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).

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

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 $\approx$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
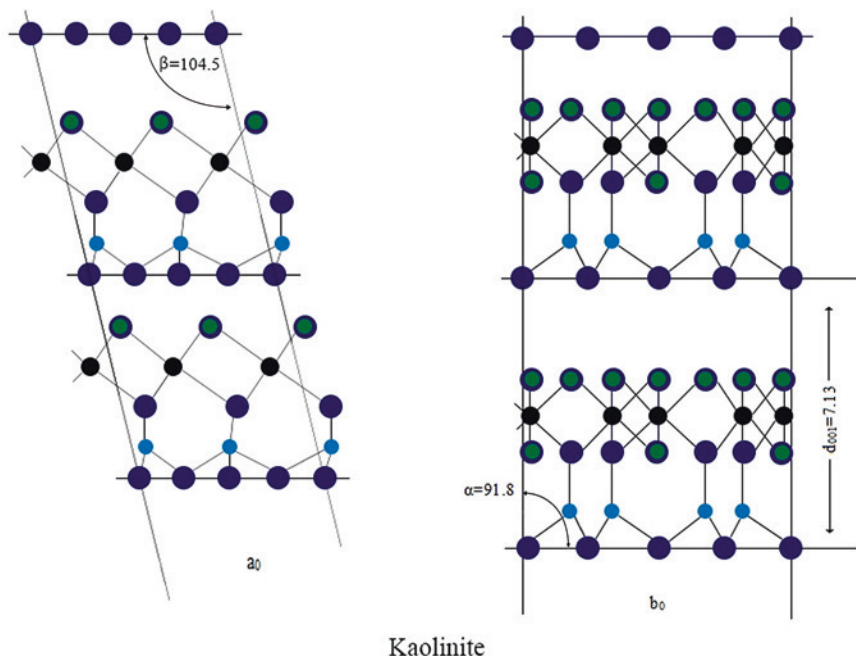
Fig. 2.1 Schematic diagram of kaolinite structure (redrawn based on Murray 2007)

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
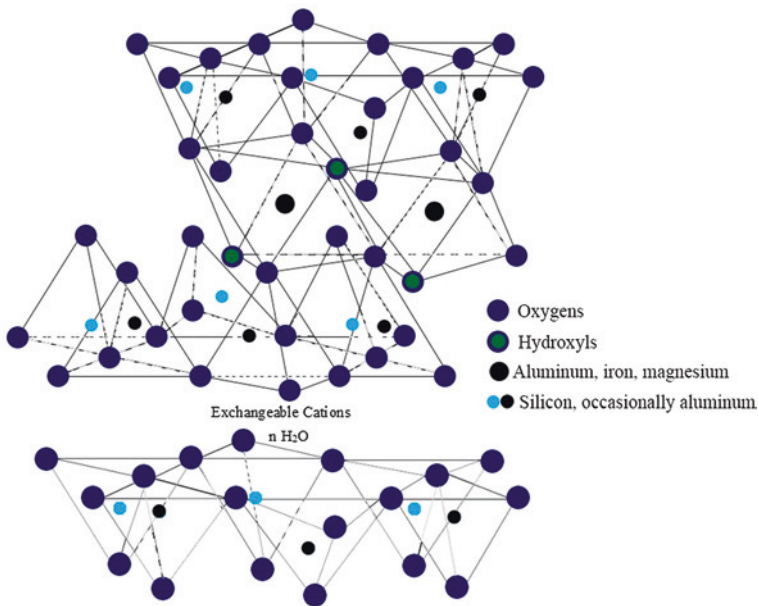

Fig. 2.2   The structure of smectite clay (redrawn based on Murray 2007)

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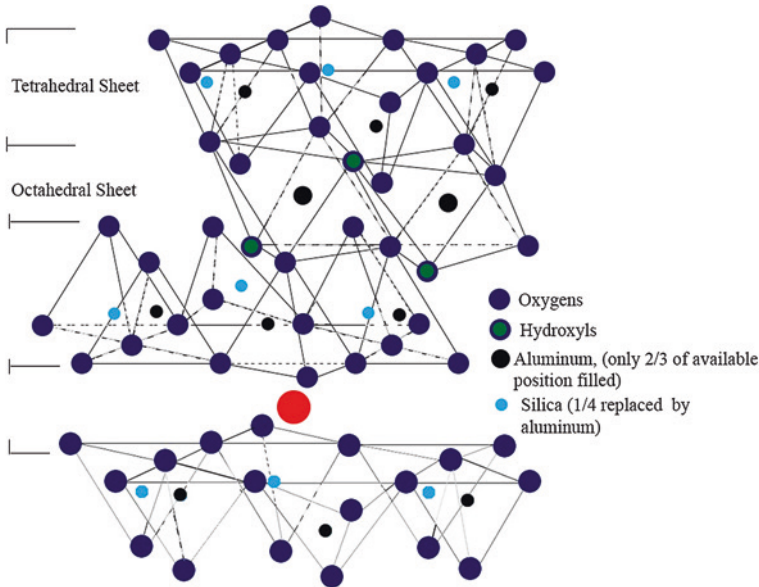
Fig. 2.3 Schematic diagram of illite structure (redrawn based on Murray 2007)

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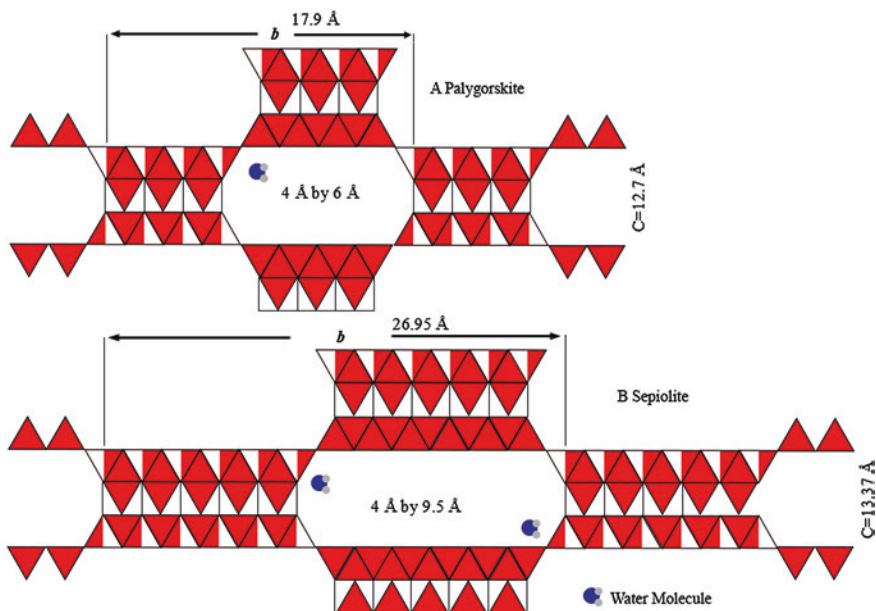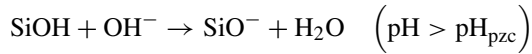
Fig. 2.4   The structure of *A* palygorskite and *B* sepiolite (redrawn based on Murray 2007)

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.

$$SiOH + H^+ \rightarrow SiOH_2^+ \quad \left(pH < pH_{pzc}\right)$$

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

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$_2$S 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$_2$S 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$_2$S 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)

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 iso-morphic 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:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$
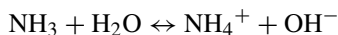
Unionized ammonia (NH_3) is harmful to aquatic organisms. The acidity and basicity (pH) of the water strongly influence the equilibrium condition between unionized ammonia and the ionized one. Unionized ammonia is toxic and its presence in water predominates when the pH is high, while in the form of 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)
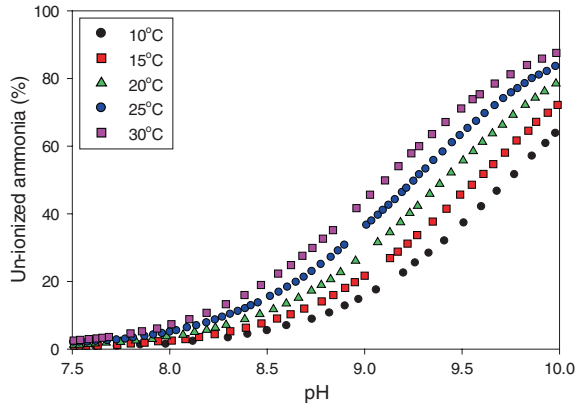
removal is the layered structure of the clay allows expansion (swelling) when con-
tacted with water, which exposes an additional mineral surface capable of ammo-
nium ion (NH_4^+) adsorption (Rozic et al. 2000). With the increase of ammonium
ions adsorbed by the surface of clay, the equilibrium reaction 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 sys-
tem, the pH of the system also fluctuates with photosynthesis process and respi-
ration 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 tet-
rahedral and octahedral sheets which are stacked together in certain ways that cre-
ates 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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