed depth–service time (BDST) model was used to analyze the experimental data. The BDST model plot at 5

ml/min (flow rate) and 100 mg/l (inlet solute concentration) was used to predict bed depth service time data at different conditions. The BDST model predicted values always coincide with experimental values with high correlation coefficients.