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# Clay Materials for Environmental Remediation

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# Preface

First of all, we would like to thank Prof. S.K. Sharma for the chance to write a monograph in his series of books (SpringerBriefs in Green Chemistry for Sustainability). This book is a comprehensive summary of the recent studies on the adsorption of hazardous substances from the water environment onto clay and clay minerals.

In our modern life, clay minerals are one of the most important materials for a number of industrial applications, from the conventional ones to the advanced applications. A substantial number of studies have been carried out to explore the possible usage of clay minerals as "super" adsorbent for removal of hazardous substances from water environment. To increase the adsorption capability of natural clay minerals, several methods have been used to modify the surface and structure of clay minerals. Often, the modification involved hazardous chemicals which ended up as waste after the process. Combination between clay minerals and other materials to form new composite materials has also been explored, and as a result, many new clay composite materials were developed for the environmental remediation purpose.

A number of literatures dedicated to clay science are available, and most of them provide important information about the science of clay minerals or materials. Different aspects of clays including geology, mineralogy, crystallography, geotechnology, and its industrial importance and applications have been given and discussed in these available books. A large number of studies have been devoted to the use of clay minerals for the removal of hazardous substances from water or wastewater; however, only a limited number of monograph books are available in this area. This book attempts to fill the gap between the science of clays and their applications, especially for water remediation.

Brief discussions about the environmental problem, particularly in water system caused by the pollution of hazardous chemicals, are presented in Chap. 1 as the introduction chapter. The subsequent chapter discusses the structure and classification of clay minerals and its role as cleaning agents in water remediation. Due to their hydrophilic nature, natural clay minerals usually are not suitable as adsorbents for some organic compounds; therefore, modification in their structure and surface chemistry is needed. Various methods are available for this purpose, and some aspects of clay modification and their application for adsorption purpose are given in Chap. 3.

Relevant adsorption equilibria and kinetic data are needed for the design and analysis of the adsorption separation process. Adsorption equilibria and kinetic data are the most important information in understanding the adsorption process. Several adsorption isotherm and kinetic models are currently available to represent the adsorption data of hazardous substances on clay minerals, and usually, more than one model can represent the adsorption equilibria of a certain system. The decision to choose or decide the suitability of the model to represent the experimental data should not only be based on the value of $r^2$ but also on the rationality of the physical meaning of each parameter. Comprehensive discussions on the validity of the available models to represent adsorption equilibria and kinetic data are given in Chaps. 4 and 6.

Chapter 5 discusses the characterization of clay minerals and its modified forms. Clay minerals are heterogeneous in both composition and pore structure; therefore, the characterization and identification of the mineralogical composition are challenging processes. With the availability of modern instrumentation, the process of characterization of clay minerals becomes much easier. Various aspects of the characterization of clay minerals for environmental application are covered in the last chapter of this book.

# Contents

# Chapter 1
# Introduction

Clay science is multi-disciplinary area; the scientists who work in this area come from diverse backgrounds with very diverse interests. The diversity of the nature of clay science is also reflected by the existence of a variety of scientific journals, books, and patents. Several of the available records such as Handbook of Clay Science, edited by Bergaya et al. (2006) provides information on the fundamental structure and surface properties of clay minerals, their industrial and environmental applications as well as analytical techniques, and the teaching and history of clay science. *Applied Clay Mineralogy* by Murray (2007) discusses about the occurrences, processing and application of kaolins, bentonites, palygorskite-sepiolite, and common clays.

Most of the available review papers just only compilation of the published literatures. This book is intended to provide a critical review of recent studies on the utilization of clay minerals and its modified forms for the water remediation purpose. The structures of clay minerals and their utilization for removal of hazardous compounds from gas and water environment are discussed in Chap. 2. The modification of clay minerals using various kinds of modifying agents such as acids, base, and surfactants is discussed in Chap. 3, while Chap. 4 deals with the adsorption isotherm models which widely used to represent the experimental adsorption data of various hazardous substances on clay minerals. The temperature dependent forms of several isotherm models are also presented in this chapter. The extension of single component isotherm to multicomponent system and its modification are also discussed. The kinetic studies of the adsorption hazardous substances onto clay minerals are described in Chap. 5. The comprehensive discussions about the physical meaning of kinetic parameters of the widely used kinetic models are also presented in this chapter. Chapter 6 describes various analytical instruments commonly employed for the characterization of clay minerals.

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## 1.1 Water Pollution

An environmental problem arises whenever there is a change in the quality or quantity of any environmental factor which directly or indirectly affects the health and well-being of man in an adverse manner. In this modern world we face very serious environmental issues that need special attention to make the environment friendlier to human. Presently, the global warming is the greatest environmental and humanitarian crisis. Clean and renewable energy is the second big issues after climate change. Water degradation and shortage, severe industrial pollution, and diminishing biodiversity are also other big environmental issues. Increasing human population at faster rate resulted in over consumption, leading to poverty and other environmental problems.

Water is an important and indispensable part of the cosmos and it plays a critical part in the proper operation of the earth's ecosystems (Ali and Gupta 2006). The water shortage has already become the daily problem for almost 1/6 of the world's population. It is also predicted that by 2025, more than 30 % of the world's population will experience water scarcity and more than 60 % will experience clean water problems due to contamination of water and water pollution. Water pollution caused by industrial activities is likewise a major global problem that demands very serious attention, therefore, the evaluation and revision of water resources and water usage policy are also required.

The contaminants enter the water environments through various ways. It can enter directly from direct discharge of industrial effluents, wastewater treatment facilities, refineries, etc. The contaminations of soil, groundwater, and the atmosphere via rain water also contribute to water pollution. Water pollution often creates severe problems for human and environment, such as poisonous drinking water, poisonous food animals, unbalanced river and lake ecosystems that can destroy the biological diversity, etc.

The presence of heavy metals in water cause serious health problems to human. Although several adverse health effects of heavy metals have been known for a long time, exposure to heavy metals continues, and is even increasing in some parts of the world, in particular in less developed countries (Jarup 2003). In view of the human health impacts, each metal imparts different effects and symptoms. Heavy metals are persistent, and therefore, very difficult to eliminate naturally from the environment, even at a presence of trace amounts. Table 1.1 lists the common heavy metals found in water environment as pollutants and its impact on human health (Febrianto et al. 2009; Arief et al. 2008).

Other pollutants commonly found in water environment are dyes, antibiotics, biocides compounds, aromatic organic compounds, and etc. As coloring agents, some dyes are resistant to degradation and their presence in water dyes might be harmful to human beings and hazardous to aquatic organisms. Even at very low concentration, the presence of dye in water is visible and could reduce aquatic diversity by blocking the passage of light through water. The presence of antibiotics and biocides compounds in the water stream cause severe environmental problems. Some of these chemicals have toxic nature toward algae and other lower

**Table 1.1** Heavy metals and its impact on human health

| Heavy metal | Impact on human health |
|---|---|
| As(V) | Damage to skin, eyes, and liver, may also cause cancer |
| Cd(II) | Provoke cancer, kidney damage, mucous membrane destruction, vomiting, diarrhea, bone damage, itai-itai disease, affect the production of progesterone and testosterone |
| Cr(III) | Allergic skin reactions and cancer in the digestive tract and lungs |
| Cr(VI) | Headache, nausea, severe diarrhea, vomiting, epigastric pain, hemorrhage, provokes cancer and has an adverse potential to modify the DNA transcription process |
| Cu(II) | Liver damage, Wilson's disease, insomnia, brain, pancreas, and myocardial damage |
| Hg(II) | Damage to the nervous system, kidneys, and vision, protoplasm poisoning |
| Mn(II) | Triggers neurotoxicity, low hemoglobin levels, and gastrointestinal accumulation |
| Ni(II) | Dermatitis, nausea, chronic asthma, coughing, bronchial hemorrhage, gastrointestinal distress, weakness and dizziness |
| Pb(II) | Anemia, damage to the kidneys, nervous system deterioration, damage the ability to synthesize protein |
| Zn(II) | Irritability, muscular stiffness, loss of appetite, nausea, depression, lethargy, neurologic signs such as seizures and ataxia, and increased thirst |

organisms which can bring about indirect effect in long terms toward ecological sustainability and some bacteria are becoming more resistant to the exposure antibiotics or biocides. Some aromatic organic compounds are important materials in the chemical process industries and usually used as the raw materials or as the solvents. Most of these chemicals are classified as dangerous chemicals and several of them are carcinogenic and/or mutagenic substances. In several less developed countries, all of these compounds are major pollutants in the water streams.

Currently, several technologies are available for the remediation of contaminated water, such as aerobic and anaerobic biological treatments, photocatalysis, advanced chemical oxidation, membrane separation, and adsorption process. Among those available technologies, the adsorption process is economically viable and highly effective across a wide range of pollutant concentrations.

## 1.2 Role of Clay Minerals in Environment Protection

Clay minerals are one of the most abundant materials in the earth. These minerals play important role in the development of human civilization. For the environment protection, the clay minerals have been used in the disposal and storage of hazardous chemicals. Clay minerals have the catalytic capability to neutralize certain organic hazardous chemicals. As the liners of hazardous chemical storage, one of the most important characteristics of clay minerals is the adsorption capability. As the base liners, the clay minerals must be able to prevent any leakage of hazardous substances into the subsoil or the environment. The capability of clay minerals to retain hazardous substances depend on their cation exchange capacity (CEC) since the process of retaining toxic materials mainly occurs by the adsorption or ion exchange.

Due to its high cation exchange capacity, clay minerals are very effective for the adsorption of cations from the solution, therefore these materials are widely used for the removal of heavy metals from the solution. Clay minerals The uptake of heavy metals by clay minerals involves a series of complex adsorption mechanisms, such as direct bonding between metal cations with the surface of clay minerals, surface complexation, ion exchange, etc. Although the most of clay materials are negatively charged (Churchman et al. 2006), due to their high surface area and pore volume, these materials still can adsorb organic and non-ionic substances in significant amounts. Churchman et al. (2006) mentioned that in their natural state the clay minerals are hydrophilic and in the aqueous solution usually they have low adsorption capacity toward small non-ionic organic compounds. The adsorption capacity of natural clay minerals can be enhanced by modification using various kinds of acid, base, salts, surfactants and other organic or inorganic chemicals. Through this modification the clay minerals become hydrophobic and organophilic, and it will enhance the uptake of small non-ionic organic compounds. Details of modification using various kinds of chemicals are discussed in Chap. 3.

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# Chapter 2
# Natural Clay Minerals as Environmental Cleaning Agents

**Abstract** Clays and clay minerals are very important industrial minerals; they have been in use as raw materials for hundreds of industrial applications due to its abundant availability and inexpensive. Clay minerals are usually classified according to its structure and layer type. The classification of Grim becomes the basis for outlining the nomenclature and the differences between the various clay minerals. A simple classification of clay minerals also available in the literatures, in this classification clay mineral divided into four main groups: kaolinite group, illite group, smectite group, and vermiculite. Clay minerals play important role in the environment protection. These minerals have been used in the disposal and storage of hazardous chemicals as well as for remediation of polluted water. The use of clay minerals as the adsorbents for the adsorption of various hazardous substances (heavy metals, dyes, antibiotics, biocide compounds, and other organic chemicals) has been widely studied by a large number of researchers. Some important information about current studies is given and discussed in this chapter.

**Keywords** Clay classification · Clay structure · Clay properties · Adsorption · Adsorbent

Clay minerals belong to the family of phyllosilicate or sheet silicate family of minerals, which are distinguished by layered structures composed of polymeric sheets of $SiO_4$ tetrahedra linked into sheets of (Al, Mg, Fe)$(O,OH)_6$ octahedra. Clay minerals are layer-type aluminosilicates that are formed as products of chemical weathering of other silicate minerals at the earth's surface (Sposito et al. 1999). These minerals have a platy morphology because of the arrangement of atoms in the structure. Clays and clay minerals are very important industrial minerals; they have been in use as raw materials for hundreds of industrial applications due to its abundant availability and inexpensive. Clays are utilized in agricultural applications, in engineering and construction applications, in environmental remediation, in geology, pharmaceuticals, food processing, and many other industrial applications (Murray 2007).

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## 2.1 Types, Structures, and Characteristics of Clay Minerals

### *2.1.1 Types and Classifications of Clay Minerals*

The classification of clay minerals was firstly proposed by Grim (1962), and this classification becomes the basis for outlining the nomenclature and the differences between the various clay minerals (Murray 2007). The Grim's classification of clay minerals is as follows (Murray 2007):

1. Amorphous
   Allophane group
2. Crystalline
   (a) Two-layer type (sheet structures composed of units of one layer of silica tetrahedrons and one layer of alumina octahedrons)
      - Equidimensional:
        Kaolinite group
        Kaolinite, dickite and nacrite
      - Elongate
        Halloysite

   (b) Three-layer types (sheet structures composed of two layers of silica tetrahedrons and one central dioctahedral or trioctahedral layer)
      - Expanding lattice
         – Equidimensional
           Smectite group
           Sodium montmorillonite, calcium montmorillonite, and beidellite
           Vermiculite
         – Elongate
           Smectite
           Nontronite, saponite, hectorite
      - Non-expanding lattice
        Illite group

   (c) Regular mixed-layer types (ordered stacking of alternate layers of different types)
       Chlorite group
   (d) Chain-structure types (hornblende-like chains of silica tetrahedrons linked together by octahedral groups of oxygens and hydroxyls containing Al and Mg atoms)
       Sepiolite
       Palygorskite (attapulgite)

Another classification of clay minerals is based on the layer type and charge per formula unit, this classification is given in Table 2.1. 1:1 layer structure consists of a unit

**Table 2.1** Classification of clay minerals is based on the layer type and charge per formula unit

| Layer type | Group | Subgroup | Species |
|---|---|---|---|
| 1:1 | Kaolin-serpentine x = 0 | Kaolin | Kaolin, dickite, nacrite, halloysite |
| | | Serpentine | Chrysotile, lizardite, amesite |
| 2:1 | Pyrophyllite-talc x = 0 | Pyrophyllite | Pyrophyllite |
| | | Talc | Talc |
| | Smectite x = 0.2–0.6 | Montmorillonite (dioctaheralsmectite) | Montmorillonite, beidellite, nontronite |
| | | Saponite (trioctahedralsmectite) | Saponite, hectorite, |
| | Vermiculite x = 0.6–0.9 | Dioctaheral vermiculite | Dioctaheral vermiculite |
| | | Trioctaheral vermiculite | Trioctaheral vermiculite |
| | Mica x = 0.5–1.0 | Dioctaheral mica | Muscovite, illite, glauconite, paragonite |
| | | Trioctaheral mica | Phlogopite, biotite, lepidolite |
| | Brittle mica x = 2.0 | Dioctaheral brittle mica | Margarite |
| | | Trioctaheral brittle mica | Clintonite, anandite |
| | Chlorite x = variable | Dioctaheral chlorite | Donbassite |
| | | Di,trioctaheral chlorite | Cookeite, sudoite |
| | | Trioctaheral chlorite | Chlinochlore, chamosite, nimite |
| | Palygorskite-sepiolite x = variable | Sepiolite | Sepiolite |
| | | Palygorskite | Palygorskite |

*Note* x = charge per formula unit

made up of one octahedral and one tetrahedral sheet, with the apical $O_{2}$– ions of the tetrahedral sheets being shared with the octahedral sheet, while 2:1 layer structure consists of two tetrahedral sheets with one bound to each side of an octahedral sheet.

A simple classification of clay minerals also available in the literatures, in this classification clay mineral divided into four main groups: kaolinite group, illite group, smectite group, and vermiculite. Kaolinite group includes kaolinite, dickite, nacrite, and halloysite; formed by the decomposition of orthoclase feldspar (e.g. in granite). Illite group—also includes hydrous micas, phengite, brammalite, celadonite, and glauconite (a green clay sand); formed by the decomposition of some micas and feldspars; predominant in marine clays and shales. Smectite group—also includes montmorillonite, bentonite, nontronite, hectorite, saponite and sauconite.

Martin et al. (1991) provide a classification of clay minerals based on a scheme for planar hydrous phyllosilicate structures. These phyllosilicates are divided by layer type, and within layer type, by groups based on charge per formula unit, further subdivisions by subgroups based on dioctahedral or trioctahedral character, and finally by species based on chemical composition. The classification scheme is based on details of structure, and it also corresponds to a succession of stages of refinement in identification (Guggenheim et al. 2006). Table 2.2 summarizes the classification of clay minerals based on a scheme for planar hydrous phyllosilicate structures.

**Table 2.2** Classification of planar hydrous phyllosilicates (Guggenheim et al. 2006)

| Layer type | Interlayer material | Group | Octahedral character | Species |
|---|---|---|---|---|
| 1:1 | None or $H_2O$ only, x = 0 | Serpentine-kaolin | Trioctahedral | Lizardite, berthierine, amesite, cronstedtite, nepouite, kellyite, fraipontite, brindleyite. |
| | | | Dioctahedral | Kaolinite, dickite, nacrite, halloysite (planar) |
| | | | Di,trioctahedral | Odinite |
| 2:1 | None (x = 0) | Talc-pyrophyllite | Trioctahedral | Talc, willemseite, kerolite, pimelite |
| | | | Dioctahedral | Pyrophyllite, ferripyrophyllite |
| | Hydrated exchangeable cations (x = 0.2–0.6) | Smectite | Trioctahedral | Saponite, hectorite, sauconite, stevensite, swinefordite |
| | | | Dioctahedral | Montmorillonite, beidellite, nontronite, volkonskoite |
| | Hydrated exchangeable cations (x = 0.6–0.9) | Vermiculite | Trioctahedral | Trioctahedral vermiculite |
| | | | Dioctahedral | Dioctahedral vermiculite |
| | Non-hydrated monovalent cations, (≥55 % monovalent, x = 0.85–1.0 for dioctahedral) | True (flexible) mica | Trioctahedral | Annite, phlogopite, lepidolite, aspidolite |
| | | | Dioctahedral | Muscovite, celadonite, paragonite |
| | Non-hydrated mono- or divalent cations (x = 0.6–0.85) | Interlayer-deficient mica | Trioctahedral | Illite, glauconite, brammallite |
| | | | Dioctahedral | Wonesite |
| | Non-hydrated divalent cations, (≥55 % divalent, x = 1.8–2.0) | Brittle mica | Trioctahedral | Clintonite, kinoshitalite, bityite, anandite |
| | | | Dioctahedral | Margarite, chernykhite |
| | Hydroxide sheet (x = variable) | Chlorite | Trioctahedral | Clinochlore, chamosite, pennantite, nimite, baileychlore |
| | | | Dioctahedral | Donbassite |
| | | | Di,trioctahedral | Cookeite, sudoite |

(continued)

**Table 2.2** (continued)

| Layer type | Interlayer material | Group | Octahedral character | Species |
|---|---|---|---|---|
| 2:1 | Regularly interstratified (x = variable) | Variable | Trioctahedral | Corrensite, aliettite, hydrobiotite, kulkeite |
| | | | Dioctahedral | Rectorite, tosudite, brinrobertsite |
| 1:1, 2:1 | | | Trioctahedral | Dozyite |

## 2.1.2 *Structures and Characteristic of Clay Minerals*

The individual clay mineral particles look like tiny plates which consist of many crystal sheets which have a repeating atomic structure. The atomic structure consists of octahedral or alumina sheets and tetrahedral or silica sheets. The octahedral sheet is basically a combination of closely packed six hydroxyls or oxygen enclosing a metal atom (aluminum, magnesium, iron or other atom) (Murray 2007).

The tetrahedral or silica layer comprised of silica tetrahedral units which consist of four oxygen or possibly hydroxyl atoms at the corners, surrounding a single silicon atom. These tetrahedrons are arranged to form a hexagonal network repeated infinitely in two horizontal directions to form what is called the silica tetrahedral sheet (Murray 2007).

The basic building block of all clay minerals is the same; they consist of two basic structures: the tetrahedral and octahedral sheets which are stacked together in certain ways. The variation of the basic structures makes the composition of major clay minerals (smectites, kaolin, palygorskite, sepiolite) is very different. The structures and characteristics of several clay minerals are discussed in the subsequent paragraphs.

Allophane is a generic term for amorphous hydrated aluminosilicate with a Si:Al ratio of ≈1–2. Allophane is a derivative of the weathering of volcanic ash. Allophane group is naturally occurring hydrous aluminosilicate minerals that are not totally amorphous but are short-range (partially) ordered. The empirical formula of allophane is $(Al_2O_3)(SiO_2)_{1.3}\cdot 2.5(H_2O)$. The main characteristic of the allophane structure is the dominance of Si–O-Al bonds in which the most of the aluminum atoms are arranged in both of tetrahedral and hexahedral coordinations. The Al:Si ratio of allophane is normally between 2 and 3 Allophane particles appears as rings and three dimensionally may be hollow spherules or polyhedrons with a diameter of 35–50 Å and wall thickness of 10 Å or less (Henmi and Wada 1976). In the allophane structure, the aluminum enters octahedral coordination and Si is present in tetrahedral coordination.

Kaolinite group—includes kaolinite, dickite, nacrite, and halloysite; formed by the decomposition of orthoclase feldspar (e.g. in granite). Dickite and nacrite are rather rare and usually are found mixed with kaolinite in deposits of hydrothermal origin (Murray 2007). The structure of the kaolinite group composed of units of one

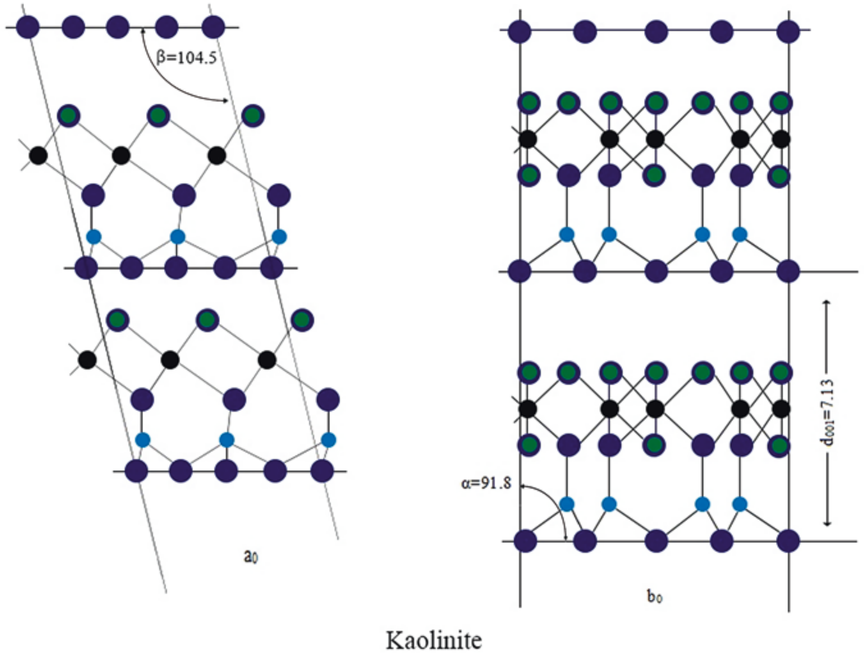

**Fig. 2.1** Schematic diagram of kaolinite structure (redrawn based on Murray 2007)

layer of silica tetrahedrons and one layer of alumina octahedrons. Kaolinite is called as 1:1 clay mineral due to the stacking of one layer of each of the two basic sheets. The schematic diagram of Kaolinite structure is given in Fig. 2.1. Kaolinite, dickite and nacrite possess similar chemical composition, and this kaolinite group has the molecular formula $Al_2Si_2O_5(OH)_4$. The chemical composition of the kaolinite group majority is $SiO_2$, $Al_2O_3$, $H_2O$ and minor amounts of Mg, K, Fe, Ti, etc. The differences in the kaolin minerals are the manner in which the unit layers are stacked above each other with the thickness of the unit layer around 7.13 Å (Murray 2007).

Dickite is a monoclinic crystal system with the unit cell consists of two unit layers, in which a shared layer of corner-sharing tetrahedra filled by a plane of oxygens and hydroxyls along with a sheet of edge-sharing octahedra with every third site left empty. Dickite possesses perfect cleavage in the (001) direction. Nacrite also has a monoclinic crystal system with irregular pseudo-hexagonal and aggregates plates. Similar to dickite, nacrite also has perfect cleavage in the (001) direction. Halloysite exists in two forms: hydrated form and dehydrated form.

The hydrated form of halloysite has the basal spacing 10 Å, while in the dehydrated form it has the basal spacing 7.2 Å. Naturally, the crystal of halloysite is in the form of small cylinder with the average diameter of 300 Å and lengths between 0.5 and 10 μm (Brindley 1952).

Kaolin is one of the important clay in kaolinite group for industrial application. This clay mineral is also the principal constituent in china clay. The main constituent of kaolin is kaolinite mineral. The primary industrial application of kaolin is in the paper making as the coating and paper filler. As filler, the kaolin is mixed with the cellulose fibers in wood pulp and as a coating; the kaolin is mixed with water, adhesives, and various additives and coated onto the surface of the paper (Murray 2007). Kaolin is also widely used as filler in the plastics industry because of its inert chemical nature and its unique size, shape and structure. Due to the white color, fine particle size and plate-like structure, kaolin is suitable as the pigment for paint, ceramic raw material, functional filler, extender, cosmetic, food additive, adhesives, Portland cement, sealant, etc. It also holds importance as a raw material in refractory applications, catalysts, concrete, fiberglass, and can be employed as the adsorbent for removal of organic compounds.

The structure and composition of smectite are different with kaolinite, therefore both of these clays possess different physical and chemical properties. Smectites are one of the largest and most important classes of the phyllosilicate clay-mineral group. The Equidimensional smectite group includes sodium montmorillonite, calcium montmorillonite, beidellite (aluminum montmorillonite) and vermiculite, while elongate smectite includes nontronite (iron montmorillonite), saponite (magnesium montmorillonite), and hectorite (lithium montmorillonite). The basic structural unit of smectite clay is a layer consisting of two inward-pointing tetrahedral sheets with a central alumina octahedral sheet (Fig. 2.2). The layers are continuous in the *a* and *b* directions, but the bonds between layers are weak and have excellent cleavage, allowing water and other molecules to enter between the layers causing expansion in the *c* direction (Grim 1962). In the octahedral layer of

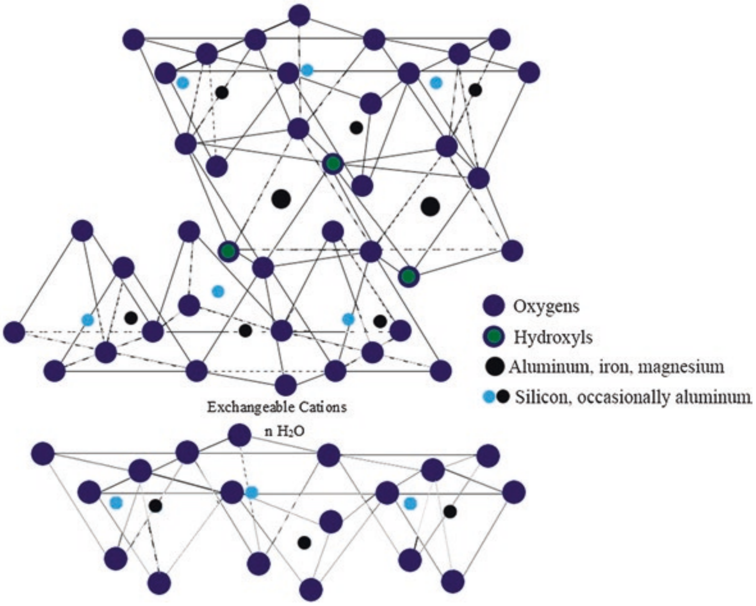

**Fig. 2.2** The structure of smectite clay (redrawn based on Murray 2007)

the smectite in which all three octahedral positions are filled is called trioctahedral and when only two-thirds of the possible positions are filled is called dioctahedral (Murray 2007).

The general molecular formula of smectite group is $(Ca,Na,H)(Al,Mg,Fe,Zn)_2(Si,Al)_4O_{10}(OH)_2$-$xH_2O$. One characteristic in smectite clay is considerable substitution in the octahedral sheet and some of the tetrahedral sheet. In the octahedral sheet there is substitution of magnesium and iron for aluminum, while substitution of aluminum for silicon occurs in the tetrahedral sheet. If the octahedral positions are mainly filled with aluminum, the smectite mineral is beidellite; if filled with magnesium, the mineral is saponite; if by iron, the mineral is nontronite and if it is filled with lithium the clay mineral called as hectorite (Murray 2007).

Calcium montmorillonite and sodium montmorillonite are the most important clay minerals in smectite group. The main structural difference between calcium and sodium montmorillonite is at the water layer, calcium montmorillonite possesses two water layers in the interlayer position while for sodium montmorillonite only have one water layer (Murray 2007). With only one water layer in the interlayer position, sodium montmorillonite has significantly different properties with calcium-bentonite. Sodium montmorillonite has the much higher swelling capacity and viscosity than calcium montmorillonite.

Several applications of smectite minerals are as follow: Adsorbents, adhesives, animal feed bonds, bleaching earths, barrier clays, catalysts, cement, ceramics, cosmetics, deodorizer, drilling fluids, dessicants, detergents, emulsion stabilizer, food additives, foundry bonds, herbicide carrier, industrial adsorbents, insecticide carrier, medicines, nanoclays, organo-clays, paint, paper, pesticides carrier, pharmaceuticals, pillared clays, plasticizers, sealants, seed growth, soil stabilization, etc.

Illite is an important constituent of clay soils. Illite group includes hydrous micas, phengite, brammalite, celadonite, and glauconite (green clay sand); formed by the decomposition of some micas and feldspars. In the term of substitution of $Al^{3+}$ for $Si^{4+}$ in tetrahedral sheet, illite differs from muscovite. In illite only one-sixth of of the $Si^{4+}$ is replaced by $Al^{3+}$, while in muscovite one-fourth is replaced (Muray 2007). The structure of illite is comprised of a silica-gibbsite-silica sandwich, with the tips of the silica tetrahedra pointing towards the octahedral gibbsite sheet and the oxygen at the tips being common with the octahedral sheet. Isomorphous substitution of aluminium for silicon in the tetrahedral sheet results in a negative charge on the surface of these layers. This charge is balanced by potassium, cesium and ammonium ions between the 2:1 layers; these ions fit tightly in the 1.32-Angstrom-radius holes in the bases of the silica sheet and as a result are fixed in position and are not exchangeable (Mukherjee 2013). The schematic structure of illite is shown in Fig. 2.3. The general formula of illite is $K_yAl_4(Si8_{-y},Al_y)O_{20}(OH)_4$, the value of y usually between 1 and 1.5. Due to possible imbalance of charge, sometimes Ca and Mg can also substitute for K. Illite clays are non-expanding clays due to the presence of K (or sometime Ca and Mg) interlayer cations which prevent the intrusion of water molecules into the clay structure.

Chlorite is commonly present in shales and also in underclays associated with coal seams (Murray 2007). Chlorite group includes baileychlore, borocookeite,

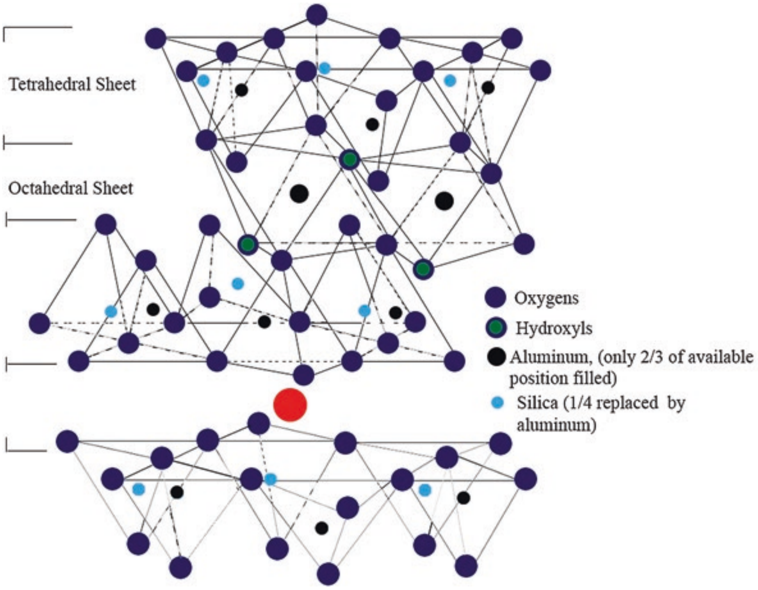

**Fig. 2.3** Schematic diagram of illite structure (redrawn based on Murray 2007)

chamosite, clinochlore, cookeite, donbassite, franklinfurnaceite, nimite, orthochamosite, and sudoite. The structure of chlorite group mostly monoclinic (triclinic or orthorhombic sometimes also can be found) micaceous phyllosilicate minerals with a structure consisting of tetrahedral—octahedral—tetrahedral (2:1) layers. The silicate tetrahedral layers apices pointing towards each other, separated by an interlayer that may be simple octahedrally coordinated cations or which may be a brucite ($Mg(OH)_2$) layer of two sheets of closely packed OH groups with the interstices between sheets providing the octahedral coordination site.

The simple chemical formula of the common member of chlorite group is $(Mg,Fe,Li)_6AlSi_3O_{10}(OH)_8$. Individual group members also have their own chemical formula such as: chamosite $(Fe^{2+},Mg)_5Al(AlSi_3O_{10})(OH)_8$, cookeite $LiAl_5Si_3O_{10}(OH)_8$, orthochamosite $(Fe^{2+},Mg,Fe^{3+})_5Al(AlSi_3O_{10})(OH,O)_8$, clinochlore $(Mg,Fe^{2+})_5Al_2Si_3O_{10}(OH)_8$.

Due to its special properties, palygorskite and sepiolite have a wide range of industrial applications. Palygorskite and sepiolite are 2:1 layer silicates which contain a continuous two dimensional tetrahedral sheet and octahedral sheets only continuous in one dimension. The tetrahedral sheets are divided into ribbons, and each ribbon is linked to the next ribbon by inversion of $SiO_4$ tetrahedral along a set of Si–O–Si bonds. In sepiolite, the ribbons extend parallel to the X-axis and have an average width along Y of three linked pyroxene-like single chains while in palygorskite the average width of the ribbons is two linked chains (Galan 1996).

Sepiolite has larger channels between the ribbon strips then palygorskite as indicated in Fig. 2.4, and these channels may also contain exchangeable cations. The chemical formula of palygorskite $Mg_5Si_8O_{20}(OH)_2(OH_2)_4{\cdot}4H_2O$ while

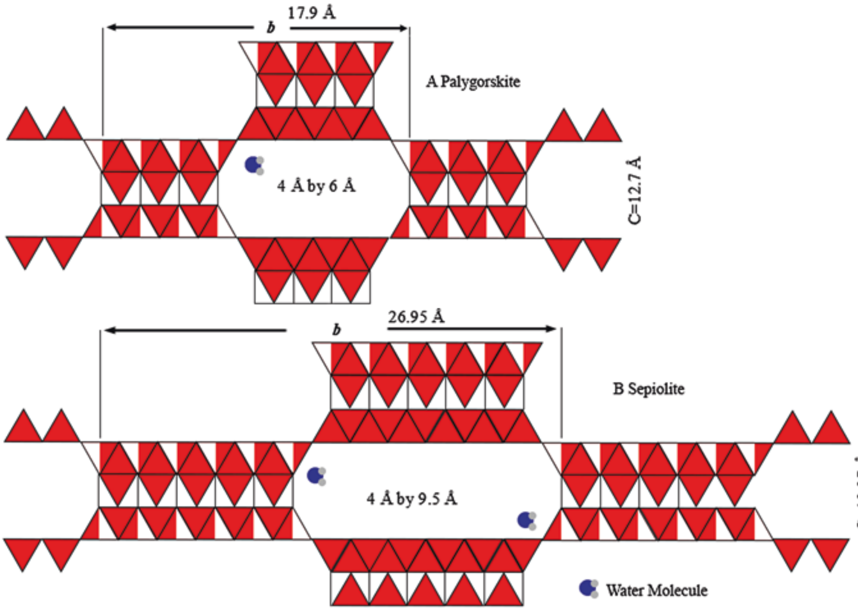

**Fig. 2.4** The structure of *A* palygorskite and *B* sepiolite (redrawn based on Murray 2007)

for sepiolite $Mg_8Si_{12}O_{30}(OH)_4(OH_2)_4{\cdot}8H_2O$. The cation exchange capacity of both palygorskite and sepiolite is quite low, just around 4–40 meq/100 g. Since palygorskite and sepiolite have a high surface area and in its structures contains micropore, both of these clay minerals are widely used as an adsorbent. Due to their high surface area, thermal stability and mechanical strength, palygorskite and sepiolite are also used as catalysts or catalyst supports. Other applications of these clay minerals are: organo-mineral derivatives, filler, paints, adhesive, sealant, fertilizer suspensions, cosmetics, drilling muds, anti-caking agent, animal nutrition applications, decolorizing material, etc. (Galan 1996).

### 2.1.3 Properties of Clay Minerals

The existence of charge in clay minerals is the basis for cation exchange and the swelling properties of the minerals. The tetrahedral and octahedral sheets of clay minerals usually possess a charge. The charge in the clay minerals exists in two forms: structural and surface charge. The structural charge is permanent and exists due to ion substitutions while the surface charges, usually depends on the value of pH. The structural charge originates within the interior of the layers. In clay minerals with 2:1 layer, the surface charge originates on the basal surface of tetrahedral sheets, while for clay with 1:1 layer type the surface charge come from both of tetrahedral and octahedral sheets. The edges of the sheets of both 1:1 and 2:1 clay also contribute the surface charge (Eslinger and Pevear 1988).

The hydrolysis of Si–OH or Al–OH bonds along the clay lattices produces the surface charge. Depending on the silica structure and the pH of the solution, the net surface charge can be either positive or negative. At pH less than $pH_{pzc}$, the clay would have an anion exchange capacity, while at pH higher than $pH_{pzc}$, the clay would have a cation exchange capacity.

$$\mathrm{SiOH} + \mathrm{H}^+ \rightarrow \mathrm{SiOH}_2^+ \quad \left(\mathrm{pH} < \mathrm{pH}_{\mathrm{pzc}}\right)$$

$$\mathrm{SiOH} + \mathrm{OH}^- \rightarrow \mathrm{SiO}^- + \mathrm{H_2O} \quad \left(\mathrm{pH} > \mathrm{pH}_{\mathrm{pzc}}\right)$$

For 2:1 layer type clay minerals, the contribution of surface charge to total charge just less than 1 %, but for 1:1 layer type clay minerals, the surface charge contributes a major portion to total charge (Eslinger and Pevear 1988).

In kaolinite structure, only two-thirds of the octahedral positions are filled by an aluminum atom. The aluminum atoms are surrounded by four oxygen and eight hydroxyls and the charges on the structure are balanced as seen in the charge distribution layer (Table 2.3). Therefore, the kaolinite is electrically neutral (Eslinger and Pevear 1988; Murray 2007). The charge distribution of the smectite layer is given in Table 2.4.

As mentioned previously, the $pH_{pzc}$ of clay minerals determines the anion or cation exchange ability. The $pH_{pzc}$ is the pH at which the total net charge is zero (point zero charge). At the $pH_{pzc}$ the surface could be uncharged or charged with

**Table 2.3** Charge distribution of the kaolinite layer (Murray 2007)

| Ion | Number of ions | Total charge |
|---|---|---|
| $O^{2-}$ | 6 | −12 |
| $Si^{4+}$ | 4 | +16 |
| $O^{2-} + (OH)^-$ | 4 $O^{2-}$ and 2 $(OH)^-$ | −10 (layer shared by the tetrahedral and octahedral sheets) |
| $Al^{3+}$ | 4 | +12 |
| $(OH)^-$ | 6 | −6 |

**Table 2.4** Charge distribution of the smectite layer (Murray 2007)

| Ion | Number of ions | Total charge |
|---|---|---|
| $O^{2-}$ | 6 | −12 |
| $Si^{4+}$ | 4 | +16 |
| $O^{2-}$ and $(OH)^-$ | $4O^{2-}$ and $2(OH)^-$ | −10 (layer shared by the tetrahedral and octahedral sheets) |
| $Al^{3+}$ | 4 | +12 |
| $O^{2-}$ and $(OH)^-$ | $4O^{2-}$ and $2(OH)^-$ | −10 (layer shared by the tetrahedral and octahedral sheets) |
| $Si^{4+}$ | 4 | +16 |
| $O^{2-}$ | 6 | −12 |

**Table 2.5** $pH_{pzc}$ of several clay minerals

| Clay minerals | Origin | $pH_{pzc}$ | References |
|---|---|---|---|
| Kaolin | Georgia, USA | 3.00 | Tschapek et al. (1974) |
| Illite | Zhejiang, China | 2.50 | Wang et al. (2008) |
| Kaolinite | Nigeria | 4.40 | Unuabonah et al. (2008) |
| Bentonite | Fluka | 3.00 | Anirudhan et al. (2008) |
| Montmorillonite | Milos, Greece | 9.40 | Balomenou et al. (2008) |
| Ca-bentonite | Pacitan, Indonesia | 3.85 | Putra et al. (2009) |
| Montmorillonite | Sigma Aldrich | 3.40 | Ijagbemi et al. (2009) |
| Montmorillonite | Sipovo, Bosnia | 7.70 | Dakovic et al. (2012) |
| Smectite | Tunisia | 8.20 | Arfaoui et al. (2012) |
| kaolinite | Thailand | 4.00–5.00 | Khawmee et al. (2013) |

**Table 2.6** CEC values of several clay minerals

| Clay mineral | CEC, meq/100 g |
|---|---|
| Allophane | 70 |
| Kaolinite | 3–15 |
| Halloysite ($2H_2O$) | 5–10 |
| Sodium montmorillonite | 80–130 |
| Calcium montmorillonite | 40–70 |
| Hectorite | 80–130 |
| Palygorskite | 30–40 |
| Sepiolite | 30–40 |
| Illite | 10–40 |
| Vermiculite | 100–150 |

equal densities of positive and negative charges. The $pH_{pzc}$ of several clay minerals can be seen in Table 2.5.

Cation exchange capacity (CEC) is one of the important properties in clay minerals. CEC is a measure of the capacity of clay minerals to exchange cations from the solution. CEC is also a measure of the concentration of unfixed cations in the interlayers and surface layers, which depends on the magnitude of the total layer charge. Since the surface layer charge is the function of pH, thus, CEC also varies with pH and usually CEC is measured at pH 7 (Eslinger and Pevear 1988). CEC values of several clays are given in Table 2.6. The common metallic cations found in exchange positions in clay minerals are $Ca^{2+}$, $Mg^{2+}$, $Na^{+}$, and $K^{+}$.

## 2.2 Selective Pollutant Gas Adsorption by Clay Minerals

Many investigations have been made of the sorption of non-polar and polar gases and vapor molecules by various forms of clay minerals. Various industrial activities release a number of toxic gases pollutants. The abatement of gaseous pollutants, especially volatile organic compounds using thermal oxidation are expensive due to the high energy requirement. The more efficient process by combining with adsorption technology has been developed to improve the efficiency of thermal or catalytic oxidation (Pires and Pinto 2010). Activated carbons are considered as good adsorbents for the removal of those toxic gaseous pollutants; however, the main drawback of these adsorbents is in their combustion property (combustible) which create the difficulties during the regeneration process. Clay minerals are another type of adsorbents that can be used for toxic gaseous pollutant abatement.

Pillared clays have intermediate hydrophobic–hydrophilic properties between activated carbons and the more common zeolites and could be an interesting alternative as adsorbents for toxic gaseous pollutant removal or abatement (Pires and Pinto 2010). Pillared clays are obtained by cation exchange between the alkali cations (generally $Na^+$) of the original clay and hydroxy metal cations from a solution in which the clay is dispersed (Pinnavaia 1983). Table 2.7 summarizes a number of studies on the adsorption of volatile organic compounds onto clays and pillared clays.

Hydrogen sulfide is a colorless gas with the characteristic of rotten egg odor; it is very corrosive, flammable, poisonous, and explosive. The hydrogen sulfide also classified as a noxious gaseous pollutant. A number of studies utilized the clay minerals for the removal of this gas from the environment (Molina-Sabio et al. 2004; Thanh et al. 2005; Stepova et al. 2009; Batista et al. 2014; Zhang et al. 2014). The adsorption of $NH_3$ and $H_2S$ onto activated carbon-sepiollite pellets was studied by Molina-Sabio et al. (2004). In this case, the sepiolite acts as a binder and as the adsorbent. The adsorption isotherm of $H_2S$ on activated carbon—sepiollite has a shape very similar to combination of activated carbons and sepiolite. The

**Table 2.7** Adsorption of volatile organic compounds onto clays and pillared clays

| VOC | Clay mineral | Type of pillars | Amount adsorbed, $cm^3/g$ | Reference |
|---|---|---|---|---|
| Benzene | Montmorillonite | $SiO_2$–$TiO_2$ | 0.100 $cm^3/g$ | Yamanaka et al. (1992) |
| Cyclohexane | | | 0.065 $cm^3/g$ | |
| *n*-Hexane | | | 0.09 $cm^3/g$ | |
| Benzene | Montmorillonite | $Cr_2O_3$ | 0.13 $cm^3/g$ | Sychev et al. (2001) |
| Benzene | | $TiO_2$ | 0.14 $cm^3/g$ | |
| *p*-xylene | Na-montmorillonite | – | 21.314 mg/g | Çakanyıldırım and Cabbar (2008) |
| Toluene | Montmorillonite | Si–$TiO_2$ | 2.23 mg/g | Chen et al. (2011) |
| Ethyl acetate | | | 3.41 mg/g | |
| Ethanethiol | | | 4.50 mg/g | |
| Acetone | Na-montmorillonite | Al/Ce | 0.4898 mmol/g | Zuo et al. (2012) |
| Benzene | | | 0.0442 mmol/g | |
| Ethylbenzene | | | 0.0405 mmol/g | |
| *n*-Hexane | Montmorillonite | – | 0.185 $cm^3/g$ | Morozov et al. (2014) |
| Benzene | | – | 0.179 $cm^3/g$ | |

low uptake of $H_2S$ by activated carbon—sepiollite pellets compared to activated carbon indicated that sepiolite possesses the lower adsorption capacity (Molina-Sabio et al. 2004).

The modification of Na-bentonite with iron in order to introduce active centers for hydrogen sulfide adsorption was conducted by Thanh et al. (2005). The pillared clay samples were tested as hydrogen sulfide adsorbents. Iron-doped samples showed a significant improvement in the capacity for $H_2S$ removal, despite of a noticeable decrease in microporosity compared to the initial pillared clay. The smallest capacity was obtained for the clay modified with iron oxocations. Variations in adsorption capacity are likely due to differences in the chemistry of iron species, the degree of their dispersion on the surface, and accessibility of small pores for the $H_2S$ molecule (Thanh et al. 2005).

A few numbers of studies were made considering the adsorption of ammonia gas, which is also considered as a dangerous gaseous pollutant (Molina-Sabio et al. 2004; Benco and Tunega 2009). In the work of Molina-Sabio et al. (2004), the activated carbon—sepiollite was employed as the adsorbent for ammonia gas removal. Very strong interaction between sepiolite and $NH_3$ was observed. Sepiollite has special affinity towards $NH_3$ (Dandy 1971), specific interactions between ammonia with the acid groups of the sepiollite surface produces very strong adsorption energy (Molina-Sabio et al. 2004).

## 2.3 Adsorption of Hazardous Substances from Aqueous Solution Using Clay Minerals

### *2.3.1 Adsorption of Heavy Metals*

The presence of heavy metals in air, soil and water is known to be harmful to living species. Several heavy metals of highest concern include: mercury, arsenic, lead, cadmium, chromium, copper, cobalt, manganese, nickel, and tin. Some heavy metals such as iron, selenium, copper, zinc, molybdenum in the certain amount are essential to humans for the metabolism. In view of the human health impacts, each metal imparts different effects and symptoms. Mercury (Hg) has been identified to cause damage to the nervous system, kidneys, and vision. Lead (Pb) is one of the most lethal heavy metals; it causes anemia, damage to the kidneys, nervous system deterioration, damage the ability to synthesize protein, etc. Arsenic (As) Causes damage to skin, eyes, and liver, may also cause cancer. The expose of Cadmium to human cause severe health risks such as provoke cancer, mucous membrane destruction, kidney damage, bone damage, and also affects the production of progesterone and testosterone.

The source of heavy metals in the environment comes from natural sources, mining activities, industrial activities, Agrochemicals, wastewater treatment system, etc. Mercury (Hg) enter the environment through various routes such as coal burning, household, e leaching of soil due to acid rain, and industrial activities.

The sources of lead (Pb) include mining waste, automobile exhaust, industries, incinerator ash, and water from lead pipes, while the sources of cadmium (Cd) are electroplating, mining, plastic industries, and sewage.

Various kinds of adsorbents ranging from agricultural waste to industrial by-products have been explored for the removal of heavy metals from aquatic environments and the results indicate that they may be an alternative to more costly materials such as commercial activated carbons or synthetic ion exchange resins. Even though those alternative adsorbents are abundantly available and cheap, the major drawback of these adsorbents is poor adsorption capacity.

Clay and clay minerals have also been explored as the adsorbents for the removal of heavy metals from aqueous solution. The advantages of using clay minerals as the alternative adsorbents for the removal of heavy metals are high ion sorption/exchange capacity, low permeability, swelling ability, chemical and mechanical stability, and large specific surface area. Different types of clay minerals have been tested for the removal of heavy metal ions from water and wastewater. Table 2.8 summarizes recent studies of utilization clay minerals as the adsorbent for heavy metals removal.

**Table 2.8** Recent studies of the removal heavy metals using clay minerals

| Clay mineral | Heavy metal | Remarks | References |
|---|---|---|---|
| Bentonite | Zn(II) | Bentonite was modified with HCl | Hajjaji and El Arfaoui (2009) |
| Montmorillonite | Cr(VI) | Effect of activation and modification on the adsorption performance was studied | Akar et al. (2009) |
| Bentonite | Pb(II) | The bentonite was pillared by $MnCl_2$ | Eren et al. (2009) |
| Montmorillonite | Cu(II) | The bentonite was pillared by poly-hydroxyl ferric | Wu et al. (2009) |
| Kaolin | Pb(II) | The influences of initial concentration, pH, equilibration time, dosage and temperature on the adsorption performance were studied | Tang et al. (2009) |
| Palygorskite | Cd(II) | Palygorskite was also modified with HCl | Frini-Srasra and Sasra (2010) |
| Bentonite | Pb(II) | Bentonite was modified with HCl | Kul and Koyuncu (2010) |
| Montmorillonite | As(III) and As(V) | Montmorillonite was pillared by $TiCl_4$ | Na et al. (2010) |
| Kaolinite and montmorillonite | Cu(II) | Clay minerals were modified with $H_2SO_4$ | Bhattacharyya and Gupta (2011) |
| Kaolin | Cr(III) | kaolin-supported bacterial biofilm of Bacillus sp | Fathima et al. (2012) |
| Bentonite | Ni(II) and Cd(II) | Chitosan-clay was crosslinked to epichlorohydrin | Tirtom et al. (2012) |

(continued)

**Table 2.8** (continued)

| Clay mineral | Heavy metal | Remarks | References |
|---|---|---|---|
| Kaolinite | Pb(II) | The Kaolinite was modified with polyvinyl alcohol | Unuabonah et al. (2012) |
| Montmorillonite | Cu(II) | Chitosan-montmorillonite beads were prepared by crosslinking with pentasodium tripolyphosphate. | Pereira et al. (2013) |
| Montmorillonite | Co(II) | Montmorillonite was modified with chitosan | Wang et al. (2014) |
| Vermiculite | Hg(II) | To study the influence of humic acid on the adsorption performance | Nascimento and Masini (2014) |
| Smectite, Illite, calcite | Cu(II), Zn(II) | To evaluate the adsorptive capacity of three different natural clays | Musso et al. (2014) |
| Kaolinite | Cd(II) | The Kaolinite was pillared using $MnO_2$ | Sari and Tuzen (2014) |
| Kaolinite | Pb(II) and Cd(II) | Cd(II) and Pb(II) sorption isotherms were performed at different pH value | Mascia et al. (2014) |
| Montmorillonite | Hg(II) | Influence of pH, ionic strength and the treatment with different cations | Dos Santos et al. (2015) |

The adsorption of heavy metals from aqueous solution using clay minerals are influenced by several factors such as pH, temperature, the presence of other compounds, initial concentration, etc. The pH of the solution is a crucial factor in the adsorption of heavy metals onto clay minerals. As mentioned in the previous section, the surface layer charge of the clay minerals varies with the pH and the exchange capacity also as a function of pH. The pH value significantly influences the solution chemistry of heavy metals (precipitation, hydrolysis, complexation, redox reaction, etc.). In certain range of pH, the uptake of heavy metals by the clay minerals increases with the increase of pH to certain value and then followed by reduction of the amount uptake on a further increase of pH.

Dos Santos et al. (2015) studied the effect of pH and ionic strength on the removal of Hg(II) using montmorillonite as the adsorbent. The study was conducted at a range of pH from 2 to 8 (Na-montmorillonite and K10 montmorillonite) and at a pH from 3 to 8 for Ca-montmorillonite. The pH of the solution influences the surface charge of the clay minerals. At the pH below the $pH_{pzc}$ of the clay mineral, the surface of the clay mineral becomes positively charged, and the ion exchange between Hg(II) and $Ca^{2+}$, $Na^+$, or $K^+$ on the surface of montmorillonites can lead the adsorption of Hg(II) on montmorillonites. The decrease in the Hg(II) adsorption by all of the montmorillonites with increasing of $[H^+]$ (low pH) is indicative of a competitive ion exchange between $H^+$ and Hg(II) to the cations on the surface of montmorillonite. However, at pH above 8, the formation of metal hydroxides or intermediate species occurred, hindering to estimate the decrease of the ion concentration in solution (Dos Santos et al. 2015).

Temperature is also one crucial process parameter in the adsorption of heavy metals onto clays. Depending on the structure of clay minerals, the temperature has an impact on the adsorption capacity, to a certain extent. In the case of physical adsorption the temperature is known to have a negative effect on the amount uptake by the adsorbent, the amount uptake decreases with the increase in temperature. However, if the chemisorption is the control mechanism, Increasing in temperature also increase the amount uptake by the adsorbent.

A number of adsorption studies have been performed concerning the effect of temperature on the metal uptake. The impact of temperature on the adsorption of Pb(II) by natural and activated bentonite at a certain pH was examined by Kul and Koyuncu (2010). They found that the uptake of the metal ions increased with the increase of temperature. This trend was also reported by other research groups (Dal Bosco et al. 2006; Unuabonah and Adebowale 2009; Nathaniel et al. 2011; Sandy et al. 2012; Rivera-Hernandez and Green-Ruiz 2014). In contrast, Na et al. (2010) obtained the opposite behavior for the temperature effect on adsorption capacity. In her study, higher temperature leads to a lower adsorption capacity of Ti-pillared montmorillonite.

The use of allophane as the raw material for industrial applications and construction is scarcely reported. However, due to its surface characteristic and cation exchange capacity, this clay mineral can be used as adsorbent for contaminant removal from water and wastewater. It has good adsorption capacity toward phosphorus (Yuan and Wu 2007; Elsheikh et al. 2009), and Arsenate (As(V)) (Arai et al. 2005; Shukla et al. 2011).

### *2.3.2 Adsorption of Dyes*

Dyes have been used by human since the beginning of human civilization, and all colorant used were from natural origin. Synthetic dye manufacturing started in 1856, and in the early of 20th century, synthetic dyestuffs had almost completely supplanted natural dyes. Based on their structure, synthetic dyes can be classified into 20–30 groups such as azo (monoazo, diazo, triazo, polyazo), anthraquinone, phthalocyanine, triarylmethane, diarylmethane, indigoid, azine, oxazine, thiazine, xanthene, nitro, nitroso, methine, thiazole, indamine, indophenol, lactone, aminoketone, etc.

The largest class of synthetic dyes in the color index is acid dyes, and this class of dyes is anionic compounds and mostly is azo, anthraquinone or triarylmethane groups. Reactive dyes are dyes with reactive groups that form covalent bonds with OH-, NH-, or SH-groups in fibers. The reactive group is often a heterocyclic aromatic ring substituted with chloride or fluoride, e.g. dichlorotriazine. Another common reactive group is vinyl sulphone. Other classes of dyes are metal complex dyes, direct dyes, basic dyes, mordant dyes; disperse dyes, pigment dyes, vat dyes, anionic dyes and ingrain dyes, sulfur dyes, solvent dyes and fluorescent brighteners.

Many dyes are visible in the water even at very low concentrations (1 ppm). As dyes are designed to be chemically and photolytically stable, they are highly persistent in natural environments. The release of dyes may therefore present an ecotoxic hazard and introduces the potential danger of bioaccumulation that may eventually affect man by transport through the food chain. Depending on their chemical structures, some of synthetic dyes are very toxic to human and environment. Some of the available synthetic dyes are carcinogenic, mutagenic, or teratogenic to aquatic biota and human. Long exposure of chromium based dyes causes severe damage to kidney, liver, central nervous system, and reproductive system. Azo dyes are toxic because their presence in water environment will release toxic amines. Anthraquinone based dyes are very resistant to degradation and its color will fade away for a long time. Reactive dyes are very stable dyes due to its chemical structure, and very resistant to biodegradation.

A number of physical, chemical, and biological pre-treatment technologies are available and can be employed to remove color from dye containing wastewaters such as chemical oxidation, coagulation, adsorption, aerobic and anaerobic microbial degradation, membrane separation, etc. For a low concentration of dye, the adsorption using various adsorbents is still the best choice for the treatment of water or wastewater.

A large number of studies have been dedicated to finding suitable and cheap adsorbents for the treatment or removal of dyes from water and wastewater, however, industrial scale application is still limited due to lack of comprehensive feasibility study of a potential dye adsorbent and also the complexity of the adsorption systems. Some of clay minerals possess a high adsorption capacity towards several classes of dyes and their adsorption capabilities are comparable to those activated carbons. Recent studies of the adsorption of dyes using clay minerals and its modified forms are summarized in given in Table 2.9. From Table 2.9 it can be seen that some of natural clay minerals (mostly is montmorillonite/bentonite) show significant dye removal capacities; while others still need modification in order to enhance its adsorption capacities. The adsorption performance of clay minerals and its modified forms also depend strongly on class of dye. Many of natural clay minerals have a high adsorption capacity for binding basic (cationic) dyes (Hajjaji and Arfaoui 2009; Kurniawan et al. 2011) but often hardly to remove dyes from other groups or classes of dyes.

Similar to the other liquid phase adsorption systems, the factors that affecting the adsorption of dyes onto clay minerals and its modified forms are solution pH, temperature, initial dye concentration, the presence of other substances, etc. In most liquid phase adsorption system, the efficiency of adsorption is dependent on the pH of the system, the variation of pH leads to the variation of surface charge of the adsorbent and the degree of ionization of the absorbing molecule. The adsorption ability of the surface and the type of surface active centers are indicated by the significant factor that is $pH_{pzc}$ (Yagub et al. 2014).

Bhattacharyya et al. (2014a) studied the adsorption of Rhodamine B from aqueous solution using kaolinite and montmorillonite. The adsorption experiments were conducted at a pH range from 2 to 12. The $pH_{pzc}$ of kaolinite and

**Table 2.9** Several recent studies of the removal of dyes from aqueous solution using clay minerals or its modified forms

| Clay | Dye | Performance | References |
|---|---|---|---|
| Bentonite | Methylene blue | Maximum adsorption capacity of bentonite 2.22 mmol/g, after acid activation the adsorption capacity decreases to 1.56 mmol/g | Hajjaji and Arfaoui (2009) |
| Attapulgite | Congo red | Maximum adsorption capacity of HTMA-bentonite 189.39 mg/g | Chen and Zhao (2009) |
| Bentonite | Acid green 25 | Maximum adsorption capacity of CTA-bentonite 3.723 mmol/g | Koswojo et al. (2010) |
| Bentonite | Reactive red 120 | Adsorption capacity of cetylpyridinium-bentonite 81.97 mg/g | Tabak et al. (2010) |
| Bentonite | Acid blue 12 | Adsorption capacity of bentonite of bentonite 0.76 mmol/g, and for CTA-bentonite 2.76 mmol/g | Yesi et al. (2010) |
| Na-montmorillonite | Methyl orange | Adsorption capacity of Na-montmorillonite 22.83 mg/g, modified by cethyltrimethyl ammonium bromide 42.04 mg/g, anionic surfactant tants sodium stearate 121.97 mg/g | Chen et al. (2011a) |
| Bentonite | Methylene blue | Adsorption capacity of bentonite 194 mg/g, and for rarasaponin-bentonite 256 mg/g | Kurniawan et al. (2011) |
| Rectorite | Methylene blue | Adsorption capacity of acid modified rectorite 37 mg/g | Zhang et al. (2011) |
| Na-bentonite | Congo red | Adsorption capacity of natural bentonite 19.5 mg/g, acid activation 69.44 mg/g, thermal activation 54.64 mg/g, combination acid and thermal 75.75 mg/g | Toor and Jin (2012) |
| Kaolin | Malachite green | Adsorption capacity of Kaolin 0.509 mmol/g, rarasponin modified kaolin 0.919 mmol/g | Suwandi et al. (2012) |
| Kaolinite | Coomassie Brilliant Blue R 250 | Adsorption capacity 22.89 mg/g, acid treated kaolinite 30.08 mg/g | de Sales et al. (2013) |
| Bentonite | Evans blue | Adsorption capacity 0.263 mmol/g, treated with rarasaponin 0.516 mmol/g | Chandra et al. (2013) |

(continued)

**Table 2.9** (continued)

| Clay | Dye | Performance | References |
|---|---|---|---|
| Alunite | Acid red 88 | The adsorption capacity of calcined alunite 832.31 mg/g | Akar et al. (2013) |
| Bentonite | Methylene blue | Adsorption capacity of chitosan-bentonite composite 142.86 mg/g | Bulut and Karaer (2015) |
| Bentonite | Orange II | Adsorption capacity of Alkyltriphenyl phosphonium-bentonite 53.78 mg/g | Bouzid et al. (2015) |
| Bentonite | Amido black 10B | Adsorption capacity of cross-linked chitosan/bentonite composite 323.6 mg/g | Liu et al. (2015) |

its acid treated forms were 2.9 (kaolinite), 4.0 (0.25 M acid-treated kaolinite), and 4.2 (0.50 M acid treated kaolinite). Montmorillonite in their study did not show $pH_{pzc}$ in the studied pH range from pH 2.0 to pH 12.0 suggesting that even at a very low pH, montmorillonite surface remained negatively charged. They reported that the uptake of Rhodamine B increased with the increased of pH from 2 to 4, and further increase of pH, the uptake of the dye decreased significantly (Bhattacharyya et al. 2014a). Rhodamine B is a xanthane dye existing in the form of three species:

- $RhBH^+$ at pH 1.0–3.0
- $RhBH_2^{2+}$ at $pH < 1.0$
- Zwitterion $RhB^{\pm}$ at $pH > 4.0$

As mentioned in the previous section, at $pH < pH_{pzc}$, the net surface charge of the clay is positive and the clay becomes the anion exchange. The surface of solid becomes repulsive to $RhBH^+$, as the results the uptake of Rhodamine B by the kaolinite and its modified forms were low (the maximum uptake was around 24 mg/g). In the case of montmorillonite, the uptake of Rhodamine B much higher than Kaolinite and its acid-modified forms, due to the negatively charged of the surface of the entire range of the pH studied (Bhattacharyya et al. 2014a). The negative charge value of the surface of montmorillonite is attributed to the isomorphic substitutions of lattice-constituent metal ions by cations of lower charge and the deprotonated silanol and aluminol groups at the pH-dependent edge faces (Cottet et al. 2014).

Temperature is another significant physico-chemical process parameter in the adsorption system. Changing the temperature can alter the dye adsorption rate while after the equilibrium has been reached it can affect the adsorption equilibrium of the adsorbent for a particular adsorbate (Cottet et al. 2014). In most of dye—clay mineral adsorption systems, the temperature possess a positive effect on the uptake of solute, with the increase of temperature, the amount of dye adsorbed by clay also increase (Hong et al. 2009; Kurniawan et al. 2011; Auta and Hameed 2012; Rehman et al. 2013; Bhattacharyya et al. 2014b; Cottet et al. 2014; Fan et al. 2014; Liu et al. 2014a, 2015), however, in several systems the temperature gave negative effect on the adsorption capacity (Vimonses et al. 2009; Suwandi et al. 2012; Chandra et al. 2013; Öztürk and Malkoc 2014).

The adsorption of the cationic dye onto smectite clays is an instantaneous process; the organic cations replace the exchangeable cations in the interlayer space and on the external surfaces and formation of dye aggregates occur (Pentrák et al. 2012). The interaction between methylene blue and montmorillonite can be used for the characterization of layer charge of montmorillonite. Pentrák et al. (2012) studied the change in layer charge of clay minerals upon acid treatment using adsorption of methylene blue. They found that decreased values of cation exchange capacity (CEC) upon HCl attack confirmed reduction of layer charge of all the systems studied.

### 2.3.3 Adsorption of Antibiotics

Antibiotic was discovered in 1928 by Alexander Fleming. The first natural antibiotic called as penicillin. Currently, with the advances in medicinal chemistry, large number of antibiotics are commercially available in the market. Most of the available antibiotics are semi synthetic modifications of various natural compounds such as beta-lactam antibiotics, the cephalosporins, and the carbapenems, only aminoglycosides are still isolated from living organisms. Antibiotics have been proven to be powerful drugs to treat various bacterial infections, from minor to life-threatening ones (Anggraini et al. 2014). The antibiotics available in the market are classified according to several classifications and one of them is as follows:

- β-lactam antibiotics are a broad class of antibiotics, consisting of all antibiotic agents that contain a β-lactam ring in their molecular structures, examples: penicillins (amoxicillin, ampicillin, etc.), cephalosporins, carbapenems, monobactams, etc.
- Aminoglycosides are a group of bactericidal antibiotics, which act by inhibiting bacterial protein synthesis, examples: Gentamicin, Tobramycin, Amikacin, streptomycin, neomycin, etc.
- Quinolones are synthetic, bactericidal antibacterial agents with broad-spectrum activity, examples: Ciprofloxacin, levofloxacin, lomefloxacin, cinoxacin, etc.
- Macrolide antibiotics are a class of antibiotics found in streptomycetes. They are natural lactones with a large ring, consisting of 14 to 20 atoms, examples: erythromycin, fidaxomicin, azithromycin, clarithromycin, etc.
- Tetracycline are a family of broad-spectrum antibiotics effective against a remarkably wide variety of organisms.
- Tetracyclines able to inhibit protein synthesis in gram positive and gram negative bacteria by preventing the attachment of aminoacyl-tRNA to the ribosomal acceptor (A) site (Fuoco 2012), example: tetracycline
- Lincosamides are broad-spectrum antibiotics that inhibit gram-positive and gram-negative bacterial protein synthesis, example: clindamycin.
- Cyclic peptides: Vancomycin, Streptogramins, Polymyxins, etc.

- Sulfa antibiotics are synthetic antimicrobial agents that contain the sulfonamide group, examples: sulfisoxazole, Sulfadimethoxine, Sulfadoxine, etc.
- Oxazolidinoes are a chemical class of synthetic antimicrobial agents. They exhibit a unique mechanism of protein synthesis inhibition and generally display bacteriostatic activity against many important human pathogens (Diekema and Jones 2000), example: Linezolid.

The excessive use of antibiotics creates serious problems to the environment; about 30–90 % of the given dose would remain undegradable in human or animal body, largely excreted as active compound (Putra et al. 2009). Currently, as a consequence of their overuse, bacteria have developed antibiotic resistance as opposed to the oldest compounds. The removal of antibiotic from the environment can be conducted effectively using adsorption process. The utilization of clay minerals as the adsorbents for the antibiotics removal has been conducted by a large number of researchers, mostly using the synthetic aqueous solution as the model for aquatic environments (Chang et al. 2009a, b; Putra et al. 2009; Wu et al. 2010; Li et al. 2010a, b, 2011; Molu and Yurdakoc 2010; Wang et al. 2010, 2011; Liu et al. 2012; Lu et al. 2012; Parolo et al. 2012; Yan et al. 2012; Zhao et al. 2012; Jiang et al. 2013; Lv et al. 2013; Wu et al. 2013a, b; Zhang et al. 2013; Anggraini et al. 2014; Hamilton et al. 2014; Sturini et al. 2015).

Adsorption and intercalation of ciprofloxacin on montmorillonite have been studied by Wu et al. (2010). Quantitative desorption of exchangeable cations confirmed cation exchange as the most important mechanism of ciprofloxacin adsorption on montmorillonite. High removal of ciprofloxacin was achieved at pH less than $pKa_2$ value of ciprofloxacin. The intercalation of ciprofloxacin onto interlayer of montmorillonite was also observed through the increase of basal spacing of the montmorillonite. A similar phenomenon was also observed by Chang et al. (2009a) on the adsorption of tetracycline onto Na-montmorillonite. They found that the intercalation was an important mechanism on the adsorption antibiotics onto smectite clay.

Adsorption of ciprofloxacin onto montmorillonite, rectorite and illite was studied by Wu et al. (2013a). The displacement of exchangeable cations indicates that the cation exchange as important for ciprofloxacin adsorption on illite, while significant contribution to the adsorption also given by hydrogen bonding between ciprofloxacin carboxylic groups basal oxygen atoms on external surface of clay minerals. Wu et al. (2013b) studied the adsorption of the quinolone antibiotic nalidixic acid onto montmorillonite and kaolinite. The study was conducted at different pH of the solution and initial concentration of antibiotic. At the pH below the pKa of nalidixic acid, the antibiotic existed mainly in neutral form and hydrophobic interaction was responsible for high uptake of antibiotic. When the pH increased above the pKa value, electrostatic repulsion between the anionic form of nalidixic acid and negatively charged mineral surface reduced the uptake of nalidixic acid. The expansion of basal spacing around 0.09 nm was a strong indication that the intercalation of nalidixic acid in the interlayer space also occurred.

### 2.3.4 Adsorption of Biocides and Other Organic Compounds

A biocide substance is a chemical compound which can inhibit the metabolism, render harmless, and even eliminate any harmful organisms. The utilization of biocides substances and products in the medicine, agriculture, forestry, and various kinds of industries are very common. Thousands of biocides are available in the market, and many of them possess a broad spectrum of antimicrobial activity (Ong et al. 2014). There are four main groups of biocides: disinfectants and general biocidal products, preservatives, pest control, and other biocidal products. Disinfectants and general biocidal products include human hygiene biocidal products, Veterinary hygiene biocidal products, private area and public health area disinfectants and other biocidal products, etc. Preservatives include fiber, leather, rubber and polymerized materials preservatives, wood preservatives, etc. Pest control includes pesticides, herbicides, insecticides, repellents, etc., while other biocidal products include antifouling products, etc.

Because biocides are intended to kill living organisms, the massive uses of biocidal products pose significant risk to human health and welfare, and also cause significant adverse effects on the natural environment. The disposal of waste and direct discharge of wastewater containing biocides cause serious and potentially long-lasting damage to the environment. The treatment of biocides compounds in wastewater treatment plants usually are conducted using a combination of physical, chemical and biological processes. Since some biocidal compounds are persistent, some small or trace amount of the biocidal compounds still present in the effluent. The degradation of several biocidal compounds also produces some toxic organic compounds such as the trihalomethanes, dioxins, and benzenes, which are known to be carcinogenic substances (Tatarazako et al. 2004; Rule et al. 2005; Buth et al. 2010). As the consequence, the supplementary treatment process on the regular wastewater treatment plant should be incorporated to manage a maximum elimination of those hazardous residues.

Adsorption has proven as an effective process for removal various kinds of hazardous substances from gas and water environment. A number of adsorbents including clay minerals have been in use for that purpose. As the adsorbent, clay minerals should possess the ability to select and retain certain minor constituent from gases or liquids. Modification using physical or chemical methods usually is conducted to enhance the adsorption capacity.

Benzalkonium chloride and triclosan are the commonly used biocides for cleaning products, cosmetics, and other household disinfectant products. These biocides have been known to raise severe environmental problems such as pathogen resistance and the existence of the toxic compounds in reclaimed water (Ong et al. 2014). The removal of benzalkonium chloride and triclosan using surfactant modified bentonite (dodecyltricetyl ammonium—bentonite/DTA-bentonite). The experiment results indicate that the modified bentonite has a much higher adsorption capacity toward triclosan than untreated bentonite. Organophilic cation facilitates the anchoring of hydrophobic triclosan, but slightly limits the adsorption of benzalkonium chloride by occupying the active cation exchange site in the bentonite structure (Ong et al. 2014).

Clopyralid (3,6-dichloro-2-pyridinecarboxylic acid) is an auxin-mimic type herbicide and more selective than some other auxin-mimic herbicides to control of broad leaf weeds, especially thistles and clovers. This acid herbicide often in their anionic form at the pH of soil and water environments, and the ability of the soils to retain this herbicide is weak; therefore it has a tendency to contaminate ground and surface water (Celis et al. 2012). The preparation of Montmorillonite-chitosan bionanocomposites as adsorbents of the herbicide clopyralid in aqueous solution and soil/water suspensions was studied by Celis et al. (2012). The composites gave very well adsorption performance at all pH levels, in where both of the anionic form (pKa = 2.30) or cationic form (pKa = 6.30) of the herbicide predominated. The adsorption capability of montmorillonite-chitosan composites depended on the amount and arrangement of chitosan in the samples. The adsorption of herbicide was rapid and the addition of salt at high concentration promoted the desorption of herbicides from the composites (Celis et al. 2012).

Simazine is an effective herbicide to inhibit the photosynthetic electron transport processes in plant leaves, used for weed removal from corn, sorghum, sugarcane, banana, pineapple, tea gardens and rubber plantations etc. (Paul et al. 2010). The acid activated beidellite was employed for the removal of this herbicide from aqueous solution. Different types of binding mechanisms between beidellite and simazine were observed, the binding mechanisms involve were van der Waals interactions, hydrogen bonding, and ion-dipole interactions (Paul et al. 2010) Other studies of the adsorption of various biocides compounds and other organic pollutants using clay minerals and its modified forms are given in Table 2.10.

## 2.4 Application Clay Minerals as Cleaning Agents in Aquaculture and Other Systems

In the water the ammonia ($NH_3$) exists in its equilibrium form with the ammonium ion ($NH_4^+$) according to the following equilibrium chemical reaction:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

Unionized ammonia ($NH_3$) is harmful to aquatic organisms. The acidity and basicity (pH) of the water strongly influence the equilibrium condition between unionized ammonia and the ionized one. Unionized ammonia is toxic and its presence in water predominates when the pH is high, while in the form of ammonium ion ($NH_4^+$) is relatively nontoxic and predominates when pH is low. Temperature also has the same influence as pH to the equilibrium condition of ammonia and ammonium ion. In general, less than 10 % of ammonia are in the toxic form when the pH is less than 8.0 (Hargreaves and Tucker 2004). The effect of pH and temperature on the amount of unionized ammonia is given in Fig. 2.5.

Ammonia is released into the aquatic system by various kinds of human and industrial activities. Wastewater treatment plants, agricultural activities, fertilizer production, food processing, intensive animal-rearing facilities are the major contributors of the ammonia pollution in aquatic systems. The ecological impact of

**Table 2.10** Recent studies on the adsorption of biocides and other organic pollutants using clay minerals

| Clay | Organic compound | Modification | References |
|---|---|---|---|
| Bentonite | Chlorobenzene | Acid (HCl) and thermal activation (100–500 °C) | Sennour et al. (2009) |
| Montmorillonite | p-nitrophenol | tetradecyltrimethylammonium bromide was employed for modification of montmorillonite | Park et al. (2011) |
| Bentonite | *o*-, *m*- and *p*-nitrophenols | Two organobentonites (HDTMA-B and PEG-B) were synthesized using hexadecyltrimethylammonium bromide (HDTMABr) and poly(ethylene glycol) butyl ether (PEG) | Koyuncu et al. (2011) |
| Montmorillonite | Phenol | – | Djebbar et al. (2012) |
| Kaolin | 4-nitro-phenol | – | Ahmedzeki et al. (2013) |
| Bentonite | Aniline | The bentonite was modified by bis-pyridinium dibromides | Gu et al. (2014) |
| Montmorillonite | Triclosan | Different ester-containing Gemini surfactant-modified montmorillonite (EMMT) were prepared under microwave irradiation | Liu et al. (2014b) |
| Montmorillonite | Phenol and catechol | Organo-clays were prepared by two novel hydroxyl-containing Gemini surfactants | Liu et al. (2014c) |
| Montmorillonite | 2-Naphthol | Na-montmorillonite was modified by Gemini surfactants with different spacers | Yang et al. (2014) |

ammonia on aquatic ecosystems is likely to occur through chronic toxicity to fish and benthic invertebrate populations as a result of reduced reproductive capacity and reduced growth of the young. Another problem is the eutrophication of fresh waters.

Various methods for the removal of ammonia from water and wastewater have been developed, and one of them is adsorption process. Natural clays and its modified forms have been used for the ammonia removal from aqueous solution (Rozic et al. 2000; Bedelean et al. 2010; Zhang et al. 2012; Zhao et al. 2013; Zamparas et al. 2013). One of the advantages of using clays as the adsorbent for ammonia

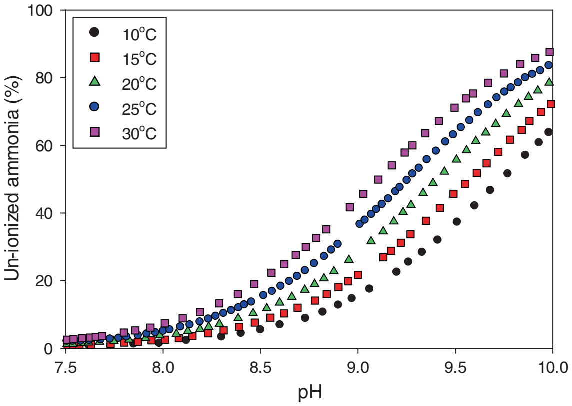

**Fig. 2.5** The effect of pH and temperature on the proportion of un-ionized ammonia ($NH_3$)

removal is the layered structure of the clay allows expansion (swelling) when contacted with water, which exposes an additional mineral surface capable of ammonium ion ($NH_4^+$) adsorption (Rozic et al. 2000). With the increase of ammonium ions adsorbed by the surface of clay, the equilibrium reaction is shifted towards the formation of $NH_4^+$, leading to the decrease of ammonia concentration in water, and this phenomenon enhances the removal of ammonia. Ammonium removal from aqueous solution by clays is the result of ion exchange and adsorption.

In aquaculture system, the main source of ammonia in the system is from the fish excretion. The rate at which fish excrete ammonia is directly related to the feeding rate and the protein level in the field. As dietary protein is broken down in the body, some of the nitrogen is used to form protein (including muscle), some is used for energy, and some is excreted through the gills as ammonia. (Hargreaves and Tucker 2004). Another source of ammonia in aquaculture system is from the decomposition of organic matter which also produces ammonia.

In open aquaculture system, most of the ammonia excreted by the fist is taken up by the algae and available water plants in the system In open aquaculture system, the pH of the system also fluctuates with photosynthesis process and respiration of aquaculture organisms. The fluctuation of the pH influence un-ionized ammonia concentration in the water and according to Hargreaves and Tucker (2004) the toxic form of ammonia ($NH_3$) predominates during the late afternoon and early evening and ammonium ($NH_4^+$) predominates from before sunrise through early morning.

In order to control the concentration of ammonia ($NH_3$) in the aquaculture system, usually the fish farmer uses one type of a group silicate mineral called as zeolites. Chemically, zeolites are similar to clay minerals. Zeolites molecules are connected in a framework structure that is characterized by spaces or pores between the molecule groups, while in clay minerals are characterized by the tetrahedral and octahedral sheets which are stacked together in certain ways that creates loosely connected plates. Some exchangeable cations such as $K^+$, $Na^+$, $Mg^{2+}$ and $Ca^{2+}$ are available in the structure of zeolite molecules, and these cations are not strongly bound to the molecule so they can easily exchange with other cations such as $NH_4^+$ (Malekian et al. 2011; Moussavi et al. 2011; Huang et al. 2014; Zhou and Boyd 2014).

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# Chapter 3
# Modification of Clay Minerals for Adsorption Purpose

**Abstract** The chemical nature and pore structure of clay materials generally influence their adsorption capability. In order to increase its adsorption capacity, modification of the pore structure of clay materials has been conducted chemically as well as physically. Inorganic acids, bases, salts, and surfactants have been used for modification of clay minerals. A combination of chemical and physical treatment process has also been employed to modify the surface and structure of clay minerals. The modification of clay minerals using acid can alter the crystalline structure of the clay minerals. The clay minerals modified with quaternary ammonium surfactant have a high affinity towards most of hydrophobic organic compounds. Even though the anionic surfactants are cheaper than other types of surfactants, the anionic surfactants are seldom used for clay modification compared to the cationic and nonionic surfactants. Nonionic surfactant organoclays were more chemically stable than cationic surfactant organoclays. This chapter also describes the use of Gemini surfactants as well as natural surfactant for modification of various clay minerals.

**Keywords** Acid-leached · Impregnation · Surfactants · Rarasaponin · Clay composite

The chemical nature and pore structure of clay materials generally influence their adsorption capability. However, due to the hydrophilicity of most clay materials, the natural clay minerals usually are not effective for the adsorption of organic contaminants such as dyes, antibiotics, pesticides, and biocidal compounds (Koswojo et al. 2010; Kurniawan et al. 2011). In order to increase its adsorption capacity, modification of the pore structure of clay materials has been conducted chemically as well as physically. The modification of clay materials using chemical modifying agents usually conducted by a simple impregnation method.

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## 3.1 Modification of Clay Minerals Using Acids, Bases, and Salts

The modification of the surface of clay minerals through impregnation using acids, bases, and salts has been conducted by various researchers. Usually inorganic acid such as hydrochloric acid (HCl), sulfuric acid ($H_2SO_4$), nitric acid ($HNO_3$) are used for that purpose. While for the modification using base, the solution the alkali and alkali earth metal hydroxide such as NaOH, KOH, $Ca(OH)_2$, or $Al(OH)_3$ were employed as impregnating agents. The anion salts such as potassium dihydrogen phosphate ($KH_2PO_4$), orthophosphate, tri-polysulphate, and sodium tetraoxosulphate(VI) has also been used for surface modification of several clay minerals.

### *3.1.1 Acid-Leached Clay Minerals*

Acid leaching of clays and clay minerals causes disaggregation of the clay particles, elimination of impurities, and dissolution of the external layers. The purpose of inorganic acid modification is to enhance the adsorption capability of clay minerals through the increasing of surface area, pore volume, and number of acid sites.

The use of acid to increase the specific surface area and pore volume of bentonite has been conducted in industrial scale. The product, acid-leached bentonite also known as bleaching earth has been used for decolorization of vegetable oils. The most widely used acids for this purpose is sulfuric acid ($H_2SO_4$). The modification of bentonite using acid can alter the crystalline structure of the clay mineral. The chemical composition of the raw bentonite, acid concentration, temperature, and leaching time play significant roles in the chemical composition and mineralogical of the bleaching earth (Temuujin et al. 2006).

Temuujin et al. (2006) studied the influence of acid concentration on the pore structure, crystalline phases, and chemical composition of montmorillonite. The chemical composition of the clay used in their study was 40 % montmorillonite, 40 % amorphous compounds, 4 % cristobalite, 5 % feldspar, 2 % calcite and traces of quartz. Since the clay contains large amount of impurities, the purification of clay increased the montmorillonite content to 92.8 %. The acid concentration and the duration of the acid modification strongly affected the pore structure and the acidity of the montmorillonite. The acidity of the montmorillonite clay arises from $H^+$ in the surface exchange sites (Brønsted acid sites). These acid sites were generated by the exchange of interlamellar cations ($Mg^{2+}$ and $Al^{3+}$) of the octahedral sheet of montmorillonite with protons ($H^+$) from the sulfuric acid. With increasing acid concentration and impregnation time, considerably greater amounts of octahedral $Al^{3+}$ and $Mg^{2+}$ were removed, leading to a decrease in the Lewis acidity (Temuujin et al. 2006).

Combination of acid and thermal treatment process to increase the adsorption capacity of montmorillonite has been studied by Sennour et al. (2009). The thermal activation of montmorillonite was conducted at temperatures of 100–500 °C. Quartz and cristoballite as the impurity material was removed by dispersing montmorillonite powder into distilled water. Carbonate and organic compounds were removed by HCl (1 N) and hydrogen peroxide solution, respectively. The acid and thermal modified montmorillonite were used to remove chlorobenzene from aqueous solution. The adsorption experimental results indicate that the thermal modified montmorillonite has better adsorption performance than acid montmorillonite.

Panda and his co-workers (2010) studied the influence of acid concentration on the physico-chemical characteristics of kaolin clay. The results indicate that high acid strength treatment provoked amorphization and structural transformation to form an amorphous silica type phase. The improvement of pore characteristics such as specific surface area and pore volume was observed after acid treatment. A similar study of the acid activation of kaolin was also conducted by Alkan et al. (2008). The effect of molar concentrations and acid to solid impregnation ratios was studied and they found that the partial distortion of layer structure and specific adsorption of $H^+$ ions onto the clay surface reduced the active patches of kaolin.

The influence of acid treatments on the adsorption capacity of sepiolites was studied by Kilislioglu and Aras (2010). The acid-treated forms of clays show a significant increase in the specific surface area. Even though the acid treatments produced clays with higher specific surface area, however, the adsorption capacity of acid-sepiolites towards $UO_2^{2+}$ ions was smaller than the untreated sepiolites. This phenomenon occurred likely due to the leaching of most of $Mg^{2+}$ interlayer ions and the collapse of octahedral layer.

Tunisian smectite-rich clay was modified by Chaari and coworkers (2008) using two inorganic acids (HCl and $H_2SO_4$). The modification using $H_2SO_4$ gave a better adsorption performance than HCl on the removal of Pb(II) from aqueous solution. Compared to non-activated clay, both acid-activated clays have a higher number of active surface sites for the binding of lead cations.

Low adsorption capacity is the main problem of utilization of clay minerals as the adsorbents for industrial scale wastewater treatment. Toor and Jin (2012) studied the modification of sodium bentonite used thermal activation, acid activation, and combined acid and thermal activation. The effects of process parameters of the activation such as contact time, dye concentration, bentonite dosage, pH and temperature on the adsorption performance of modified bentonite for the removal of Congo red were also studied. The bentonite modified by combining an acid and thermal activation gave a better adsorption performance compared to standalone thermal activation and acid activation.

### *3.1.2 Impregnation Clay Minerals with Base and Salts*

Compared to the acid modification, the impregnation of clay minerals using base solutions for environmental purpose is seldom used. Sodium hydroxide solution was used to regenerate a spent bleaching earth from an edible oil refinery by Mana et al. (2008). After alkali treatment, the spent bleaching earth was subsequently treated with thermal treatment at 100 °C. The clay structure was not apparently affected by the treatment and the impregnated organic matter was quantitatively removed. The treated spent bleaching earth exhibited a significantly higher sorption capacity than virgin bleaching earth as well as fast kinetics uptake at the same metal concentration (Mana et al. 2008).

The influence of acid, base and salt modifications of clay in its rates of naphthalene adsorption was examined by Owabor et al. (2012). The chemical modifiers used in their study include hydrochloric acid (HCl), citric acid ($C_6H_8O_7$), sodium hydroxide (NaOH), ammonium hydroxide ($NH_4OH$), sodium chloride (NaCl) and zinc chloride ($ZnCl_2$). Sodium hydroxide modified clay showed relatively good adsorption performance on the removal of naphthalene from the bulk solution, while ammonium hydroxide modified clay showed a slow rate of adsorption of naphthalene from the bulk solution (Owabor et al. 2012). Sodium hydroxide was also used for modification of illite by Lakevičs et al. (2014). The experimental results indicate that the adsorption performance of illite towards methylene blue increased after the modification process.

Chemical conditioning is another technique to chemically tailoring the surface chemical nature of clays and clay minerals. In the chemical conditioning process, the certain exchangeable cations in the clay layers are exchanged with other cations from the solution. The performance of natural and modified clinoptilolite as the cation exchange for $Ag^+$ ions was studied by Lihareva et al. (2010). The replacement of $K^+$, $Ca^{2+}$, and $Mg^{2+}$ interlayer cations with $Na^+$ enhances the cation exchange capability of Na-clinoptilolite towards $Ag^+$ due to more mono-ionic character of the clay. Similar study dealing with chemical conditioning of clinoptilolite using NaCl and HCl solutions, has been conducted by Coruh (2008) for the removal of zinc ions. He found that sodium modified clinoptilolite exhibit higher effective ion exchange capacity due to lower Si to Al ratio.

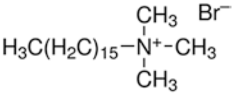
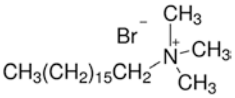
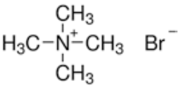
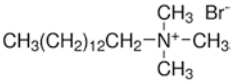
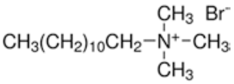
## 3.2 Modification of Clay Minerals Using Surfactant

Surfactants are organic compounds which possess polar and non-polar characteristics. Surfactants are a big group of surface active compounds with a large number of applications. The classification of surfactants is based on their dissociation in water: cationic surfactants, anionic surfactants, and non-ionic surfactants. Cationic surfactants mostly are linear alkyl amines and alkyl ammoniums substances (fatty amine salts and quaternary ammoniums). Anionic surfactants include alkybenzene sulfonates, soaps, di-alkyl sulfosuccinate, lauryl sulfate, lignosulfonates, etc. The non-ionic surfactants are not dissociated in water and these surfactants include ethoxylated linear alcohols, ethoxylated alkyl phenols, fatty acid esters, amine and amide derivatives, etc. Currently various surfactants have been used for modification of clay materials in order to improve the adsorption performance. The main purpose of the intercalation of surfactant ions onto the clay mineral structure is to convert the initially hydrophilic clay mineral particles into hydrophobic organo-clays.

### 3.2.1 *Cationic Surfactants*

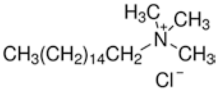
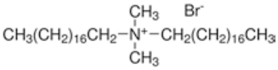
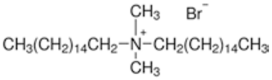
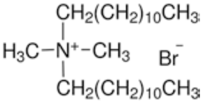
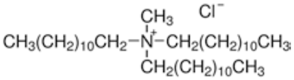
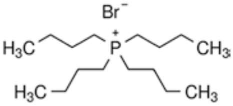
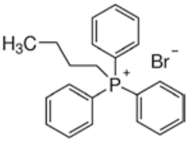
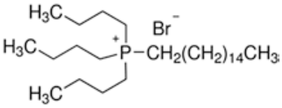
In water, cationic surfactant will be dissociated into an amphiphilic cation and an anion. Even though the cationic surfactants are not good detergents nor foaming agents, these substances still widely employed as modifying agents for clay modification due to their positive charge. The most common cationic surfactants used for clay modification, are quaternary ammonium salts, such as CTAB (Yilmaz and Yapar 2004; Ma et al. 2010; Yesi Sisnandy et al. 2010; Koswojo et al. 2010; Chen et al. 2011; Rahardjo et al. 2011), ODTMA (Hedley et al. 2007; Huang et al. 2007; Siebdrath et al. 2012), TMA (Siebdrath et al. 2012), TMAB (Yilmaz and Yapar 2004; Singla et al. 2012; Anggraini et al. 2014), DTAB (Singla et al. 2012), HDTMA (Anirudhan and Ramachandran 2007), and other (He et al. 2010). Quaternary phosponium surfactants were also used for the modification of clay mineral by several authors (Hedley et al. 2007). Table 3.1 summarizes a number of quaternary ammonium salts and quaternary phosphonium which are widely used for clay modification. The surface modification of clays and clay minerals with cationic surfactants involves both cation exchange process and the bonding of the hydrophobic moiety in the clay layers.

**Table 3.1** Cationic surfactants which are widely used for clay modification

| No | Name | Molecular structure | Physical properties |
|---|---|---|---|
| 1 | Cetyltrimethylammonium bromide or hexadecyltrimethylammonium bromide ($CH_3(CH_2)_{15}N(Br)(CH_3)_3$) |  | CTAB is soluble in $H_2O$ and readily soluble in alcohol. Melting point: >230 °C (decompose) |
| 2 | Trimethyloctadecylammonium bromide or Octadecyltrimethylammonium bromide ($CH_3(CH_2)_{17}N(Br)(CH_3)_3$) |  | ODTMA is soluble to 10 mM in DMSO and to 100 mM in ethanol, melting point: 250 °C |
| 3 | Tetramethylammonium bromide ($(CH_3)_4N(Br)$) |  | Melting point: >300 °C |
| 4 | Myristyltrimethylammonium bromide or Tetradecyltrimethylammonium bromide, ($CH_3(CH_2)_{13}N(Br)(CH_3)_3$) |  | TMAB solubility in water: soluble10 % (w/v) melting point: 245–250 °C |
| 5 | Dodecyltrimethylammonium bromide or Lauryltrimethylammonium bromide $CH_3(CH_2)_{11}N(CH_3)_3Br$ |  | DTAB soluble in water. Melting point: 246 °C |

(continued)

**Table 3.1** (continued)

| | | | |
|---|---|---|---|
| 6 | Hexadecyl trimethylammonium chloride or Cetyltrimethylammonium chloride ($CH_3(CH_2)_{15}N(Cl)(CH_3)_3$) |  | HDTMA melting point: 232–237 °C |
| 7 | Dioctadecyl dimethylammonium bromide or Distearyldimethylammonium bromide, $[CH_3(CH_2)_{17}]_2N(Br)(CH_3)_2$ |  | Melting point: 160 °C |
| 8 | Dihexadecyl dimethylammonium bromide or dimethyldihexadecylammonium bromide, $[CH_3(CH_2)_{15}]_2N(CH_3)_2(Br)$ |  | Melting point: 159–162 °C |
| 9 | Didodecyl dimethylammonium bromide or dimethyldidodecylammonium bromide, $[CH_3(CH_2)_{11}]_2N(CH_3)_2(Br)$ |  | Melting point: 157–162 °C |
| 10 | Tridodecylmethylammonium chloride or methyltridodecylammonium chloride, $[CH_3(CH_2)_{11}]_3N(Cl)CH_3$ |  | Melting point: 110–112 °C |
| 11 | Tetrabutylphosphonium bromide ($(CH_3CH_2CH_2CH_2)_4P(Br)$) |  | TBP melting point: 100–103 °C |
| 12 | Butyltriphenylphosphonium bromide, $(C_6H_5)_3P(Br)CH_2CH_2CH$ |  | BTPP melting point: 240–243 °C |
| 13 | Hexadecyltributylphosphonium bromide or Tributylhexadecylphosphonium bromide, $CH_3(CH_2)_{15}P^+[(CH_2)_3CH_3]_3Br^-$ |  | HDTBP melting point: 56–58 °C |

In recent years, the use of clay minerals modified with cationic surfactants for removal of hazardous pollutant from aqueous environment and landfill liner (to protect soil and groundwater from hydrophobic organic compounds pollution) has increased significantly. The clay minerals modified with quaternary ammonium surfactant have a high affinity towards most of hydrophobic organic compounds (Kan et al. 2011). The studies of the removal hydrophobic organic compounds using modified bentonite have been conducted by many researchers (Lee et al. 2004; Zhu et al. 2011).

Smectite clays have been proven as suitable materials for surface or structure modification by cationic surfactants due to their cation exchange capacity and large surface area. The final properties (hydrophobicity, oleophilicity, interlayer spacing, particle size, and thermal properties) of the surfactant modified smectite materials strongly depend on the length of the alkyl chain and the functional groups of the surfactants (Shah et al. 2013). Quaternary ammonium salts with different alkyl chain lengths and a benzyl substitute group has been in use by Shah et al. (2013) for the modification of montmorillonite clay. Hexadecyldimethylbenzylammonium bromide, tetradecyldimethylbenzylammonium bromide, tetradecyltrimethylammonium bromide, dodecyltrimethylammonium bromide were the cationic ammonium surfactants used for the modification. The modification with quaternary ammonium surfactants which have benzyl substitute group resulted in water-non-wettable and superhydrophobic surface, whereas clays modified with quaternary ammonium surfactants without benzyl substitute group became more water-wettable and hydrophilic than the pristine clay (Shah et al. 2013).

The effects of cationic tetradecytrimethylammonium bromide, anionic sodium tetradecyl sulfonate and nonionic Brij 30 surfactants on the electrokinetic and rheological properties of Na-bentonite and sepiolite suspensions have been investigated by Tunc et al. (2012). The presence of cationic tetradecytrimethylammonium bromide altered the negative surface charge of Na-bentonite and sepiolite to the positive charge. Na-bentonite–surfactant suspensions showed a thixotropic behavior; on the other hand sepiolite–surfactant suspensions displayed a rheopexic or thixotropic behavior depending on the surfactant concentration (Tunc et al. 2012).

The surface modification of sodium montmorillonite using cation surfactant of quaternary ammonium salt in the alkane solvent environment was studied by Sun et al. (2013). The intercalation and ion exchange reaction in alkane solvents dramatically changed the surface structure and properties of the montmorillonite. The modification of sodium montmorillonite in the organic medium produced dispersal of organo-montmorillonite.

### *3.2.2 Anionic Surfactants*

The anionic surfactants are the most commonly used surfactants for various applications. Alkylbenzene sulfonates (detergents), soaps, lauryl sulfate, di-alkyl sulfosuccinate, and lignosulfonates are the most important surfactants for household and industrial applications. Even though the anionic surfactants are cheaper than other types of surfactants, the anionic surfactants are seldom used for clay modification compared to the cationic and nonionic surfactants.

The functionalization of the surface chemistry of clay minerals using an intercalation method with anionic surfactant has been carried out by Gunawan et al. (2010), Nathaniel et al. (2011), Akbulut et al. (2012) and Sandy et al. (2012). The preparation of organo-bentonite using linear alkylbenzene sulfonat (LAS) as the anionic surfactant was carried out by Nathaniel et al. (2011). The bentonite used in their study was obtained from Pacitan, East Java, Indonesia. The elemental compositions of the bentonite were: Al 39.12 %, Si 47.89 %, Fe 3.44 %, Ca 0.15 %, Mg 0.45 %, K 0.24 %, Na 0.47 %, Mn 0.03 %. The microwave radiation method was also employed to assist the modification process. The selection of the microwave heating procedure is due to the time efficiency and energy-saving (Nathaniel et al. 2011). The FTIR analysis revealed that after modification with LAS, the existence of new absorption peaks which belong to the asymmetric and symmetric vibration of C–H stretch of methylene groups $(\text{–CH}_2)_n$ in the aliphatic carbon chain was observed. The intercalation of LAS molecules the interlayer spacing of bentonite, causing an expansion of its interlamellar spacing from 1.36 to 1.46 nm. Similar procedure of Nathaniel et al. (2011) was also employed by Sandy et al. (2012) for modification of bentonite using anionic surfactant (linear alkylbenzene sulfonat). The concentration of the surfactant used in their study was 1.5 times the cation exchange capacity (CEC) of the natural bentonite. The increase of interlayer spacing from 1.724 to 2.012 nm after modification indicates that the LAS molecules were partially intercalated into the interlayer spacing of bentonite.

### 3.2.3 *Nonionic Surfactants*

Due to the hydrophilic nature in its surface, natural clay materials are not effective adsorbents for nonpolar nonionic organic compounds. Nonionic surfactant was used for the first time by Shen (2001) for modification of the bentonite interlayer structure. Nonionic surfactants used in his study were Brij 78 ($C_{18}H_{37}(CH_2CH_2O)_{20}OH$), polyethylene glycol ether (($C_9H_{19}C_6H_4(CH_2CH_2O)_{10}OH$) and ($C_9H_{19}C_6H_4(CH_2CH_2O)_{20}OH$)), and for comparison purpose, dodecylpyridinium chloride ($C_{12}H_{25}C_6H_4NH^+Cl^-$), was used as cationic surfactant. The results indicated that organobentonites derived from nonionic surfactants show larger interlayer spacing and higher organic carbon content than organobentonite from cationic surfactant. Further, the nonionic surfactant organobentonites were more chemically stable than cationic surfactant organobentonite (Shen 2001).

Nonionic surfactants offer several advantages compared to the cationic or anionic surfactants (Guegan et al. 2015):

- Biodegradable and non-toxic (Shen 2001)
- Good thermal and chemical stabilities (Beall and Goss 2004; Guegan 2013)
- Preserve of the exchangeable inorganic cations after adsorption onto clay minerals (Deng et al. 2006; de Paiva et al. 2008; Guegan 2010)
- The possibility of cation exchange of the resulting nonionic organoclay with both organic and inorganic cations Guegan (2010, 2013).

While a large number of works dedicated to the improvement of the sequestration of organic contaminants by using cationic organoclays, Guegan et al. (2015) developed nonionic organoclay for the adsorption of organic pollutants from aqueous solutions. Sodium montmorillonite was employed as the starting clay material and the triethylene glycol mono n-decyl ether (C10E3) as an unconventional nonionic surfactant. The preparation of nonionic organoclay was conducted at a concentration below the critical micelle concentration (cmc), at this condition the nonionic surfactant is in a monomer state. The adsorption performance of nonionic organoclay was tested to remove three organic micro-pollutants (benzene, dimethylphthalate and paraquat) and the results were compared with pristine montmorillonite. The adsorption results indicate that the chemical nature of the micro-pollutants play important role in the performance of nonionic organoclay (Guegan et al. 2015).

### *3.2.4 Gemini Surfactants*

Gemini surfactants (sometimes also called as bis-surfactants) are surfactants which consist of two conventional surfactant molecules that chemically bonded together by a rigid or flexible spacer. Several functional groups such as short or long methylene groups, polyether, aliphatic, and aromatic groups can be used as spacer. Gemini surfactants are a class of amphiphilic molecules containing two head groups and two aliphatic chains (Kirby et al. 2003). In the recent years, gemini surfactants have attracted attention many researchers for modification of clay and clay minerals (Li and Rosen 2000; Liu et al. 2011, 2014; Yang et al. 2014). Gemini surfactants have been claimed to have many advantages compared to the conventional surfactants, such as higher efficiency in reducing the oil/water interfacial tension, better wetting, lower critical micellar concentration (CMC), foaming, and antibacterial activities (Yang et al. 2014).

Critical micellar concentration (CMC) is the concentration above which monomeric surfactant molecules abruptly aggregate to form micelles (Hait and Moulik 2002). CMC values of several conventional and gemini surfactants are given in Table 3.2. The increase of the hydrophobic chain length of the molecule decreases the value of the CMC of the surfactant as seen in Table 3.2.

**Table 3.2** CMC values of several conventional and gemini surfactants

| Surfactant | Molecular formula | CMC/mM |
|---|---|---|
| Dodecyltrimethylammonium bromide | $C_{12}H_{25}N^+(CH_3)_3Br^-$ | 14 |
| Tetradecyltrimethylammonium bromide | $C_{14}H_{29}N^+(CH_3)_3Br^-$ | 4–5 |
| Cetyltrimethylammonium bromide | $C_{16}H_{33}N^+(CH_3)_3Br^-$ | 0.92–1.0 |
| Trimethyloctadecylammonium bromide | $C_{18}H_{37}N^+(CH_3)_3Br^-$ | 0.35 |
| Butanediyl-1,4-bis(hexadecyl hydroxyethyl methyl ammonium bromide) | $C_{16}H_{33}N^+(CH_3)$ $C_2H_4OH(CH_2)_4C_2H_4OH(CH_3)$ $N^+C_{16}H_{33}2Br^-$ | 0.0018 |
| Butanediyl-1,4-bis(decyl dimethyl ammonium bromide) | $C_{10}H_{21}N^+(CH_3)_2\ (CH_2)_4\ (CH_3)_2N^+C_{10}H_{21}2Br^-$ | 0.795 |
| Butanediyl-1,4-bis(dodecyl dimethyl ammonium bromide) | $C_{12}H_{25}N^+(CH_3)_2\ (CH_2)_4\ (CH_3)_2N^+C_{12}H_{25}2Br^-$ | 0.164 |
| Butanediyl-1,4-bis(tetradecyl dimethyl ammonium bromide) | $C_{14}H_{29}N^+(CH_3)_2\ (CH_2)_4\ (CH_3)_2N^+C_{14}H_{29}2Br^-$ | 0.00782 |
| Butanediyl-1,4-bis(hexadecyl dimethyl ammonium bromide) | $C_{16}H_{33}N^+(CH_3)_2\ (CH_2)_4\ (CH_3)_2N^+C_{16}H_{33}2Br^-$ | 0.00225 |

Glycol bis-N-cetylnicotinate dibromide a cationic gemini surfactant has been used by Kan et al. (2011) for modification of bentonite. The XRD and FTIR results revealed that the cationic gemini surfactant successfully intercalated into the bentonite layer. For the comparison, the authors also modified the bentonite using conventional cationic surfactant (cetyltrimethyl ammonium bromide). As expected, the gemini surfactant modified bentonite has a better adsorption capacity than CTA-bentonite. However, the adsorption efficiency of gemini surfactant modified bentonite decreased rapidly at pH above 6. The decrease of the adsorption efficiency at alkaline environment possibly due to the hydrolysis of the ester groups in the gemini surfactant molecules.

Modification of bentonite or montmorillonites using gemini surfactants with different spacers has been conducted by Yang et al. (2014). The results showed that gemini surfactants containing longer spacer group arranged relatively loose in the interlayer though, the strong hydrophobic interaction between the adsorbed surfactants and organic pollutants facilitated the adsorption capacity of organo-clays (Yang et al. 2014). The adsorption performance of modified bentonite was evaluated through adsorption of 2-Naphtol from aqueous phase solution. The adsorption experimental results indicate that the optimum condition for 2-Naphtol removal was achieved at pH = 6.

The functionalization of sodium montmorillonites using geminal hexadecyl hydrophobic buttress via a cationic exchange process has been carried out by El-Achaby et al. (2013). The resulting organo-clay exhibits a large d-spacing of 3 nm between silicate layers and showed a high thermal stability compared to the commonly used clay modified alkyl ammonium salts.

### 3.2.5 Natural Surfactants

The use of synthetic surfactants to modify the adsorption capacity of clay materials sometimes creates quite serious problems to the environment due to the unused of excess surfactants. The surfactants could possess poisonous effects to the aquatic life, especially if these chemical compounds are present in sufficient amounts. The surfactants have the capability to destruct mucus layers of the fish and cause severe damage of the gills. These mucus layers are the active protector of the fish against the parasites and bacteria. The ability to lower the surface tension of the water is another big problem of the presence of the surfactants in the water environment. With lower surface tension, the organic compounds easily dissolve in water and absorbed by the fish or other aquatic creature. The toxicity of a surfactant is related to its chemical structure, the longer the fatty chain, the more toxic the surfactant is to aquatic organisms. Therefore, the study on the utilization and modification of clay materials for environmental remediation and wastewater treatment purpose should be directed towards the application of environmental friendly or natural chemicals as modifying agents (Kurniawan et al. 2011).

Rarasaponin extracted from the berry soap (*Sapindus rarac* DC) was employed as modifying agent to improve adsorption capacity several clay materials by

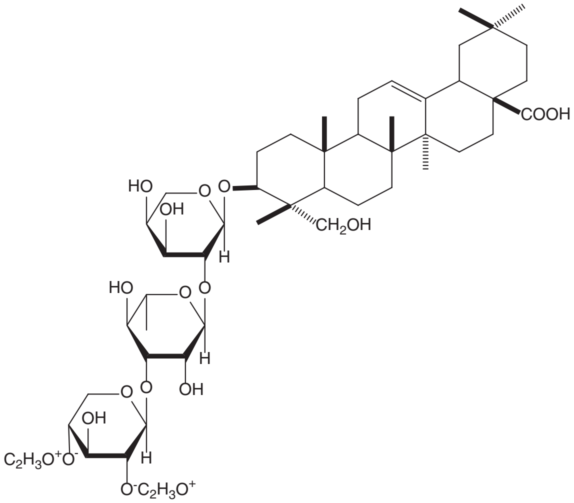


**Fig. 3.1** The molecular structure of Rarasaponin derived from *Sapindus rarak DC*

Ismadji's research group (Kurniawan et al. 2011, 2012; Suwandi et al. 2012; Chandra et al. 2013). The molecular structure of rarasaponin is given in Fig. 3.1. Rarasaponin belongs to the alkaloid group which has one or more oligosaccharide. Several functional groups exist in the structure of rarasaponin such as hydroxyls, ester carbonyls, aromatic rings, and also alkanes group both in aliphatic and alicyclic structure (Kurniawan et al. 2011). The rarasaponin was extracted from *Sapindus rarac* DC by the maceration method at a temperature of 80 °C and extraction time of 60 min.

Kurniawan et al. (2011) have utilized the extract from berry soap for the preparation of organo-bentonite. The bentonite was used as the raw material for rarasaponin-bentonite preparation. The bentonite was obtained from bentonite mining located in Pacitan, East Java province, Indonesia. Prior the modification, the impurities of bentonite were removed by impregnation using hydrogen peroxide solution. The impregnation combined with microwave radiation methods was employed to prepare the rarasaponin-bentonite/organo-bentonite. After intercalation using rarasaponin, the increment of basal spacing ($d_{001}$) of the bentonite was observed (1.42 for bentonite and 2.67 nm for rarasaponin-bentonite). The increase of basal spacing in organo-bentonite indicates that rarasaponin molecules were partially intercalated at bentonite interlayer spaces and expanded its interlamellar spacing The adsorption capacity of rarasaponin-bentonite was examined through the adsorption of methylene blue. The highest adsorption capacity of rarasaponin-bentonite obtained in their study was 256 mg/g while for raw bentonite was 194 mg/g at 60 °C.

The formation of rarasaponin-bentonite from intercalation of rarasaponin surfactant with the bentonite are described with the following reaction mechanisms (Kurniawan et al. 2011): the first mechanism is the deacylation reaction of rarasaponin structure, rarasaponin contains two acyl groups ($C_2H_3O^+$) attached to carbonyl structure. These alkyl groups attached to carbonyl structure will be decimated when it is dissolved in polar solvents such as water. This phenomenon causes the oxygen atoms in carbonyl groups become negatively charged. The second step is the protonation of the surface of the silanol group (Si-OH) due to the excess of $H^+$ in the solution. The final mechanism is the attachment of protonated silanol groups into negatively charged oxygen atoms in carbonyl groups.

Suwandi et al. (2012) studied the modification of kaolin using rarasaponin surfactant. Modification of kaolin was conducted by soaking kaolin in rarasaponin solution for 24 h at room temperature. The XRD spectra for kaolin and rarasaponin-kaolin indicate that the alternation of basal spacing of kaolin occurred after intercalation of the rarasaponin molecules into interlamelar spacing of kaolin. In relation with environment protection, Chandra et al. (2013) employed rarasaponin surfactant as the modifying agent for the preparation of organo-bentonite. The rarasaponin-bentonite was prepared based on the method of Kurniawan et al. (2011). They used the X-ray fluorescence method to determine the chemical composition of the bentonite and rarasaponin-bentonite. The chemical composition of rarasaponin–bentonite in general was slightly different from the natural one due to the attachment of rarasaponin molecules into interlamelar spacing of bentonite.

## 3.3 Clay Composite Materials for Environmental Remediation

Organic compounds have been used to modify the surface of clay minerals and other related layered silicates, mainly because they exhibit a very rich intercalation chemistry which allows them to be chemically modified and made compatible with organic polymers and other materials for various applications (Mambrini et al. 2013). The combination of organo-clays with different polymers or biopolymers to create composites or nanocomposites have been widely studied (Sölener et al. 2008; Unuabonah et al. 2008, 2012; Zhu et al. 2011; Kredatusova and Brozek 2012; Zhou et al. 2012; Natkanski et al. 2012; Mandal et al. 2012; Urbano et al. 2012; Tirtom et al. 2012; Gorrasi et al. 2013; Rytwo et al. 2013; Hassan and El-Nemr 2013; Shirsath et al. 2013; Pereira et al. 2013; Lopes et al. 2014; Unuabonah and Taubert 2014; Wu et al. 2014; Alcantara et al. 2014; Bhattacharyya and Ray 2014; Vanamudan et al. 2014). Table 3.3 summarizes studies of the preparation of organo-clay and polymers or biopolymers composites for the environmental application.

Starch is a carbohydrate consisting of a large number of glucose units joined by glycosidic bonds, and is the most common carbohydrate in human diets and also economically important used biomass in nature. Due to its abundant availability in nature, some researchers have tried to utilize this biomass for removal organic pollutants from water ecosystem. However, native starch has weak adsorbing functional groups in its backbone (Xing et al. 2012), therefore, the modification by introducing various active groups, such as carboxylate, acrylonitrile, acrylamide, phosphate, etc. have been carried out in order to make this biomass has the ability to adsorb hazardous pollutants. The main drawback of chemically modified starch for adsorption purpose cost effectiveness. Cost-effective cationic starch intercalated clay composite

**Table 3.3** Clay/organo-clay and polymer or biopolymers composites for the environmental application

| Clay/Organo-clay | Polymer/biopolymer | Application | References |
|---|---|---|---|
| Kaolinite | Polyvinyl alcohol | Removal of Pb(II) | Unuabonah et al. 2012 |
| Wyoming montmorillonite | Polyacrylate | Removal of Fe(III) | Natkanski et al. 2012 |
| Montmorillonite | Poly[N-(4-vinyl benzyl)-N-methyl-D-glucamine | Removal of As(V) | Urbano et al. 2012 |
| Bentonite | Chitosan | Removal of Ni(II) and d(II) | Tirtom et al. 2012 |
| Hydrotalcite | Sodium alginate | Removal of fluoride and Orange II dye | Mandal et al. 2012 |
| Montmorillonite | Cellulose acetate | Removal of Acid Scarlet anionic dye | Zhou et al. 2012 |
| Montmorillonite | Chitosan | Removal of herbicide clopyralid | Celis et al. 2012 |
| Na-montmorillonite | Ethylene propylene diene monomer (EPDM) rubber | Removal of Remacryl blue 3G–Basic blue 3, Nylson navy N-RBL–Acid blue 13, Remazol brilliant blue BB–Reactive blue 19, Samaron red 2BSL–Disperse red 60 | Hassan and El-Nemr 2013 |
| Kaolin | Polyacrylic acid | Removal of brilliant green | Shirsath et al. 2013 |
| Palygorskite | Cellulose | Removal of phenol | Wu et al. 2014 |
| Sepiolite and palygorskite | Polysaccharides | Removal of Cu(II) and Pb(II) | Alcantara et al. 2014 |
| Bentonite | Chitosan and acrylic copolymer | Removal of malachite green and methyl violet dyes | Bhattacharyya and Ray 2014 |
| Montmorillonite | Pectin | Removal of Basic Yellow 28 | Nesic et al. 2014 |
| Montmorillonite | Chitosan-g-(N-vinylpyrrolidone) | Removal of Rhodamine 6G | Vanamudan et al. 2014 |
| Montmorillonite | Chitosan | Removal of Co(II) | Wang et al. 2014 |

matrix for removal of reactive dye (brilliant blue X-BR) was prepared by Xing et al. (2012). The adsorption capacity of such kind of composite was controlled by the variation of the weight ratio of clay and cationic starch. The adsorption experimental results showed that the adsorption capacity increased greatly with increasing the weight ratio of clay to cationic starch from 0.1 to 0.2, and then decreased when the weight ratio up to 0.3 (Xing et al. 2012).

Cationic layered clay minerals, such as montmorillonite, saponite and hectorite, feature peculiar ion exchange, swelling, and large surface areas in aqueous systems. The modification and shaping of these clay minerals into functional materials has received much attention over the past decades, especially in adsorption and separation process (Zhou et al. 2012). The preparation of novel paper-like composites from cellulose acetate and organo-montmorillonite clays have been conducted by Zhou and his co-workers (2012). A simple method was used to prepare the composites, the method consists of the dispersion of cellulose acetate and organo montmorillonite in organic solvent followed by evaporation and drying. The adsorption of Acid Scarlet G (ASG) anionic dye in aqueous solution onto the CA/OMMT composites was tested by varying the pH value of the dye solution, the temperature and time, and the initial dye concentration. The adsorption capacity of the composites increased with the decrease of the ratio of CA to OMMT and the pH value of the dye solution (Zhou et al. 2012).

Polyethylene glycol is nontoxic, biocompatible, and soluble in water. This compound is widely used pharmaceutical industries, biomaterial production, tissue culture, and also as the adsorbent for environmental purpose. As the adsorbent, the polyethylene glycol must be polymerized to introduce several functional groups in its structure (Bhattacharyya and Ray 2015) and subsequently functionalized with vinyl groups at the chain-ends such as polyethylene glycol diacrylate and these active vinyl groups may be crosslinked to form PEG based superabsorbent hydrogel (Kwak et al. 2013; Bhattacharyya and Ray 2015). Bhattacharyya and Ray (2015) studied the preparation of nano clay filled composite hydrogels of poly acrylic acid and polyethylene glycol for the adsorption of dyes. Nano clay filled composite hydrogels were synthesized by incorporating 0.5, 1.0 and 1.5 wt% nano size bentonite fillers in the hydrogels. The adsorption experimental results indicate that nano clay filled composite hydrogels were excellent adsorbent for the removal of Congo red and methyl violet in almost entire range of dye concentrations.

Easy route to activate clay honeycomb monoliths for environmental application was proposed by Cifredo et al. (2010). The method consists of mixing the clay with coal before the extrusion, and the removal of coal from the monolith was conducted by heating the mixture in the presence of air at a certain low temperature. The adsorption capacity of the activated clay honeycomb was tested toward the removal of methylene blue from synthetic wastewater solution.

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# Chapter 4
# The Equilibrium Studies in the Adsorption of Hazardous Substances Using Clay Minerals

**Abstract** The most important information to understand the adsorption process is the adsorption equilibria. The adsorption equilibria relate the amount of a solute in the surface of adsorbent at equilibrium condition and the equilibrium concentration of the solute in the liquid phase. The adsorption equilibria of a system are described by adsorption isotherm. A number of adsorption equations which originally developed for the gas phase adsorption can be used to represent the liquid phase adsorption equilibria. The theoretical approaches of several adsorption equations are discussed in this chapter. The most widely used isotherm equations for the correlation of adsorption experimental data of hazardous substance—clay mineral systems are the Langmuir and Freundlich equations. Other two and three parameters isotherms such as Dubinin-Radushkevich, Temkin, Toth, Sips, BET, and Redlich-Patterson also have been used to correlate the liquid phase adsorption of various solutes onto clay minerals. The temperature dependent forms of several models and its applicability to describe the adsorption experimental data also given in this chapter. The extension of single component models to multicomponent adsorption system is also discussed. The thermodynamic aspects of the adsorption process also given in this chapter.

**Keywords** Isotherm model · Single component · Multicomponent · Temperature dependent · Adsorption thermodynamic

Adsorption arises as a result of the unsaturated and unbalanced molecular forces that are present on every solid surface. When the surface of the solid is contacted with a solute, the interaction force between the surface and the solute occurs, the solid surface tends to balance these residual forces by attracting and retaining on its surface the molecules of the solute. This results in a greater concentration of the solute in the near vicinity of the solid surface than in the bulk liquid (Bansal and Goyal 2005).

There are two kinds of forces involve in the adsorption process: physical forces (dipole moments, polarization forces, dispersive forces, or short range repulsive

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interactions) and chemical forces (involving chemical reaction and the interactions are essentially those responsible for the formation of chemical compounds) (Bansal and Goyal 2005). In the physical adsorption, the forces predominantly are the attractive dispersion forces and short-range repulsive forces. In the chemical adsorption which also known as chemisorption, on the other hand, involves the exchange or sharing of electrons between the adsorbate molecules and the surface of the adsorbent resulting in a chemical reaction (Bansal and Goyal 2005).

The most important information to understand the adsorption process is the adsorption equilibria. The adsorption equilibria relate the amount of a solute in the surface of adsorbent at equilibrium condition and the equilibrium concentration of the solute in the liquid phase. The adsorption equilibria of a system are described by adsorption isotherm. Several adsorption isotherms which originally developed for gas phase adsorption are available and have been used to correlate the adsorption equilibria of various substances onto clay materials. These isotherms are Langmuir equation, Freundlich isotherm, Sips equation, Toth model, etc. (Yesi et al. 2010; Zhou et al. 2012; Chandra et al. 2013; Anggraeni et al. 2014; Ong et al. 2014). The application of these isotherm models to represent the adsorption equilibrium data of hazardous substances onto clay materials will be discussed in the subsequent sections.

## 4.1 Langmuir Isotherm

A coherent theory of adsorption onto a flat surface was proposed by Langmuir in 1918. This theory of adsorption was based on a kinetic principle, in which the rate of adsorption onto flat surface equal to the rate of desorption from the surface to maintain zero rate of accumulation at the surface at equilibrium condition (Do 1998). The Langmuir model is the first theoretically developed adsorption isotherm that was derived using thermodynamic and statistical approaches. Three simple assumptions were used by Langmuir to develop his model: surface is homogeneous, adsorption on the surface is localized, and each active site on the surface of adsorbent can accommodate only one molecule. The Langmuir equation is written in the following form:

$$q_e = q_{\max} \frac{K_L C_e}{1 + K_L C_e} \tag{4.1}$$

where $q_e$ is the amount of the solute adsorbed onto the adsorbent surface at equilibrium condition, $q_{\max}$ is the adsorption capacity of an adsorbent, while $K_L$ and $C_e$ are affinity constant and the equilibrium concentration of solute in the bulk liquid, respectively. The parameter $K_L$ measures of how strong an adsorbate molecule is attracted onto a surface (Do 1998).

Theoretically, when the value of parameter $K_L$ is larger, the interaction between the surface of adsorbent and the solute molecules become stronger, and the surface of adsorbent will be covered more with the solute molecules. The effect of the value of parameter $K_L$ on the amount of solute adsorbed by the adsorbent is depicted in Fig. 4.1.

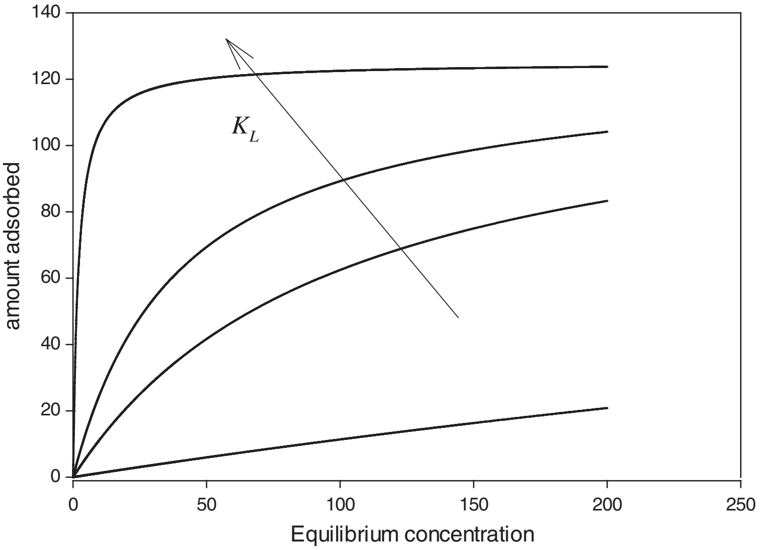

**Fig. 4.1** The effect of the value of parameter $K_L$ on the amount of solute adsorbed by the adsorbent

Langmuir equation is one of the most widely used isotherm models to represent the liquid adsorption equilibrium data. This equation can describe the adsorption equilibria data of many solute-adsorbent systems. Langmuir equation possesses Henry's law at very low concentration and limit saturation capacity at high concentration of solute. At saturation capacity, all of the adsorption active sites are covered by the solute or adsorbate molecules, this phenomenon is called as monolayer coverage (Do 1998). Table 4.1 summarizes a number of recent studies that employ the Langmuir equation to correlate the adsorption experimental data.

The parameters ($q_{\max}$ and $K_L$) of Langmuir equation are usually obtained by a nonlinear regression method using various kinds of software such as SigmaPlot (Putra et al. 2009; Yesi et al. 2010; Rahardjo et al. 2011; Zhou et al. 2012; Suwandi et al. 2012; Chandra et al. 2013; Anggraeni et al. 2014; Ong et al. 2014). Even though the use of nonlinear regression method is more convenient and gives more accurate results than the linear one, however, many researchers still prefer to use the linear form of the Langmuir model to extract the values of the parameters due to its simplicity (Bhattacharyya and Gupta 2006; Zhang et al. 2006; Wang and Wang 2007; Tang et al. 2009; Rawajfih and Nsour 2010; Frini-Srasra and Srasra 2010; Eloussaief and Benzina 2010; Bhattacharyya and Gupta 2011; Urbano et al. 2012; Tirtom et al. 2012; Campos et al. 2013; Peng et al. 2013; Shirsath et al. 2013; Tiwari et al. 2014; Jones et al. 2015). The linear forms of the Langmuir equation can be written as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{K_L q_{\max}} \tag{4.2}$$

**Table 4.1** Langmuir parameters for adsorption of hazardous substances onto clay materials and its modified forms

| System | Operation condition | $K_L$ | $q_{\max}$ | References |
|---|---|---|---|---|
| Nano clay composite hydrogels of PAA, PEG + congo red and methyl violet | pH = 3.5–9.0 | 0.003–0.008 L/mg (congo red), 0.007–0.008/mg (methyl violet) | 110–225 mg/g (congo red), 92.14–111 mg/g methyl violet) | Bhattacharyya and Ray (2015) |
| MTA-montmorillonite + amoxicillin and ampicillin | $T = 30$, 40, and 50 °C<br>pH = 2–11 | 122.94–182.58 L/mmol (amoxicillin) and 141.11–206.44 L/mmol (ampicillin) | 0.124–0.133 mmol/g (amoxicillin) and 0.143–0.157 mmol/g (ampicillin) | Anggraeni et al. (2014) |
| DTA, and saponin-bentonite + Benzalkonium chloride and triclosan | $T = 30$, 40, and 50 °C | 0.0302–0.0315 L/µmol (DTA-bentonite + triclosan), 0.0901–0.0902 L/µmol (DTA-bentonite + benzalkonium), 0.0317–0.0319 L/µmol (saponin-bentonite + triclosan), 0.0902–0.0904 L/µmol (saponin-bentonite + benzalkonium) | 12.2803–12.3807 µmol/g (DTA-bentonite + triclosan), 5.3689–5.6478 µmol/g (DTA-bentonite + benzalkonium), 12.5028–12.5316 µmol/g (saponin-bentonite + triclosan), 5.6448–5.6528 µmol/g (saponin-bentonite + benzalkonium) | Ong et al. (2014) |
| Montmorillonite + phenol and 4-nitrophenol | $T = 20$ °C pH = 3, 5, and 8 | 1.35 L/mmol (phenol at pH 3) | 0.13 mmol/g (phenol at pH 3) | Houari et al. (2014) |
| | | 2.36 L/mmol (phenol at pH 5) | 0.11 mmol/g (phenol at pH 5) | |
| | | 4.10 L/mmol (phenol at pH 8) | 0.05 mmol/g (phenol at pH 8) | |
| | | 3.09 L/mmol (4-NP at pH 3) | 0.11 mmol/g (4-NP at pH 3) | |
| | | 4.14 L/mmol (4-NP at pH 5) | 0.07 mmol/g (4-NP at pH 5) | |
| | | 7.06 L/mmol (4-NP at pH 8) | 0.05 mmol/g (4-NP at pH 8) | |
| $Fe_3O_4$/sepiolite magnetic composite + antrazine | $T = 24$, 45, and 65 °C<br>pH = 6.5 | 14.6–15.9 µg/m$^2$ | 0.571–0.647 L/mg | Liu et al. (2014a) |
| Alunite + acid red 88 | $T = 25$ °C pH 2–10 | 1840 L/mol (raw alunite), 45,800 L/mol (calcined alunite) | $5.24 \times 10^{-5}$ mol/g (raw alunite), $2.08 \times 10^{-5}$ mol/g (calcined alunite) | Akar et al. (2009) |

(continued)

**Table 4.1** (continued)

| System | Operation condition | $K_L$ | $q_{\max}$ | References |
|---|---|---|---|---|
| poly(acrylic acid) hydrogel loaded with kaolin clay + Brilliant Green | $T = 15$, 25, and 35 °C<br>pH = 4–9 | 0.13 L/mg (15 °C), 0.20 L/mg (25 °C), 0.33 L/mg (35 °C) | 24.90 mg/g (15 °C),<br>25.60 mg/g (25 °C),<br>26.31 mg/g (35 °C) | Shirsath et al. (2013) |
| Cationic starch-clay composite + brilliant blue X-BR | $T = 20$ °C | 0.67–2.22 L/mg | 89.3–122.0 mg/g | Xing et al. (2012) |
| Water-insoluble polymer–clay nanocomposite + arsenic | pH = 3 and 6 | 4.15 L/mg (pH = 3),<br>12.9 L/mg (pH = 6) | 53.47 mg/g (pH = 3),<br>55.24 mg/g (pH = 6) | Urbano et al. (2012) |
| Zinc-exchanged montmorillonite + aflatoxin B1 | pH = 3 and 7 | 3.51 L/mg (montmorillonite),<br>4.66 L/mg (Zn-montmorillonite) | 40.98 mg/g (montmorillonite), 60.17 mg/g (Zn-montmorillonite) | Dakovic et al. (2012) |
| cetylpyridinium-bentonite + Reactive red 120 | $T = 25$–65 °C pH = 2–11 | 0.20 L/mg | 81.97 mg/g | Tabak et al. (2010) |
| Ti-pillared Montmorillonite + Arsenic | $T = 25$ °C | 3.091 L/mg (As(III)),<br>7.141 L/mg (As(V)) | 14.72 mg/g (As(III)),<br>12.503 mg/g (As(V)) | Na et al. (2010) |
| Acid activated bentonite + $\gamma$-picoline | $T = 30$, 45, and 60 °C | 0.009 L/mg (30 °C) 0.016 L/mg (45 °C) 0.017 L/mg (60 °C) | 21 mg/g (30 °C) 26 mg/g (45 °C) 46 mg/g (60 °C) | Rawajfih and Nsour (2010) |
| Palygorskite + Cd (II) | – | 0.001 L/mg (natural palygorskite) 0.001 L/mg (acid treated palygorskite) | 227.272 mg/g (natural palygorskite) 149.253 mg/g (acid treated palygorskite) | Frini-Srasra and Srasra (2010) |
| Activated clay minerals + methylene blue | – | 0.011–0.041 L/mg | 99–558 mg/g | El-Mouzdahir et al. (2010) |
| Acid-activated clays + Pb (II) | $T = 20$, 30, and 40 °C<br>pH = 4.0–7.5 | 0.018–0.074 L/mg | 17.84–40.75 mg/g | Eloussaief and Benzina (2010) |

$$\frac{1}{q_e} = \left(\frac{1}{K_L q_{\max}}\right) C_e + \frac{1}{q_{\max}} \tag{4.3}$$

$$q_e = q_{\max} - \left(\frac{1}{K_L}\right)\frac{q_e}{C_e} \tag{4.4}$$

$$\frac{q_e}{C_e} = K_L q_{\max} - K_L q_e \tag{4.5}$$

The essential characteristics of the Langmuir isotherm equation are represented through the dimensionless constant called the equilibrium parameter, $R_L$ (Kurniawan et al. 2011), which can be expressed by the following equation

$$R_L = \frac{1}{1 + K_L C_o} \tag{4.6}$$

where $C_o$ is the initial solute concentration in the liquid phase. The classification of parameter $R_L$ as the nature of adsorption is as follows: favorable—convex isotherms ($0 < R_L < 1$), unfavorable—concave isotherms ($R_L > 1$), linear ($R_L = 1$) or highly favorable/non-reversible ($R_L = 0$).

Since the Langmuir equation was developed according to three ideal assumptions, there are significant limitations in the interpretation of the adsorption data because of its idealized character (Bansal and Goyal 2005). In some cases, this equation failed to represent the adsorption equilibria data of the adsorption systems (Vanamudan et al. 2014; Randelovic et al. 2014; Jones et al. 2015).

## 4.2 Freundlich Isotherm

Freundlich isotherm is one of the most widely used adsorption models to represent the liquid phase adsorption equilibrium data. This equation is also one of the earliest empirical equations used to describe adsorption equilibria data (Do 1998). The Freundlich isotherm has the form as follows:

$$q_e = K_F C_e^{1/n} \tag{4.7}$$

where $K_F$ and $n$ are Freundlich parameters. The parameter $K_F$ indicates the adsorption capacity of the adsorbent, while parameter $n$ indicates the heterogeneity of the system. In the linearized logarithmic form the Freundlich model has a mathematical expression as follows:

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{4.8}$$

The plot of ln $q_\mathrm{e}$ versus ln $C_e$ has a slope with the value of $1/n$ and an intercept magnitude of ln $K_F$. The behavior of parameter $n$ to the amount of solute adsorbed by the adsorbent is given in Fig. 4.2.

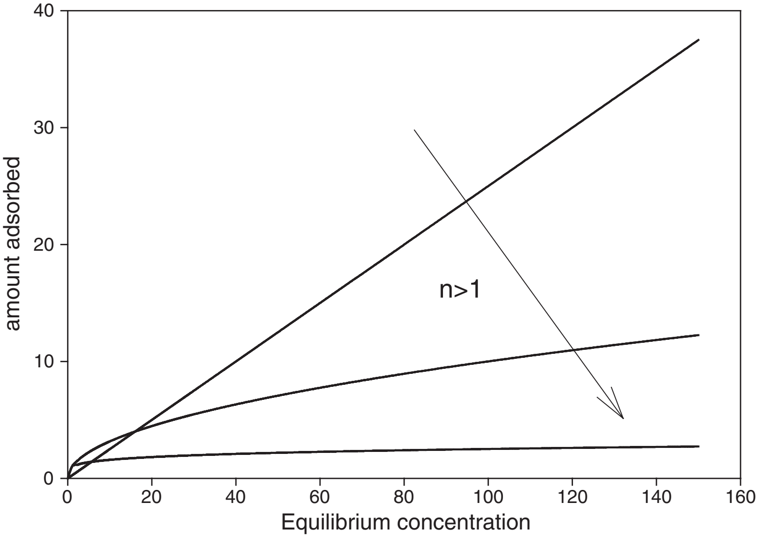

**Fig. 4.2** The effect of the value of parameter *n* on the amount of solute adsorbed by the adsorbent

In most adsorption systems, the parameter *n* usually greater than unity (Do 1998). On average, a favorable adsorption tends to have Freundlich parameter *n* between 1 and 10 (Febrianto et al. 2009). When the parameter *n* is equal to 1, the adsorption is linear; at this condition the identical adsorption energies for all adsorption active sites (homogeneous system) are observed. From Fig. 4.2 it can be seen that the larger is the value of *n* the system deviates from linear behavior, the interaction between the adsorbent and the solute/adsorbate become stronger. If the value of parameter *n* is more than 10, the system is approaching irreversible condition, the solute attaches to the surface with extremely strong interaction, and at this condition the adsorption has the tendency to become chemisorption.

In most cases the Freundlich model can represent the adsorption equilibria data quite well and is especially excellent for fitting data from highly heterogeneous adsorbent systems (Dal Bosco et al. 2006; Chen and Zhao 2009; Djebbar et al. 2012; Zhou et al. 2012; Xing et al. 2012; Dı´az-Nava et al. 2012; Hajjaji et al. 2013; Kadu and Chikate 2013; Wang et al. 2013; Chen and Liu 2014). Freundlich model only applicable in a narrow range of solute concentration since this isotherm equation does not have a proper Henry law behavior at low concentration, and it does not have a finite limit when the solute concentration is sufficiently high (Do 1998).

Freundlich equation was developed as an empirical equation; however, this equation also can be derived from a theoretical basis. The theoretical derivation of Freundlich model is based on the assumption that the surface is heterogeneous in the sense that the adsorption energy is distributed and the surface topography is patch wise, that is sites having the same adsorption energy are grouped together into one patch. There is no interaction between independent patches, and each patch only can accommodate or adsorb one molecule of adsorbate. Details on the derivation of the theoretical Freundlich model can be seen in Do (1998).

## 4.3 Other Two Parameters Isotherms

A certain model might be invalid to describe the adsorption experimental data in a particular situation, and in most cases, more than one model can represent the adsorption equilibria of a certain system. Several models initially developed for gas phase adsorption can be directly implemented to correlate the adsorption equilibria data of many hazardous substances onto the surface of clay minerals. Some of these equations contain two fitting parameters such as Temkin isotherm, Flory–Huggins, BET equation, and Dubinin–Raduskevich equations. The use of these equations to correlate the adsorption experimental data of the hazardous chemical and clay mineral systems are discussed in this sub-section.

### *4.3.1 Dubinin Radushkevich Equation*

The Dubinin-Radushkevich equation is a semi-empirical equation which was proposed by Dubinin and his co-workers for sub critical vapors in microporous solids, where the adsorption process follows a pore filling mechanism (Do 1998). For the adsorption in the liquid phase, the Dubinin-Radushkevich equation is written in the following form:

$$q_e = q_{\max} \exp\left(-\left(\frac{RT\ln\left(C_e/C_s\right)}{\beta E_o}\right)^2\right) \tag{4.9}$$

The parameter $\beta$ represents an affinity coefficient; this parameter is proportional to the liquid molar volume. While parameter $E_o$ represents the characteristic energy. The solute solubility at a given temperature is represented by $C_s$. Applications of the Dubunin-Radushkevich equation to liquid-phase adsorption are scarce because of the complexities associated with other factors such as pH and ionic equilibria that are inherent in such systems (Ismadji and Bhatia 2001).

The behavior of the Dubinin-Radushkevich equation as the function of characteristic energy is given in Fig. 4.3. From Fig. 4.3 it can be seen that the adsorption become stronger as the characteristic energy increases. The increase of solute uptake by the adsorbent as the characteristic energy increases due to the stronger energy possessed by the solid adsorbent therefore the interaction between the solid and solute also become stronger and more solute attached to the surface of the adsorbent.

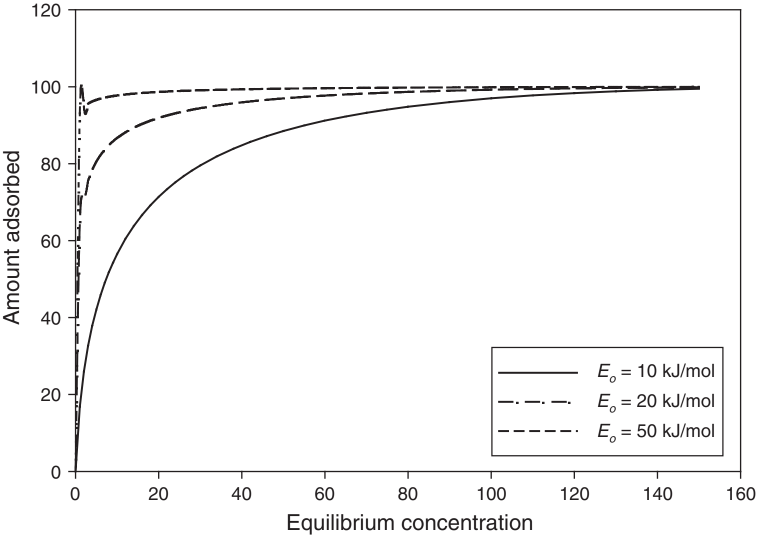

**Fig. 4.3** Plots of Dubinin-Raduskevich equation as function of characteristic energy

The Dubinin-Radushkevich equation has been employed by several researchers to correlate their adsorption equilibria data of hazardous substances and clay systems (Atun and Kilislioglu 2003; Kubilay et al. 2007; Hajjaji and El Arfaoui 2009; Tang et al. 2009; Randelovic et al. 2012, 2014; Kadu and Chikate 2013; Guegan et al. 2015). The Dubinin-Radushkevich equation has a 'tool' to measure the applicability of the model called as a characteristic curve. The adsorption process is temperature-dependent, if the adsorption data at different temperatures are plotted as the logarithm of the amount adsorbed versus the square of potential energy, all the suitable data shall in general lie on the same characteristic curve (Febrianto et al. 2009). If most or all of the data lie in the characteristic curve, the Dubinin-Radushkevich model can represent the adsorption experimental data. This characteristic curve can be used for initial measure for the applicability of the Dubinin-Radushkevich equation in expressing the adsorption equilibria data. However, since most of the adsorption experimental data of hazardous compounds—clay mineral systems were obtained at a single temperature, the application of this characteristic curve to determine the validity of the Dubinin-Radushkevich cannot be found in the literature. In the case that the fitting procedure gives high correlation values, but the characteristic curve obtained from the analyzed data does not lie in the same curve, the validity of the ascertained parameters is still questionable (Febrianto et al. 2009).

### 4.3.2 Temkin Isotherm

Temkin isotherm initially was proposed by Slygin and Frumkin (1935) to correlate the adsorption equilibria data of hydrogen onto the platinum electrode in acidic solution. This model was developed based on the chemisorption mechanism. This isotherm is one of the available isotherm models which often used to correlate the liquid phase adsorption experimental data of hazardous compounds—clay mineral system (Gao et al. 2013; Ahmedzeki et al. 2013). The Temkin isotherm was derived based on the assumption that the decline of the heat of sorption as a function of temperature is more linear rather than logarithmic. Temkin isotherm has the form as follows

$$q_e = \frac{RT}{b_T} \ln (A_T C_e) \tag{4.10}$$

where $A_T$ and $b_T$ are equilibrium binding constant and parameter constant, respectively. This equation is similar to Freundlich isotherm; it does not have a correct Henry law limit and finite saturation limit.

In most adsorption of hazardous compound—clay mineral system, Temkin isotherm is incapable to represent the adsorption equilibria data. Temkin isotherm is an empirical model and lack of fundamental basis. Even this model quite superior to represent the gas phase adsorption equilibria, for more complex system such as the adsorption in the liquid phase, this model often fails to represent the adsorption equilibria data. In general, the adsorption in the liquid phase is much more complex compared to the gas phase adsorption. In the liquid phase adsorption, the presence of solvent molecules and formation of micelles from adsorbed molecules give strong effect on the amount of solute adsorbed onto the surface of adsorbent. The interaction between the solute-solvent and solvent-adsorbent also occur, the adsorbed molecules in here do not necessarily organized in a tightly packed structure with identical orientation add to the complexity of liquid phase adsorption. Several factors including pH, solubility of adsorbate in the solvent, temperature and surface chemistry of the adsorbent influence the adsorption from liquid phase.

### 4.3.3 Flory–Huggins Isotherm

Compared with other adsorption isotherm models, the Flory–Huggins isotherm is seldom used to correlate the adsorption equilibria data of hazardous substances—clay mineral system. The Flory–Huggins isotherm is usually chosen to correlate the adsorption experimental data in order to account for the surface coverage characteristic degree of the solute on the surface of adsorbent. Based on the surface coverage characteristics, this model also can express the feasibility and spontaneous nature of an adsorption process. The Flory–Huggins isotherm has the form

$$\frac{\theta}{C_o} = K_{FH}(1 - \theta)^{n_{FH}} \tag{4.11}$$

where $\theta$ is the degree of surface coverage and is defined as

$$\theta = 1 - \frac{C_e}{C_o} \tag{4.12}$$

Flory–Huggins isotherm equilibrium constant indicated by symbol $K_{FH}$ and $n_{FH}$ is Flory–Huggins isotherm model exponent (usually also correlate to the number of solute molecules present on the adsorbent surface), while $C_o$ is the initial concentration of the solute.

Kadu and Chikate (2013) employed the Flory–Huggins isotherm to correlate the adsorption equilibria data of magenta dye onto Fe–Ni sandwiched montmorillonite. They obtained the parameters $K_{FH}$ and $n_{FH}$ from the slope and intercept of the linear plot of the isotherm. The maximum value of $n_{FH}$ was achieved for in situ composite (FeNi-in situ-25 %) while for the other composites the value of parameter $n_{FH}$ is similar.

### *4.3.4 Brunauer-Emmet-Teller (BET) Model*

Most of the adsorption equations in this chapter are for adsorption with 'monolayer' coverage except Freundlich isotherm and Dubinin-Radushkevich equation. The concept of the BET theory is an extension of the Langmuir theory, which is a theory of monolayer molecular adsorption, to multilayer adsorption. In the Langmuir isotherm, the derivation of the model was based on three simple assumptions, and one of the assumptions is adsorption only occurs at the unoccupied adsorption sites (monolayer coverage). In developing the BET model, the same assumptions of Langmuir theory was used except the monolayer coverage adsorption. Figure 4.4 depicts multi-layer adsorption in a flat surface.

The BET model originally developed for gas adsorption, and currently this model is also applied for the liquid phase adsorption. In the BET model development, the surface area of the flat surface covered by no layer ($S_o$), one layer ($S_1$), two layers ($S_2$), three layers ($S_3$), and n layers of adsorbate molecules. Then the concept of the Langmuir model about kinetic of adsorption and desorption process is applied to this multiple layering process. The rate of adsorption on any layer is equal to the rate of desorption from that layer. Using the similar approach, the rate of evaporation from (n + 1)th layer should equal to the rate of adsorption onto nth layer. The volume of solute adsorbed on the flat surface covering by one layer of molecules is the fraction occupied by one layer of molecules multiplied by the monolayer coverage. Since the proposed theory allows for infinite layers on top of flat surface the amount adsorbed must be infinity when the solute concentration is equal to solute solubility. Based on the above theory, the BET equation for liquid phase can be written as follows

$$\frac{q_e}{q_{\max}} = \frac{BC_e}{\left(C_s^* - C_e\right)\left(1 + (B-1)\left(C_e/C_s^*\right)\right)} \tag{4.13}$$

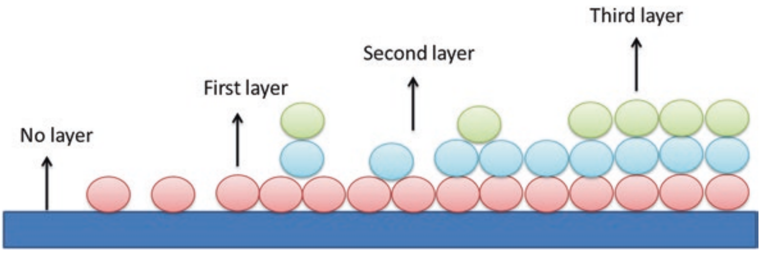

**Fig. 4.4** Multiple layering in BET theory (Do 1998)

where $B$ and $C_s^*$ are constant related to the energy of adsorption and the saturation concentration of solute, respectively. Details about the derivation of BET model are given in Do (1998). Figure 4.5 shows the plots of the BET equation versus reduced concentration $(C_e/C_s^*)$ with parameter $B$ is the varying parameter. Figure 4.5 clearly shows that the multilayer form of BET plot is achieved at high values of $B$ and the convexity of the isotherm increases towards low concentration of solute (Do 1998). If $B$ and $B * (C_e/C_s^*)$ is very high, the BET equation is simplified in the following form

$$\frac{q_e}{q_{\max}} = \frac{1}{1 - C_e/C_s^*} \tag{4.14}$$

The BET model has been used by several researchers to correlate the adsorption experimental data of several substances onto clays (Gao et al. 2013; Randelovic et al. 2014). Gao et al. (2013) used this model to represent the adsorption phosphate

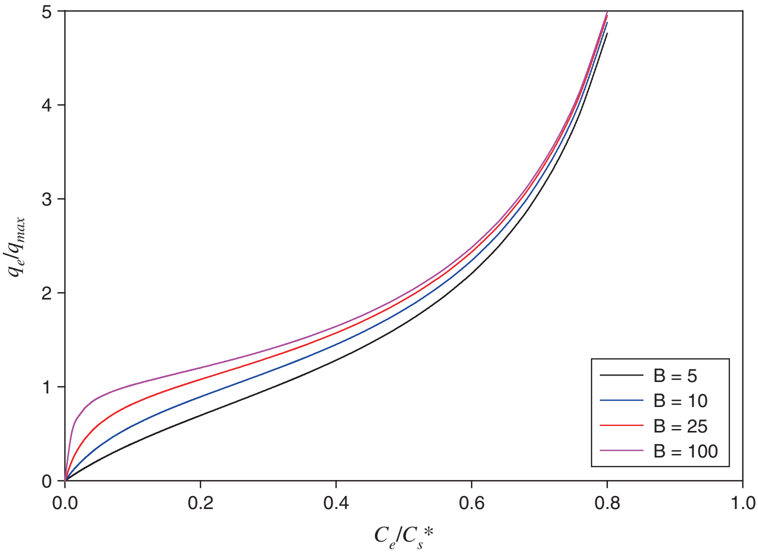

**Fig. 4.5** Plots of the BET equation versus reduced concentration

from aqueous solution using clay composite material. From the fitting of the experimental data, the values of parameter $B$ were less than 1 ($r^2 > 0.91$). The parameter $B$ relates to the energy of adsorption and can be defined as

$$B = \exp\left(\frac{E_A - E_L}{RT}\right) \tag{4.15}$$

where $E_A$ is the heat of adsorption in the first layer and $E_L$ is the heat of liquefaction in subsequent layers. The heat of adsorption in the first layer is larger than the heat of liquefaction (Do 1998), therefore the value of parameter $B$ is usually very large. After verification the values of fitted parameter $B$ obtained by Gao et al. (2013) with the physical meaning of the parameter, it is obvious that the BET equation is not adequate to correlate their experimental data.

## 4.4 Three Parameters Isotherms

In some cases the available two parameters isotherm models are not sufficient for the correlation of the adsorption experimental data, therefore the addition more parameters or modify the existing isotherm models are necessary. Currently there are several isotherm models with three or more parameters such as Sips, Toth, Redlich-Peterson, Unilan, and Keller-Staudt. Unilan and Keller-Staudt models have never been in use to correlate the adsorption equilibria of hazardous substance—clay systems.

### *4.4.1 Sips Isotherm*

Sips isotherm also known as Langmuir–Freundlich was proposed by Sips in 1948. This equation possesses a similar form to Langmuir and Freundlich models. The improvement of this equation is it has a finite saturation capacity at sufficiently high concentration.

$$q_e = q_{\max} \frac{(K_S C_e)^{1/n_s}}{1 + (K_s C_e)^{1/n_s}} \tag{4.16}$$

The parameter $K_S$ represents the adsorption affinity, while the parameter $n_S$ is regarded as the parameter characterizing the system's heterogeneity. The heterogeneity could stem from the clay minerals or the solutes, or a combination of both. If the system is homogeneous ($n_S = 1$), the Eq. 4.16 becomes Langmuir isotherm (Eq. 4.1).

The behavior of Sips isotherm as function of $n_S$ is depicted in Fig. 4.6. Since the Sips isotherm is the improvement of Freundlich model, its behavior is the same as that of the Freundlich equation except that the Sips equation possesses a finite saturation limit when the concentration is sufficiently high (Do 1998). The behavior of Sips isotherm at low solute concentration is shown in Fig. 4.7. Figure 4.7 clearly indicates that Sips model still possesses the major drawback of the lack of Henry's law at very low concentration.

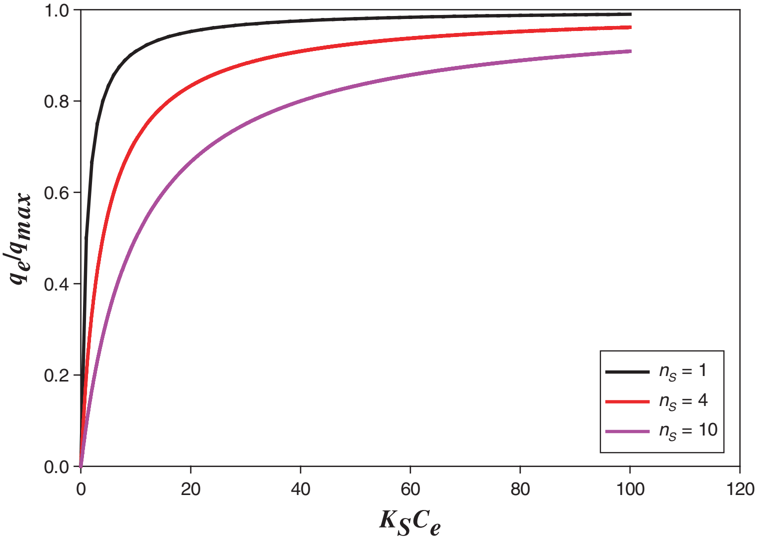

**Fig. 4.6** The behavior of Sips isotherm at high solute concentration

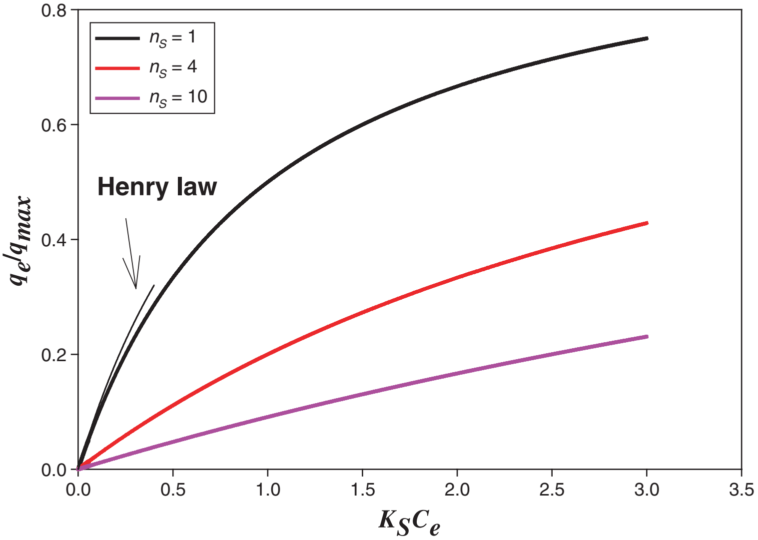

**Fig. 4.7** The behavior of Sips isotherm at low solute concentration

Sips isotherm has been used by several researchers to interpret their adsorption experimental data (Yao et al. 2014; Yahyaei et al. 2014; Bhattacharyya and Ray 2015). Yao et al. (2014) studied the adsorption of methylene blue onto clay-biochar composites; they employed montmorillonite and kaolinite as the clay minerals. The Sips isotherm could represent their adsorption experimental data fairly well. Bhattacharyya and Ray (2015) also utilized this isotherm to represent the adsorption data of congo red and methyl violet onto nano clay filled composite hydrogels of poly acrylic acid and polyethylene glycol. The validity of isotherms was examined based on the value of statistical parameters such as $r^2$, $\chi^2$, and $F$. From the values of statistical parameters they concluded that three parameter Sip model or four parameter Fritz–Schlunder (FS) model gives better fitting than two-parameter Langmuir or Freundlich models. It is not surprising that three and four parameter gave better performance than two parameter model. However, it should be noted that the decision to choose the correct isotherm should not be based just only on the statistical parameters; the decision should be based on the physical meaning of each fitted parameter obtained.

### 4.4.2 Toth Model

Toth equation is three parameter isotherm model which is popularly used to describe gas phase adsorption data. This empirical equation has the correct Henry law type behavior for low concentration and limit saturation capacity for high concentration. Toth equation has the mathematical form as follows

$$\frac{q_e}{q_{\max}} = \frac{K_T C_e}{\left[1 + (K_T C_e)^{n_T}\right]^{1/n_T}} \tag{4.17}$$

Parameter $K_T$ is the adsorption affinity and $n_T$ is a parameter represent the system heterogeneity. Both of these parameters are specific for adsorbate-adsorbent pairs. Unlike Freundlich or Sips equation, the parameter $n_T$ is usually has a value less than one. If this parameter is deviated further away from unity, the system is said to be more heterogeneous. If the value of this parameter equal to 1, the Toth equation reduces to the Langmuir isotherm. Being the three-parameter model, the Toth equation can describe well many liquid phase adsorption data of hazardous substances—clay mineral system (Unuabonah and Adebowale 2009; Chandra et al. 2013).

### 4.4.3 Redlich–Peterson (R–P) Isotherm

Another three parameter equation which capable to represent adsorption equilibria over a wide concentration range is Redlich-Peterson isotherm. Redlich-Peterson equation has the form as follows

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{\beta}} \tag{4.18}$$

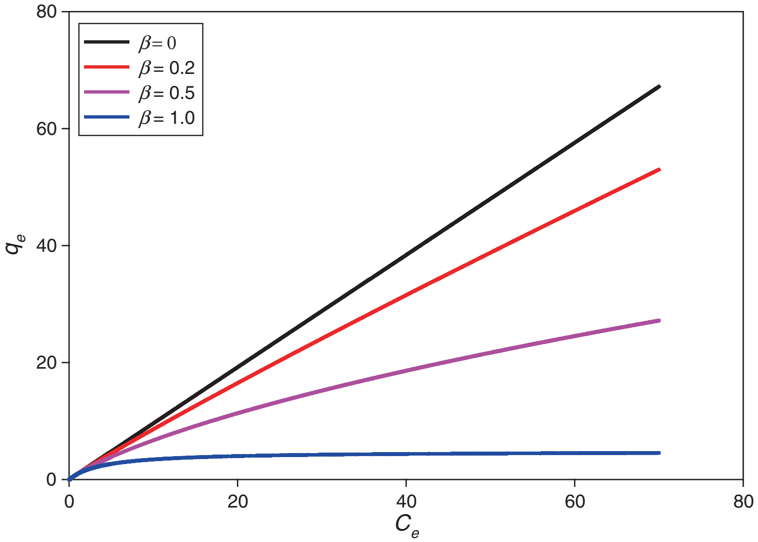

Fig. 4.8 The behavior of Redlich-Peterson isotherm at various value of $\beta$

where $K_R$, $a_R$, and $\beta$ are adsorption affinity, constant parameter, and parameter characterizing the heterogeneity of the system, respectively. This equation is quite popular for the prediction of hazardous substances adsorption onto clay minerals (Peng et al. 2013; Kadu and Chikate 2013; Ahmedzeki et al. 2013; Auta and Hameed 2012; Yao et al. 2014). This isotherm combines both of the characteristics of the Langmuir and Freundlich into a single equation. It reduces to a linear isotherm at low surface coverage and to the Langmuir isotherm when $\beta$ is equal 1. The influence of parameter $\beta$ on the adsorption isotherm behavior is given in Fig. 4.8.

## 4.5 Temperature Dependent Forms

The relevant equilibrium adsorption data provide the most important information for understanding a given adsorption process, since these are needed for the design and analysis of adsorption systems (Ismadji and Bhatia 2000). In most studies of adsorption of hazardous compounds using clay minerals as the adsorbents, the adsorption equilibria data were obtained at a single temperature, some of the studies conducted the adsorption experiments at various temperatures (Yesi et al. 2010; Kurniawan et al. 2011; Nathaniel et al. 2011; Kurniawan et al. 2012; Suwandi et al. 2012; Sandy et al. 2012; Chandra et al. 2013; Anggraini et al. 2014; Ong et al. 2014).

The adsorption of solute onto the surface of the adsorbent is affected by temperature. For physical adsorption, the temperature has a negative effect on the amount adsorbed, and for the chemisorption the amount adsorbed increase with the increase of temperature. In most of the studies, the fitting the adsorption equilibria data obtained from the experiments with isotherm models have been made at a single temperature. Since the adsorption equilibria are temperature dependent, it is important to include the temperature dependence forms of adsorption models in correlating the experimental data. In this sub-section, the temperature dependence forms of four adsorption equations are discussed.

### *4.5.1 Langmuir Isotherm*

The Langmuir theory is based on a kinetic principle that is the rate of adsorption is equal to the rate of desorption from the surface. The parameters $q_m$ and $K_L$ of the Langmuir isotherm (Eq. 4.1) usually are obtained through the fitting procedure using linear or nonlinear regression method. The values of parameters $q_m$ and $K_L$ are temperature dependent. The temperature dependence forms of the Langmuir isotherm parameters ($q_{\max}$ and $K_L$) can be written in the following forms:

$$q_m = q^o_{\max} \exp\left(\delta(T - T_o)\right) \tag{4.19}$$

and

$$K_L = K^o_L \exp\left[\frac{Q}{RT_o}\right] \tag{4.20}$$

where $q^o_{\max}$ is the adsorption capacity of the adsorbent at a reference temperature $T_o$ (usually 25 °C is taken as the reference temperature). The parameter $\delta$ is the expansion coefficient of solute or adsorbate. The parameter $K^o_L$ is the adsorption affinity of the Langmuir isotherm at a reference temperature, while $Q$ is a parameter represents the isosteric heat of adsorption.

The parameter $\delta$ is specific for a given component and independent of the type of adsorbent and of the order of $10^{-3}$/K. The parameter $K^o_L$ has the physical meaning similar to parameter $K_L$ in Eq. 4.1. This parameter can be estimated according to the following equation

$$K^o_L = \frac{\alpha}{k_d\sqrt{2\pi MRT_o}} \tag{4.21}$$

The parameter $\alpha$ is the sticking coefficient, which accounts for non-perfect sticking. The rate constant for desorption is represented by parameter $k_d$. The parameter $K^o_L$ is inversely proportional to the square root of the molecular weight.

The parameter $Q$ is the isosteric heat of adsorption and is equal to the activation energy for desorption. When the isosteric heat of adsorption $Q$ increase, the amount of solute adsorbed on the surface of adsorbent increases due to the higher energy barrier that adsorbed molecules have to overcome to evaporate and diffuse back to the bulk liquid phase (Do 1998). An increase in the temperature will decrease the amount adsorbed at a given solute concentration. This is due to the greater energy acquired by the adsorbed molecule to evaporate (Do 1998).

The capability of the temperature dependence forms of the Langmuir model was examined by several researchers. Table 4.2 summarizes the use of temperature dependent forms of the Langmuir model to correlate the adsorption experimental data of hazardous substances—clay mineral system. The temperature dependence of the Langmuir model generally can represent the adsorption system well as indicated by the value of $r^2$ higher than 0.95. The decision to choose or decide the suitability of the model to represent the experimental data should not only be based on the value of $r^2$ but should be based on the rationality of the physical meaning of each parameter.

The values of parameter $q^o_{\max}$ listed in Table 4.2 are reasonable, the adsorption capacity of clays increase after modification, and this phenomenon is in accordance with the purpose of the modification of clay minerals is to increase the adsorption capacity. The next parameter is the expansion coefficient of solute or adsorbate ($\delta$), as mentioned before, this parameter is specific to a given component and independent of the type of adsorbent, from Table 4.2 it can be seen that the Langmuir model with its temperature dependent forms fails to give the consistent fitted parameter $\delta$. Therefore, this model is not suitable to represent the adsorption experimental data for the system listed in Table 4.2.

**Table 4.2** The fitted temperature dependence parameters of Langmuir model

| Clay mineral | Hazardous substance | Parameter | | | | References |
|---|---|---|---|---|---|---|
| | | $q^o_{\max}$, mmol/g | $\delta \times 10^3$/K | $K^o_L$, L/mmol | $Q$, kJ/mol | |
| Ca-bentonite | Acid blue 129 | 1.05 | 16.00 | 4.17 | 3.85 | Yesi et al. (2010) |
| CTA-bentonite | Acid blue 129 | 1.59 | 15.20 | 768.09 | 11.55 | Yesi et al. (2010) |
| Ca-bentonite | Pb(II) | 0.047 | 0.17 | $1.24 \times 10^{-4}$ | 27.71 | Nathaniel et al. (2011) |
| LAS-bentonite | Pb(II) | 0.193 | 1.89 | $1.45 \times 10^{-5}$ | 33.49 | Nathaniel et al. (2011) |
| LAS-bentonite | Cu(II) | 0.285 | 9.50 | 1036.8 | −8.94 | Sandy et al. (2012) |
| Kaolin | Malachite green | 0.365 | 3.80 | 4.392 | 21.83 | Suwandi et al. (2012) |
| Rarasaponin-kaolin | Malachite green | 0.497 | 6.20 | 34.534 | 46.25 | Suwandi et al. (2012) |
| Ca-bentonite | Evans blue | 0.167 | 3.40 | 0.452 | 0.88 | Chandra et al. (2013) |
| Rarasaponin-bentonite | Evans blue | 0.527 | 0.70 | 0.114 | 3.15 | Chandra et al. (2013) |

*Note* $r^2$ for all fitting >0.95

### 4.5.2 Freundlich Isotherm

The parameters $K_F$ and $n$ of the Freundlich isotherm (Eq. 4.7) are dependent on temperature. Do (1998) has mentioned that the dependence of the parameters $K_F$ and $n$ on temperature is very complex, and should not be extrapolated them outside their range of validity. The complete derivation of temperature dependence of Freundlich isotherm should be referred to Do (1998). The temperature dependence forms of Freundlich isotherm can be written as follows:

$$K_F = K_F^o \exp\left(-\frac{\eta R_g T}{A_o}\right) \tag{4.22}$$

and

$$\frac{1}{n} = \frac{R_g T}{A_o} \tag{4.23}$$

The parameter $K_F^o$ is assumed as the Freundlich adsorption capacity at reference temperature $T_o$. The parameters $A_o$ and $\eta$ represent the characteristic adsorption energy of surface and constant parameter of Clapeyron, respectively. For most of the adsorption system, the parameter $n$ is higher than one, indicates that the molar thermal energy $R_g T$ is lower than the characteristic adsorption energy of surface $A_o$ (Do 1998).

Table 4.3 summerizes the fitted values of temperature dependence parameters of Freundlich isotherm. The reasonable fitted value of $K_F^o$ was obtained only by Chandra et al. (2013), while others either too high or too low. The fitted value of constant parameters of Clapeyron, $\eta$, for rarasaponin-bentonite and the Evans blue system was also reasonable and comparable to the value available in the literature (Do 1998). The removal of Evans blue using Ca-bentonite and rarasaponin-bentonite was conducted at three different temperatures: 303, 318, and 333 K (Chandra et al. 2013). The molar thermal energy at those temperatures are 2.52, 2.64, and 2.76 kJ/mol. As mentioned before, the value of heterogeneity of the system $n$ mostly is higher than one, therefore, the characteristic adsorption energy of surface $A_o$ must be higher than the molar thermal energy $R_g T$, and the fitted values of parameter $A_o$ for both systems are still consistent with its physical meaning.

The system heterogeneity could stem from the solid or the adsorbate or a combination of both. Kurniawan et al. (2011) have mentioned about the deacylation and attachment of the acyl ($C_2H_3O^+$) groups to the protonated silanol groups which are available in tetrahedral sheet of natural bentonite. The heterogeneity of the system increase with the attachment of rarasaponin molecule into the interlayer structure of Ca-bentonite (Chandra et al. 2013). In Freundlich equation the degree of heterogeneity of the system is indicated by parameter $n$, the larger is this parameter, the higher is the degree of heterogeneity. From Eq. 4.2 it can be seen that the value of parameter $1/n$ is a linear function of $1/A_o$, the larger value of $A_o$ the larger value of $n$. This phenomenon was not captured by parameter $A_o$ in Freundlich model, the value of this parameter decreases with increase of the

**Table 4.3** The fitted temperature dependence parameters of Freundlich isotherm

| Clay mineral | Hazardous substance | Parameter | | | References |
|---|---|---|---|---|---|
| | | $K_F^o$, (mmol/g) (mmol/L)$^{-n}$ | $\eta$ | $A_o$, kJ/mol | |
| Ca-bentonite | Acid blue 129 | 32.25 | 2.384 | −175.92 | Yesi et al. (2010) |
| CTA-bentonite | Acid blue 129 | 204.33 | 2.421 | −153.23 | Yesi et al. (2010) |
| Ca-bentonite | Pb(II) | 0.0034 | −0.339 | 0.318 | Nathaniel et al. (2011) |
| LAS-bentonite | Pb(II) | 0.0081 | −0.535 | 0.413 | Nathaniel et al. (2011) |
| LAS-bentonite | Cu(II) | 0.0061 | −0.015 | 9.57 | Sandy et al. (2012) |
| Kaolin | Malachite green | 8.974 | 0.247 | 176.42 | Suwandi et al. (2012) |
| Rarasaponin-kaolin | Malachite green | 47.582 | 0.308 | 171.11 | Suwandi et al. (2012) |
| Ca-bentonite | Evans blue | 0.274 | 1.646 | 3.121 | Chandra et al. (2013) |
| Rarasaponin-bentonite | Evans blue | 0.612 | 1.457 | 2.858 | Chandra et al. (2013) |

*Note* $r^2$ for all fitting >0.95

system heterogeneity (Chandra et al. 2013). These evidences indicate that the Freundlich model with its dependence temperature forms failed to represent the adsorption equilibria data of heavy metals—clay minerals system or dyes—clay mineral system.

### 4.5.3 *Sips Isotherm*

For better applicability at various temperatures, Sips isotherm also possesses temperature dependence forms as follows

$$K_S = K_S^o \exp\left(\frac{Q}{R_g T_o}\left(\frac{T_o}{T} - 1\right)\right) \tag{4.24}$$

$$\frac{1}{n_S} = \frac{1}{n_S^o} + \alpha_S\left(1 - \frac{T_o}{T}\right) \tag{4.25}$$

here $K_S^o$ is adsorption affinity constant at a reference temperature, $n_S^o$ is the parameter characterizing the system heterogeneity at a reference temperature, and $\alpha_S$ is a constant. The temperature dependence of affinity constant of Sips isotherm is similar to Eq. 4.20, the difference is in the physical meaning of parameter $Q$. The parameter $Q$ in the Langmuir equation measure isosteric heat of adsorption which is invariant with surface loading (Do 1998), while the parameter $Q$ in Sips isotherm only the measure of the heat of adsorption.

The correlation between the heat of adsorption and isosteric heat of adsorption can be obtained through van't Hoff equation (Do 1998)

$$\frac{(-\Delta H)}{R_g T^2} = \left(\frac{\partial C}{\partial T}\right)_\theta \tag{4.26}$$

where $\theta = \frac{q_e}{q_{\max}}$, and the Sips model becomes

$$\theta = \frac{(K_S C_e)^{1/ns}}{1 + (K_S C_e)^{1/ns}} \tag{4.27}$$

By assuming $(K_S C_e)^{1/ns} = y$, the Sips isotherm can be written as

$$\theta = \frac{y}{1+y} \tag{4.28}$$

At the constant loading $\mathrm{d}\theta = 0$, and $\mathrm{d}y = 0$, and using the temperature dependence forms of Sips isotherm (Eqs. 4.24 and 4.25) we can obtain

$$-\Delta H = Q - n_S \alpha_S R_g T_o \ln (K_S C_e) \tag{4.29}$$

And in the term of surface fractional loading

$$-\Delta H = Q - n_s^2 \alpha_S R_g T_o \ln \left(\frac{\theta}{1-\theta}\right) \tag{4.30}$$

From Eq. 4.30, it is obvious that the isosteric heat of adsorption will equal to the heat of adsorption when the surface fractional loading is 0.5. Thus the physical meaning of parameter $Q$ in Eq. 4.24 is the isosteric heat at the fractional loading of 0.5. The temperature dependence forms of Sips model have been used to correlate the adsorption experimental data of several substances on clay mineral and the results are summarized in Table 4.4.

Table 4.4 reveals that there are several inconsistencies of the fitted values with the physical meaning of each parameter. The Sips with its temperature dependence forms can represent the experimental data well for the adsorption of acid blue onto Ca-bentonite and CTA-bentonite (Yesi et al. 2010), and the adsorption of malachite green onto kaolin and rarasaponin-kaolin (Suwandi et al. 2012).

### *4.5.4 Toth Model*

The parameters $K_T$ and $n_T$ in Toth model are temperature dependent and can be written mathematically in the following forms

$$K_T = K_T^o \exp\left[\frac{Q}{R_g T_o}\left(\frac{T_o}{T} - 1\right)\right] \tag{4.31}$$

**Table 4.4** The fitted temperature dependence parameters of Sips isotherm

| Clay mineral | Hazardous substance | Parameter | | | | | | References |
|---|---|---|---|---|---|---|---|---|
| | | $q^o_{\max}$, mmol/g | $\delta \times 10^3$/K | $K^o_S$, L/mmol | $Q$, kJ/mol | $n^o_S$ | $\alpha_S$ | |
| Ca-bentonite | Acid blue 129 | 0.76 | 29.3 | 1.53 | 10.88 | 0.88 | 1.68 | Yesi et al. (2010) |
| CTA-bentonite | Acid blue 129 | 2.76 | 30.5 | 1.79 | 38.59 | 1.54 | 1.27 | Yesi et al. (2010) |
| Ca-bentonite | Pb(II) | 0.047 | 9.6 | 8.574 | 13.57 | 1.04 | 4.86 | Nathaniel et al. (2011) |
| LAS-bentonite | Pb(II) | 0.204 | 0.11 | 9.528 | 19.37 | 1.11 | 5.72 | Nathaniel et al. (2011) |
| LAS-bentonite | Cu(II) | 0.326 | 7.8 | 17.59 | −13.67 | 1.45 | 1.37 | Sandy et al. (2012) |
| Kaolin | Malachite green | 0.509 | 7.6 | 1.681 | 10.01 | 1.48 | 1.31 | Suwandi et al. (2012) |
| Rarasaponin-kaolin | Malachite green | 0.919 | 7.9 | 2.410 | 21.72 | 2.37 | 1.40 | Suwandi et al. (2012) |
| Ca-bentonite | Evans blue | 0.185 | 0.810 | 0.542 | 5.29 | 1.02 | 0.299 | Chandra et al. (2013) |
| Rarasaponin-bentonite | Evans blue | 0.575 | 1.330 | 0.367 | 9.64 | 1.01 | 0.405 | Chandra et al. (2013) |

$$n_T = n^o_T + \alpha_T \left(1 - \frac{T_o}{T}\right) \tag{4.32}$$

Here $K^o_T$ is the adsorption affinity at a reference temperature $T_o$, and similar to Sips isotherm the parameter $Q$ is only a measure heat of adsorption. Table 4.5 summarizes the fitted values of temperature dependence forms of Toth isotherm for the adsorption of several compounds on clay minerals. Based on the examination of the physical meaning of the value of each parameter listed in Table 4.5, it can be concluded that the Toth equation could represent the adsorption data of Pb(II) onto Ca-bentonite and LAS-bentonite and evans blue onto Ca-bentonite and rarasaponin-bentonite quite well.

Similar to Sips isotherm, the heat of adsorption can be correlated to the isosteric heat of adsorption using van't Hoff equation (Eq. 4.26), and in the term of surface fractional loading, the correlation between the isosteric heat of adsorption and heat of adsorption is written as

$$(-\Delta H) = Q - \frac{1}{n_T}\left(\alpha_T R_g T_o\right)\left[\ln\left(\frac{\theta}{\left(1-\theta^{n_T}\right)^{1/n_T}}\right) - \frac{\ln\theta}{\left(1-\theta^{n_T}\right)}\right] \tag{4.33}$$

**Table 4.5** The fitted temperature dependence parameters of Toth isotherm

| Clay mineral | Hazardous substance | Parameter | | | | | | References |
|---|---|---|---|---|---|---|---|---|
| | | $q^o_{\max}$, mmol/g | $\delta \times 10^3$/K | $K^o_T$, L/mmol | $Q$, kJ/mol | $n^o_T$ | $\alpha_T$ | |
| Ca-bentonite | Acid blue 129 | 1.05 | 16 | 1.135 | 2.814 | 1 | 0 | Yesi et al. (2010) |
| CTA-bentonite | Acid blue 129 | 1.54 | 14 | 0.144 | 12.17 | 0.96 | 0.46 | Yesi et al. (2010) |
| Ca-bentonite | Pb(II) | 0.049 | 7.9 | 8.66 | 29.14 | 0.87 | 8.45 | Nathaniel et al. (2011) |
| LAS-bentonite | Pb(II) | 0.207 | 8.2 | 11.39 | 38.92 | 0.77 | 10.77 | Nathaniel et al. (2011) |
| LAS-bentonite | Cu(II) | 0.344 | 6.7 | 59.2 | 4.02 | 0.54 | 1.80 | Sandy et al. (2012) |
| Kaolin | Malachite green | 0.709 | −2.9 | 0.419 | 12.27 | 0.407 | −0.14 | Suwandi et al. (2012) |
| Rarasaponin-kaolin | Malachite green | 1.956 | 27.1 | 0.253 | 8.76 | 0.151 | 0.15 | Suwandi et al. (2012) |
| Ca-bentonite | Evans blue | 0.263 | 2.380 | 2.051 | 9.63 | 0.77 | 0.97 | Chandra et al. (2013) |
| Rarasaponin-bentonite | Evans blue | 0.516 | 2.230 | 2.524 | 11.43 | 3.38 | 4.24 | Chandra et al. (2013) |

At $\theta = 0$, the value of isosteric heat of adsorption is infinity, and at $\theta = 1$ (very high loading), the value of isosteric heat of adsorption is minus infinity. Based on the fitted value of the heat of adsorption of Pb(II) onto Ca-bentonite and LAS-bentonite, the isosteric heat of adsorption of the system is estimated as the function of surface functional loading and the results are depicted in Fig. 4.9. As seen in Fig. 4.9, the isosteric heat of adsorption decreases with loading.

## 4.6 Multicomponent Models

Most of the studies on the adsorption of hazardous substances using clay minerals have focused on the single component uptake. The single component adsorption provides the basic foundation for the design of industrial adsorption processes. In the real application, most or all of the systems usually involve multicomponent, and therefore adsorption equilibria involving competition between molecules of different type are needed in order to understand the system as well as for the

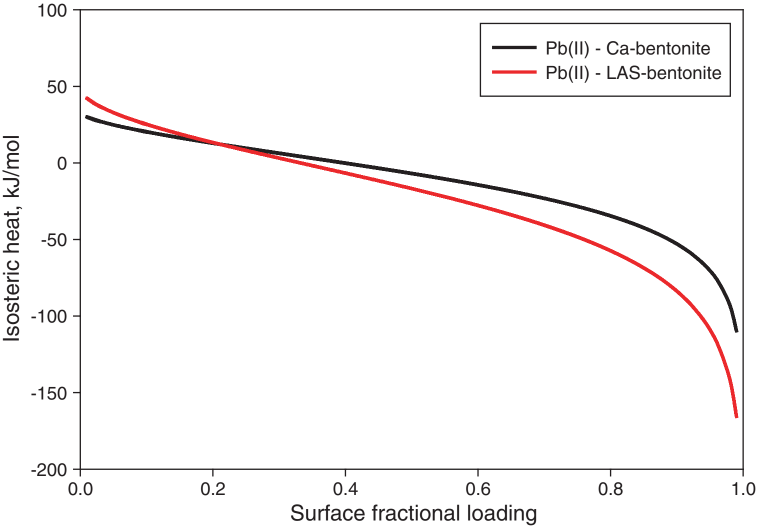

**Fig. 4.9** Plot isosteric heat of adsorption for Pb(II) onto Ca-bentonite and LAS-bentonite

design purposes (Do 1998). A proper model of multicomponent adsorption equilibria data may provide a complete description of the adsorption process in the practical application, yet, it is a challenging task to build it.

Several multi-component adsorption isotherms are available, some of the isotherms are purely empirical or semi-empirical, and some of them have the fundamental thermodynamic basis. The currently available multi-component models which widely used to correlate the multicomponent adsorption data are extended Langmuir isotherm equation, various versions of Ideal Adsorption Solution Theory (IAST), empirical isotherm based on the Langmuir equation (multicomponent Sips isotherm), Real Adsorption Solution Theory (RAST), the potential theory, etc. Most of the available empirical or semi-empirical adsorption models often lack of the theoretical basis and may not be able to accurately predict the multicomponent adsorption behavior (Ong et al. 2014).

Since the multicomponent adsorption is much more complex compared to single component adsorption, only a limited number of studies were conducted considering the multicomponent adsorption of hazardous substances onto clay minerals.

### *4.6.1 Extended Langmuir Isotherm and Its Modified Forms*

Compared to single component adsorption, to obtain multicomponent adsorption equilibria data is much more difficult. Therefore, the easiest way to estimate multicomponent adsorption equilibria is based on single solutes adsorption equilibria.

However, this approach often fails to represent the multicomponent adsorption equilibria accurately. When multicomponent solutes exist in the solution and each component has the possibility to occupy the same adsorption sites, the isotherm relationships become more complex due to the competition of the components for the same adsorption sites.

A model for competitive sorption on the basis of kinetic considerations of the Langmuir equation has been proposed by Markham and Benton (1931) to describe the sorption equilibrium in multi-component systems. This extended model of Langmuir isotherm is only applicable when each component in the system obeys Langmuir behavior in a single-solute adsorption system. In the development of the extended Langmuir model for multi-component system, the similar assumptions of the single solute system were also used (Do 1998). The rate of adsorption of solute $i$ on the surface of the adsorbent is:

$$R_{a,i} = K_{a,i} C_{e,i} \left( 1 - \sum_{j=1}^{n} \theta_j \right) \tag{4.34}$$

If the rate of desorption of the solute $i$ is proportional to its fractional loading

$$R_{d,i} = K_{d,i} \theta_i \tag{4.35}$$

At equilibrium condition, the rate of adsorption of solute $i$ is equal to the rate of desorption

$$K_{a,i} C_{e,i} \left( 1 - \sum_{j=1}^{n} \theta_j \right) = K_{d,i} \theta_i \tag{4.36}$$

If $K_{L,i} = K_{a,i} / K_{d,i}$ and $\sum_{j=1}^{n} \theta_j = \theta_T$ is total fractional coverage, the Eq. 4.36 can be written as

$$K_{L,i} C_{e,i} (1 - \theta_T) = \theta_i \tag{4.37}$$

If the number of solute in the solution is $n$, and the summation for $n$ component, the total fractional coverage can be written as

$$\theta_T = \frac{\sum\limits_{j=1}^{n} K_{L,j} C_{e,j}}{1 + \sum\limits_{j=1}^{n} K_{L,j} C_{e,j}} \tag{4.38}$$

And the fractional coverage contributes by component $i$ is

$$\theta_i = \frac{K_{L,i} C_{e,i}}{1 + \sum\limits_{j=1}^{n} K_{L,j} C_{e,j}} \tag{4.39}$$

Equation 4.39 can be written in the term of amount adsorbed at equilibrium condition as follow

$$\frac{q_{e,i}}{q_{\max,i}} = \frac{K_{L,i}C_{e,i}}{1 + \sum_{j=1}^{n} K_{L,i}C_{e,i}} \tag{4.40}$$

Equation 4.40 is known as the extended Langmuir equation, and for binary components

$$\frac{q_{e,1}}{q_{\max,1}} = \frac{K_{L,1}C_{e,1}}{1 + K_{L,1}C_{e,1} + K_{L,2}C_{e,2}} \tag{4.41}$$

and

$$\frac{q_{e,2}}{q_{\max,2}} = \frac{K_{L,2}C_{e,2}}{1 + K_{L,1}C_{e,1} + K_{L,2}C_{e,2}} \tag{4.42}$$

where $q_{e,1}$ and $q_{e,2}$ are the amount of solute 1 and solute 2 adsorbed at equilibrium condition, while $C_{e,1}$ and $C_{e,2}$ are the equilibrium concentration of solute 1 and solute 2. The adsorption capacity of adsorbent toward solute 1 and solute 2 is indicated by parameter $q_{\max,1}$ and $q_{\max,2}$. The parameters $q_{\max,1}$, $q_{\max,2}$, $K_{L,1}$, and $K_{L,2}$ are obtained from single component adsorption isotherm.

The extended Langmuir model was applied to correlate the binary adsorption experimental data for several systems such as basic textile dyes on bentonite (Turabik and Gozmen 2013), Cd(II)–Ni(II) on bentonite, Zn(II)–Cd(II) on sepiolite and Pb(II)–Cu(II) on vermiculite (Padilla-Ortega et al. 2013), heavy metals on chitosan immobilized on bentonite (Futalan et al. 2011), Pb(II)-Cd(II) on beidellite (Etci et al. 2010), dye-surfactant on clay (Atun et al. 2009), Acid red 18—Acid yellow 23 on bentonite based composite (Qiao et al. 2009).

For a binary system, Fig. 4.10 shows theoretical plots of fractional coverage of component 1 as the function of component 2 (varying parameter). From this figure, it is clear that of the additional component 2 causes a decrease in the amount adsorbed of the component 1 and vice versa due to the competition between two solutes.

The evaluation of binary adsorption equilibrium data using extended Langmuir model was performed by inserting the values of parameters $K_L$ and $q_{\max}$ obtained from single system adsorption to calculate the theoretical value of $q_e$ and compared it with experimental results. For several systems, the calculation using this procedure may give good correlation result; however, the results may be not correct, especially if the adsorbent exhibits a microporous or heterogeneous structure (Kurniawan et al. 2012). As mentioned before, in the binary liquid phase adsorption, the competition between adsorbate species for the adsorption sites on the solid surface occur and may act as the sorption-controlling factor. Since the parameters $K_L$ and $q_{\max}$ from single system do not account the competition between adsorbate species in the system, it is obvious that both of these parameters cannot be adequately used to describe adsorption behaviors in binary system.

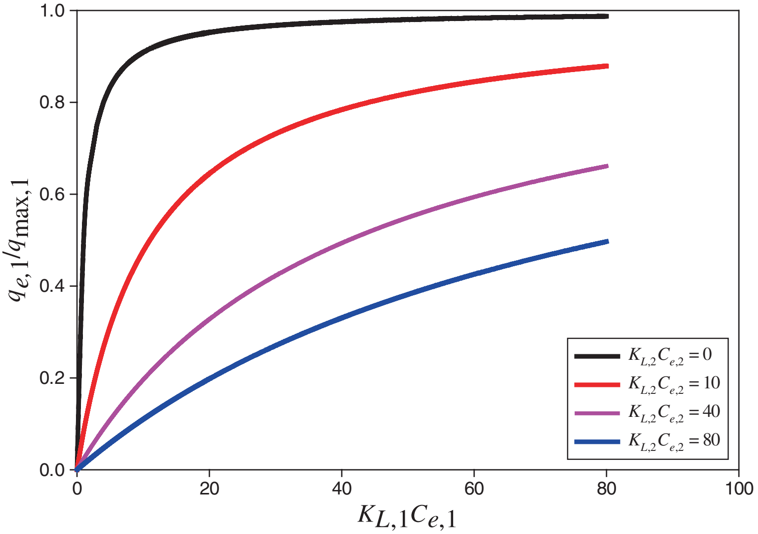

**Fig. 4.10** Theoretical plots of fractional coverage of extended Langmuir equation for binary component

Kurniawan et al. (2012) have proposed revisited models for parameters $K_L$ and $q_{\max}$ for the binary adsorption system as follows

$$q_{\max,bin} = q_{\max,1}\Theta_1 + q_{\max,2}\Theta_2 \tag{4.43}$$

$$K_{L,1(bin)} = K_{L,1} \exp\left(\frac{-\Theta_2}{\Theta_1}\right) \tag{4.44}$$

$$K_{L,2(bin)} = K_{L,2} \exp\left(\frac{-\Theta_1}{\Theta_2}\right) \tag{4.45}$$

where $\Theta_1$ and $\Theta_2$ are parameters representing fractional loading of each adsorbate species on the adsorbent surface. The substitution of Eqs. (4.43)–(4.45) in (4.41) and (4.42) give the results as follow

$$q_{e,1} = \frac{\left(q_{\max,1}\Theta_1 + q_{\max,2}\Theta_2\right)K_{L,1} \exp\left(-\Theta_2/\Theta_1\right)C_{e,1}}{1 + \left(q_{\max,1}\Theta_1 + q_{\max,2}\Theta_2\right)K_{L,1} \exp\left(-\Theta_2/\Theta_1\right)C_{e,1} + \left(q_{\max,1}\Theta_1 + q_{\max,2}\Theta_2\right)K_{L,2} \exp\left(-\Theta_1/\Theta_2\right)C_{e,2}} \tag{4.46}$$

$$q_{e,2} = \frac{\left(q_{\max,1}\Theta_1 + q_{\max,2}\Theta_2\right)K_{L,2} \exp\left(-\Theta_1/\Theta_2\right)C_{e,2}}{1 + \left(q_{\max,1}\Theta_1 + q_{\max,2}\Theta_2\right)K_{L,1} \exp\left(-\Theta_2/\Theta_1\right)C_{e,1} + \left(q_{\max,1}\Theta_1 + q_{\max,2}\Theta_2\right)K_{L,2} \exp\left(-\Theta_1/\Theta_2\right)C_{e,2}} \tag{4.47}$$

Equations (4.46) and (4.47) reduce to single Langmuir model if only one solute available in the solution. The above equations could represent the adsorption experimental data of malachite green—methylene blue on rarasaponin-bentonite quite well. The inclusion of fractional surface coverage in the extended Langmuir model could increase the performance of the traditional extended model in representing the experimental data.

Ong et al. (2014) proposed a modification of the extended Langmuir model to represent the binary adsorption equilibria data of biocidal compounds on organo-bentonite (dodecyltricetyl ammonium-bentonite). Their proposed model incorporates the thermodynamic property of adsorption. They used a similar approach as Kurniawan et al. (2012), the modification was conducted to the parameters $K_L$ and $q_{\max}$. Based on the value of parameter $q_{\max}$ in a single system, the binary maximum adsorption capacity in the equilibrium condition was assumed equal to the log mean value of each maximum sorption capacity of the solute in the single adsorption system

$$q_{\max,bin} = \frac{q_{\max,2} - q_{\max,1}}{\ln\left(\frac{q_{\max,2}}{q_{\max,1}}\right)} \tag{4.48}$$

where $q_{\max,2} > q_{\max,1}$. By introducing the concept of Gibb's free energy, the adsorption affinity for binary components is given by the following equations:

$$K_{L,1(bin)} = K_{L,1}\left(\frac{\Delta G_1^o C_{o,1}}{\Delta G_1^o C_{o,1} + \Delta G_2^o C_{o,2}}\right) \tag{4.49}$$

$$K_{L,2(bin)} = K_{L,2}\left(\frac{\Delta G_2^o C_{o,2}}{\Delta G_1^o C_{o,1} + \Delta G_2^o C_{o,2}}\right) \tag{4.50}$$

The competitive behavior of the solutes is given as the ratio of the multiplication value between standard Gibb's free energy change and initial concentration of certain solute to the summation of those values for both solutes. The adsorption affinity of an adsorbate species in the binary adsorption system is reduced from its adsorption affinity in the single adsorption system without the presence of adsorbates competition (Ong et al. 2014).

In order to test the validity of their proposed model, the binary component adsorption of triclosan and benzalkonium chloride were conducted at three different temperatures in the static mode system. They found that the incorporation of the log mean value of maximum adsorption capacity and the Gibb's free energy ratio in the extended Langmuir model gave a better representation of the experimental data than the original extended Langmuir model. Incorporation of the Gibb's free energy on the affinity constant of the extended Langmuir equation may attribute robust predictive ability of the binary adsorption model (Ong et al. 2014).

### 4.6.2 Freundlich Multicomponent Adsorption Isotherm

Most of the available single component adsorption isotherm, in principle can be extended to fit the multicomponent adsorption equilibria data. One of the extended forms of adsorption isotherm, which also used to correlate multicomponent adsorption data is extended Freundlich isotherm. The extended Freundlich model has the form as follows (Do 1998)

$$q_{e,1} = \frac{n\left(\frac{K_{F,1}}{n}\right)^{1/n} C_{e,1}}{\left[\left(\frac{K_{F,1}}{n}\right)^{1/n} C_{e,1} + \left(\frac{K_{F,2}}{n}\right)^{1/n} C_{e,2}\right]^{1-n}} \tag{4.51}$$

$$q_{e,2} = \frac{n\left(\frac{K_{F,2}}{n}\right)^{1/n} C_{e,2}}{\left[\left(\frac{K_{F,1}}{n}\right)^{1/n} C_{e,1} + \left(\frac{K_{F,2}}{n}\right)^{1/n} C_{e,2}\right]^{1-n}} \tag{4.52}$$

Equations (4.51) and (4.52) assume that the heterogeneity of the system toward solute 1 and solute 2 is the same ($n_1 = n_2 = n$), in the case of unequal heterogeneity between adsorbent and solutes ($n_1 \neq n_2 \neq n$) more complicate equations are obtained:

$$q_{e,1} = \frac{\overline{n}\left(\frac{K_{F,1}}{n_1}\right)^{1/n_1} C_{e,1}}{\left[\left(\frac{K_{F,1}}{n_1}\right)^{1/n_1} C_{e,1} + \left(\frac{K_{F,2}}{n_2}\right)^{1/n_2} C_{e,2}\right]^{1-\overline{n}}} + \Delta F_r \tag{4.53}$$

$$q_{e,2} = \frac{\overline{n}\left(\frac{K_{F,2}}{n_2}\right)^{1/n_2} C_{e,2}}{\left[\left(\frac{K_{F,1}}{n_1}\right)^{1/n_1} C_{e,1} + \left(\frac{K_{F,2}}{n_2}\right)^{1/n_2} C_{e,2}\right]^{1-\overline{n}}} + \Delta F_r \tag{4.54}$$

where

$$\begin{aligned}\Delta F_r =& (n_1 - n_2) \frac{\left(\frac{K_{F,1}}{n_1}\right)^{1/n_1} C_{e,1} \left(\frac{K_{F,2}}{n_2}\right)^{1/n_2} C_{e,2}}{\left[\left(\frac{K_{F,1}}{n_1}\right)^{1/n_1} C_{e,1} + \left(\frac{K_{F,2}}{n_2}\right)^{1/n_2} C_{e,2}\right]^{2-\overline{n}}} \\ & \times \ln\left[\left(\frac{K_{F,1}}{n_1}\right)^{1/n_1} C_{e,1} + \left(\frac{K_{F,2}}{n_2}\right)^{1/n_2} C_{e,2}\right]\end{aligned} \tag{4.55}$$

$$\overline{n} = \frac{\left[n_1\left(\frac{K_{F,1}}{n_1}\right)^{1/n_1} C_{e,1} + n_2\left(\frac{K_{F,2}}{n_2}\right)^{1/n_2} C_{e,2}\right]}{\left[\left(\frac{K_{F,1}}{n_1}\right)^{1/n_1} C_{e,1} + \left(\frac{K_{F,2}}{n_2}\right)^{1/n_2} C_{e,2}\right]} \tag{4.56}$$

where $K_{F,1}$, $K_{F,2}$, $n_1$, and $n_2$ are parameters derived from the corresponding single component Freundlich isotherm equations.

Extended Freundlich isotherm has successfully been applied to correlate several multicomponent adsorption experimental data, such as basic red 46—basic yellow 28 on bentonite (Turabik and Gozmen 2013), toluidine blue—cetyltrimethylammonium bromide on clay (Atun et al. 2009), 4-nitrophenol—basic yellow 28 on iron organo–inorgano pillared montmorillonite clay (Zermane et al. 2010), and humic acid—basic yellow 28 on iron organo–inorgano pillared clay and two Hydrous Ferric Oxides (Zermane et al. 2013).

## 4.7 Thermodynamics of Adsorption

Adsorption thermodynamic relates the equilibrium of adsorption to those properties which cannot be directly measured from the experiment, and these properties are activation energy ($E_a$), the change of standard Gibb's free energy ($\Delta G^o$), the change of the standard enthalpy ($\Delta H^o$), and the change of standard entropy ($\Delta S^o$). The spontaneity of the adsorption process is indicated by the change of standard Gibb's free energy, therefore this thermodynamic property is one of the most important criteria in the adsorption process. The change of standard Gibb's free energy can be related to adsorption equilibrium constant by the following simple equation:

$$\Delta G^o = RT \ln K_D \tag{4.57}$$

where $K_D$ is the linear sorption distribution coefficient, defined as a ratio between the equilibrium surface concentration of adsorbed solute and the equilibrium solute concentration in the liquid phase. The value of $K_D$ is obtained from the plot of $\ln(q_e/C_e)$ versus $C_e$. The change of standard enthalpy and entropy are obtained from classical van't Hoff equation:

.

$$\ln K_D = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \tag{4.58}$$

Table 4.6 summarizes the values of thermodynamic parameters for single adsorption of some hazardous substances on clay minerals obtained from several studies conducted in 2014. The negative values of $\Delta G^o$ indicate that the adsorption is thermodynamically feasible and spontaneous with high preference of solutes to the surface, while the positive values of the Gibb's free energy change indicate the non-spontaneous nature of the adsorption. From Table 4.6 it can be seen that most of the systems have negative values of $\Delta G^o$, indicate that the adsorption of some

**Table 4.6** Thermodynamic parameters for adsorption of several hazardous substances in single component systems

| Adsorbent | Compound | T (K) | Thermodynamic parameters | | | References |
|---|---|---|---|---|---|---|
| | | | $\Delta G^o$ (kJ/mol) | $\Delta H^o$ (kJ/mol) | $\Delta S^o$ (kJ/mol K) | |
| Bentonite | Amoxicillin | 303.15 | −5.55 | 43.8 | 0.1628 | Anggraeni et al. (2014) |
| | | 313.15 | −7.18 | | | |
| | | 323.15 | −8.81 | | | |
| | Ampicillin | 303.15 | −8.78 | 45.3 | 0.1784 | |
| | | 313.15 | −10.56 | | | |
| | | 323.15 | −12.35 | | | |
| Organo-bentonite | Amoxicillin | 303.15 | −9.92 | 48.1 | 0.1914 | |
| | | 313.15 | −11.84 | | | |
| | | 323.15 | −13.75 | | | |
| | Ampicillin | 303.15 | −12.12 | 49.6 | 0.2036 | |
| | | 313.15 | −14.16 | | | |
| | | 323.15 | −16.19 | | | |
| Organo-bentonite | Anillin | 298.15 | 11.29 | −10.56 | −0.0372 | Gu et al. (2014) |
| | | 308.15 | 11.67 | | | |
| | | 318.15 | 12.04 | | | |
| | | 328.15 | 12.43 | | | |
| Organo-bentonite | 2-Naphthol | 298.15 | −10.10 | −7.20 | 0.0096 | Yang et al. (2014) |
| | | 308.15 | −10.20 | | | |
| | | 318.15 | −10.30 | | | |
| | | 328.15 | −10.40 | | | |
| Organo-montmorillonite | Catechol | 298.15 | −8.50 | 8.05 | 0.0555 | Liu et al. (2014b) |
| | | 308.15 | −9.06 | | | |
| | | 318.15 | −9.61 | | | |
| | | 328.15 | −10.17 | | | |
| | Phenol | 298.15 | −10.38 | −6.13 | 0.0142 | |
| | | 308.15 | −10.52 | | | |
| | | 318.15 | −10.66 | | | |
| | | 328.15 | −10.80 | | | |
| Chitosan-clay composite | Methylene blue | 303.15 | −1.43 | 29.99 | 0.103 | Auta and Hamed (2012) |
| | | 313.15 | −2.05 | | | |
| | | 323.15 | −3.46 | | | |

hazardous substances on clay minerals and its modified forms were feasible and spontaneous in nature.

The positive values of $\Delta H^o$ are an indication that the adsorption process is endothermic and the binding between solute and adsorbent is strong. The negative values of $\Delta H^o$ suggest that the adsorption process is exothermic, and the binding between solute and adsorbent mainly through physical binding or van der Waals attraction force. Furthermore, the magnitude of $\Delta H^o$ values may give an idea whether the adsorption belongs to physisorption (2.1–20.9 kJ/mol) or chemisorption (80–200 kJ/mol). The combination between the combination of physisorption and chemisorption often observed for the adsorption of hazardous substances on clay minerals (Anggraeni et al. 2014; Auta and Hameed 2012).

The thermodynamic property of $\Delta S^o$ is as a measure of randomness in the system. The positive values of $\Delta S^o$ reflect a high affinity of solute to the sorption sites, also the increased randomness at the solid/solution interface during adsorption process. Usually the $\Delta S^o$ of the system increase after the modification process. In the modification significant changes in the internal structure of the adsorbent occurred, and during the adsorption process, the change of the internal structure of the adsorbent cause the system to gain extra translational and rotational entropies, such as from the displacement of adsorbed water by the adsorbate, the partitioning of solute in the hydrophobic alkyl chain of the intercalated surfactant, etc. All of those phenomena increase the randomness of the process and increased the values of $\Delta S^o$ (Anggraini et al. 2014). The negative value of $\Delta S^o$ reflects the decrease of randomness of the adsorption system.

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# Chapter 5
# The Characterization of Clay Minerals and Adsorption Mechanism onto Clays

**Abstract** The characterization of the solid provides the most valuable information to understand the behavior of the process. Various modern analytical instruments are available for the characterization of clay minerals. Chapter 6 describes several methods which widely used for the characterization of clay minerals for environmental purpose. The methods include nitrogen sorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR). The analyzing of nitrogen sorption isotherms is used to characterize porous materials, allowing for the determination of specific surface area, pore size distribution as well as the pore volume. The lack of BET method based on nitrogen sorption isotherms is presented in this chapter. The X-ray diffraction provides fingerprint characterization of crystalline materials and the determination of their structure. The scanning electron microscope (SEM) analysis provides surface topography of the clay minerals. The functional groups of the modified clay minerals can be determined by FTIR method.

**Keywords** Characterization · BET · X-ray powder · FTIR

Currently, the identification and characterization of clay minerals much more easier, modern analytical instruments are available for identification and quantification of the clay minerals in various samples. Several analytical instruments which are widely used for the identification and characterization of clay minerals include nitrogen sorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared spectroscopy, etc.

The analyzing of nitrogen sorption isotherms is used to characterize porous materials, allowing for the determination of specific surface area, pore size distribution as well as the pore volume. Usually the nitrogen adsorption isotherm is obtained by measuring the amount of gas adsorbed across a wide range of relative pressures at boiling point of nitrogen (77.15 K). The desorption isotherm is obtained by measuring the amount of gas removed from the system by reducing the pressure of the system. The pore characteristics of porous materials are

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determined by application of several adsorption models such as BET equation on the nitrogen sorption isotherms.

The X-ray diffraction method has been applied for identification of clay minerals since 1920s. X-ray diffraction analysis is a unique method to determine the crystallinity of the compounds. XRD analysis is based on constructive interference of monochromatic X-rays and a crystalline sample and the XRD pattern analysis provides a unique fingerprint of the crystals present in the sample.

The scanning electron microscope (SEM) analysis provides surface topography of the solid sample. The scanning electron is routinely used to generate high-resolution images of shapes of objects and to show spatial variations in chemical composition. SEM analysis is also used to identify the phases of clay minerals.

## 5.1 Nitrogen Sorption

Nitrogen sorption analysis is very useful method to characterize the pore structure of clay minerals. The calculation of specific surface area is based on the monolayer formation of gas molecules on the surface of solid, while the principle of capillary condensation is used to determine the presence of pores, pore volume and pore size distribution. Porous materials are characterized in the term of pore sizes obtained from nitrogen gas sorption data, and the classification of pore sizes is based on the IUPAC convention (Alothman 2012). The IUPAC classification of adsorption isotherms is given in Fig. 5.1.

Type I isotherm indicates that the adsorbents are microporous. Types II, III, and VI are the characteristics of nonporous or macroporous solids, while the mesoporous materials are represented by types IV and V. It is widely accepted that the shape of the hysteresis loop correlates with the structure of mesoporous materials (pore size distribution, pore geometry, and pore network connectivity).

Figure 5.2 depicts the relation between the hysteresis of sorption isotherm and the pore shape. According to IUPAC classification, the isotherm with type H1 hysteresis is associated with mesoporous materials consisting of well-defined cylindrical like pore channels or agglomerates of approximately uniform spheres. The H2 isotherm relates to disordered materials with not well defined pore size distribution and shape. The isotherm with type H3 hysteresis belongs to materials which have slit-shaped pores. Type H4 hysteresis is associated with narrow slit pores (Alothman 2012).

The nitrogen sorption isotherms of bentonite from Pacitan, East Java, Indonesia are shown in Fig. 5.3. According to IUPAC classification, the bentonite from Pacitan possesses type H3 hysteresis, the material with type H3 hysteresis has slit-shaped pore characteristic. As the basic information about the mesoporous adsorbents, the pore size distribution is perhaps the most important information on the characterization of the pore structure of such mesoporous adsorbents. The pore size distribution is a statistical representation of the size property of individual pores and closely related to both the equilibrium and kinetic features of

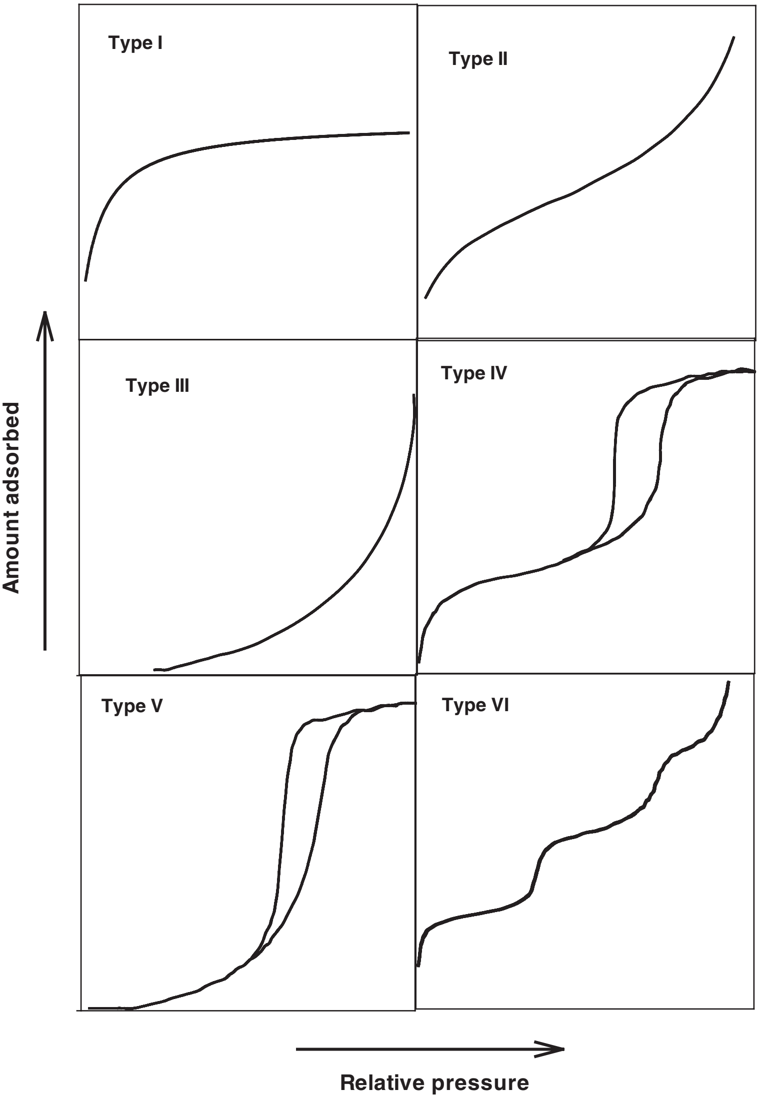


**Fig. 5.1** The IUPAC classification of adsorption isotherm (Alothman 2012)

adsorption in these mesoporous materials (Ismadji and Bhatia 2001). The pore size distribution of the bentonite from Pacitan was calculated based on the density functional theory method (DFT) with medium regularization, and the result is given in Fig. 5.4. The DFT analysis reveals that the bentonite from Pacitan does not have a uniform pore structure as indicated in Fig. 5.4. Most of the pores are in the mesoporous region (>2 nm), the bentonite also possesses a small amount of micropore structure (<2 m). Table 5.1 summarizes the structural properties of several natural clays obtained from nitrogen sorption isotherms.

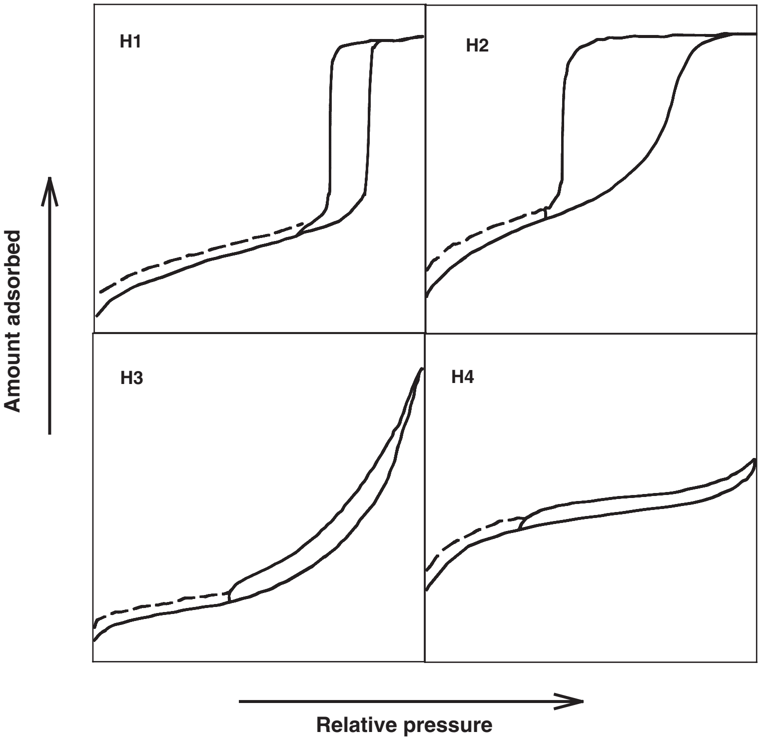


**Fig. 5.2** Relation between the hysteresis of sorption isotherm and the pore shape (Alothman 2012)

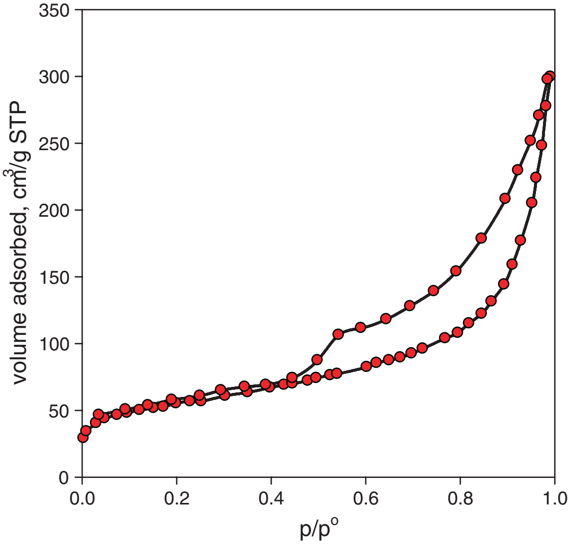


**Fig. 5.3** Nitrogen sorption isotherms of bentonite from Pacitan, East Java, Indonesia

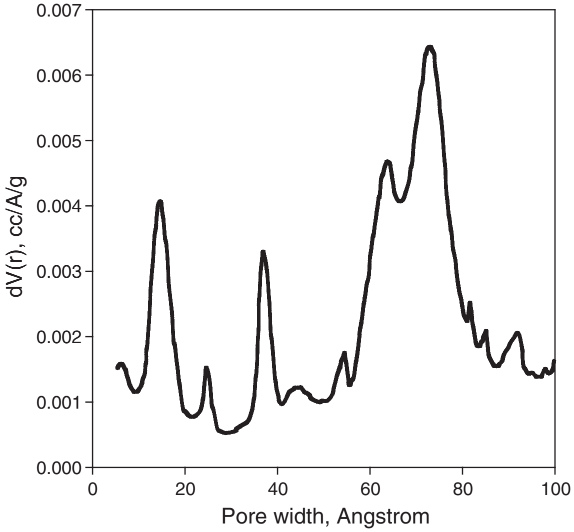


**Fig. 5.4** The DFT pore size distribution of bentonite from Pacitan

**Table 5.1** Structural properties of several natural clays

| Clay material/ mineral | Cation exchange capacity (mmol/100 g) | BET surface area (m$^2$/g) | Pore volume (cm$^3$/g) | References |
|---|---|---|---|---|
| Ca-montmorillonite | – | 80.40 | 0.150 | Wang et al. (2004) |
| Kaolinite | 11.3 | 3.80 | – | Bhattacharyya and Gupta (2006) |
| Kaolinite | 8.5 | 24.95 | – | Koyuncu et al. (2007) |
| Beidellite | – | 18.00 | 0.070 | Paul et al. (2010) |
| Ca-bentonite | 45.0 | 118.00 | 0.480 | Koswojo et al. (2010) |
| Palygorskite | – | 59.70 | 0.349 | Frini-Srasra and Srasra (2010) |
| Montmorillonite | 125.0 | 243.00 | – | Wang et al. (2010) |
| Ca-bentonite | 67.2 | 92.30 | 0.610 | Kurniawan et al. (2011) |
| Montmorillonite | 76.4 | 42.71 | 0.089 | Park et al. (2011) |
| Na-montmorillonite | 97.0 | 82.50 | 0.085 | Zaghouane-Boudiaf and Boutahala (2011) |
| Na-bentonite | 95.0 | 25.70 | – | Toor and Jin (2012) |
| Na-bentonite | 88.0 | 12.74 | 0.037 | Gu et al. (2014) |
| Kaolinite | – | 18.40 | 0.060 | Sari and Tuzen (2014) |

There are two methods to obtain the surface area from the nitrogen sorption isotherms of certain adsorbent with unknown surface character: BET method and χ theory method. The BET is widely used for the determination of surface area and this method has been available since 1938. The BET surface area analysis is based on the BET equation as follows

$$\frac{V}{V_m} = \frac{C\frac{P}{P_o}}{\left(1 - \frac{P}{P_o}\right)\left[1 + (C-1)\frac{P}{P_o}\right]} \tag{5.1}$$

where $V$ is the volume gas adsorbed at STP, $V_m$ is the volume of gas required for a monolayer adsorption, $P_o$ is the saturation pressure at the temperature of measurement, $P$ is adsorptive pressure, and $C$ is a constant. The linear form of Eq. (5.1) can be written as follows:

$$\frac{P/P_o}{V(1-P/P_o)} = \frac{1}{CV_m} + \frac{C-1}{CV_m}(P/P_o) \tag{5.2}$$

The slope and intercept of Eq. (5.2):

$$Slope_{BET} = \frac{C-1}{CV_m} \tag{5.3}$$

$$Int_{BET} = \frac{1}{CV_m} \tag{5.4}$$

$V_m$ can be calculated by the following equation

$$V_m = \frac{1}{slope_{BET} + Int_{BET}} \tag{5.5}$$

and

$$C = \frac{1}{V_m Int_{BET}} \tag{5.6}$$

For the BET surface area calculation, the value of $V_m$ can be related to the number of moles of a monolayer coverage. To convert the value of $V_m$ into BET surface area the following equation is used:

$$S_{BET} = \frac{n_m a}{m} N_A = \frac{(V_m/22,400)a}{m} N_A \tag{5.7}$$

where $S_{BET}$ is a BET surface area (m$^2$/g), $m$ is the mass of the sample (g), $N_A$ is Avogadro number. The unit of $V_m$ is cm$^3$/g. The effective molecular cross-sectional area, $a$ is calculated by the following equation:

$$a = 1.091\left(\frac{M}{N_A \rho}\right) \tag{5.8}$$

Here, $M$ and $\rho$ are the molar mass of the gas and the liquid density of gas, respectively, the constant 1.091 is the packing factor.

Although the technique for determination surface area and other pore structural characteristic using gas sorption isotherms have long been established and tested, however, the results should always be treated with caution when accurate values are required (Michot and Villieras 2006). In many cases, especially for microporous solids, the lack of accuracy of the BET method for surface area calculation has already been pointed (Do 1998; Ismadji and Bhatia 2001).

The measured sorption isotherms of clay minerals are also strongly dependent on the operating condition such as degassing temperature and time, the gas probe, and type of clay minerals itself. Clay minerals are hydrophilic materials, the correct choice of degassing temperature is very important; the degassing process should be able to remove all of weakly absorbed water molecules, the structural water molecules must not be affected by the degassing process. High vacuum condition and narrow range of degassing temperature are required for several types of clay minerals such as palygorskite (25–100 °C) and sepiolite (25–200 °C). The influence of degassing condition and type of clay minerals on the measured adsorption isotherms has been studied by a number of researchers (Grillet et al. 1988; Cases et al. 1991; Michot and Villieras 2006).

Different gases such as $N_2$, Ar, Kr, and $CO_2$ have been used for measurements of specific surface area and pore structure. Mostly the nitrogen gas is used as the primary standard for that purpose as suggested by Emmett and Brunauer (1937). For certain solid samples, the use of nitrogen as the probe is the best choice, but for several systems such as for clay minerals, the use of this gas as the adsorption probe has been questioned. The main reason is the quadrupole moment of nitrogen gas can interact with hydroxyl or other polar groups in solid samples, and this phenomenon can change the cross sectional area of the adsorbed molecule. The use of argon as the probe gas for the characterization of solid materials has been conducted by many researchers. The adsorption measurements usually conducted at the boiling point of argon (87.15 K). The reason of using argon as the probe molecule is the fact that argon is a symmetrical non-polar atom which should be less subject to specific interactions affected by changes in the chemical nature of surfaces (Aylmore 1973). However, the main drawback of using argon as the gas probe is this gas is less strongly adsorbed than nitrogen, raising some doubts as to whether the BET procedure provides a satisfactory estimate of the monolayer capacity (Aylmore 1973).

Aylmore (1973) compared the specific surface area of several clay minerals obtained by application of the BET theory to nitrogen, argon, krypton, and carbon dioxide isotherms, and the values are summarized in Table 5.2. For the BET calculation, the molecular area of each gas is as follows: nitrogen 0.162 $nm^2$, argon 0.141 $nm^2$, carbon dioxide 0.221 $nm^2$, and krypton 0.195 $nm^2$. As seen in Table 5.2, it is obvious that the calculation of specific surface area using sorption isotherms of different gases gave the different BET surface area. Much larger BET specific surface areas were obtained from carbon dioxide sorption at 196 K on goethite, hematite and gibbsite than from nitrogen, argon and krypton sorption at 78 K. Carbon dioxide is more energetic gas (larger quadrupole moment and high polarizability) compared to nitrogen, argon and krypton; therefore it can penetrate

**Table 5.2** Specific surface areas obtained by application of BET theory for gas sorption onto clay minerals (Aylmore 1973)

| Clay | BET surface area ($m^2/g$) | | | |
|---|---|---|---|---|
| | Nitrogen | Argon | Carbon dioxide | Krypton |
| Sodium A.P.I.-5 Kaolinite | 23.1 | 17.6 | 12.1 | 22.2 |
| Cesium A.P.I.-5 Kaolinite | 22.7 | 17.6 | 21.7 | – |
| Calcium A.P.I.-5 Kaolinite | 18.9 | 16.9 | 13.5 | – |
| Lanthanum A.P.I.-5 Kaolinite | 20.7 | 18.3 | 12.9 | – |
| Sodium Fithian Illite | 95.6 | 86.8 | 95.6 | 123 |
| Cesium Fithian Illite | 97.2 | 87.4 | 104.4 | – |
| Calcium Fithian Illite | 96.8 | 89.2 | 94.3 | – |
| Lanthanum Fithian Illite | 87.2 | 87.7 | 86.4 | – |
| Sodium Willalooka Illite | 185 | – | 183 | 200 |
| Goethite | 39.2 | 35.9 | 56.3 | 42.0 |
| Hematite | 18.0 | 14.4 | 25.2 | 13.8 |
| Gibbsite | 35.2 | 29.5 | 40.9 | 39.3 |

further into microporous region of the clays, in which this pore region is inaccessible to nitrogen, argon and krypton (Aylmore 1973).

Considerably lower BET specific surface areas were obtained for $CO_2$ sorption on kaolinite than were obtained for other gases. The presence of hydroxyl groups on one surface of the plate shaped kaolinite crystals might somehow result in a reduced adsorption of carbon dioxide. The specific surface areas obtained by application of the BET theory to gas sorption isotherms on clay mineral systems are subject to significant variations in apparent molecular areas with variations in surface structure, exchangeable cation and microporosity (Aylmore 1973).

## 5.2 X-Ray Diffraction

The development of modern X-ray diffraction instruments has contributed substantial improvement in the quality and number of structural characterizations of clay minerals. X-ray diffraction technique has been in use for the fingerprint characterization of crystalline materials and the determination of their structure. Each solid crystalline material possesses a unique characteristic X-ray powder pattern, and it can be used as a “fingerprint” for its identification. The unique X-ray powder pattern depends on the unit cell size for the peak position, and depends on the type of atoms present and on their arrangement in the crystal for the peak intensity. If the material has been identified, X-ray crystallography may be used to determine its structure. Clay minerals are difficult to identify and quantify due to their great structural and chemical composition diversity. Therefore, the X-ray diffraction method is still the most important characterization tool to identify clay minerals.

There are several advantages of using X-ray powder diffraction analysis to characterize the clay minerals, such as only a small quantity of clay are required, non-destructive, can determine the actual chemical compounds, and automatically determines the crystal type. However, this method still has limitations such as: this method is not possible to identify amorphous substances, component in mixture occurring below 5 % by weight, etc.

Bragg's law provides a simple relationship between the wavelength of the X-ray, the *d*-spacing, and diffraction angle.

$$d = \frac{n\lambda}{2\sin\theta} \tag{5.9}$$

where $n$ is the order of diffraction, $\lambda$ is the wavelength of the X-ray, $d$ is the interplanar spacing and $\theta$ is diffraction angle. In most cases, the value of $n$ is taken to be 1. The characteristic of wavelength ($\lambda$) of several X-ray sources (Cullity 1963) is given in Table 5.3.

In nature clay minerals exist as mixed-layer clay minerals. Mixed layer clay minerals are characterized by two or more types of unit cells or layers. The positions of the peaks are intermediate between those of the pure end-members, and peak broadening can be highly variable, depending on the distance between the corresponding end-member peaks (Srodon 2006). The identification of clay minerals using XRD definitions is based on the positions of 0 0 *l* reflections of samples. Basic crystallographic property information and position h k *l* reflections of several pure clay minerals is given in Table 5.4 and the crystal structures of all known minerals are classified into seven crystal system are summarized in Table 5.5 (http://www.webmineral.com).

Ouellet-Plamondon et al. (2014) studied the effect of cationic, non-ionic and amphiphilic surfactants on the intercalation of bentonite. X-ray diffraction patterns of the surfactant modified bentonite were measured at different surfactant concentrations. The interlayer basal spacing of the bentonite was 1.24 nm. The XRD spectra of the modified bentonite indicate that the peaks shifted to lower angles suggesting an increase of basal spacing as intercalated molecules were introduced into the montmorillonite galleries. The non-ionic surfactants (PPG 1200 and PPG 2000)

**Table 5.3** The characteristic of wavelength of several X-ray sources (Cullity 1963)

| Element | Wavelength (nm) | | | | |
|---|---|---|---|---|---|
| | Weighted average $K_\alpha$ | $K_{\alpha 1}$ (strongest) | $K_{\alpha 2}$ (strong) | $K_\beta$ (weak) | $L_\alpha$ |
| Chromium | 0.229092 | 0.228962 | 0.229351 | 0.208480 | – |
| Cobalt | 0.179021 | 0.178892 | 0.179278 | 0.162075 | – |
| Copper | 0.154178 | 0.154051 | 0.154433 | 0.139217 | 1.3357 |
| Iron | 0.193728 | 0.193597 | 0.193991 | 0.175653 | – |
| Manganese | – | 0.210175 | 0.210568 | 0.191015 | – |
| Molybdenum | 0.071069 | 0.070926 | 0.0713543 | 0.0632253 | 0.540625 |
| Nickel | – | 0.165784 | 0.166169 | 0.150010 | 0.147635 |
| Zinc | – | 0.143511 | 1.43894 | 0.129522 | 1.2282 |

**Table 5.4** Crystallographic data and position hkl reflections of the clay minerals

| Clay mineral | Crystal system | Space group | Cell dimensions | h k *l* reflections |
|---|---|---|---|---|
| Kaolinite | Triclinic | $C_1$ | $a = 5.1554$ | $d_{001} = 0.717$ nm |
| | | | $b = 8.9448$ | $d_{002} = 0.358$ nm |
| | | | $c = 7.4048$ | |
| | | | $\alpha = 91.700°$ | |
| | | | $\beta = 104.862°$ | |
| | | | $\gamma = 89.822°$ | |
| Dickite | Monoclinic | $C_c$ | $a = 5.1375$ | $d_{001} = 0.715$ nm |
| | | | $b = 8.9178$ | |
| | | | $c = 14.389$ | |
| | | | $z = 4$ | |
| | | | $\beta = 96.74°$ | |
| Nacrite | Monoclinic | $C_c$ | $a = 8.909$ | $d_{001} = 0.718$ nm |
| | | | $b = 5.146$ | |
| | | | $c = 15.697$ | |
| | | | $z = 4$ | |
| | | | $\beta = 113.7°$ | |
| Halloysite | Monoclinic | $C_c$ | $a = 5.14$ | $d_{001} = 1.00$ nm |
| | | | $b = 8.90$ | |
| | | | $c = 14.70$ | |
| | | | $z = 4$ | |
| | | | $\beta = 101.9°$ | |
| Montmorillonite | Monoclinic–prismatic | $C_{2/m}$ | $a = 5.17$ | $d_{001} = 1.66–1.72$ nm (Na-montmorrilonite) |
| | | | $b = 8.94$ | |
| | | | $c = 9.95$ | |
| | | | $z = 1$ | |
| | | | $\beta = 99.9°$ | |
| Vermiculite | Monoclinic–prismatic | $C_{2/m}$ | $a = 5.26$ | $d_{001} = 1.45$ nm |
| | | | $b = 9.23$ | |
| | | | $c = 14.97$ | |
| | | | $z = 2$ | |
| | | | $\beta = 96.82°$ | |
| Nontronite | Monoclinic–prismatic | $C_{2/m}$ | $a = 5.23$ | $d_{001} = 1.52$ nm |
| | | | $b = 9.11$ | |
| | | | $c = 15.25$ | |
| | | | $z = 2$ | |
| | | | $\beta = 96°$ | |
| Saponite | Monoclinic–prismatic | $C_{2/m}$ | $a = 5.3$ | $d_{001} = 1.23$ nm |
| | | | $b = 9.16$ | |
| | | | $c = 12.4$ | |
| | | | $z = 2$ | |
| | | | $\beta = 96.5°$ | |

(continued)

**Table 5.4** (continued)

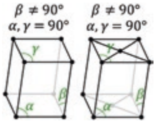
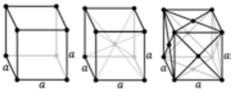
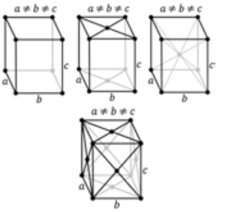
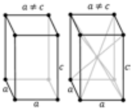
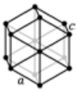
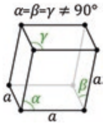
| Clay mineral | Crystal system | Space group | Cell dimensions | h k *l* reflections |
|---|---|---|---|---|
| Hectorite | Monoclinic–prismatic | $C_{2/m}$ | $a = 5.25$ | $d_{001} = 1.53$ nm |
| | | | $b = 9.18$ | |
| | | | $c = 16$ | |
| | | | $z = 3$ | |
| | | | $\beta = 99°$ | |
| Illite | Monoclinic–prismatic | $C_{2/m}$ | $a = 5.18$ | $d_{001} = 0.998–1.00$ nm |
| | | | $b = 8.98$ | $d_{001} = 1.033$ nm ($NH_4^+$ illite) |
| | | | $c = 10.92$ | |
| | | | $z = 2$ | $d_{060} = 0.150$ nm ($Al^{3+}$ illite) |
| | | | $\beta = 101.83°$ | |
| | | | | $d_{060} = 0.151$ nm ($Fe^{3+}$ illite and $K^+$ illite) |
| Chlorite | Orthorombic | – | $a = 5.00$ | $d_{001} = 1.40$ nm |
| | | | $b = 8.90$ | $d_{060} > 1.53$ nm |
| | | | $c = 29.80$ | |
| | | | $z = 2$ | |
| Sepiolite | Orthorombic-dipyramidal | $P_{nan}$ | $a = 13.43$ | $d_{110} = 1.20–1.29$ nm |
| | | | $b = 26.88$ | |
| | | | $c = 5.281$ | |
| | | | $z = 4$ | |
| Palygorskite | Monoclinic-Prismatic | $C_{2/m}$ | $a = 12.33$ | $d_{110} = 1.03–1.05$ nm |
| | | | $b = 17.89$ | |
| | | | $c = 5.24$ | |
| | | | $z = 4$ | |
| | | | $\beta = 105.2°$ | |

increased the interlayer basal spacing of bentonite from 1.24 to 1.83 nm at 2.00 CEC (Ouellet-Plamondon et al. 2014).

The modification of montmorillonite with polyacrylic acid or its salts caused an increase in the interlayer distance, without destruction of the montmorillonite structure as observed by Natkanski et al. (2012). The addition of polyacrylic acid to montmorillonite resulted in more distinct growth in $d_{001}$ spacing due to the introduction of the polymer into the montmorillonite interlayers. The intercalation of montmorillonite with sodium polyacrylic resulted largest expansion of the composite and increasing the crystallinity of the composite (Natkanski et al. 2012).

He et al. (2010) studied the preparation of organo-montmorillonite from montmorillonites with different cation exchange capacity. The XRD patterns indicate that the basal spacing of the organo-montmorillonites increased with surfactant loading, while the maximum basal spacing increased as the alkyl chain length of the surfactant increased. For the same surfactant, the cation exchange capacity of the montmorillonite gave little influence on the maximum basal spacing of organo-montmorillonite. For a given alkyl chain length, the basal spacing increased when the chain number increased from one to two (He et al. 2010). Table 5.6 lists some

**Table 5.5** Classes of crystal

| Crystal family | Axis | Axis angles | Bravais lattices |
|---|---|---|---|
| Triclinic | A ≠ B ≠ C | $\alpha \neq \beta \neq \gamma \neq 90°$ |  |
| Monoclinic | A ≠ B ≠ C | $\alpha = \gamma = 90°, \beta > 90°$ |  |
| Cubic | A = B = C | $\alpha = \beta = \gamma = 90°$ |  |
| Orthorhombic | A ≠ B ≠ C | $\alpha = \beta = \gamma = 90°$ |  |
| Tetragonal | A = B ≠ C | $\alpha = \beta = \gamma = 90°$ |  |
| Hexagonal | A = B ≠ C | $\alpha = \beta = 90°, \gamma = 120°$ |  |
| Rhombohedral | A = B = C | $\alpha = \beta = \gamma \neq 90° < 120°$ |  |

studies which employed the XRD technique for the characterization of clay materials, clay composites, and organo-clays.

## 5.3 SEM Analysis

Scanning electron microscopy (SEM) is one of the available methods for the characterization of solid materials. SEM analysis can provide information about the surface topography of the sample. The SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid samples. The interactions between the electron and sample produce signals that reveal information

**Table 5.6** The characterization of clay materials, clay composites, and organo-clays using XRD

| Clay | X-ray source | Remarks | References |
|---|---|---|---|
| Bentonite | Cu $K_\alpha$ | XRD analysis shown the presence the main minerals are montmorillonite and opal CT, in the subordinate quantity illite | Zivica and Palou (2015) |
| Bentonite | Cr $K_\alpha$ | Bentonite exhibits a strong reflection at $2\theta = 6.8°$ corresponding to a basal spacing of 1.31 nm. The silylation reaction has had a negligible effect on the basal spacing of the bentonite indicated by slightly change of the 001 reflection ($d_{100} = 6.9°$) | D'Amico et al. (2014) |
| Bentonite | Cu $K_\alpha$ | The XRD patterns of sodium bentonite and organo-bentonite indicate that the enlargement of $d_{001}$ spacing of bentonite from 1.2294 to 1.3627 nm was observed after modification. The thickness of montmorillonite unit was 0.2694 nm and for organo-bentonite was 0.4027 nm | Gu et al. (2014) |
| Kaolin and montmorillonite K10 | Cu $K_\alpha$ | The interlayer spacing of the clay minerals did not increase significantly with the presence of ciprofloxacin in the physical blends. Based on the XRD pattern, the interlayer spacing of montmorillonite K10 become larger as the concentration of ciprofloxacin increased | Hamilton et al. (2014) |
| Montmorillonite | Cu $K_\alpha$ | The expansion of interlayer space due to the intercalation of gemini surfactants was indicated by the shifting of $d_{001}$ peaks of organo-montmorillonites towards lower angle. Typical basal spacing 1.41 nm appeared at the XRD patterns of all organo-clays. The molecule chains of surfactants lying parallel to the siloxane surfaces and forming monolayers | Yang et al. (2014) |
| Kaolinite and montmorillonite | Cu $K_\alpha$ | Two kaolin samples show structural differences in terms of crystallinity and order–disorder structure: well-ordered and poorly-ordered kaolin. Kaolin used in the study consists of silanol and aluminol layers as surface sites | Campos et al. (2013) |
| Rectorite | Cu $K_\alpha$ | *d* spacing of raw rectorite 2.41 nm, when the uptake of ciprofloxacin less than 0.29 CEC, $d_{001} = 2.325$ nm and $d_{002} = 1.153$ nm, when the uptake >0.44 CEC, $d_{001} = 2.51$ nm, and maximum value of $d_{001}$ was 2.58 nm achieved at 0.88 CEC | Jiang et al. (2013) |
| Montmorillonite | Cu $K_\alpha$ | Organo-montmorillonite exhibits an intense peak at 2.14° corresponding to a basal spacing of 4.13 nm ($d_{001}$ spacing) | Sun et al. (2013) |

(continued)

**Table 5.6** (continued)

| Clay | X-ray source | Remarks | References |
|---|---|---|---|
| Bentonite and Kaolin | Cu $K_\alpha$ | XRD analysis indicated that nalidixic acid adsorption to montmorillonite at pH 4.0 resulted in an expansion of basal spacing around 0.9 Å, suggesting adsorption and intercalation of nalidixic acid in the interlayer space | Wu et al. (2013) |
| Montmorillonite | Cu $K_\alpha$ | The basal spacing of air-dried $Na^+$ -montmorillonite and $Fe^{3+}$- montmorillonite were 1.25 and 1.34 nm, respectively. After reducing the $Fe^{3+}$ on the clay surface of smectite by $NaBH_4$, the basal spacing increases to 14.5° | Jia and Wang (2012) |
| Bentonite | Cu $K_\alpha$ | The XRD patterns indicate at the main composition of bentonite is Ca-montmorillonite with $d_{100} = 1.54$ nm with the impurities: illite, quartz, feldspar, and clinoptilolite. The crystallinity of Ca-montmorillonite decreases by increasing in HCl concentration as indicated by the decrease in intensity and the increase in full width at half-maximum (FWHM) peak height on the 0 0 1 XRD reflections | Yener et al. (2012) |

on the external sample morphology or topography, chemical composition, crystalline structure, and orientation of minerals making up the sample.

The SEM micrograph of Ca-bentonite from Pacitan, East Java, Indonesia is given in Fig. 5.5. The SEM analysis conducted on a JEOL JSM-6390 field emission SEM at an accelerating voltage of 15 kV, spot size of 8, aperture of 4, and working distance of 9.6 mm. The Ca-bentonite was coated with a thin layer of platinum to make it electronically conductive, using an Eiko IB-5 sputter–coater operated at 6 mA for 3 min in argon atmosphere. The SEM micrograph of the Ca-bentonite indicates that the clay exhibited a disordered and heterogeneous surface structure.

Energy-dispersive X-ray spectroscopy (EDX) or sometimes called as energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA) is an analytical technique used for the elemental analysis or chemical characterization of a sample. The EDX mapping of the Ca-bentonite from Pacitan is presented in Fig. 5.6. The EDX analysis shows that the bentonite from Pacitan contains carbon in quite significant amounts. This carbon content possibly comes from humic or other organic substances.

The use of SEM technique for characterization of clay minerals and its modified forms does not provide any significant information about the structural characteristic of the materials; it only provides the information about the surface topography of the materials. However, this method still widely used by many researchers for the characterization of clay minerals, clay composites, and

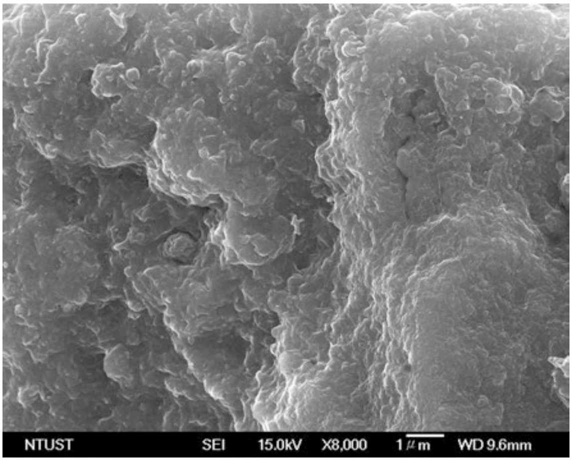


**Fig. 5.5** SEM analysis of Ca-bentonite from Pacitan, East Java, Indonesia

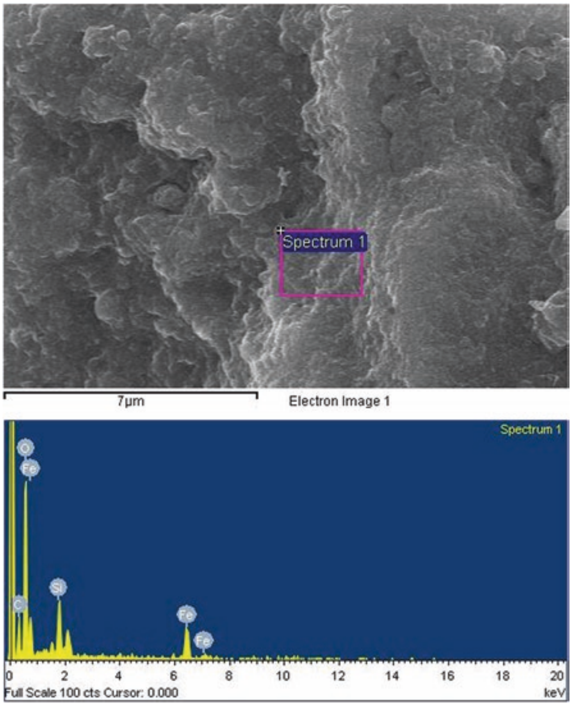


**Fig. 5.6** EDX spectra of Ca-bentonite from Pacitan, East Java, Indonesia

organo-clays, especially for environmental purpose (Bhattacharyya and Ray 2014, 2015; Islam et al. 2015; Alcantara et al. 2014; Nesic et al. 2014; Wu et al. 2014; Yao et al. 2014; Hajjaji et al. 2013; Mambrini et al. 2013; Tirtom et al. 2012; Zhou et al. 2012; Ely et al. 2011).

## 5.4 FTIR Analysis

Fourier transform infrared spectroscopy (FTIR) is an analytical method used to identify organic matter and a limited number of inorganic compounds. FTIR technique is based on the vibrations of atoms in molecules. The IR spectrum of a clay mineral is sensitive to its chemical composition, isomorphous substitution and layer stacking order. This makes Fourier transform infrared (FTIR) spectroscopy, the most informative single technique for assessing the mineralogy and crystal-chemistry of a clay mineral sample (Petit 2006).

The absorption of infrared radiation by clay minerals, strongly depends on atomic mass, and the length, strength and force constants of inter-atomic bonds in the structure of clay minerals. The overall symmetry of the unit cell as well as the local site symmetry of each atom within the unit cell also influences the absorption of infrared radiation (Petit 2006). So far, the characterization of clay minerals using the FTIR method in most of literatures was conducted in the middle infrared region (4000–300 $cm^{-1}$) where the fundamental vibrational modes appear, and the KBr pellet method was employed.

FTIR method has been used for the characterization of clay minerals and its modified forms by a large number of recent studies (Bhattacharyya and Ray 2015; Islam et al. 2015; Bhattacharyya and Ray 2014; Rasouli et al. 2014; Wu et al. 2014; Yang et al. 2014; Campos et al. 2013; Chandra et al. 2013; Sun et al. 2013; Jia and Wang 2012; Tirtom et al. 2012; Zhou et al. 2012; Bhattacharyya and Gupta 2011; Kurniawan et al. 2011; Zaghouane-Boudiaf and Boutahala 2011; Frini-Srasra and Srasra 2010; Paul et al. 2010; Rawajfih and Nsour 2010; Yesi et al. 2010). Zhou et al. (2012) used the FTIR method to characterize sodium and calcium montmorillonite, and the formation of organically modified montmorillonite. Several important characteristics of montmorillonite were revealed, such as the stretching vibration of O–H groups, the stretching vibration and bending vibration of water molecules for the hydration in the lattice of montmorillonite, hydrogen bonds between water molecules in the interlayer of the montmorillonite, stretching vibration of the Si–O bonds, and bending vibration of Si–O–Al bonds. The vibrations of the O–H groups are very slightly dependent on the vibrations of the rest of the structure. The O–H vibrations are affected by the octahedral cations to which the O–H group is coordinated, and to a lesser degree, by the tetrahedral and interlayer environments (Petit 2006).

FTIR method is extensively used to study the clay minerals—organic intercalation. The intercalation of organic species, especially from surfactants into the interlayer space of clay minerals is widely studied using this method (Liu et al. 2011, 2014a, b; Ouellet-Plamondon et al. 2014; Rasouli et al. 2014; Yang et al. 2014; Chandra et al. 2013; El-Achaby et al. 2013; Shah et al. 2013; Sun et al. 2013; Suwandi et al. 2012; Tunc et al. 2012; Zhou et al. 2012; Chen et al. 2011; Kurniawan et al. 2011; Koswojo et al. 2010; Nathaniel et al. 2011; Yesi et al. 2010). FTIR technique was often used to show the intercalation and solvation of organic molecules (surfactants) into smectite. Upon intercalation, the hydrogen bonds between the inner surface hydroxyls and the siloxane of the next adjacent layer is replaced by those between the smectite and the intercalated molecules. A number of studies also used the FTIR method to characterize the surface functional groups of clay mineral composites (Bhattacharyya and Ray 2015; Auta and Hameed 2014; Das et al. 2014; Hamilton et al. 2014; Vanamudan et al. 2014; Wang et al. 2014; Wu et al. 2014; Campos et al. 2013; Luo et al. 2013; Jia and Wang 2012; Tirtom et al. 2012; Xing et al. 2012).

One of the important things in clay minerals is the interaction of water and clay. Water molecules that are strongly hydrogen-bonded exhibit different vibrational properties from those that are weakly bonded to the oxygen atoms of the silicate anions. The absorbed water molecules in the clay minerals, especially in smectites, can occupy the available pores or directly coordinated to exchangeable cations (Petit 2006). The absorption band of water around 1630 $\mathrm{cm}^{-1}$ and it varies with the water content on the clay minerals as indicated by several studies (Gu et al. 2014; Yang et al. 2014; Shah et al. 2013; Chen et al. 2011; Kurniawan et al. 2011; Suwandi et al. 2012; Koswojo et al. 2010; Putra et al. 2009).

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# Chapter 6
# The Kinetic Studies in the Adsorption of Hazardous Substances Using Clay Minerals

**Abstract** For the design of the adsorption system, reliable adsorption kinetic data are required. Different concepts are employed to develop a reliable adsorption kinetic model. Most of the available models were developed according to mass transfer principles or the concept of chemical reaction occurring on the surface of a solid. The models based on the surface-reaction kinetic step as controlling the sorption rate have also been proposed, these models include pseudo-first order kinetic (also called as Lagergren model), pseudo-second order kinetic, and Elovich equation. This chapter discusses various aspects of pseudo-first order kinetic and pseudo-second order kinetic in representing the adsorption kinetic data of some hazardous compounds onto clay minerals. The pseudo-first order kinetic is the earliest known equation to describe the rate of sorption in the liquid phase system. The behavior of time constant parameters $k_1$ and $k_2$ of pseudo-first order kinetics and pseudo-second order kinetics as a function of initial concentration as well as the temperature is discussed in this chapter. One of the kinetic models which also widely used to represent the sorption kinetic data is an intraparticle diffusion model also briefly discussed in this chapter.

**Keywords** Adsorption kinetic · Pseudo-first · Pseudo-second · Intraparticle diffusion

Adsorption kinetics are expressed as the solute removal rate that controls the residence time of the solute in the solid–solution interface. Reliable sorption kinetic data are of substantial value for adsorption separation system design. Various models have been developed to adequately describe the kinetics of sorption of the solid—liquid system. However, due to its complexity compared to the description of adsorption equilibria, the progress of development of various sorption kinetics appears to be limited. In general, the adsorption of solute from aqueous solution

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into the surface interior of the adsorbent can be represented by the following mechanisms (Plazinski et al. 2009):

- Transport of solute in the bulk of the solution
- Diffusion of solute across liquid film (interface) of the adsorbent
- Intraparticle diffusion
- Adsorption and desorption of solute molecules on/from the adsorbent surface (also called as “the surface reaction”).

Any step or combination of those mechanisms may control the overall sorption rate. A numerous adsorption kinetic models have been proposed based on those mechanisms. The kinetic models based on “the surface reaction” are most the widely used equations to predict the behavior of the kinetic experimental data (Plazinski et al. 2009). According to Plazinski et al. (2009) the “surface reaction” term may not necessarily mean the actual chemical reaction occurring on the adsorbent surface involving the formation of chemical bonds, Interactions of physical nature (van der Waals forces, for instance) may also play a role.

The concept of chemical reaction occurring on the surface of solid has also been employed to develop the adsorption kinetic models such as Langmuir kinetics (Langmuir 1918), first order and second order reversible, first and second order irreversible reactions based on the solute concentration (Plazinzki et al. 2009). The models based on the surface-reaction kinetic step as controlling the sorption rate have also been proposed. These models include pseudo-first order kinetic (also called as Lagergren model), pseudo-second order kinetic, and Elovich equation. Pseudo first and pseudo second order equations are the most widely used to correlate the kinetic adsorption data of various compounds onto clay minerals.

## 6.1 The Pseudo-first Order Kinetic

The pseudo-first order kinetic is well known model to correlate the adsorption kinetic data for various solutes—clay mineral systems. The original form of this model was proposed by Lagergren in the 19th century (Lagergren 1898) and the earliest known equation to describe the rate of sorption in the liquid phase system. This equation is known as Lagergren’s first-order rate equation. The expression of Lagergren equation as the pseudo-first order was given by Sharma et al. (1990) to correlate the adsorption kinetic of Ni(II) in wollastonite. The pseudo-first order kinetic expression based on the solid capacity is written in the following form:

$$\frac{dq}{dt} = k_1(q_e - q) \tag{6.1}$$

Integration of Eq. (6.1) with the boundary conditions as follows: $t = 0 \rightarrow q = 0$, and $t = t \rightarrow q = q$, gives the result as follow

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{6.2}$$

or

$$q = q_e(1 - \exp(k_1 t)) \tag{6.3}$$

where $k_1$ and $q_e$ are the parameters of pseudo-first order. The physical meaning of $k_1$ is the time-scaling factor the value which decides how fast the equilibrium in the system can be reached (Plazinzki et al. 2009). Figure 6.1 depicts the theoretical plots of pseudo-first order as a function of parameter $k_1$. From this figure, it can be seen that increasing $k_1$ value results in shorter times required for a system to reach equilibrium.

The experimental kinetic studies on the adsorption of hazardous compounds onto clays and its modified forms have confirmed that the initial concentration of the solute influences the value of parameter $k_1$ as summarized in Table 6.1. The value of parameter $k_1$ decreases with the increasing of initial concentration of solute in the bulk liquid phase. This phenomenon indicates that the parameter $k_1$ can be treated as a time-scaling factor as suggested by Plazinzki et al. (2009).

In many cases the pseudo-first order model failed to describe the adsorption kinetic data (Bhattacharyya and Gupta 2006, 2011; Akar et al. 2009; Chen and Zhao 2009; Koswojo et al. 2010; Kurniawan et al. 2011; Toor and Jin 2012; Vanamudan et al. 2014; Wang et al. 2014; Dos Santos et al. 2015). Kurniawan et al. (2011) found the inconsistency of the fitted value of parameter $k_1$ with its physical meaning, the value of $k_1$, increase with the increasing of initial solute concentration, hence the pseudo-first order model is not the correct choice to represent the kinetic experimental data.

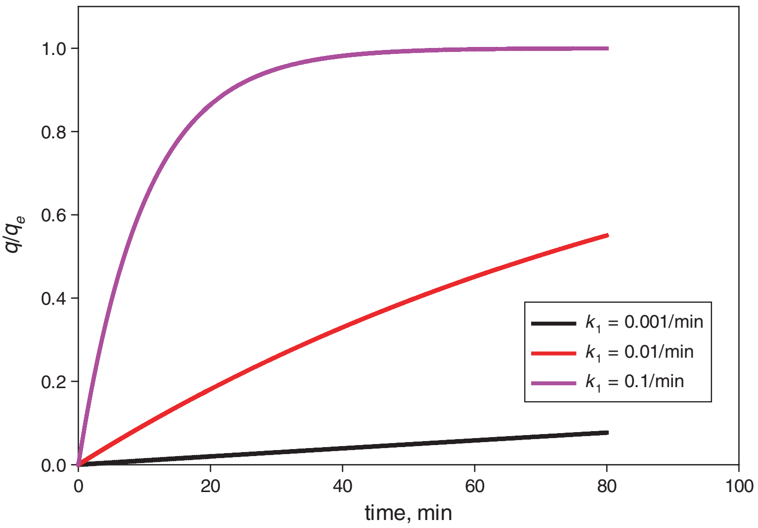

**Fig. 6.1** Pseudo-first order plots as a function of parameter $k_1$

**Table 6.1** Pseudo-first order equation for prediction of adsorption kinetic data of several systems

| Clay | Solute | $C_o$ (mg/L) | $q_{e,exp}$ (mg/g) | Parameter | | | References |
|---|---|---|---|---|---|---|---|
| | | | | $q_e$ (mg/g) | $k_1$ (1/time) | $R^2$ | |
| Chitosan-clay composite | Methylene blue | 30 | 26.93 | 29.56 | 0.128 | 0.974 | Auta and Hameed (2012) |
| | | 100 | 79.76 | 80.78 | 0.116 | 0.967 | |
| | | 300 | 193.23 | 190.47 | 0.106 | 0.982 | |
| Bentonite supported Fe/Pd | Methyl orange | 200 | – | – | 0.2396 | 0.984 | Wang et al. (2013) |
| | | 500 | – | – | 0.0721 | 0.994 | |
| | | 800 | – | – | 0.0325 | 0.924 | |
| Acid-activated bentonite | γ-picoline | 25 | – | 46.30 | $1.2 \times 10^{-3}$ | 0.998 | Rawajfih and Nsour (2010) |
| | | 50 | – | 59.58 | $9.2 \times 10^{-4}$ | 0.998 | |
| | | 100 | – | 75.21 | $6.9 \times 10^{-4}$ | 0.994 | |
| | | 200 | – | 115.69 | $4.6 \times 10^{-4}$ | 0.999 | |
| Kaolin | Pb(II) | 80 | – | 0.095 | 0.143 | 0.982 | Tang et al. (2009) |
| | | 160 | – | 16.273 | 0.061 | 0.991 | |
| | | 320 | – | 30.323 | 0.045 | 0.762 | |

## 6.2 The Pseudo-second Order Kinetic

The pseudo-second order kinetic is commonly associated with the situation when the rate of direct adsorption/desorption process controls the overall sorption kinetics (Plazinzki et al. 2009). The mathematical expression of the pseudo-second order kinetic model was given by Blanchard et al. (1984) as follows:

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{6.4}$$

Solving the Eq. 6.4 with the boundary conditions: $t = 0 \to q = 0$, and $t = t \to q = q$, gives the following result

$$q = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \tag{6.5}$$

where $k_2$ is the pseudo-second order rate constant and the value of this parameter strongly depends on the applied operating conditions. The influence of parameter $k_2$ on the pseudo-second order plots are given in Fig. 6.2.

Figure 6.2 clearly indicates that the parameter $k_2$ possesses similar physical meaning with parameter $k_1$ in pseudo-first order equation. The higher the value of parameter $k_2$, the shorter times required to reach the equilibrium condition. Similar to the pseudo-first order, the value of $k_2$ is also affected by the initial solute concentration, the higher initial solute concentration the longer time required to reach an equilibrium ($k_2$ decreases with the increasing of $C_o$). The dependence of parameter $k_2$ on the initial solute concentration was observed by a number of researchers

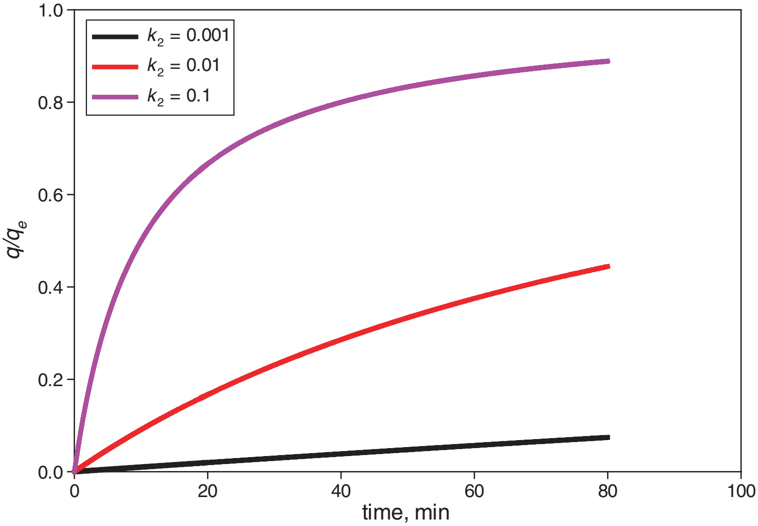

**Fig. 6.2** Pseudo-second order plots as a function of parameter $k_2$

(Tang et al. 2009; Rawajfih and Nsour 2010; Kurniawan et al. 2011; Wang et al. 2013; Auta and Hameed 2012).

The influence of temperature on the value of parameter $k_2$ was studied by Koswojo et al. (2010). The change of temperature of the system results in the change of the equilibrium condition, indicated by the change of amount adsorbed at equilibrium condition ($q_e$). The increase temperature resulting the increase of $q_e$, the higher value of $q_e$ requires a longer time for the system to reach equilibrium, and as the consequence the value of $k_2$ decreases. The value of $q_e$ should be equal to those determined from the measurements of the equilibrium sorption isotherm.

In most adsorption systems using clay minerals and its modified forms as the adsorbents, the pseudo-second order kinetic model could represent the experimental data much better than the pseudo-first order kinetic (Bhattacharyya and Gupta 2006, 2011; Tsai et al. 2007; Akar et al. 2009; Chen and Zhao 2009; Koswojo et al. 2010; Kul and Koyuncu 2010; Kurniawan et al. 2011; Toor and Jin 2012; Auta and Hameed 2012; Lv et al. 2014; Vanamudan et al. 2014; Wang et al. 2014; Dos Santos et al. 2015). A potential advantage of the pseudo-second order equation as an expression estimating the $q_e$ values is its small sensitivity to the influence of the random experimental error (Plazinzki et al. 2009).

Theoretical approaches of the pseudo-second order kinetic have also been proposed by a number of researchers (Azizian 2004, 2006; Rudzinski and Plazinski 2006, 2007, 2009), however, these theoretical pseudo-second order kinetic models are rarely used to describe the adsorption kinetic data of hazardous substance—clay mineral systems.

## 6.3 Intraparticle Diffusion Model

One of the kinetic models which also widely used to represent the sorption kinetic data is an intraparticle diffusion model. This model has the form as follows:

$$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{Dn^2\pi^2}{r^2} t\right) \tag{6.6}$$

where $D$ is the intraparticle diffusion coefficient and $r$ is the particle radius. The intraparticle diffusion model is applicable when the rate-determining step is the mass transfer of adsorbate to the solid surface sites (Marco-Brown et al. 2014). When the ratio of $q_t/q_e$ is less than 0.3, the Eq. 6.6 reduced to

$$q_t = k_p\sqrt{t} + c \tag{6.7}$$

where parameter $k_p$ and $c$ are the intra particle diffusion rate constant and a constant representing mass transfer resistance due to boundary layer, respectively. In general, the plots consist of three linear portions which confirm that the external mass transfer at the initial stage is followed by intra particle pore diffusion into macropores, mesopores and micropores. The slope of the second linear portion is the rate constant for intra particle diffusion while its intercept is proportional to the boundary layer thickness (Bhattacharyya and Ray 2015).

The intra particle diffusion model could represent the adsorption kinetic data quite well for several systems such as congo red—nano clay filled composite hydrogels and methyl violet—nano clay filled composite hydrogels (Bhattacharyya and Ray 2015), Basic yellow 28—amidated pectin/montmorillonite composite (Nesic et al. 2014), Rhodamine 6G—chitosan-g-(N-vinyl pyrrolidone)/montmorillonite composite (Vanamudan et al. 2014), Cobalt(II)—chitosan–montmorillonite (Wang et al. 2014), Indigo carmine—CdSe montmorillonite composite (Chikate and Kadu 2014), picloram herbicide—montmorillonite (Marco-Brown et al. 2014), phenol and cathecol—gemini surfactant modified montmorillonite (Liu et al. 2014).

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