

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Clay mineral

2.1.1 What is clay mineral [11-12]

The clay mineral is predominant in the colloidal fractions of soils, sediments, rocks and water, and generated by the reactions inherited from sedimentary rocks or formed directly in the soil by weathering. They are defined as hydrous aluminosilicates or phyllosilicates (silicate clays) and mostly have small particle sizes ($< 2 \mu\text{m}$) [13]. The crystalline structure of clay minerals is the layer-lattice type, which is called the layered silicate clay, similar to the mica. They may contain the variable amounts of alkali metals (Na^+ or K^+), alkali earths (Mg^{2+} or Ca^{2+}) and other cations inside the interlayer of clay minerals. Moreover, the natural properties are high specific surface area, negatively charge surface and the sorption ability for cations [14].

2.1.2 Structure of layered silicate clay

2.1.2.1 Modular unit of layered silicate clay [12-13]

The two modular units, a sheet of corner-linked tetrahedra and a sheet of edge-linked octahedra, are basic structures of silicate clay and can form the layered silicate clay by packing octahedral and tetrahedral sheets via sharing of an apical oxygen.

Tetrahedral sheet

The structure of tetrahedral sheet (Figure 2.1b) is composed of a tetrahedral unit of Si (Figure 2.1a), which is four O^{2-} atoms coordinating around one central Si^{4+} atom. The SiO_4 tetrahedral units link infinitely in two dimensions through the oxygens of all three corners with three others to generate a sheet of the hexagonal network.

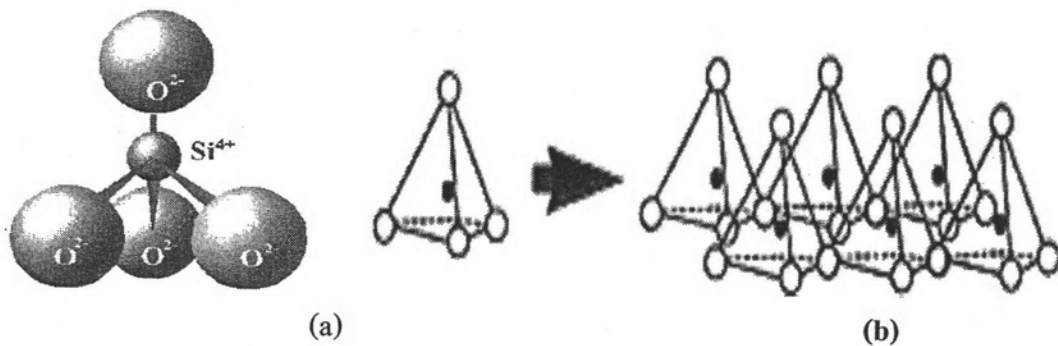


Figure 2.1 Structure of a silica tetrahedral unit (a) and a tetrahedral sheet (b) [15].

Octahedral sheet

A unit of octahedral (Figure 2.2a) consists of six oxygen ions coordinating around a central cations which usually are Al^{3+} , Mg^{2+} or Fe^{2+} . Each octahedral unit infinitely arranges in two dimensions by connecting to neighbored oxygen ions to form a sheet of edge-linked octahedral, called an octahedral sheet as in Figure 2.2b.

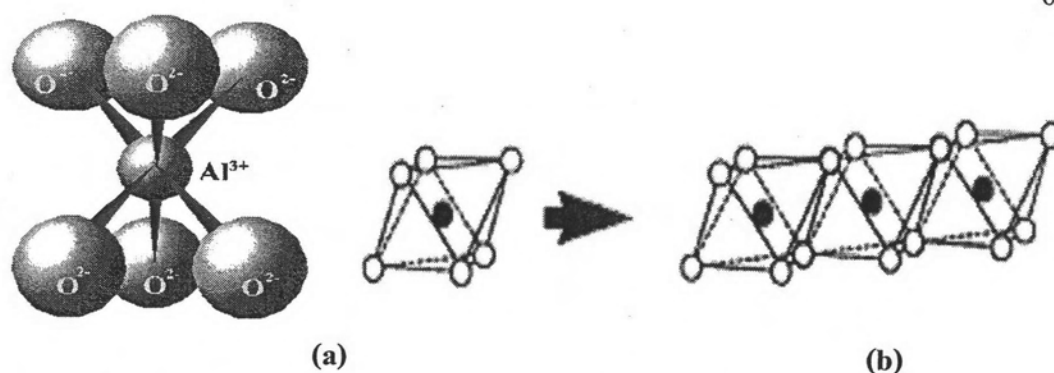


Figure 2.2 Structure of an octahedral unit (a) and an octahedral sheet (b) [15].

2.1.2.2 Types of layered silicate clay [12]

The modular units, the tetrahedral and octahedral sheets, linking together by sharing oxygens at the corners of the tetrahedral and octahedral sheets, gives the layered silicate structures. They can be classified under the two types as following:

1:1 layer type (T:O)

The structural unit of 1:1 layer silicate is formed by superimposing a tetrahedral sheet (T) on an octahedral sheet (O). The apical oxygen atoms of the tetrahedral sheet connect to the octahedral sheet by sharing oxygens (Figure 2.3a). Moreover, the 1:1 layers are held together strongly by hydrogen bonds between the hydroxyl groups of the octahedral sheet and the oxygen ions of the tetrahedral sheet. The crystalline structure of kaolinite, as the example of 1:1 layer type clay with no interlayer cation, is shown in Figure 2.3b.

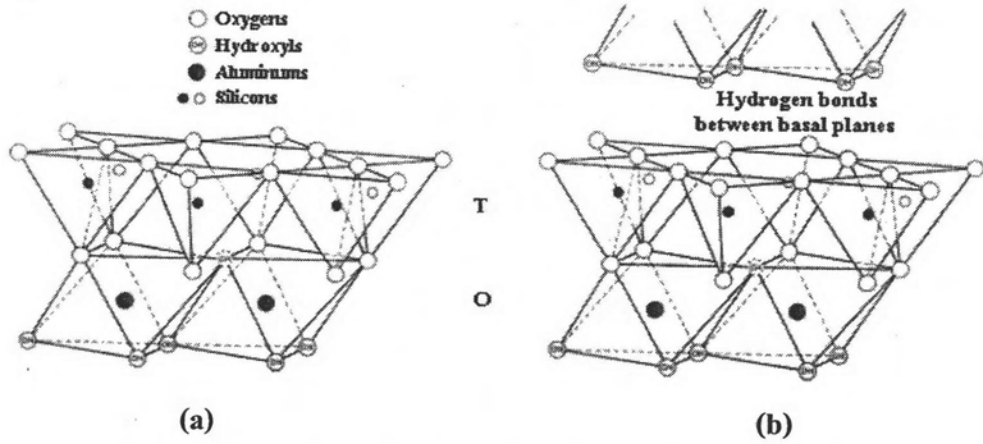


Figure 2.3 The 1:1 layer type, T:O (a) and the structure of kaolinite (b).

2:1 layer type (T:O:T)

The 2:1 layer silicate is formed by sandwiching an octahedral sheet between two tetrahedral sheets through sharing apical oxygen atoms [1] (Figure 2.4a). In addition, the 2:1 layers are held together by Van der Waals forces (Figure 2.4b) and to give the crystalline 3-dimensions structure. The clay minerals such as bentonite, montmorillonite and hectorite are in a group of 2:1 layered type with a permanent charge, called smectite clays [11].

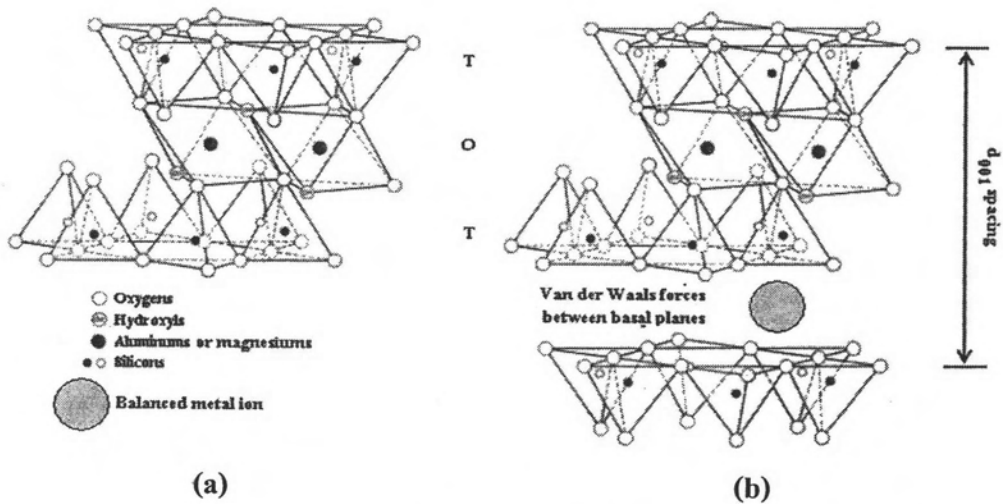


Figure 2.4 The 2:1 layer type, T:O:T (a) and the structure of smectite (b).

2.1.3 Hectorite clay [11]

Smectite clay, which is the group of the clay species e.g. montmorillonite, beidellite, saponite and hectorite, are 2:1 layer silicates and derived from the minerals talc and pyrophyrite. Both minerals of a stacking of charged-neutral layers with the compositive of $Mg_6Si_8O_{20}(OH)_4$ and $Al_4Si_8O_{20}(OH)_4$, respectively [16]. Furthermore, smectite minerals have extensive isomorphous substitution, being substitution of Fe^{3+} and Mg^{2+} for Al^{3+} in the octahedral sheet and Al^{3+} for Si^{4+} in the tetrahedral sheet. This substitution results in net negative charge in the layered structure depending on the central cation of octahedral and tetrahedral sheet. This charge must be balanced by various cations, either inside the interlayer space or around the edges. The magnitude of charge per formula unit, which is balanced by external cations (e.g. Na^+ , K^+ , Mg^{2+} and Ca^{2+}) to the unit layer, is called the “layer charge”, having the value about 0.5 to 1.2 per formula unit.

The distance between the repeating layer silicate clay is called the basal spacing (d_{001}) (Figure 2.4b). This value is easily determined by X-ray diffraction technique and varied by the type of exchangeable cation and the degree of interlayer solvation. The basal spacing of smectite clays can fully swell up to 20.0 Å.

Hectorite is one of 2:1 smectic clays, similar to a bentonite, but there are different cation types at the central of octahedral sheet. The central cation of octahedral sheet of hectorites are magnesium ions (Mg^{2+}) which is partly substituted by Li^+ (Li/Mg substitution) [17]. The general formular of hectorite is $(Si_8)(Mg_{6-x}Li_x)O_{20}(OH)_4 A_x.nH_2O$ (where A is a monovalent or divalent cation) [18].

2.1.4 Properties of clay minerals [11, 19]

Ion exchange

In the lattice of smectites, either the octahedral or tetrahedral sheet, the isomorphous substitution of cation by lower valent ions, such as the substitution of Al^{3+} for Si^{4+} , Mg^{2+} and/or Fe^{3+} for Al^{3+} or sometimes Li^+ for Mg^{2+} , can take place and give rise to a residual negative charge in the lattice. Thus, this generated charges must be balanced by exchangeable cations in the interlayer of the clays. The interlayer cation can be exchanged with cations in aqueous solutions when clay mineral is swelled. The degree of exchangeable cations is in term of the cation exchange capacity (CEC), usually measured in milliequivalents per 100 g of dried clay. Smectite groups have the highest CEC in the range of 70-120 meq/100 g. The structural defects at layer edges cause an additional CEC and a small amount of anion exchange capacity.

In addition, in the interlayer of clay minerals, the common exchangeable cations can be calcium, magnesium, hydrogen, potassium, ammonium and sodium ions, which are relatively abundant in aqueous solutions. The exchangeability of cations associated with the clay minerals by cations of a specific aqueous solution is determined by:

- The nature of the clay mineral
- The nature of the cation, e.g. hydration energy, size, valency
- The concentration of the electrolyte and pH of the exchange solution
- The population of exchange sites on the clay

The cations of small size/high valency are very effective in replacing the interlayer exchangeable cations of a clay.

Swelling

The swelling of the clays depends on (i) the type of clays, (ii) the energy released by the salvation of interlayer cation that must be adequate to overcome the attractive force (hydrogen bonding and van der waals interaction) between the adjacent layers and (iii) the layer charge. From these reasons, the clay minerals undergo different degree at expansion of the interlayer spacing.

In the case of 1:1 clay minerals of kaolinite groups, water molecules form strong hydrogen bonds with hydroxyl groups on hydrophilic octahedral layers, allowing swelling to occur. While 2:1 of smectite group has an evident characteristic swelling ability, due to the favorable adsorption of water and the other polar molecules between their layers. However, the other 2:1 clay minerals such as mica and vermiculite do not swell readily due to the excessively high layer charge, that cause strong electrostatic forces holding the anionic layers and the alternate interlayer cations together.

Acidity

The interlayer cations contribute the acidity to clay minerals. Some of these cations may be protons or polarizing cations (e.g. Al^{3+}), which give rise to strong Brönsted and Lewis acidity, respectively. The higher the electronegativity of M^+ cations, the stronger the Lewis acidic sites. Brönsted acidity also stems from the terminal hydroxyl groups and the bridging oxygen atoms. In addition, clay minerals have layer surface and edge defects, which would result in weak Brönsted and/or Lewis acidity, generally at low concentrations.

2.1.5 Modification of clay surface

Naturally occurring clay minerals have unique features such as high specific surface area, ion exchange property, thermal stability, swelling behavior, surface with negative charge and hydroxyl groups. For these reasons, clays are widely applied in many fields and one of the application is the use as adsorbent material for the elimination of heavy metals [1, 5-6] and other pollutants. However, inherent limitations of the natural clays, when applied as adsorbents of heavy metals, are the low loading capacity, relatively weak binding strength and low selectivity towards some heavy metals (Hg and Pb) [5, 10]. Moreover, the pollutants in water other than heavy metal e.g. anions and organic molecules can not be extracted by clay mineral due to their high hydrophilicity. These limitations have been overcome by surface modification with selected organic molecules (e.g. 2-mercaptobenzimidazole, hexadecyltrimethyl ammonium bromide, organosilanes, etc.). There are two types of surface modification: physical process (i.e. impregnation or ion exchange) and chemical process (i.e. grafting) [7, 20]. These two processes can change the surface of clays from hydrophilic to hydrophobic or organophilic.

(i) Physical process

Ion exchange is accomplished via the replacement of inorganic exchangeable cations, such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} within the interlayer space of clay lattice by organic cations. The widely used molecules are quaternary ammonium cations of the form $[(\text{CH}_3)_3\text{NR}]^+$ or $[(\text{CH}_3)_2\text{NRR}']^+$, where R and R' are aromatic for alkyl hydrocarbon species [11]. Modified clays could be used as adsorbents of certain pollutants, for example, hexadecyltrimethyl ammonium bromide-modified clay as adsorbent for chromate [8] and phenol [21], bromide hexadecyl pyridine-modified clay

for the adsorption of phenol [22] and 2-mercapto-benzimidazole-clay for the removal of mercury(II) [2].

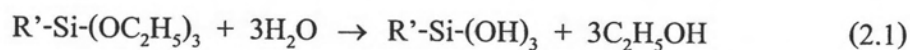
(ii) Chemical process

The chemical process includes organo-functionalization or grafting of silane molecules onto the surface of clay. It is the reaction between alkoxy groups of silane molecules ($R'-SiX_3$) with the surface hydroxyl groups via condensation reaction [5, 23] (Scheme 2.1). In silane molecules, X is alkoxy groups (e.g. methoxy ($-OCH_3$), ethoxy ($-OC_2H_5$)) and R' represents alkyl chain and/or alkyl chain containing organic functional group (e.g. amino ($-NH_2$), mercapto ($-SH$)).

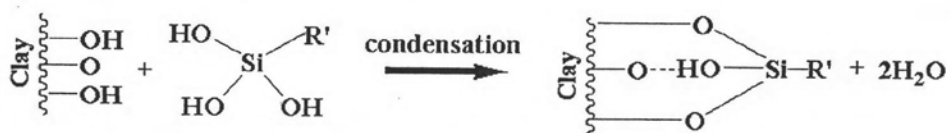


Scheme 2.1 The reaction of alkoxy groups of organosilane with the silanol groups on the clay surface.

In some cases, the alkoxy groups of silane molecules are converted to silanol groups by hydrolysis [7, 20], as presented in equation 2.1.



Then, the hydrolyzed silanol groups of silane molecules can also react with the surface hydroxyl groups and/or bridging oxygen atoms on the clay surface by condensation reaction, shown in Scheme 2.2.



Scheme 2.2 The reaction of hydrolyzed silanol groups of organosilane with the surface hydroxyl groups and/or oxygen atoms on the clay surface.

After the modification, the surface of clays can well adsorb the heavy metals ions and organic molecules in a higher degree or higher selectivity. For example, 3-mercaptopropyltrimethoxysilane [10], 3-(2-aminoethylamino)propylmethydimethoxysilane [27] and *N*-(2-aminoethyl)-3-amino-propyltrimethoxysilane [20] can be used to modify the clay surface for removal of Hg, Pb and 4-nitrophenol, respectively.

2.2 Heavy metals in the environment

Heavy metals in water, may be generated by the natural (e.g. soil weathering) and in particular by human activities (e.g. mining and ore processing, industrial processing and agriculture). The contamination of heavy metals in water is a critical environmental problem because they are harmful to plant, animal and human life [1]. Thus, the removal of heavy metals from water before releasing to the environment is necessary. In Thailand, the residual concentration of heavy metals in released water has to be within the limits of the regulation of the Pollution Control Department, PCD (Table 2.1).

Table 2.1 The maximum levels of heavy metal acceptable in drinking water and wastewater [25]

| Contaminant | Maximum acceptable concentration (mg L ⁻¹) | |
|-------------|--|--------------------------------|
| | Drinking water | Wastewater from the industrail |
| Arsenic | 0.05 | 0.25 |
| Cadmium | 0.005 | 0.03 |
| Copper | 1.0 | 2.0 |
| Lead | 0.05 | 0.2 |
| Mercury | 0.002 | 0.005 |
| Silver | 0.05 | - |

2.3 Background information of metals

2.3.1 Mercury [14]

Mercury has atomic number of 80, atomic weight of 200.6, melting point of -38.8 °C, specific gravity of 13.55 g cm⁻³, vapor pressure of 1.22×10⁻³ mmHg at 20 °C and the oxidation states of Hg⁰, Hg⁺(mercurous) and Hg²⁺ (mercuric). Moreover, it can be in the form of inorganic (e.g. HgCl₂, Hg(OH)₂ and HgS) or organic (e.g. CH₃HgCH₃) compounds, depending upon the type of ligand and pH of solution. Figure 2.5 shows species distribution of mercury at different pH of aqueous solution.

Mercury compound are widely applied in industries such as chlor-alkali manufacturing industry, oil refinery, paint, battery industry, pulp and paper industry and dentistry (dental amalgams) and in agriculture such as a seed dressing in grain, potatoes, flower bulbs, etc. and a foliar spray against plant diseases. These activities could cause the contamination of mercury in the environment. It can affect the human health such as carcinogenic, mutagenic, teratogenic and promote tyrosnemia. Uptake

of high concentration of mercury causes impairment of pulmonary and kidney function, chest pain and dyspnoea [26]. The best known example of the dangerous effects of mercury on human health is the Minamata disease.

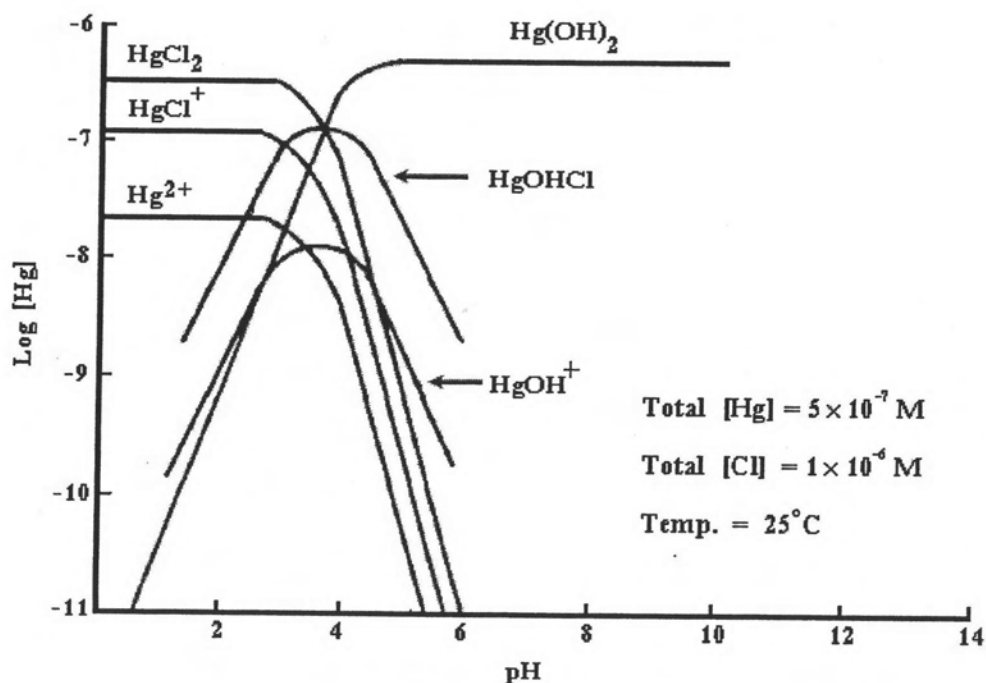


Figure 2.5 The diagram of mercury speciation as a function pH [27].

2.3.2 Silver [14]

Silver has atomic number of 47, atomic mass of 107.87 and specific gravity of 10.5 g cm^{-3} . Silver has the oxidation numbers of 0, 1, 2 and 3 and Ag^0 and Ag^+ are the most common, while Ag^{2+} and Ag^{3+} are rare. The major industrial use of silver is in photographic manufacturing and the other industries such as in the production of electrical contacts and conductors, batteries, catalysts, brazing alloys and solders, jewelry and mirrors. These industries release solid and liquid silver wastes into the environment [28]. The silver wastes do not directly affect human life but it can cause allergic reactions of skin such as rashes, burning and swelling [29]. Furthermore, Ag^+

has been considered to be hazardous to zooplankton, aquatic lives (plants, fishes, molluscs and crustaceans) and mammals [28].

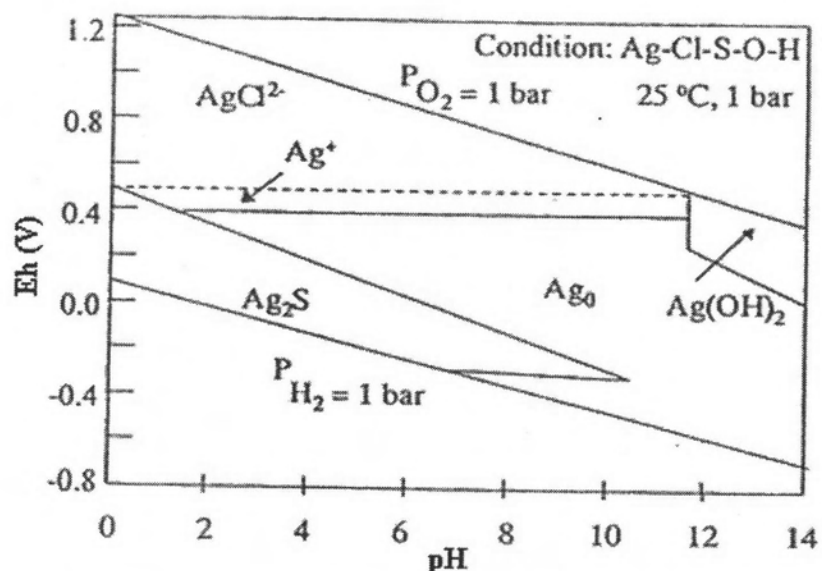


Figure 2.6 The diagram of silver speciation as a function pH [14].

2.4 Chelation

The chelation mechanism occurs between the ligands or the electron donor atoms, and metal electron acceptor by coordination. Several chelating ligands consist of electron donor atoms such as nitrogen (e.g. N present in azo groups, amines, nitriles and imino groups), oxygen (e.g. O present in carboxylic, hydroxyl, phenolic, ether and carbonyl groups) and sulfur (e.g. S present in thiols, thiocarbamates and thioethers and etc.). The chelating ligands can bind different metal ions with different affinity, and it can be explained by the hard-soft acid-base principle (HSAB).

Pearson propounded that "hard acids bind strongly to hard bases and soft acids bind strongly to soft bases". The binding of hard acids to hard bases and soft acids to soft bases occur via the ionic and covalent bonds, respectively. In case of the borderline acids, which have an intermediate characteristics, they possess affinity for

both hard and soft bases. Table 2.2 presents the classification of hard-soft acids and hard-soft bases [30].

However, the binding ability between the metal ions in solution and the chelating ligands attached onto the solid support also depends on various factors as followings:

- Nature, charge and size of the metal ions
- Nature of the donor atoms present in the ligand
- The pH of solution which would favor the extraction and binding of certain metal ions by active donor or groups
- Nature of the solid support (e.g. hydrophilicity of adsorbent should be considered in case of the extraction in the aqueous solution.)

Table2.2 The classification of hard-soft acids and hard-soft bases [30]

| Acids | Bases |
|--|--|
| Hard | |
| $H^+, Li^+, Na^+, K^+(Rb^+, Cs^+)$ | NH_3, RNH_2, N_2H_4 |
| $Be^{2+}, Be(CH_3)_2, Mg^{2+}, Ca^{2+}, Sr^{2+}(Ba^{2+})$ | $H_2O, OH^-, O^{2-}, ROH, RO^-$, |
| $Se^{3+}, La^{3+}, Ce^{4+}, Gd^{3+}, Lu^{3+}, Th^{4+}, U^{4+}, UO_2^{2+}, Pu^{4+}$ | R_2O |
| $Ti^{4+}, Zr^{4+}, Hf^{4+}, VO^{2+}, Cr^{3+}, Cr^{6+}, MoO^{3+}, WO^{4+}$ | $CH_3COO^-, CO_3^{2-}, NO_3^-, PO_4^{3-},$ |
| $Mn^{2+}, Mn^{7+}, Fe^{3+}, Co^{3+}$ | SO_4^{2-}, ClO_4^- |
| $BF_3, BCl_3, B(OR)_3, Al^{3+}, Al(CH_3)_3, AlCl_3, AlH_3,$ | $F^- (Cl^-)$ |
| Ga^{3+}, In^{3+} | |
| $CO_2, RCO^+, NC^+, Si^{4+}, Sn^{4+}, CH_3Sn^{3+}, (CH_3)_2Sn^{2+}$ | |
| $N^{3+}, RPO_2^+, ROPO_2^+, As^{3+}$ | |
| $SO_3, RSO_2^+, ROSO_2^+$ | |

Table 2.2 The classification of hard-soft acids and hard-soft bases (continued)

| Acids | Bases |
|--|---|
| Hard | |
| $\text{Cl}^{3+}, \text{Cl}^{7+}, \text{I}^{5+}, \text{I}^{7+}$ | |
| HX (hydrogen-bonding molecules) | |
| Borderline | |
| $\text{Fe}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}$ | $\text{C}_6\text{H}_5\text{NH}_2, \text{C}_5\text{H}_5\text{N}, \text{N}_3^-, \text{N}_2$ |
| $\text{Rh}^{3+}, \text{Ir}^{3+}, \text{Ru}^{3+}, \text{Os}^{2+}$ | $\text{NO}_2^-, \text{SO}_3^{2-}$ |
| $\text{B}(\text{CH}_3)_3, \text{GAH}_3$ | Br^- |
| $\text{R}_3\text{C}^+, \text{C}_6\text{H}_5^+, \text{Sn}^{2+}, \text{Pb}^{2+}$ | |
| $\text{NO}^+, \text{Sb}^{3+}, \text{Bi}^{3+}$ | |
| SO_2 | |
| Soft | |
| $\text{Co}(\text{CN})_5^{3-}, \text{Pd}^{2+}, \text{Pt}^{2+}, \text{Pt}^{4+}$ | H^- |
| $\text{Cu}^+, \text{Ag}^+, \text{Au}^+, \text{Cd}^{2+}, \text{Hg}^+, \text{Hg}^{2+}, \text{CH}_3\text{Hg}^+$ | $\text{R}^-, \text{C}_2\text{H}_4, \text{C}_6\text{H}_6, \text{CN}^-, \text{RNC},$ |
| $\text{BH}_3, \text{Ca}(\text{CH}_3)_2, \text{GaCl}_3, \text{GaBr}_3, \text{GaI}_3, \text{Tl}^+, \text{Tl}(\text{CH}_3)_3$ | CO |
| CH_2 , carbenes | $\text{SCN}^-, \text{R}_3\text{P}, (\text{RO})_3\text{P}, \text{R}_3\text{As}$ |
| π acceptors: trinitrobenzene, chloroanil, etc. | $\text{R}_2\text{S}, \text{RSH}, \text{RS}^-, \text{S}_2\text{O}_3^{2-}$ |
| $\text{HO}^+, \text{RO}^+, \text{RS}^+, \text{RSe}^+, \text{Te}^{4+}, \text{RTe}^+$ | I^- |
| $\text{Br}_2, \text{Br}^+, \text{I}_2, \text{I}^+, \text{ICN}$, etc. | |
| $\text{O}, \text{Cl}, \text{Br}, \text{I}, \text{N}, \text{RO}, \text{RO}_2$ | |
| M^0 (metal atoms) and bulk metals | |

R refers to hydrocarbon compounds.

2.5 Adsorption [14]

Adsorption is a phenomena of the sorption that occurs between the liquid or gas phase and solid phase. The analytes in the liquid or gas phase are moved and can be attracted on the surface of solid phase, which is called mass transfer. The solid phase and the analyte in the liquid or gas phase are called adsorbent and adsorbate, respectively. The adsorption can be further split into two types, the physisorption and chemisorption.

Physisorption

This physical adsorption is the attraction between adsorbates and adsorbents via van der Waals force, generating from London dispersion force and the electrostatic force. Furthermore, it can occur the multilayer sorption on the adsorbent surface, when the concentration of adsorbates increases. The reaction of this adsorption is called outer-sphere surface reaction or non-specific (Figure 2.7a), that the analytes are independently adsorb on the surface of adsorbents and the adsorption is the reversible. The reversibility of reaction depends upon the attraction forces of analytes with adsorbent, the concentration of analytes and temperature.

Chemisorption

The interaction between analytes and adsorbent in chemisorption is the chemical or covalent bonds, which is stronger than van der Waals force in physisorption. This mechanism may occur when the surface of adsorbents has active sites specific for analytes. The adsorption of analytes occurs in the monolayer regime and the reaction is irreversible. The chemical adsorption can be called inner-sphere surface reaction (Figure 2.7b).

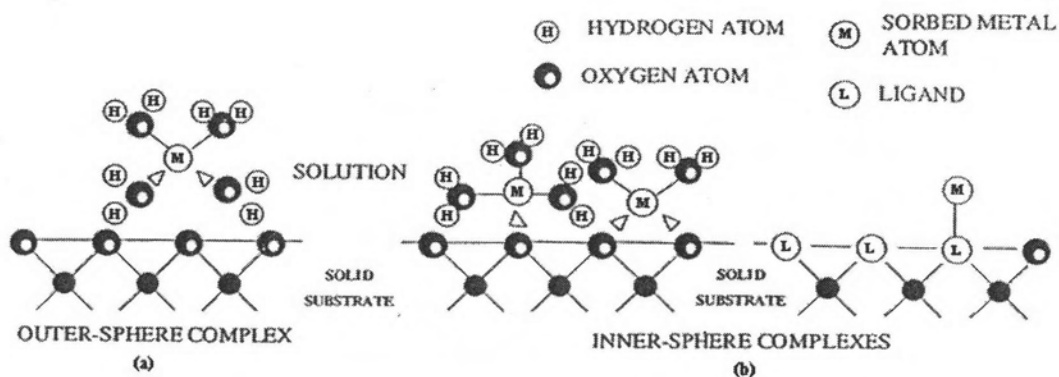


Figure 2.7 The outer-sphere (a) and inner-sphere (b) surface reation [14].

2.5.1 Rate of mass transfer

The adsorption occurs when analytes in liquid or gas phase are transferred to adsorbent, which is called mass transfer. The mass transfer is divided into three main steps as follows: (i) bulk transport, (ii) film transport and (iii) intraparticle transport (Figure 2.8). Moreover, it is important to understand the adsorption kinetics because the kinetics is useful in the prediction the time needed to reach the adsorption equilibrium when applied the adsorbents. The step that controls the rate of mass transfer at equilibrium is the slowest step of the adsorption mechanism.

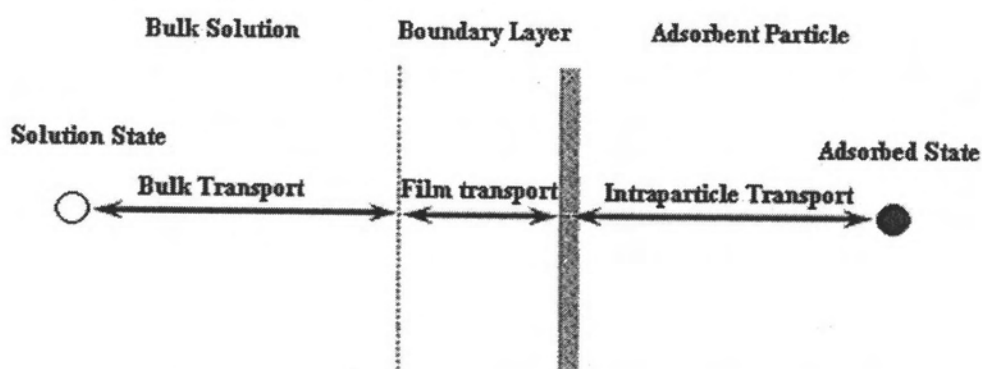


Figure 2.8 The steps of adsorption on the adsorbent surface [31].

(i) Bulk transport

In this step, the analytes move from the bulk solution to the surface of the boundary layer. It is the very fast process.

(ii) Film transport

The analytes transport from the boundary layer to the surface of the adsorbent, which is called film diffusion or external diffusion. Film transport may occur slowly and can be considered as the step that controls the adsorption rate.

(iii) Intraparticle transport

The final step is one of the steps that can be the rate limiting steps of the adsorption. The analytes transfer from the adsorbent surface to the inside or into the pores of adsorbent and react with the active sites. This step is called the internal diffusion.

2.5.2 Adsorption isotherms [12]

The adsorption process that refers to the partition of analytes between the aqueous phase and adsorbent (solid phase) at equilibrium of constant temperature is called adsorption isotherm. Moreover, the relation of the amount of adsorbate on adsorbent and the concentration of analytes in solution at equilibrium can be applied to describe adsorption at equilibrium by fitting with the adsorption isotherm models such as Langmuir and Freundlich isotherm models (Figure 2.9 and 2.10).

2.5.2.1 Langmuir isotherm

The Langmuir model derived for adsorption is initially based on the assumptions: (i) a constant energy of adsorption that is independent of the extent of a homogeneous surface, (ii) the adsorption takes place at specific sites of adsorbent and no further adsorption can take place at that sites and (iii) the phenomena of adsorption is the monolayer and the maximum adsorption capacity of the adsorbent for that analyte at equilibrium can be predicted. The general form of the Langmuir relation is shown in equation (2.2).

$$q = \frac{q_m b C_e}{1 + b C_e} \quad (2.2)$$

The equation 2.2 is further arranged into the form of linear equation, as shown in equation (2.3).

$$\frac{C_e}{q} = \frac{1}{b q_m} + \frac{C_e}{q_m} \quad (2.3)$$

where C_e = equilibrium concentration of the analyte in aqueous solution
(mg L^{-1} or mol L^{-1})

q = adsorption capacity of adsorbent (mg g^{-1} or mol g^{-1})

q_m = maximum adsorption capacity of sorbent (mg g^{-1} or mol g^{-1})

b = Langmuir constant related to the affinity of binding sites
(L mg^{-1} or L mol^{-1})

A plotting of $\frac{C_e}{q}$ versus C_e yields a straight line with a slope of $\frac{1}{q_m}$ and intercept of $\frac{1}{b q_m}$ (Figure 2.9b).

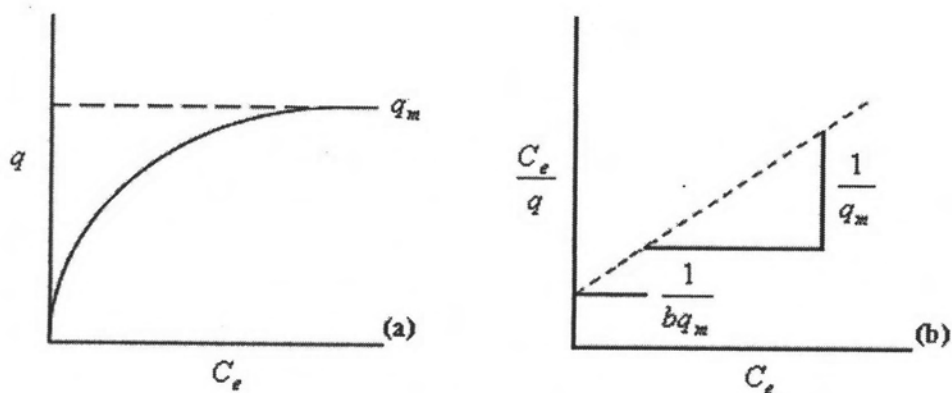


Figure 2.9 The shape (a) and the linear plot (b) of Langmuir adsorption isotherm [32].

2.5.2.2 Freundlich isotherm

The Freundlich equation was derived theoretically by assuming the adsorption of analytes on heterogeneous surface or surface active sites of varied affinities. The common form of the Freundlich equation is presented in equation (2.3).

$$q = K_f C_e^{1/n} \quad (2.3)$$

The linear form of the Freundlich isotherm is the logarithmic form according to equation 2.4.

$$\log q = \log K_f + \frac{1}{n} \log C_e \quad (2.4)$$

where K_f = Freundlich constant related to adsorption capacity
(mg g^{-1} or mol g^{-1})

n = Freundlich constant related to adsorption intensity

A linear plotting $\log q$ versus $\log C_e$ gives a slope of $\frac{1}{n}$ and intercept of $\log K_f$ (Figure 2.10b).

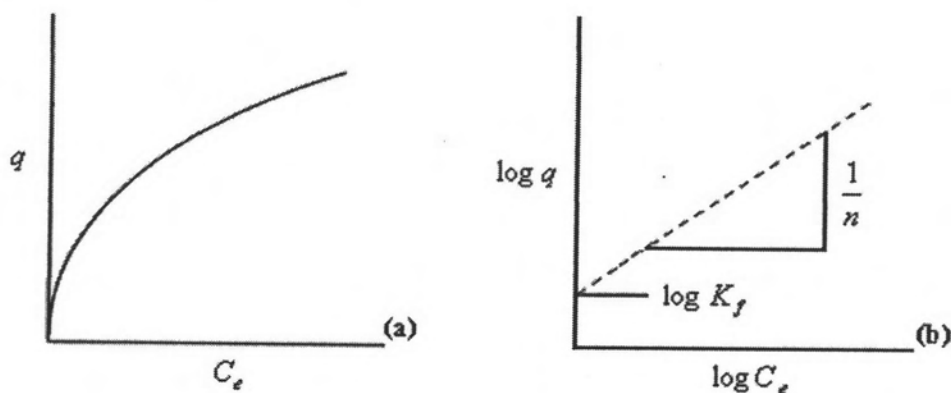


Figure 2.10 The shape (a) and the linear plot (b) of Freundlich adsorption isotherm [32].

2.6 Literature review

The properties of clay minerals, such as ion exchange, swelling and intercalation, high specific surface area and the presence of hydroxyl groups on the surface, draw interest in using these materials as adsorbents for removal of heavy metal ions in water. There are many researches investigating the use of the clay minerals as followings.

Mellah et al. [33] used the natural bentonite clay for removal of zinc from aqueous solutions and studied on the effect of various parameters (agitation speed, solid-liquid ratio, temperature, particle size and initial zinc concentration) to the rate of adsorption. The results showed that the maximum adsorption capacity according to Langmuir isotherm was 52.91 mg g^{-1} at 20°C and the adsorption was physisorption. Dafonseca et al. [1] removed Cd^{2+} , Zn^{2+} , Mn^{2+} and Cr^{3+} from aqueous solutions by vermiculite clay. The effect of pH, contact time and cation concentration were investigated. The adsorbent showed good sorption potential for these four cations and

the adsorption isotherms fitted to the Langmuir model. In addition, Sajidu et al. [78] applied unmodified clay to remove Hg^{2+} and Pb^{2+} ions in solutions, having the initial concentration of 5 mg L^{-1} and initial pH of 6.5 and 7.6, respectively. The results showed that the removal efficiency was 60 % and 95 % for Hg^{2+} and Pb^{2+} ions, respectively.

Furthermore, the clay minerals have been treated and modified to achieve the greater adsorption efficiency of metal ions. Vengris et al. [34] reported the activation of natural montmorillonite by treatment with HCl and subsequent neutralization with NaOH. Then, the adsorbent was used to extract metal ions (e.g. Ni^{2+} , Cu^{2+} and Zn^{2+}) in wastewater. It was concluded that the acid treatment led to the decomposition of the montmorillonite structure and the uptake capacity of the modified clay for all metal ions increased significantly. Krishna et al. [8] modified the clay by using cationic surfactant (hexadecyl trimethylammonium (HDTMA) bromide) for the adsorption of chromate. It was found that the surfactant-modified clay showed maximum adsorption at pH below pH 1, but between pH 2 and 6, the adsorption efficiency was one half of that observed at pH 1. The adsorption data obtained were well described by Langmuir adsorption isotherm. In addition, the anionic surfactant (sodium dodecylsulfate (SDS)) was also used in the modification of montmorillonite by Su et al [9]. This SDS-modified adsorbent was taken to investigate the efficiency in removal of heavy metal ions (Cu^{2+} and Zn^{2+}) from water. The results showed that the removal efficiency for both metal ions increased with an increasing of pH. The equilibrium time was attained within 2 hr. The kinetics was fitted to the pseudo-first-order model, having the rate constants of 6.64×10^{-4} and $3.14 \times 10^{-3} \text{ min}^{-1}$ at 25°C for adsorption of Zn^{2+} and Cu^{2+} , respectively.

From these researches, it was observed relatively weak binding strength occurring between the clay surface and metal ions or chemical reagents used the modification. The adsorption studies of some metal ions (Hg^{2+} and Pb^{2+}) by clays showed low loading capacity and low affinity of the clay surface towards these metal

ions. Furthermore, these disadvantages must be solved by modifying clay surface with chelating ligands. Monohar et al. [2] modified kaolinite with 2-mercaptobenzimidazole and studied the removal of mercury(II) ions from aqueous solutions and chlor-alkali industry wastewater by the modified clay. It was found that the removal efficiency of Hg^{2+} ions increased, compared to unmodified kaolinite and the optimum pH for adsorption was in the range of 4-8. Erdemoglu et al. [7] modified the pyrophyllite with 3-(2-aminoethylamino)propylmethydimethoxysilane (APMDS) for removal of Pb^{2+} ions and the characterization of the adsorbents were performed by using XRD, FTIR and SEM technique. It was proposed that hydrogen bonding took place between the hydroxyl groups and/or oxygen atoms within the structure of pyrophyllite and hydroxyl groups of APMDS. The APMDS-modified pyrophyllite adsorbed approximately 93% of Pb^{2+} ions, while natural pyrophyllite could adsorb only 35% when used the solution containing 20 mg L^{-1} of Pb^{2+} under the same condition. Tonle et al. [5] studied the grafting of silane agents (γ -aminopropyltriethoxysilane and 3-mercaptopropyltrimethoxysilane) on smectite via reaction with the hydroxyl groups on clay surface for the application in mercury(II) ions uptake. TGA, EA, FTIR and surface area analysis were performed to characterize the grafted clay. It was found a decrease of porosity and amounts of surface hydroxyl groups, due to the presence of aminopropyl or mercaptopropyl groups attached onto the aluminosilicate structure. The adsorption efficiency of the grafted smectite was greater than that of the natural smectite for the uptake of Hg^{2+} ions. Mercier et al. [10] investigated the preparation, characterization and applications of montmorillonite grafted with (3-mercaptopropyl)trimethoxysilane. The new material was characterized by XRD, TGA, FTIR, XRF and ^{13}C solid-state NMR and it was demonstrated to be an effective adsorbent for Pb^{2+} and Hg^{2+} ions 70 and 65 mg of metal / g of adsorbent, respectively.

The grafting reaction of organosilane agents onto clay surface was investigated in detail by Park et al. [35], who grafted the external surface of laponite with octylsilane groups and by Shanmugaraj et al. [36], who functionalized

montmorillonite clay by using 3-aminopropyltriethoxysilane in various solvent media. The grafted clays were characterized by XRD, TGA, FTIR and ^{13}C solid-state NMR.

Moreover, the other substrates (e.g. silica, hexagonal mesoporus silica, MCM-41 and poly(EGDMA-HEMA)microbeads) were also modified for removal of mercury and silver ions. It was observed that the functional groups on the modification reagent must contain the nitrogen and/or sulfur atom in the molecule such as, dithizone [24], 2-mercaptothiazoline [37], 3-mecaptopropyltrimethoxysilane [4, 38], di(n-propyl) thiuram disulfide [39] and 1,5,9,13-tetrathiacyclohexadecane-3,11-diol [40]. Both nitrogen and sulfur atoms have the lone pair electrons that can be used in the binding with metal ions according to the hard-soft acid-base principle [30].

In this research, we are interested in the modification of hectorite clay with 2-(3-(2-aminoethylthio)propylthio)ethanamine (AEPE) (Figure 2.11), due to the presence of sulfur and nitrogen donor atoms in the molecule and the ease of synthesis, to improve the removal efficiency of mercury and silver ions in water.

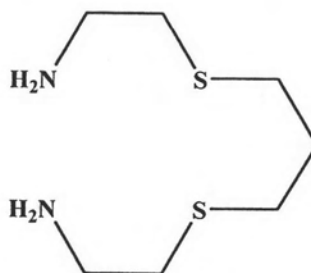


Figure 2.11 The structure of AEPE ligand.