



## CHAPTER II

### THEORETICAL BACKGROUNDS

#### 2.1 Heavy metals

The term heavy metal generally has been used to describe those metals having atomic numbers higher than iron (molecular weight > 59) or having density greater than 5 g/ml. From the environmental standpoint, metals may be classified into two groups. The first is essential metals, which are required in trace amount for microorganisms as nutritional components, but are toxic in greater amount. This group consist of As, Cr, Co, Cu, Ni, Se, Va and Zn etc. The second group is highly poisonous and is not known to have any nutritional value. This group consists of Pb, Hg, Cd, Ur, Ag and Be etc (Kojima and Lee, 2001)

Problems with heavy metals differ greatly from most other forms of pollution. This is primarily because metals do not undergo degradation. Moreover, most heavy metals only require relatively low dosages to cause toxicity. Examples of the threshold limits and the effects caused by heavy metal uptake are given in Table 2.1.

Muhammad *et al.*, 2004 have recommended that environmental problems of the textile industry are mainly caused by discharges of wastewater. Textile processing employs a variety of chemicals, depending on the nature of the raw material and product. Industrial processes generate wastewater containing mixture contaminants, for example; heavy metals, enzymes, detergents, dyes, acids, sodas, and salts. Since most of heavy metals are non-degradable into non-toxic end products, their concentrations must be reduced to acceptable levels before discharging them into environment.

The method of separation / preconcentration for heavy metal have determines: these include precipitation / co-precipitation (Atanassova *et al.*, 1998), liquid-liquid extraction (El-Hussaini *et al.*, 2004), and solid phase extraction (SPE) (Soylak *et al.*, 2006). Recently, toxic heavy metal removal has been already established after the serious disaster caused by the heavy metal pollution as for

example; Minamata case in Japan. To date the majority of heavy metals in wastewater are increasing and have many study to removed them such as by means of precipitation by adding calcium hydroxide, in which large amounts of nontoxic metal compounds such as calcium sulfate are also precipitated together with heavy metals as a precipitated sludge. (Kedar *et al.*, 2007)

**Table 2.1** Heavy metals, their threshold limiting values (TLV) and poisoning effect (Friberg *et al.*, 1979).

Heavy metals	TLV (mg/l)	Effect of poisoning
Pb	0.05	Toxicity to fetus, reduces fertility in women, altered spermatogenesis for men, impaired kidney function
Cd	0.005	Bronchitis, pneumonitis, nausea, gastroenteritis, intense pain in bones, cancer, damage to kidneys, lungs and liver
Cu	1.0	Damage to liver, vomiting, nausea
Ni	No TLV	Lung cancer
Cr	0.5	Irritant, vomiting, nausea, carcinogenic
Hg	0.1	Damage to nerve system, liver and kidney
Zn	No TLV	Vomiting, nausea

Moreover, now there had many researches about heavy metals adsorption by use adsorbents, such as active carbon (Strelko *et al.*, 2004), modified resin (Kumar *et al.*, 2001), nanometer-sized materials (Yin *et al.*, 2005), fullerene (Munoz *et al.*, 2002), and silica-coated magnetic nanoparticle (Chaozhang and Bin, 2007).

## 2.2 Dyes

A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an

aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber.

Both dyes and pigments appear to be colored because they absorb some wavelengths of light preferentially. In contrast with a dye, a pigment generally is insoluble, and has no affinity for the substrate. Some dyes can be precipitated with an inert salt to produce a lake pigment, and based on the salt used they could be aluminum lake, calcium lake or barium lake pigments. Dyes can be categorized by origin in 2 types:

- 1.) Natural dyes: are dyes that made from plant and animal
- 2.) Synthetic dyes: are dyes that made from chemical mechanism

Synthetic dyes quickly replaced the natural dyes. They cost less, they offered a vast range of new colors, and they imparted better properties upon the dyed materials. Dyes are classified according to how they are used in the dyeing process in 11 types (Hiranchit, 1996):

- 1.) Acid dyes
- 2.) Direct dyes
- 3.) Basic or Cationic dyes
- 4.) Disperse dyes
- 5.) Reactive dyes
- 6.) Azoic dyes
- 7.) Vat dyes
- 8.) Mordant or Chrome dyes
- 9.) Ingrain dyes
- 10.) Oxidation dyes
- 11.) Sulfur dyes

### 2.2.1 Methylene Blue

Methylene blue (MB) is a heterocyclic aromatic chemical compound with molecular formula:  $C_{16}H_{18}ClN_3S$ . It has many uses in a range of different fields, such as biology and chemistry. At room temperature it appears as a solid, odorless, dark green powder, that yields a blue solution when dissolved in water. The hydrated

form has 3 molecules of water per molecule of MB. Methylene blue should not be confused with methyl blue, another histology stain, new methylene blue, nor with the methyl violets often used as pH indicators.

Methylene blue is widely used as a redox indicator in analytical chemistry. Solutions of this substance are blue when in an oxidizing environment, but will turn colorless if exposed to a reducing agent. In biology methylene blue is used as a dye for a number of different staining procedures, such as Wright's stain and Jenner's stain. Since it is a temporary staining technique, methylene blue can also be used to examine RNA or DNA under the microscope or in a gel: as an example, a solution of methylene blue can be used to stain RNA on hybridization membranes in northern blotting to verify the amount of nucleic acid present.

Methylene blue is used in endoscopic polypectomy as an adjunct to saline or epinephrine, and is used for injection into the submucosa around the polyp to be removed. This allows the submucosal tissue plane to be identified after the polyp is removed, which is useful in determining if more tissue needs to be removed, or if there has been a high risk for perforation. Methylene blue is also used as a dye in chromoendoscopy, and is sprayed onto the mucosa of the gastrointestinal tract in order to identify dysplasia, or pre-cancerous lesions. Intravenously injected methylene blue is readily released into the urine and thus can be used to test the urinary tract for leaks or fistulas.

In surgeries such as sentinel lymph node dissections, methylene blue can be used to visually trace the lymphatic drainage of pertinent tissues. Similarly, methylene blue is added to bone cement in orthopedic operations to provide easy discrimination between native bone and cement. Additionally, methylene blue accelerates the hardening of bone cement, increasing the speed at which bone cement can be effectively applied.

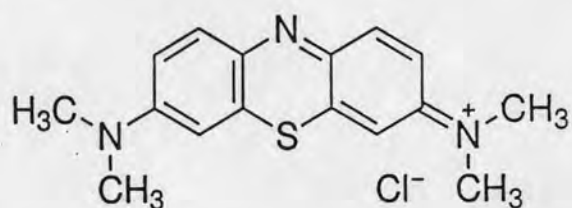


Figure 2.1 Molecular structure of Methylene blue



## 2.3 Surfactants

Surfactant, or surface active agent, has an amphipathic structure consisting of two dissimilar parts in one molecule which is a hydrophilic polar head group and a hydrophobic non-polar tail (Rosen, 1989; and Rouse, 2001). The hydrophilic head group is attracted to polar environments, such as water, while the hydrophobic tail comprised a long chain hydrocarbon is attracted to nonpolar environments, for example oil. Consequently, the surfactants can dissolve either in water or oil and have the capability to solubilize water or oil to create homogeneous system (Uppgård, 2002). Based on the charge of surfactant head group, surfactants are classified into four categories; anionic, cationic, nonionic, and zwitterionic (Hill, 1999).

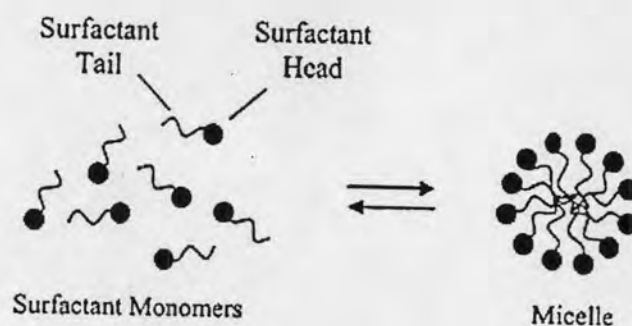
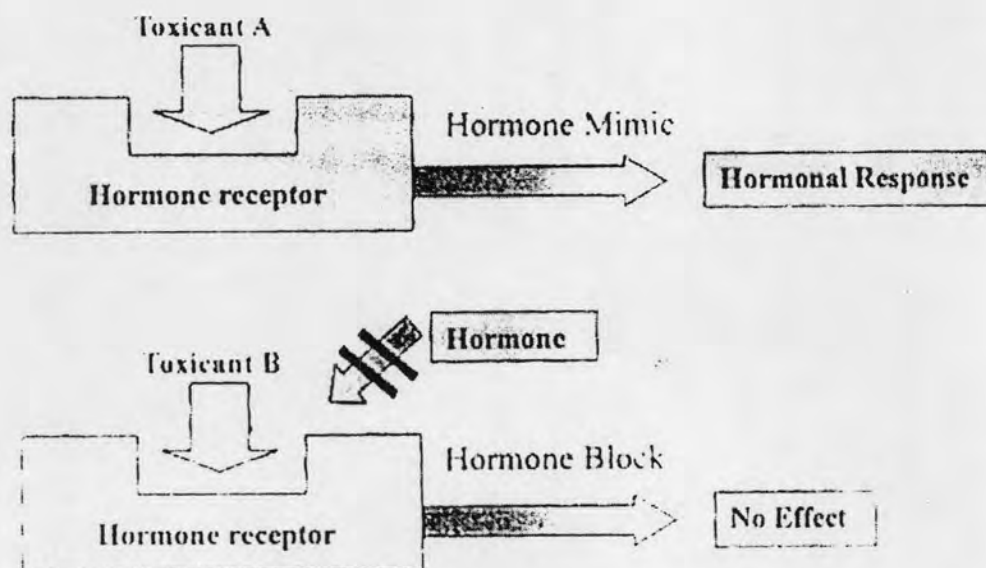


Figure 2.2 Schematic illustration of the reversible monomer-micelle thermodynamic. (Rangel-Yagui *et al.*, 2004)

### 2.3.1 Alkylphenol polyethoxylate (APnEOs)

APnEOs constitute the most prevalent surface active agents. They are found in important industrial applications including detergent production, textile industries, commercial laundries and tanning industries. Biological transformation of APnEOs has been shown to occur in natural ecosystems and in aerobic and anaerobic wastewater treatment plants (Figure 2.3). Their primary degradation proceeds exclusively on their hydrophilic parts via oxidative shortening of the polythoxylate chain while complete mineralization of APnEOs appears to be very poor because of the presence of highly branched alkyl substitutes on the aromatic ring. The result of





**Figure 2.4** Functional or receptor-based toxicology. Exogenous chemicals may act at hormone receptor site by mimicking and endogenous hormone to create a response or by blocking an endogenous hormone from producing an effect. (McLanchlan *et al.*, 1993)

### 2.3.3 Uses and exposure

APnEOs make up the world's third largest group of surfactants in terms of production and have been used widely in various applications for nearly 50 years. Every year about 500,000 metric tones of APnEOs are produced worldwide (Rener *et al.*, 1997). Nonylphenol polyethoxylates are the most important APnEOs, accounting for about 80% of the total APnEOs volume. The concentration of APnEOs in industrial wastewater in Canada was reported in range from 2 to 117.57 mg/l (Lee *et al.*, 2002). Now in Western Europe and U.S. the APnEOs was replaced by alcohol ethoxylates (AE) in household application, but APnEOs are still being used in substantial amounts in institutional and industrial applications.

## 2.4 Mesoporous Silicate

### 2.4.1 Synthesis and Formation Mechanism of Mesoporous Silicate

A mesoporous material is a material containing pores with diameters between 2 and 50 nm. The synthesis of mesoporous silicate uses cooperation between

organic surfactants as a liquid crystal templating mechanism (LCT) and silicate species in the aqueous phase (silicate-organic complex) (Thieme and Schüth, 1999). These materials were first described as “ordered mesoporous molecular sieve” and collectively designated M41S by a research group of the former Mobil Oil Company (Kresge *et al.*, 1992). The M41S family of mesoporous materials was synthesized using silica source and different organic structure directing agents, e.g., cationic surfactants containing long alkyl chain quaternary ammonium compounds containing 10-20 carbons, often followed with addition of co-surfactants. There are three main liquid crystalline phases with hexagonal, cubic, and lamellar structures.

The synthesis mechanisms of mesoporous silicates have two pathways. In the first way, the alkyltrimethylammonium surfactant of type  $C_nH_{2n+1}(CH_3)_3N^+$  species organize into lyotropic liquid crystal phase, which can serve as template for the formation of hexagonal MCM-41 (Mobil Catalytic Material, number 41) structure. Firstly, the surfactant micelle aggregate into a hexagonal array of rods, followed by interaction of silicate or aluminate anions present in the reaction mixture with the surfactant cationic head groups. Thereafter condensation of the silicate species occurs, leading to the formation of an inorganic polymeric species. After combusting of the surfactant template by calcination, hexagonally arranged inorganic hollow cylinders are produced. In the second way, the silicate species added to the reaction mixture influence the ordering of the isotropic rod-like micelles to the desired liquid crystal phase.

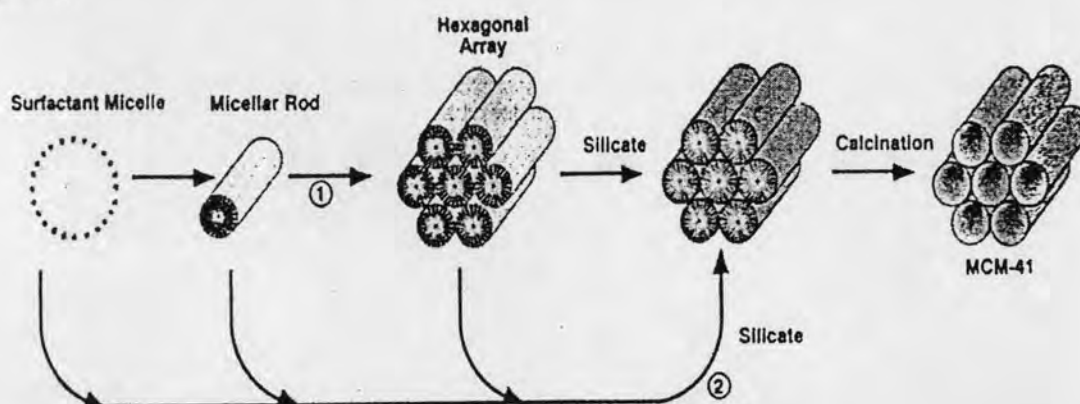


Figure 2.5 Possible mechanism pathways for the formation of MCM-41 (Beck *et al.*, 1992).

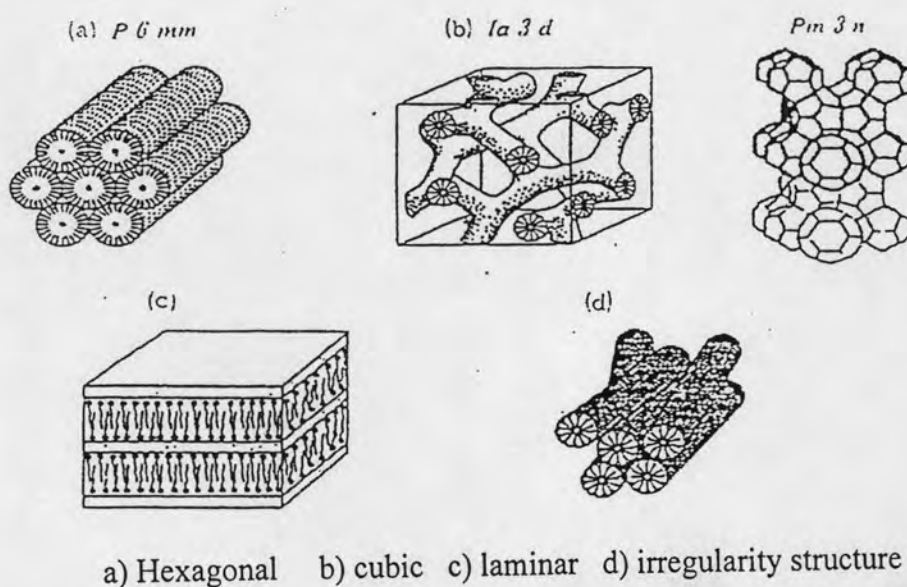


### 2.4.2 Category and structure of Mesoporous Silicate

Structure of mesoporous silicate was categorized by crystalline structure, shape and size of pores, composition of structure and formation. Table 2.2 shows the category of mesoporous silicate. Crystalline structure was classified as hexagonal, cubic, laminar, etc., depending on the kind of chemical and synthesis condition.

**Table 2.2** Categories of uniformity mesoporous materials (Punyapalukul and Takizawa, 2004)

Crystalline Structures	- Hexagonal - Cubic - Laminar - Irregularity Structure
Pore size	1.5-10 nm, 3-7 nm, 5-30 nm, 0.4-1.5 nm
Composition of structures	$\text{SiO}_2$ , $\text{SiO}_2\text{-MO}_{n/2}$ (M = Al, Ti, V, B, Mn, Fe, Ga, Zr) $\text{Al}_2\text{O}_3$ , $\text{TiO}_2$ , $\text{ZrO}_2$ , $\text{Ta}_2\text{O}_5$ , $\text{Nb}_2\text{O}_5$ , $\text{SnO}_2$ , $\text{HfO}_2$ , $\text{AlPO}_4$
Formation	Powder, Particle, Sphere, etc.



**Figure 2.6** Crystalline structure of mesoporous materials (Punyapalukul and Takizawa, 2004)

### 2.4.3 Synthesis Methods of Hexagonal Mesoporous Silicate (HMS)

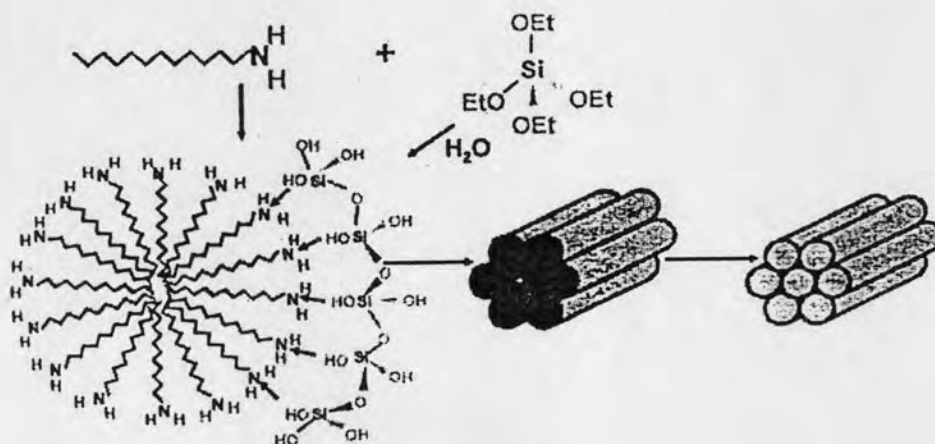
Tanev and Pinnavaia (1996) proposed Hexagonal Mesoporous Silicate (HMS) produced by the neutral synthesis pathway ( $S^{\circ}I^{\circ}$ ), which was carried out in the presence of neutral inorganic precursors and uncharged surfactants such as primary amines. In this case, hydrogen bonding rather than electrostatic interaction is a driving force for the cooperative organization of the organic-inorganic mesophase. This neutral  $S^{\circ}I^{\circ}$  templating route produces mesostructures with larger wall thickness, small scattering domain sizes, and complementary textural mesoporosities relative to materials produced by other pathway (Tanev and Pinnavaia, 1996; Kruk *et al.*, 1997).

Tanev and Pinnavaia (1996) proposed hexagonal mesoporous silicas (HMS) having thicker pore walls, high thermal stability and smaller crystallite size but having higher amounts of interparticle mesoporosity and lower degree of long-range ordering of pores than MCM-41 materials. The formation of neutral primary amine surfactant molecule ( $S^{\circ}$ ) and neutral  $\text{Si}(\text{OC}_2\text{H}_5)_{4-x}(\text{OH})_x$  precursor ( $I^{\circ}$ ) into rodlike assemblies as shown in Figure 2.7. Hydrogen bonding interactions between the precursor silanol hydrogens and the lone electron pairs on the surfactant head groups changes the head-to-chain volume ratio (i.e., the preferred packing) of the surfactant-inorganic complexes and most likely facilitates the assembly of rodlike micelles. Further hydrolysis and condensation of the silanol groups on the micelle-solution interface afford short-range hexagonal packing of the micelles and framework wall formation.

HMS was prepared by  $S^{\circ}I^{\circ}$  assembly pathways in water : ethanol solvent mixtures. In reaction media, tetraethyl orthosilicate (TEOS) intensively served as the neutral silica precursor and dodecylamine (DDA) is the neutral liquid crystal template (LCT). Although many primary amines were studied as the neutral structure, dodecylamine was recommended as the best LCT (Tanev and Pinnavaia, 1996).

HMS material can be prepared by various methods. However, after comparison with of obtained materials by basic characterization methods, synthesis procedure, presented by Tanev and Pinnavaia, 1996, was chosen because of simplicity high stability, and applicability into laboratory facilities by following this ratio: 1 mol TEOS: 0.27 mol DDA: 9.09 mol Ethanol: 29.6 mol water: Pore sizes and surface

areas of HMS were reported as 2.4-4.2 nm and 750-1120m<sup>2</sup>/g, respectively (Tanev and Pinnavaia, 1996; Mercier *et al.*, 1997; Gontier *et al.*, 1995; Zhang *et al.*, 1997).



**Figure 2.7** Schematic representation of the S<sup>\*</sup>I<sup>\*</sup> templating mechanism of formation of HMS mesoporous molecular sieves. (Tanev and Pinnavaia, 1996)

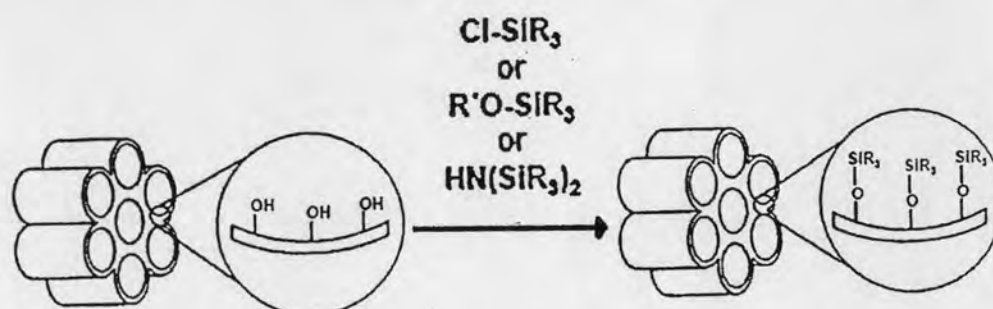
#### 2.4.4 Organic Functionalization

The application of pure mesoporous silicates or aluminosilicates as adsorbent is rather limited because of the limitations in the nature of their active sites. To utilize these mesoporous materials for several specific applications including catalysis, sorption, ion exchange, and sensing, it is essential to introduce reactive organic functional groups by modifying the inner surfaces of these materials to form inorganic-organic hybrid. Organically functionalized silicas are a subset of a larger class of hybrid organic-inorganic materials. The covalently bonded organic ligand is usually non-hydrolysable and imparts partial organic character to an inorganic siloxane network. Organic functionalization can be categorized into two general methods:

##### 2.4.4.1 Grafting Method

Grafting refers to post synthesis modification of the inner surface of mesoporous silica, where the organic functional groups are introduced as the terminal groups of an organic monolayer. A large number of surface silanol [(-SiO)<sub>3</sub>Si-OH] groups present in mesoporous silica can be utilized as convenient moieties for

anchoring of organic functional groups. The surface modification with organic functional groups is generally carried out by silylation as shown in Figure 2.8.



**Figure 2.8** Functionalization of inner walls of mesoporous silicates by grafting method. (Stein *et al.*, 2000)

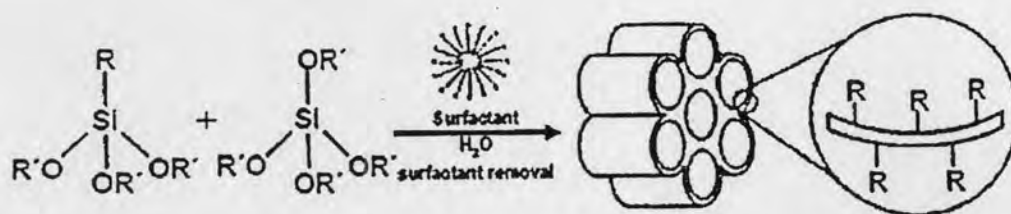
#### 2.4.4.2 Direct Co-condensation Method

In the grafting methods, organic groups are incorporated by attachment of the organosiloxane precursor with surface Si atoms through Si-O-Si-C covalent bond formation. Then Si-O bond can be cleaved under certain reaction conditions. Therefore, in some cases it would be desirable to have direct formation of a C-Si (surface) covalent bond. Thus, the “one-pot” co-condensation method, where condensation occurs between a tetraalkoxysilane and one or more trialkoxyorganosilanes through sol-gel chemistry (Figure 2.9), seems to have distinct advantages over the grafting methods. A direct co-condensation method is the one-step synthesis of organically functionalized mesoporous silica which has two different approaches of synthesis (Mercier and Pinnavaia, 2000) including:

- (1) Template exchange including the replacement of TEOS as well as alkylamine surfactant with organosilane
- (2) Addition of organosilane by replacing of TEOS with organosilane, maintaining the same alkylamine to TEOS ratio as used to synthesize the non-functionalized HMS materials.

Several research groups have employed this method to prepare inorganic-organic hybrid mesoporous materials under a wide range of synthesis condition. Usually the solvent extraction technique is used to remove the surfactant from the resultant materials.





**Figure 2.9** Synthesis of organo-functionalized mesoporous silicates by grafting co-condensation method. (Stein *et al.*, 2000)

#### 2.4.5 Properties and Application of mesoporous

Due to the unique physical properties and higher pore sizes than zeolites, mesoporous materials have been highly desirable for catalytic and adsorption applications. Many researchers have studied their properties and tried to develop surface functional groups for more applications. Functionalization of mesoporous materials has played an important role in various aspects such as immobilization of enzymes (Maria Chong and Zhao, 2004, Yiu and Wright, 2005, and Hudson *et al.*, 2005), development of new catalyst (Aprile *et al.*, 2005), and selective adsorbent (Lee *et al.*, 2001, Newalkar *et al.*, 2003, and Messina *et al.*, 2006). Many functional groups have been studied depending on purpose. Messina and Schulz (2006) modified silica mesoporous materials by TiO<sub>2</sub> augmented the adsorption capacities of reactive dyes. They suggested that this would be due to possible degradation of the dye molecule in contact with the TiO<sub>2</sub> particles in the adsorbent interior. Moreover, mesoporous silicates could be grafted on the surface by many organic functional groups to enhance its valuable. Amino-functional group having more hydrophilic than activated carbon has been studied for oxynation (Yoshitake *et al.*, 2005) and hydrophilic substances adsorption. Moreover, bi-functional mesoporous silica was applied to enhance its settlements. Lee *et al.* (2001) synthesized bi-functional porous silica (amino- and mercapto- functional groups) for heavy metal ion adsorbent. It could prevent the loss of co-condensed functional groups although hydrothermal stability and heavy metal adsorption capacities decreased introduced by hydrophilicity of amino-functional group. Punyapalukul and Takizawa (2004) developed Hexagonal Mesoporous Silica (HMS) by grafted organic functional group on surface of HMS.

The result showed amino-functional group grafted on HMS (A-HMS) had the same adsorption capacity as powder activated carbon (PAC) at high concentration. In addition, combination of amino- and mercapto- functional group which had lower surface charge than amino-functional group had higher adsorption capacity than A-HMS at higher concentration.

**Table 2.3** Physico-chemical characteristics of HMS, modified HMSs and PAC (Punyapalukul and Takizawa, 2006)

Adsorbents	Surface functional groups	Surface characteristic
HMS	Silanol	Hydrophilic
Ti-HMS	Silanol	Hydrophilic
MP-HMS	Mercapto	Hydrophobic
OD-HMS	Octyl	Hydrophobic
AM-HMS	Amino	Hydrophilic
PAC	Carboxylic, Phenyl, others	Hydrophobic

Yoshitake *et al.* (2005) studied the adsorption of oxyanion and hydrophilic substances by using amino-functional group that having more hydrophilic than activated carbon. The results found that the adsorption capacities for ferric ions on the polyamine-PrM41, amount of ferric ion adsorbed increased monotonously with the number of amino groups in the polyamine chain.

Messina and Schulz (2006) modified silica mesoporous materials by TiO<sub>2</sub> for adsorption of reactive dyes. The presence of TiO<sub>2</sub> augmented the adsorption capacities of reactive dyes. They suggested that this would be due to possible degradation of the dye molecule in contact with the TiO<sub>2</sub> particles in the adsorbent interior.

Li *et al.* (2008) grafted mesoporous silicates material by amino groups, [1-(2-amino-ethyl)-3-aminopropyl]trimethoxysilane (AAPTS) for adsorption of Cr(VI) from aqueous solution. The adsorption experiment results showed that the functionalized mesoporous silica materials show good crystallographic order and large uniform pore size. The maximum Cr(VI) loadings at 25, 35 and 45 °C were

found to reach 2.28, 2.86 and 3.32 mmol/g, respectively. The functionalized mesoporous silica materials are promising adsorption materials for reducing toxic chromate pollution. Furthermore, amimo-functional group having more hydrophilic than activated carbon has been studied for oxylanon (Yoshitake *et al.*, 2005) and hydrophilic substances adsorption.

Punyapalakul and Takizawa (2004) studied adsorption mechanism of alkylphenol polyethoxylate compound on HMS and modified HMSs (Ti-HMS, OD-HMS, and MP-HMS) and also comparison with PAC. The results showed that hydrophilic adsorbents (HMS and Ti-HMS) have higher adsorption capacities of APnEOs than hydrophobic adsorbents (PAC, OD-HMS and MP-HMS). Moreover, hydrophilic surface caused by silanol groups enhance aggregation adsorption on the external surface; on the contrary, hydrophobic surface cause semi-aggregation, which increased adsorption capacities on external surfaces of all adsorbents.

Moreover, Andrzejewska and his staffs (2006) studied about separate an anionic reactive dye from aqueous solution, and would display an intense white colour and a high adsorptive capacity. They used Syloid® 244 silica to remove C.I. Reactive Blue 19. The adsorption resulted in blue pigmentation of the silica carrier; the ensuing pigment was subjected to a comprehensive physicochemical analysis, including particle size, particle size distribution, polydispersity, tendency to form primary and secondary agglomerates and the morphology of the particle surface. It was found that a preliminary surface modification of the silica adsorbent with an NH<sub>2</sub>-silane compound was necessary. The aminosilane-modified silica could be used as a selective adsorbent in the purification of waste dye solutions; its application secured highly efficient removal of dye from solutions (in most cases over 90% and in some cases even 100%). The silica-carrier product was then used as a pigment within an exterior acrylic paint. Optimum properties were obtained using 5% silane; the ensuing pigment displayed very low polydispersity (0.030), low mean particle diameter (428 nm) and no tendency to form secondary agglomerates.

Punyapalakul and Takizawa (2006) studied selective adsorption of alkylphenol polyethoxylates (APnEOs) from synthetic textile wastewater was investigated using hexagonal mesoporous silicates (HMSs) by grafted with organic surface functional groups, i.e., n-octyldimethyl-, 3-aminopropyltriethoxy-, 3-



mercaptopropyl-groups and Ti-HMS. Triton X-100 was used as a model APnEO and either Basic Yellow 1 or Acid Blue 45 was used as cationic or anionic dyes. The results showed that all the HMSs except 3-aminopropyltriethoxy-grafted HMS had higher adsorption capacities of Triton X-100 than powdered activated carbon. FT-IR spectra proved that hydrophilic HMSs adsorbed both Basic Yellow 1 and Acid Blue 45 by hydrogen bonding. Due to negative surface charge, the anionic dye (Acid Blue 45) was not adsorbed on the four HMSs, which proves high selectivities of these HMSs for Triton X-100® over Acid Blue 45. On the contrary, a small amount of cationic dye (Basic Yellow 1) was adsorbed on all HMSs, but 3-aminopropyltriethoxy-grafted HMS showed the lowest adsorption capacity for Basic Yellow 1 due to positive surface charge.

## 2.5 Activated Carbon (AC)

Activated carbon is made of tiny clusters of carbon atoms stacked upon one another. The carbon source is a variety of materials, such as peanut shells or coal. The raw carbon source is slowly heated in the absence of air to produce a high carbon material. The carbon is activated by passing oxidizing gases through the material at extremely high temperatures. The activation process produces the pores that result in such high adsorptive properties. Most activated carbons are highly microporous. Activated carbon is used in gas purification, gold purification, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and filter masks, filters in compressed air and many other applications.

One major industrial application involves use of activated carbon in metal finishing field. It is very widely employed for purification of electroplating solutions. For example, it is a main purification technique for removing organic impurities from bright nickel plating solutions. A variety of organic chemicals are added to plating solutions for improving their deposit qualities and for enhancing properties like brightness, smoothness, ductility, etc. Due to passage of direct current and electrolytic reactions of anodic oxidation and cathodic reduction, organic additives generate unwanted break down products in solution. Their excessive build up can adversely affect the plating quality and physical properties of deposited metal.



Activated carbon treatment removes such impurities and restores plating performance to the desired level.

Activated carbon is effective for some contaminants and not effective for others. It does not remove microbes, sodium, nitrates, fluoride, and hardness (Soonglerdsongpha, 2007).

## 2.6 Adsorption Theory

### 2.6.1 Mechanism of Adsorption onto Porous Adsorbent

Adsorption is the interphase accumulation or concentration of substances at a surface or interface. Such a process can occur at an interface of any two phases, such as liquid-liquid, gas-liquid, gas-solid, or liquid-solid interfaces. While there is a preponderance of solute (sorbate) molecules in the solution, there are none in the sorbent particle to start with. This imbalance between the two environments amounts to a driving force for the solute species. First to create a sorbate layer on the surface and then the sorbate may gradually penetrate deeper into the solid. A surface phenomenon in term of adsorption can be distinguished into 2 parts including physical adsorption, is non-specific and the forces attracting the molecules to the solid are relatively weak for example covalent, electrostatic, and van der Waals force and chemisorption is specific and involves forces much stronger than in physical adsorption such as chelation of metals.

Many factors influence the adsorptive capacity for specific organic solutes of a homologous series. First, there are the adsorbate properties of group functionality, branching or geometry, polarity, hydrophobicity, dipole moment, molecular weight and size, and aqueous solubility. Second, there are solution conditions such as pH, temperature, adsorbate concentration, ionic strength, and competitive solutes. Third, there is the nature of the adsorbent with its surface area, pore size and distributions of functional groups.

#### 2.6.1.1 Properties of Sorbent Materials

The importance of the surface properties (including sorptive properties) of a given weight of material exposed to solution, increase in proportion to

the surface area of that material, and to its surface charge (or site) density or number of charged sites per unit area or weight. Surface charge may be permanent and independent of solution composition, or variable, changing with solution composition.

The surface charge of oxides, hydroxide, phosphate, and carbonates is produced chiefly by ionization of surface groups, or surface chemical reactions. For example, the pH-dependent surface charge of silicate might reflect the presence of surface species written symbolically as  $\text{SiOH}_2^+$ ,  $\text{SiOH}$ , and  $\text{SiO}^-$ . The surface species are positively charged at low pH and deprotonate as pH increase to form neutral and negatively charged species at intermediate and higher pH consistent with the amphoteric behavior of the oxide or hydroxide.

#### 2.6.1.2 Properties of Sorbates

The properties and structure of the sorbates most likely to be found in electrostatic attraction are stressed, especially dissociation constant for acid compounds. Acid dissociation constants are commonly reported as  $\text{pK}_a$  values. Acidity constants of organic compounds depend on the type of functional acid groups. For example, carboxylic acids are significant components of most contaminants originating from organic-rich wastes. The high apparent of carboxylate ions occur at higher pH of solution than  $\text{pK}_a$ , and they will be protonated to form carboxylic acids at lower pH.

Hydrogen bonding is one of the strongest types of dipole-dipole interaction. It is the importance force in water treatment at low level concentration of adsorbate (or high concentration of water) because any polar surface will undergo hydrogen bonding with water rather than attract a polar molecule that is dissolved in water. Therefore, removal of polar organics and adsorbates with ionic functional groups at low level concentration will be affected by water, while it is not result in adsorption at high level concentration of adsorbate. (Crittenden *et al.*, 2005; Soonglerdsongpha, 2007)

#### 2.6.1.3 Temperature Effect

Temperature is a crucial parameter in adsorption reactions. It was noted that the temperature can influence the sorption process. The sorptive removal of

copper ions from aqueous solution by tree fern increased with increase in temperature, which is typical for the biosorption of most metal ions from their solution (Ho, 2003). However, the magnitude of such increase continues to decline as temperatures are raised from 30 to 80°C. The decrease in adsorption with increasing temperature, suggest weak adsorption interaction between biomass surface and the metal ion, which supports physisorption. For physical adsorption, adsorption heat  $\Delta H^\circ < 0$ , adsorption reaction is exothermic and preferred at lower temperatures. For chemisorption,  $\Delta H^\circ > 0$ , adsorption reaction is endothermic and favored at higher temperatures, However, the effect of temperature is small as compared to other influencing factors.

#### 2.6.1.4 Influence of pH

Solution pH not only influences the properties of the sorbent surface, but also affects the sorbate speciation in solution. Therefore, it is an important parameter affecting sorption behaviors in many cases of the ionic adsorption, in which the adsorbent surface is charged through the protonation of functional groups and the electrostatic attraction between adsorbents and adsorbates usually plays a predominant role (Janos *et al.*, 2003). The logarithm of the conjugation acid dissociation constants ( $pK_a$ ) could be one of the key parameters in the determination of the optimum pH for charging the sites.

#### 2.6.1.5 Ionic Strength Effect

The influence of ionic strength is significantly affected ion adsorption by the electrostatic attraction. The effects of ionic strength relate to pH and surface properties. Effect of ionic strength and ionic species on TX-100 on adsorption capacity of PAC was studied by Punyapalakul and Takizawa, 2004. They plotted against adsorption capacity and ionic strength. Their results showed that ionic strength didn't affect adsorption capacities on PAC until ionic strength up to 100 mM. Moreover, applied ionic species,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{Ca}^{2+}$ , and  $\text{PO}_4^{4-}$  species didn't affected the adsorption capacities significantly.

### 2.6.1.6 Presence of Other Anions

Other sorbable ions in the solution may compete with the contaminants of interest for sorption sites. The binding of the primary is then decreased. For anion sorption, the study of anion exchange established that the selectivity of anion exchanger could be enhanced by the counter ion of higher valence, with the smaller (solvated) equivalent volume and greater polarizability, and interacting more strongly with the fixed ionic groups on the matrix and participating least in complex formation with the co-ion. The established affinity is as follows:  $\text{SO}_4^{2-} > \text{I}^- > \text{NO}_3^- > \text{CrO}_4^{2-} > \text{Br}^- > \text{SCN}^- > \text{Cl}^- > \text{F}^-$ . Therefore, it would be appropriate to use electrolytic  $\text{Cl}^-$  salts as background for ionic strength control.

Electrolyte effect on surfactant adsorption was studied by Punyapalkul and Takizawa, 2004. The adsorption capacity of adsorbent in lower pH was higher than higher pH.

### 2.6.2 Adsorption Kinetic (Eren Z., and Acar F.N., 2007)

Several models can be used to express the mechanism of solute sorption onto a sorbent. In order to investigate the mechanism of sorption, characteristic constants of sorption were determined using a pseudo-first order equation of Lagergren based on solid capacity, and a pseudo-second order equation based on solid phase sorption respectively.

#### 2.6.2.1 The pseudo-first-order-model

A simple kinetic model for sorption analysis is the pseudo-first-order rate expression of Lagergren in the form:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (1)$$

Integrating equation 1 for the boundary conditions  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$ , gives

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$



Where  $k_1$  = Lagergren rate constant (1/h)  
 $q_e$  = Amounts of solute sorbed at equilibrium (mg/g)  
 $q_t$  = Amounts of solute sorbed on the surface of the sorbent  
 at time  $t$  (mg/g).

### 2.6.2.2 The pseudo-second-order-model

The pseudo-second-order rate expression is used to describe chemisorption involving valency forces through the sharing or exchange of electrons between adsorbent and adsorbate as covalent forces. The rate of pseudo-second-order reaction may be dependent on the amount of solute sorbed on the surface of adsorbent and the amount sorbed at equilibrium. The kinetic rate equations can be written as equation 3:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)^2 \quad (3)$$

Where  $k_2$  is Pseudo-second-order rate constant ( $\text{g mg}^{-1} \text{ h}^{-1}$ ). Separating the variables in the equation 3 gives integrating this for the boundary conditions  $t = 0$  to  $t$  and  $q_t = 0$  to  $q_t$ , gives

$$\frac{t}{q_t} = \frac{1}{2k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

The advantage of using this model is that there is no need to know the equilibrium capacity from the experiments. In addition, the initial adsorption rate can also be obtained from this model as equation 5

$$h = k_2 q_e^2 \quad (5)$$

Where  $h$  is the initial sorption rate ( $\text{mg}/(\text{g min})$ ).

### 2.6.3 Adsorption Isotherm

Sorption isotherms are plot between the equilibrium adsorption capacity ( $q$ ) and the final equilibrium concentration of the residual sorbate remaining in the solution ( $C_e$ ). The equilibrium adsorption capacity,  $q$  (mg/g), can be calculated with the equation 6.

$$q = \frac{(C_0 - C_e)V}{m} \quad (6)$$

Where  $C_0$  is the initial concentration (mg/l),  $C_e$  is the residual concentration at equilibrium (mg/l),  $V$  is the solution volume (l), and  $m$  is the adsorbent mass (g). The adsorption isotherm relationship can also be mathematically expressed. Langmuir and Freundlich isotherm are the most commonly used for describing relationship.

#### 2.6.3.1 Langmuir Isotherm

The Langmuir relationship is of a hyperbolic form as shown in equation 7:

$$\text{Langmuir isotherm: } q = \frac{q_m b C_e}{1 + b C_e} \quad (7)$$

The Langmuir relationship can be linearized by plotting either  $(1/q)$  vs  $(1/C_e)$  or  $(C_e/q)$  vs  $C_e$ . Where  $q_m$  is the maximum adsorption capacity,  $b$  is a Langmuir coefficient related to the affinity between the sorbent and sorbate.

The Langmuir isotherm considers sorption as a chemical phenomenon. It was first theoretically examined in the adsorption of gases on solid surfaces. Langmuir constant  $b = 1/K$  which is related to the energy of adsorption through the Arrhenius equation. The higher  $b$  and the smaller  $K$ , the higher is the affinity of the sorbent for the sorbate.  $q_m$  can also to interpreted as the total number of binding sites that are available for sorption, and  $q$  as the number of binding sites that are in fact occupied by the sorbate at the concentration  $C_e$ .

Although the Langmuir model sheds no light on the mechanistic aspects of sorption, it provides information on uptake capabilities and is capable of

reflecting the usual equilibrium sorption process behavior. Langmuir assumed that the forces that are exerted by chemically unsaturated surface atoms (total number of binding sites) do not extend further than the diameter of one sorbed molecule and therefore sorption is restricted to a monolayer.

In the simplest case the following assumptions were made:

- a) Fixed number of adsorption sites; at equilibrium, at any temperature and gas pressure a fraction of the surface sites  $\theta$  is occupied by adsorbed molecules, and the fraction  $1 - \theta$  is free.
- b) All sorption sites are uniform (i.e. constant heat of adsorption)
- c) Only one sorbate
- d) One sorbate molecule reacts with one active site.
- e) No interaction between sorbed species.

Assumption of a value for the surface area covered per molecule then could allow computation of the active specific surface area of the sorbent using Avogadro's number. As long as its restrictions and limitations are clearly recognized, the Langmuir equation can be used for describing equilibrium conditions for sorption behavior in different sorbate-sorbent systems, or for varied conditions within any given system.

### 2.6.3.2 Freundlich Isotherm

The Freundlich Adsorption Isotherm is an adsorption isotherm, which is a curve relating the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid with which it is in contact.

The Freundlich Adsorption Isotherm is mathematically expressed as shown in equation 8:

$$\text{Freundlich Isotherm: } q = kC_e^{(1/n)} \quad (8)$$

Where:  $k$  and  $n$  are Freundlich constants

The Freundlich relationship is an empirical equation. It does not indicate a finite uptake capacity of the sorbent and can thus only be reasonably applied in the low to intermediate concentration ranges. A simple sorption isotherm indicates that the highest fraction of the sorbate species sorbed is observed at the lowest sorbate concentration, corresponding to the steepest part of the isotherm plot. Such behavior is typical of all dissolved species. Stated differently, the lower concentration of a dissolved substance in water, the greater fraction of it will be sorbed on solids. This behavior is typical of trace organic and inorganic substances at  $\mu\text{g/l}$  concentrations or lower. However, it is easier to handle mathematically in more complex calculations (e.g. in modeling the dynamic column behavior) where it may appear quite frequently. Freundlich model can be easily linearized by plotting it in a (log-log) format.

#### 2.6.4 Comparison of sorption Performance

Performance of sorbing materials often needs to be compared. The simplest case is when there is only one sorbate species in the system. The comparison of single-sorbate sorption performance is best based on a complete single-sorbate sorption isotherm curve. In order for the comparison of two or more sorbents to be "fair" it must always be done under the same conditions. These may be restricted by the environmental factors under which sorption may have to take place (pH, temperature, ionic strength, etc.).

By performance of the sorbent is usually meant its uptake ( $q$ ). The sorbents can be compared by their respective  $q_m$  values which are calculated from fitting the Langmuir isotherm model to the actual experimental data. A "good" sorbent that one always looks for would feature a high sorption uptake capacity  $q_m$ . However, also desirable is a high affinity between the sorbent and sorbate reflected in good uptake values at low concentrations ( $C_e$ ). This is characterized by a steep rise of the isotherm curve close to its origin. Performance in this region is reflected in the Langmuir coefficient  $b$ .