Heavy Metals In Water

Presence, Removal and Safety

Edited by Sanjay K. Sharma

ROYAL SOCIETY
OF CHEMISTRY

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CHAPTER 11

Natural Clays/Clay Minerals and Modified Forms for Heavy Metals Removal

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11.1   Introduction

The world's supply of clean and safe waters for human consumption and
needs is becoming more and more scarce due to various anthropogenic and
industrial activities. Such activities have inevitably released substantial
amounts of wastewater containing toxic substances, thus accounting for
great environmental concerns for many years. Heavy metals are broadly
defined as those metals and metalloids of relatively high specific gravity (at
least five times that of water) or of high relative atomic weight, which are
considered to be of sufficient dissemination and prevalence as to be in some
way environmentally or biologically significant as poisonous elements. Such
a substance is highly life-threatening towards living organisms due to its
high toxicity even at a very low concentration, non-biodegradability and
persistent nature and it is bio-accumulative (passed up the food chains to
humans).[1] Heavy metal poisoning of humans *via* inhalation, ingestion and
skin absorption can result in reduced mental and central nervous functions,
changes in numerous metabolic body processes and damage to blood

composition, kidneys, lungs, liver and other vital organs. Long-term ex-
posure may result in degeneration of physical, muscular and neurological
functions that mimics Parkinson's disease, Alzheimer's diseases, muscular
dystrophy and multiple sclerosis.[2–4] Heavy metals rich effluents are dis-
charged from many industries worldwide, such as electroplating, mining,
metal finishing, photographic, ammunition, leather tanning, textile and
dyeing, fertilizers, batteries, alloys and electronic goods manufacturing as
well as from agricultural activities to a lesser extent. Several types of toxic
heavy metals frequently pollute surface water bodies and their maximum
permissible limits according to the WHO and US EPA are presented in
Table 11.1.[5,6] In order to meet environmentally acceptable concentrations,
metal effluents that are discharged from municipal and industrial activities
should be treated properly before entering surrounding water bodies
and/or soils.

Chemical precipitation, electrodialysis, ion exchange, ultrafiltration, co-
agulation, reverse osmosis, microbial bioremediation, phytoremediation
and solvent extraction are some examples of conventional technologies for
purifying metal-contaminated effluents. The advantages and disadvantages
of these technologies are summarized in Table 11.2.[7–9] So far, the appli-
cations of these methods have encountered major obstacles and are un-
sustainable, particularly in the developing nations due to high operational
costs, generation of toxic waste sludge, complicated installation of waste-
water treatment units and poor removal effectiveness for the handling of
wastewater containing trace levels of metal ions. Lately, adsorption has be-
come a frequently used technique and a viable option for controlling the
fate, transport and bioavailability of heavy metals in terrestrial and aquatic
environments due to its simple design and operation, cost-effectiveness,
wide adaptability and high removal efficiency, which produces high-quality
effluents. Nowadays, special attention has been focused on the pursuit of

Table 11.1 Maximum acceptable limits of several toxic heavy metal ions in the surface waters based on WHO and US EPA regulations.

Heavy metal	Toxicity rank	WHO ($\mu g\ L^{-1}$)	US EPA ($\mu g\ l^{-1}$)
As	1	10	10
Pb	2	10	15
Hg	3	1	2
Cd	8	3	5
Cr, hexavalent	17	50	100
Co	52	NR[a]	100
Ni	57	70	100
Zn	75	NGL[b]	5000
Cu	125	2000	1300
Mn	140	400	50
Fe	—	—	300

[a]NR, not recorded.
[b]NGL, no guideline.

AQ:2

Table 11.2 The advantages and disadvantages of several conventional technologies for the treatment of heavy metal contaminated effluents.

Technology	Advantages	Disadvantages	Working concentration
Chemical precipitation	– Ready availability of equipment and many chemicals – Convenient, self-operating and low maintenance – Low metal concentration in the effluent is achieved	– Large volumes of sludge are generated, incurring additional waste-disposal costs – Extra coagulation–flocculation is compulsory for the complete precipitation of light tiny flocs – Regulation requirements are not always met using hydroxide and carbonate precipitation alone – Non-selective – Long-term environmental impacts of sludge disposal – Safety concerns due to working with corrosive chemicals	>10 mg L^{-1}
Electrodialysis	– Little chemical consumption – Recovery of pure metal is the added economic value	– High cost of electrodes and ion exchange membranes – Relatively short lifetime of membranes, especially when working in a high-density electrical field – Energy intensive – The formation of metal hydroxides can clog the membranes – Low removal efficiency at dilute concentrations	>10 mg L^{-1}
Ion exchange	– Highly effective for removing metal ions to a very low concentration	– High cost of ion exchanger – Partial removal of certain metal ions and highly sensitive to the pH of the solution – Cannot handling concentrated metal solutions as the ion-exchanger matrix gets easily fouled by organics and other solids in the effluent – Disposal of exhausted ion exchangers	<100 mg L^{-1}

Reverse osmosis	– High effectiveness (over 99% of all dissolved minerals can be removed) – The capability to reduce the concentration of ionic contaminants, as well as dissolved organic compounds	– High procurement and operating cost of the membranes – The use of elevated pressures makes this technique costly and sensitive to operating conditions	>10 mg L^{-1}
Biological treatment	– Fairly inexpensive and moderate capital investment – Environmentally safe and acceptable by the public – Can be conducted on site, often without causing a major disruption of normal activities – The resulting residues after treatment processes are usually harmless products, which include carbon dioxide, cell biomass and water – Self-sustaining process	– Limited to those compounds that are biologically degradable – The biodegradation products may be more persistent or toxic than the parent compound – Considerable experience and expertise may be required to design and implement a successful bioremediation process – Difficult to be adapted because the success of this process highly depends on the presence of metabolically capable microbial populations, suitable environmental growth conditions and appropriate levels of nutrients and contaminants	—
Solvent extraction	– Selective heavy metals removal – Continuous concentrated metal solution recovery	– High capital cost – Discharge of harmful solvent to environments	>100 mg L^{-1}
Phytoremediation	– —	– Difficulty for the regeneration of the plant in the further remediation – Time consuming	mg L^{-1}

natural adsorbents that possess high loading capacity, fast kinetics, a large   1
availability and are renewable and economically viable.

Numerous kinds of natural adsorbents ranging from industrial by-
products to agricultural waste have been explored for the remediation of
aquatic environments that are polluted by heavy metals and they may be an   5
alternative to more costly materials such as commercial activated carbons
or synthetic ion-exchange resins.[10–25] Despite their abundant availability
and cheapness, most of these solids show unimpressive results, associated
with poor removal capacity. Of particular interest are clays and clay min-
erals, which are highly valued for their ion sorption/exchange capacity, low   10
permeability, swelling ability, chemical and mechanical stability, large
specific surface area and ubiquitous presence on earth in the geological
deposits, terrestrial weathering environments and marine sediments.[26] In
the terrestrial environments, clay deposits may act as a natural scavenger
by taking up pollutants from water passing through the soil by ion ex-   15
change and/or adsorption mechanisms. Many types of clay materials have
been tested for the removal of heavy metal ions from waters and waste-
waters, including diatomite, illite, sepiolite, bentonite, kaolinite, clin-
optilolite, halloysite and palygorskite.[27–41] These clays and clay minerals
possess important surface reactivity, which stems from the permanent   20
negative charge within the layers. Furthermore, the natural exchangeable
alkali and alkali earth metal cations, such as Na^+, K^+, Ca^{2+} and Mg^{2+}
located between two adjacent layers, can be replaced with larger molecular
mass cations, expanding the interlayer space and consequently the
internal volume. Surface modifications of the acid–base chemistry are   25
therefore, the main aspect for broadening potential applications of clays
and clay minerals as an engineered material in new technologies. Over the
past few years, research devoted to surface modification of clays/clay
minerals as promising heavy metal sorbents, through thermal and chem-
ical activations as well as pillaring, grafting and intercalation techniques,   30
has been steadily growing and yet recent advances in this area have not
been well reported.

AQ:3

Starting from the environmental background previously outlined and the
urgent need to combat problematic heavy metal pollutions, this chapter
critically provides up-to-date information focusing on the fundamental   35
structural and surface chemistry of natural clays and clay minerals and their
various modified forms as heavy metal adsorbents. The adsorption per-
formance of natural and modified clays/clay minerals for removing heavy
metal ions from synthetic and real wastewaters has been discussed at great
depth in a large number of published studies. Considering the process de-
sign and its optimization, the knowledge of the single and multicomponent   40
adsorption behaviour of clay–heavy metal pairs, covering isotherms, kinetics
and thermodynamics, will be presented in detail. Finally, future perspectives
on the development of clay-based adsorption systems for industrial-scale
wastewater treatment is described with respect to technical and economic   45
feasibility.

11.2 Structural Features of Clays and Clay Minerals as Heavy Metals Sorbent

Clays are chemically a layer-type hydrous aluminosilicate material consisting of a mixture of micrometre-sized clay minerals and other microscopic crystals of quartz, feldspars, carbonates and metal oxides.[42] They are often referred to as earthy material that becomes plastic when mixed with limited amounts of water and will harden upon drying or firing. To date, clays have found applications in various industrial areas such as drilling fluid, foundry sand, extenders in aqueous-based paints, natural fillers in paper making, decolorizing agents in the oil industries, filtering and deodorizing agents in the petroleum refineries, building material, catalysts and adsorbent.[43–45] The origin of clays may be from gradual surface weathering and secondary sedimentary processes of a variety of minerals, typically silicate–alumina bearing rocks or low temperature hydrothermal alteration over long periods of time.[46] The properties of different clays, including specific gravity, hardness, elasticity, plasticity, swelling ability, crystallinity, *etc.*, vary considerably, depending on the place of origin and weathering conditions. Generally, clay minerals can be categorized as 1:1 or 2:1, based on the layer structure. The 1:1 clay mineral consists of one silica tetrahedral sheet and one alumina octahedral sheet and belonging to this type are serpentine, halloysite and kaolinite. This type of clay mineral can also be classified as a non-expanding clay because H-bonding holds the sheets tightly together. The alternative type, known as a 2:1 clay mineral, has two tetrahedral sheets sandwiching one octahedral sheet. Some examples of 2:1 clay minerals are talc, vermiculite, smectite, chlorite and illite/hydrous mica. Several well-known classes of clay minerals and the related information including chemical formula, cation-exchange capacity and the layer charge per unit cell are given in Table 11.3.[47,48]

Electronically, clay minerals possess a net negative layer charge due to isomorphous substitution between Al^{3+} and Si^{4+} in the tetrahedral coordination and between Mg^{2+}, Fe^{2+}, Zn^{2+} or Ca^{2+} and Al^{3+} in the octahedral coordination.[49] The negative layer charge imparts surface reactivity towards the surrounding environment, for example the clay mineral surface

AQ:4 **Table 11.3** Several well-known classes of clay minerals and their structural properties (adapted from reference 47).

Clay mineral	Chemical formula	Layer type	CEC (meq/ 100 g)	Layer charge per unit cell
Kaolinite	$[Si_4]Al_4O_{10}(OH)_8 \cdot nH_2O$ ($n = 0$ or 4)	1:1	3–15	<0.01
Illite	$M_x[Si_{6.8}Al_{1.2}]Al_3Fe \cdot 025Mg_{0.7}5O_20(OH)_4$	2:1	10–40	1.4–2.0
Smectite	$M_x[Si_8]Al_{3.2}Fe_{0.2}Mg_{0.6}O_20(OH)_4$	2:1	70–120	0.5–1.2
Vermiculite	$M_x[Si_7Al]AlFe \cdot 05Mg0.5O_20(OH)_4$	2:1	100–150	1.2–1.8
Chlorite	$(Al(OH)_{2.55})4[Si_{6.8}Al0_{1.2}]Al_{3.4}Mg_{0.6})20(OH)_4$	2:1:1	10–40	Varied

can form an electrical double-layer when exposed to aqueous electrolyte environments (*i.e.*, natural waters).[50] Therefore, water molecules can be intercalated between two adjacent layers to form an interlayer ionic solution that contributes to the swelling phenomenon related to electrical double-layer properties.[51,52] The negative layer charge from isomorphous substitution is permanent and pH independent, which is compensated by exchangeable alkali and alkali earth metal cations, such as Na^+, K^+ or Ca^{2+}, within the mineral framework. Additionally, the location of whether the layer charge derives from isomorphic cation substitutions in the tetrahedral or octahedral sheet is also an influencing factor of both hydration and cationic speciation in the interlayer spacing. Sposito demonstrated that H-bonding between basal oxygen atoms and water molecules is enhanced by tetrahedral rather than by octahedral sheet substitution.[52] The adsorbed waters, together with hydrated interlayer exchangeable cations, give rise to the clays/clay minerals surface hydrophilic character and swelling ability.

According to the theory of hard and soft acids and bases (HSAB) introduced by Pearson,[53] the 2 : 1 silicate layers and hydrated interlayer cations in the clay minerals structure can be considered as a Lewis base (electron donor or nucleophilic group) and a Lewis acid (electron donor or electrophilic group), respectively. Given this, clay minerals can be categorized as a soft or hard base, depending on how the location of the layer charge is derived. The soft base clay minerals are those whose layer charge derives from octahedral sheet substitutions (*e.g.*, Mg^{2+} or $Fe^{2+} \rightarrow Al^{3+}$) while for hard base clay minerals, the layer charge originates from tetrahedral sheet substitutions (*e.g.*, $Al^{3+} \rightarrow Si^{4+}$).[54] Among the soft base 2 : 1 silicate clay minerals are montmorillonite, hectorite, glauconite and celadonite, while among the hard base are vermiculite, saponite, beidellite and illite. Brigatti *et al.* have proven that the layer charge location at a 2 : 1 layer type clay mineral affects the hydration of the layers and, more importantly, the sorption process of the cationic species.[55] In general, hard acids (*e.g.*, metal cations) complex with hard bases and soft acids (*e.g.*, organic cations) complex with soft bases.

The Si–O–Si bonds of silica tetrahedrons form a reactive surface called a siloxane, while the O–Al–OH bonds of alumina octahedrons form an oxyhydroxy surface. The siloxane surface, typical of 2 : 1 silicate clay minerals, can be classified as inner-sphere or outer-sphere in terms of cation adsorption complexes.[50] In the inner-sphere surface complex, water molecules will not be able to penetrate siloxane ditrigonal cavities (each being nearly 0.26 nm in diameter), whereas the adsorption of cations may be still feasible due to their smaller sizes than the cavity size. Meanwhile, the outer-sphere surface complex has at least one water molecule interposed between the surface functional group and the bound ion or molecule,[50] in other words, a hydrated adsorbed cation is accommodated. The reactivity of the siloxane surface towards cationic species (*e.g.*, heavy metal ions) may stem from the negative charge-bearing patches arising from isomorphic substitution of an aluminium atom in place of a silicon atom. In this regard, the molecular interaction between metal cation and inner-sphere surface complex can be

monodentate (the ion is bonded to one oxygen atom), bidentate (the ion is bonded to two oxygen atoms), mononuclear or multinuclear.[56]

The oxyhydroxy surface is characterized by a plane of exposed hydroxyl sites underlying Mg, Al or Fe atoms in the centre of the octahedrons. Clays with a 1 : 1 layer type structure such as kaolinite and rectorite usually consist of a siloxane surface on one basal plane and an oxyhydroxy surface on another basal plane. The exposed basal hydroxyl groups are subject to dissociation, therefore they are reactive toward positively charged ions. Considering those properties, it can be implied that the sorption of cationic species onto siloxane and oxyhydroxy surfaces takes place through surface complexation phenomena.

The location of cation complexation (*i.e.*, inner-sphere or outer-sphere) and its modes are the major area that is still continuously studied to date due to the lack of theoretical understanding and incoherent data in the literature. Therefore, a number of molecular-scale investigations and computational studies have sought to investigate the adsorption mechanisms of heavy metal ions onto the surfaces of siloxane and oxyhydroxy groups and the modes of cation-surface complexes using various *in situ* molecular-scale spectroscopy techniques, such as X-ray absorption fine-structure spectroscopy, neutron scattering spectroscopy, nuclear magnetic resonance spectroscopy and Fourier transform infrared spectroscopy.[50,56] The study of Sposito and coworkers reported that excess negative charge density in the siloxane surface makes it possible for this surface to create strong adsorption complexes with cations and water molecules.[50] Electron spin spectroscopy and quasielastic neutron scattering spectroscopy can be used to probe metal ions bound in surface complexes and its adsorption modes whether inner-sphere complex (ISC), outer-sphere complex (OSC) or diffuse-layer (DL) based on the molecular time-scale.[50] The immobilization time-scale for cationic species on 2 : 1 layer-type clay minerals for ISC, OSC and DL lies between 1 and 100 ns, 10 and 100 ps and 4 and 10 ps, respectively.[50]

Systematic molecular simulation studies using Monte Carlo (MC) computer simulations have recently been conducted to examine the stability of an aqueous ionic system in the case of charge-bearing hydrated clay minerals with phase–space sampling strategies introduced by Skipper and coworkers[58,59] and Chang *et al.*[60,61] Experimental works of Wang *et al.*,[62] Sheng *et al.*[63] and Strawn *et al.*[64] have proven that the responsible adsorption mechanisms of cationic species onto surface complexes at low pH and weak ionic strength were outer-sphere complexation (*i.e.*, interlayer adsorption of hydrated cations) and ion exchange, while at high pH and ionic strength, the predominant adsorption mechanisms were inner-sphere complexation (*i.e.*, electrostatic attractions onto ligand functional groups located at the mineral discontinuities) and surface precipitate formation.

Dubbin and Goh studied the sorptive capacity of montmorillonite toward hydroxy–Cr polymers and revealed the inner-sphere complexation mode of interlayer Cr by forming covalent bonding with the basal siloxane oxygen atoms at pH of about 6 and ionic concentrations (I) of 1200–2400 cmol(+)

per kg of clay.[65] Based on previous studies, one can conclude for conveni-
ence that alkali and alkali earth metal cations primarily bound to the surface
complexes by forming outer-sphere complexes or through an ion-exchange
process (categorized as non-specific adsorption), while trace and heavy metal
cations primarily form inner-sphere complexes with surface hydroxyl groups
(categorized as specific adsorption). Furthermore, the modes of cationic
sorption complexes also depend on other factors, in addition to solution pH,
such as surface loading, contact time and types of sorbent, which are all
specific for each system.

The edge hydroxyl groups of clay minerals in particular are more active
than basal hydroxyl groups and play important roles in the sorption pro-
cess of cationic species, the two most important being silanol (Si–OH) and
aluminol (Al–OH) groups. These surface hydroxyl groups resulted from
transformation of 'broken' Si–O–Si and Al–O–Al bonds, carrying residual
negative charges along the edges of the clay mineral particles. Upon
contact with water, the anhydrous Fe- or Al-oxide surfaces can form ferrol
(Fe–OH) or aluminol groups, respectively. The defect sites of silanol and
aluminol groups are amphoteric and pH-reactive, in which these groups
carry a net positive charge at low pH (*i.e.*, Lewis acid sites), neutral at the
isoelectric point (iep) and negative at high pH (*i.e.*, Lewis base sites). Many
studies have investigated the ionizable properties of silanol and aluminol
surface groups as a function of pH, associated with protonation and
deprotonation reactions. At solution pHs lower than the pH of point zero
charge (pH_{pzc}) of the sorbent, both silanol and aluminol edge sites are
protonated due to excessive concentration of H^+ ions in the bulk solution,
while at solution pHs higher than pH_{pzc} of the sorbent, both silanol and
aluminol groups are deprotonated. The protonation and deprotonation
mechanisms of silanol and aluminol surface hydroxide groups are given as
follows:

Protonation reactions (at solution $pH < pH_{pzc}$ of the sorbent):

$$\equiv\!Si\text{–}OH + H_3O^+ \leftrightarrow \equiv\!Si\text{–}OH_2{}^+ + H_2O \tag{11.1}$$

$$\equiv\!Al\text{–}OH + H_3O^+ \leftrightarrow \equiv\!Al\text{–}OH_2{}^+ + H_2O \tag{11.2}$$

Deprotonation reactions (at solution $pH > pH_{pzc}$ of the sorbent):

$$\equiv\!Si\text{–}OH \leftrightarrow Si\text{–}O^- + H_3O^+ \tag{11.3}$$

$$\equiv\!Al\text{–}OH \leftrightarrow Al\text{–}O^- + H_3O^+ \tag{11.4}$$
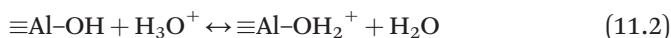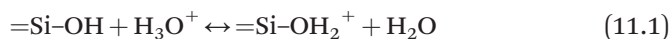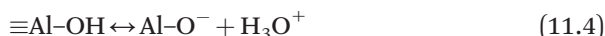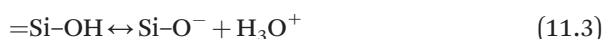
Yet Sposito *et al.* revealed that only the aluminol hydroxyl surface groups
can accept or donate protons, while the silanol hydroxyl groups is only
capable of dissociating its proton due to the larger valence of the silicon
atom.[50] In another recent study, Liu and coworkers investigated the acidity
constant of surface groups on the (0 1 0)-type edge sites of montmorillonite
and kaolinite clays using the first principles of molecular dynamics (FPMD)
based on the vertical energy gap technique.[66] This study concluded that the

values of acidic constants of silanol groups of montmorillonite and kaolinite are and, respectively. In most cases, the sorption of metal cations onto the surfaces of clays and clay minerals is favourable at elevated pH, associated with deprotonation of surface hydroxyl groups on the broken edge sites, which provide negatively charged ligands for the binding of metal cations.

The cation-exchange capacity (CEC), expressed in milliequivalents per 100 g of clays/clay minerals, or centimoles of charge per kilogram [cmol(+) per kg], is defined as the maximum holding capacity to which a clay/clay mineral can adsorb and exchange cations from the clay suspensions at a specific pH,[66] therefore it directly determines the effectiveness of clay/clay mineral sorbents in removing metal cations. Each clay/clay mineral has a specific range of exchange capacities, as shown in Table 11.3, because of structural differences and the variation of chemical compositions. The higher this number, the higher the negative charge and the more cations the clays and clay minerals can hold through electrical attraction. Generally speaking, the exchange capacities of clays and clay minerals can be enhanced by either adding organic matter or increasing the suspension pH. The latter is preferred and adopted in most sorption studies for effective removal of heavy metal ions from aqueous solutions. Increasing the pH would provide negatively charged surface sites for the binding of heavy metal ions, resulting from deprotonation of structural hydroxyl groups, mainly silanol and aluminol groups. Thus, one can infer that the acting uptake mechanism, in connection with cation-exchange capacity, is a reversible exchange reaction between cations held near a mineral surface by unbalanced electrical charges and cations in a solution in contact with the mineral. The tetrahedral–octahedral–tetrahedral (T-O-T) layer structure of 2 : 1 silicate clay minerals is also more advantageous for the sorption of heavy metal ions compared with tetrahedral–octahedral (T-O) clay, associated with a larger internal volume and a higher number of edge hydroxyl groups exposed on the surface,[67] providing more vacant spaces to accommodate higher amounts of metal cations. Other beneficial features of clays and clay minerals as heavy metal sorbents are the high specific surface area that arises from the tiny size of the particles (in the nanoscale) and good interconnectivity of the pore structures consisting of mesopores and micropores, and macropores to a lesser degree.

11.3 Surface Modification Techniques of Clays and Clay Minerals for Enhanced Heavy Metals Sorption

Improving the performance and surface compatibility of clays and clay minerals as heavy metal sorbents has becoming the hot subject area for much environmental engineering research in recent years. Surface modifications of clays/clay minerals are conducted in order to: (1) enhance metal

loading capacity and (2) alter the mineralogy, adsorptive and electrokinetic properties of the minerals so that they become widely applicable. In their native state, clays and clay minerals are potential sorbents for removing cationic species (*e.g.*, heavy metal ions) because they readily sorb onto un-altered colloidal surfaces through ion exchange or complexation mechanisms. Many efforts have been made to investigate the performance of natural clays and clay minerals to sorb various heavy metal ions.

Table 11.4 lists several studies dealing with adsorption processes of various heavy metal ions from synthetic and real effluents using natural clays and clay minerals over a six-year period from 2007 to 2012. A comparative study on lead adsorption potential on three local natural clays, namely perlite, dolomite and diatomite, has been recently conducted by Irani *et al.*[68] The removal capacities of lead ions ranked as follows: diatomite (25.01 mg g^{-1}) > dolomite (19.69 mg g^{-1}) > perlite (8.91 mg g^{-1}), which agreed well with the decreasing surface properties of clays, including the BET surface area and total pore volume. Natural kaolin and montmorillonite are both able to treat metal-contaminated waters effectively with an adsorption extent reaching 37.6% for kaolinite and 78.7% for montmorillonite, as studied by Bhattacharyya and Gupta.[69]

In another study, Chen and Wang revealed that natural palygorskite, a silicate clay with talc-like units arranged alternately along the *c*-axis of a fibrous structure, had a relatively high sorption capacity toward Pb(II) ions with a maximum uptake value of 104.28 mg g^{-1}.[70] The adsorption feasibility of expanded perlite (EP) clay for the removal processes of toxic Ag(I), Cu(II) and Hg(II) cations has been studied by Ghassabzadeh *et al.*[71] They observed excellent performance of expanded perlite in removing Ag(I) and Cu(II) ions at near-neutral pH with a removal percentage that reached 92% for Cu(II) and 100% for Ag(I), while for Hg(II) it was 35%. Natural clinoptilolite and bentonite clays have also been utilized as a low-cost material for fast uptake of bivalent lead ions from aqueous solutions in a batch mode.[72] It was found that bentonite clays were able to sorb higher amounts of Pb^{2+} ions with a removal percentage that reached 100% at ambient temperature with mild agitation. Under the same conditions, the removal percentage of clinoptilolite with particle sizes ranging between 2.5 and 5 mm and in a dust form were about 42 and 55%, respectively. This difference is due to the higher specific surface area of clinoptilolite dust than that of granular clinoptilolite, which facilitates the mobilization of transport with respect to the incoming lead ions.

The adsorption potential of two volcanic rock grains, namely Scoria (VSco) and Pumice (VPum), towards Ni(II) ions has been tested by Alemayehu and Lennartz.[73] The maximum uptake capacity of Ni(II) ions was 980 mg kg^{-1} for VSco and 1187 mg kg^{-1} for VPum at room temperature under weak acidic conditions (pH of 5). The potential application of Turkish illitic clay for removing Cd^{2+} and Pb^{2+} ions has been evaluated by Ozdes *et al.*[74] A removal efficiency of nearly 100% for Pb(II) ions and 78% for Cd(II) ions was obtained in their study.

Table 11.4 The removal capacity of various natural clays and clay minerals towards various heavy metal ions.

Clays/clay minerals	Heavy metals	Maximum sorption capacity (mg g^{-1})*	Reference
Palygorskite	Pb(II)	104.28	Chen and Wang[70]
Montmorillonite	Pb(II)	31.05	Bhattacharyya and Gupta[69]
Kaolinite	Pb(II)	11.52	Bhattacharyya and Gupta[69]
Cankiri bentonite	Zn(II)	80.64	Veli and Alyuz
Illitic clay	Cr(III)	35.70	Ghorbel-Abid et al.
	Cd(II)	52.50	
Expanded perlite	Ag(I)	8.46	Ghassabzadeh et al.[71]
	Cu(II)	1.95	
	Hg(II)	0.35	
Brazilian smectite	Cr(VI)	1.16 mmol g^{-1}	Guerra et al.
Brazilian sepiolite	As(V)	7.26×10^{-2} mmol g^{-1}	Guerra et al.
Brazilian kaolinite	U(VI)	8.37×10^{-3} mmol g^{-1}	Guerra et al.
Clinoptilolite	Pb(II)	80.93	Gunay et al.
Kaolinite	Pb(II)	11.50	Bhattacharyya and Gupta[69]
	Cd(II)	6.80	
	Ni(II)	7.10	
Montmorillonite	Pb(II)	31.10	Bhattacharyya and Gupta[69]
	Cd(II)	30.70	
	Ni(II)	21.10	
Palygorskite	Co(II)	8.88	He et al.
Diatomite	Pb(II)	25.01	Irani et al.[68]
Dolomite	Pb(II)	19.69	Irani et al.[68]
Perlite	Pb(II)	8.91	Irani et al.[68]
Apatite	Pb(II)	0.4 mmol g^{-1}	Kaludjerovic-Radoicic and Raicevic
Sericite	Ni(II)	44	Kwon and Jeon
Kaolinite	Cr(III)	$3.86–6.62 \times 10^{5}$ mmol g^{-1}	Turan et al.
Sericite	Cu(II)	1.67	Tiwari et al.[35]
	Pb(II)	4.69	
Cankiri bentonite	Cu(II)	44.84	Veli and Alyuz
Diatomite	Th(IV)	—	Sheng et al.[63]

Boron impurity (BC), a heterogeneous waste material containing clay mixtures from a boron enrichment plant, has been examined for the removal of lead and nickel ions from aqueous solutions.[75] About 81.86 and 74.28% of lead and nickel ions, respectively, were adsorbed onto the BC surface from a single-component solution within 90 min. The effectiveness of extruded clay mixtures consisting of zeolite–kaolin–bentonite for the sorption of lead ions was investigated by Salem and Sene.[76] The obtained results indicated that the simultaneous addition of bentonite and kaolin could substantially improve the compression strength and adsorption capacity. The Raschig ring-shaped adsorbent prepared at an optimum mixing ratio of 66.67 wt% zeolite,

29.17 wt% bentonite and 4.16 wt% kaolin, displayed a maximum sorption   1
capacity of 140.9 mg g^{-1}. Natural clays and clay minerals are also acquiring
prominence for nuclear waste management. In the study of Zhao *et al.*,
laboratory-grade MX-80 bentonite was used to treat tetravalent thorium ions
in aqueous solution; the adsorption is dominated by surface complexation   5
between cationic species [Th^{4+} and Th(OH)$^{3+}$] and negatively charged sur-
face sites.[77]

Despite these results, not all natural clays and clay minerals demonstrate
appreciable metal sorption capacity, which is attributed to the low specific
surface area, inaccessible inner pore channels responsible for adsorption/   10
exchange, non-expanding characteristics of the minerals and poor cation-
exchange capacity. Therefore, various modification techniques have been
employed to ameliorate the layer structure and surface chemistry of clays
and clay minerals while preserving its crystal lattices for an enhanced metal
removal process. The following sections will discuss pillaring, grafting and   15
intercalation as common techniques as well as thermal (physical) and
chemical activation methods, to a lesser extent.

11.3.1   Thermal Activation
                                                                               20
Surface modification of clays and clay minerals through thermal activation is
mostly conducted by subjecting the materials to high temperature treat-
ment, up to 1000 °C. The general purposes of thermal activation processes
are to remove any impurity (*e.g.*, organic matter) and moisture attached to
the clay particles. The resulting material, termed calcined or sintered clay,   25
possesses a lower degree of crystallinity, which is cluster-shaped or
amorphous with coarse-shaped pores, poor dispersibility in aqueous solu-
tions (*e.g.*, water) and a generally lower sorption capacity in conjunction with
a reduced specific surface area.

Talaat *et al.* studied the performance of Egyptian kaolin and bentonite   30
clays and their heat-treated forms for the removal of five heavy metal ions,
namely chromium, cadmium, nickel, zinc, copper and lead.[78] The experi-
mental results showed that all modified kaolinite clays displayed lower re-
moval capacities towards Cr(III) and Cd(II) ions, although Na-bentonite
exhibited the highest adsorptivity towards Cd(II), Cu(II), Zn(II), Pb(II) and Ni(II)   35
cations. The calcination of Turkish bentonite clay to remove the radio-
nuclide U(VI) ions from synthetic effluent has been conducted by Aytas
et al.[79] They observed a strong correlation between calcination temperatures
and U(VI) removal capacity in which the adsorptivity of uranyl ions (UO$_2$$^{2+}$)
onto thermally treated bentonite (TAB) surfaces gradually fell at extreme   40
calcination temperatures, typically above 400 °C, due to the distortion of the
internal structure of clay. In this regard, a calcination temperature of 400 °C
was selected as the optimum point that gave the highest adsorption capacity
of lead ions.

Similar attempts were made by by Alkan and colleagues to investigate the   45
sorption performance of calcined kaolin for preconcentrating copper ions

from aqueous solutions.[80] They found that the phase transition from kaolinite to the metakaolinite phase took place by calcinating clay at 600 °C. Another useful finding in their study is that the extent of copper sorption onto the clay surface decreased with increasing activation temperature due to the removal of most micropores and structural hydroxyl groups during calcination, typically at activation temperatures beyond 400 °C. The application of heat-treated palygorskite clay to sorb cadmium ions from aqueous solutions has been conducted by Wang *et al.*[81] The gradual increase in the specific surface area of heat-treated palygorskite clay from 48.66 to 128.9 $m^2\ g^{-1}$ was observed for calcination temperatures up to 300 °C, thereafter, the specific surface area gradually decreased to 64.87 $m^2\ g^{-1}$ when the calcination temperature reached 600 °C. The decreasing surface area of heat-treated clay was followed through the lower amount of adsorbed cadmium ions at equilibrium from 46.49 $mg\ g^{-1}$ at an activation temperature of 300 °C to 8.56 $mg\ g^{-1}$ at an activation temperature of 600 °C. Calcined and flux-calcined diatomite clays also displayed remarkable sorption performance for treating effluents containing radioactive waste.[82] Both these clays exhibit high selectivity and fast kinetics to sorb Th(IV) ions. With a specific surface area of 21.93 $m^2\ g^{-1}$ for calcined diatomite and 1.25 $m^2\ g^{-1}$ for flux-calcined diatomite, the removal percentage of Th(IV) ions reaches 99 ± 0.1 and $91 \pm 0.4\%$, respectively, under optimum pH conditions (pH 4). The responsible adsorption mechanism under these conditions was an electrostatic interaction between positively charged thorium acetate ion complexes (*i.e.*, $[ThCH_3COO]^{3+}$ and $[Th(CH_3COO)_2]^{2+}$) and deprotonated hydroxyl edge groups.

During the calcination process, two types of reactions, namely dehydration and dehydroxylation, take place, which are responsible for the changes on structural, textural (*e.g.*, pore size distribution) and adsorptive removal of calcined clay materials. A dehydration reaction causes the liberation of hydrated and intercalated water moieties from the clay framework, resulting in the denser packing structure. Meanwhile, dehydroxylation reactions (*i.e.*, the evolution of water from hydroxyls belonging to the clay skeleton) take place at higher temperatures than those of dehydration reactions, typically ranging from 500 to 600 °C. This reaction can be accompanied by the movement of octahedral cations within the octahedral sheets, causing phase transformation of clays/clay minerals into a meta-phase and further recrystallization of the meta-phase into a crystalline phase.[80] Calcination of clays and clay minerals at an extreme temperature causes distortion of the crystalline structure, which results in a notable decrease of adsorption capacity. Therefore, it must be taken into account that sufficient heat should be applied in order to remove impurities and adsorbed waters in the external surface and clay matrix as well as to make the octahedral layers remain intact during the treatment process. On the other hand, very high temperature treatment will deteriorate the interior structure of the mineral, leading to amorphization.

The loss of chemical constituents and any thermal reaction occurring during calcination can be monitored by simultaneous application of

thermogravimetric analysis (TGA) and differential scanning calorimetry
(DSC), which record the amount and rate of change in the mass of sample as
a function of temperature or time in a controlled atmosphere. These ther-
moanalytical techniques can differentiate between peaks associated with
mass loss and those associated with phase transformation in many solids.
The distinctive characteristics of endothermic and/or exothermic peak
temperatures that appear at a certain temperature region represent any
thermal reaction or phase transition in the solid phase and the corres-
ponding percentage of mass loss. In the study by Alkan *et al.*,[80] the structural
distortion of silica tetrahedral and alumina octahedral of kaolinite clay
could be identified at four temperature points: (1) removal of physically
bound water in pores and on the surfaces at 100 °C; (2) mass loss associated
with dehydration of a surface hydroxyl group in the alumina octahedral
sheet at about 400 °C; (3) dehydroxylation of kaolinite and formation of a
metakaolinite phase between 400 and 650 °C; and (4) decomposition of a
metakaolinite phase at 950 °C to form an Al–Si spinel phase.

11.3.2 Chemical Activation/Conditioning

Surface modification of clays and clay minerals through chemical activation
is performed by impregnating or immersing the solids in inorganic acid
solutions, such as hydrochloric acid (HCl), sulfuric acid (H_2SO_4), nitric acid
(HNO_3) or aluminium sulfate [$Al_2(SO_4)_3$], base solutions such as alkali
and alkali earth metal hydroxides [*e.g.*, NaOH, KOH, $Ca(OH)_2$ or $Al(OH)_3$] or
anion salts such as potassium dihydrogen phosphate (KH_2PO_4), orthopho-
sphate, tri-polysulfate and sodium tetraoxosulfate(VI). Chemical treatment
with inorganic acids has been widely used to improve surface and catalytic
properties of fibrous clays with respect to increased surface area, porosity
and number of acid sites compared with the parent clays. Acid leaching of
clays and clay minerals causes disaggregation of the clay particles, elimin-
ation of impurities and dissolution of the external layers.[83] In this context,
the solubility characteristics of clays and clay minerals in acids reveal certain
attributes of the mineral itself and are of fundamental importance for de-
termining the utility of various clay minerals as aluminium sources and to
produce porous and high surface area materials for catalyst supports or
adsorbents. Generally, the acid-modified clays consist of a mixture of non-
attacked clay layers and a hydrous, amorphous and partially protonated
silica phase.[83]

   The physico-chemical characteristics of H_2SO_4-leached kaolin have been
evaluated by Panda and colleagues.[84] The effect of acid molarity on the
structural and chemical properties of the resulting materials were charac-
terized using a series of techniques, including XRF, XRD, FTIR, TGA, DTA
and N_2 physisorption. The results show the leaching of interlayer and
octahedral cations upon acid treatment in which high acid strength treat-
ment provoked amorphization and structural transformation to form an
amorphous silica type phase. The specific surface area and pore volume were

found to increase after acid leaching, which is beneficial for removal purposes. Sulfuric acid-activated Tunisian green (RGC) and red (RRC) clays have been tested for the adsorption of lead metal from aqueous solution in a batch system.[85] The surface properties of acid-treated RGC and RRC clays, including specific surface area, total pore volume, internal porosity and pore size, increased and they showed maximum retention capacities of 27.15 mg g^{-1} for H_2SO_4 treated RRC and 40.75 mg g^{-1} for H_2SO_4 activated RGC, as predicted with the Langmuir adsorption model.

Jiang *et al.* also obtained $Al_2(SO_4)_3$ modified kaolin with excellent adsorption capacity and high selectivity to remove Pb(II) ions from synthetic and plating factory wastewater.[86] Compared with the parent clay, the sorption capacity of $Al_2(SO_4)_3$ modified kaolin is almost 5-fold higher with a Langmuir monolayer adsorption capacity of 32.2 mg g^{-1}. It could be that modification of kaolin clay by aluminium sulfate octadecahydrate in this study revealed that the modifying chemical did not impregnate the clay interior, but might exist on the outer surface and provide more available exchange sites for enhanced adsorption. During activation of clays/clay minerals with inorganic acids, the exchangeable cations are substituted by protons and part of the octahedral cations (mainly Al^{3+}) dissolve, creating new acid centres in the solid structure and making them amorphous, more porous and acidic. Furthermore, the acid treatment method is effective for minimizing the possible decomposition of the crystalline structure, thus generating the desired features for further thermal activation of clay materials to prepare an effective adsorbent towards heavy metals.

The influence of acid treatments on the adsorption capacity of sepiolites was evaluated by Kilislioglu and Aras to sorb radioactive uranium ions (UO_2^{2+}).[87] The acid-treated forms of the clays termed SS200 and SC200 show a dramatic increase in the specific surface area, but the uranium adsorption capacity was not solely related to the specific surface area of the materials. This study found a lower amount of UO_2^{2+} ions adsorbed onto SS200 (S_{BET} of 568.5 m^2 g^{-1}) than that adsorbed onto untreated sepiolite (S, S_{BET} of 325.2 m^2 g^{-1}), probably due to the leaching of all Mg^{2+} interlayer ions and the collapse of the octahedral layer. Acid-activation of kaolin clay at different molar concentrations and acid to solid impregnation ratios was conducted by Alkan *et al.* for removing copper ions.[80] This study obtained a lower uptake of Cu^{2+} ions onto acid-activated clay, possibly due to partial distortion of the layer structure and specific adsorption of H^+ ions onto the clay surface that reduced active patches.

Chaari *et al.* modified Tunisian smectite-rich clay using two inorganic acids, namely HCl and H_2SO_4 with an equimolar concentration for lead(II) ions adsorption.[88] They found that H_2SO_4 activated clay (labelled as AYD$_s$) demonstrated a significantly higher loading capacity towards Pb^{2+} cations than HCl activated clay (labelled as AYD$_h$). This might be attributed to the greater solubility of clay minerals in sulfuric acid than in hydrochloric acid, which resulted in the dissolution of and the formation of the phase. Compared with non-activated clay, both acid-activated clays have a higher

number of active surface sites for the binding of lead cations. Spent   1
bleaching earth (SBE), a waste by-product from an edible oil refining factory
also has value for the elimination of lead ions from water in the study by
Mana *et al.*[89] The SBE, after being thermally treated at a mild temperature
(100 °C) following NaOH impregnation treatment to form SBTE material,   5
exhibited a significantly higher sorption capacity than those of virgin
bleaching earth and pristine SBE, as well as faster kinetics uptake at the
same metal concentration. Modification of bentonite using phosphate and
sulfate anion salts has been carried out by Olu-Owolabi and Unuabonah.[90]
Although the modification process causes the specific surface area of ben-   10
tonite clays to decrease due to blockading of the pores, the CEC, as well as
adsorption capacity towards bivalent zinc and copper ions, increased due to
the presence of more binding sites introduced from the physisorbed sulfate
and chemisorbed phosphate anions, in which the latter were preferentially
adsorbed onto the Al–OH and Al–H$_2$O surface functional groups of   15
bentonite clay.

Another efficient pathway to chemically tailoring the surface chemical
nature of clays and clay minerals is through chemical conditioning. Chem-
ical conditioning is a technique with the aim of removing certain ex-
changeable cations from the clay layers and locating more easily removable   20
ones that are more willing to undergo ion-exchange processes. Lihareva *et al.*
studied the behaviour of natural and sodium-loaded clinoptilolite as a cation
exchanger of monovalent silver ions.[91] The Na form of clinoptilolite showed
an improved ability for cation exchange of Ag$^+$ ions due to the more
monoionic character of modified clay from the replacement of K$^+$, Ca^{2+} and   25
Mg^{2+} interlayer cations. The introduced exchangeable Na$^+$ cations from the
conditioning treatment help to increase the exchange performance to
remove Ag$^+$ ions.

Similar work dealing with chemical conditioning of clinoptilolite using
NaCl and HCl solutions has been conducted by Coruh for the removal of zinc   30
ions.[92] They found that the conditioned clays, irrespective of the types of
chemicals, exhibit higher effective ion-exchange capacity due to lower Si to Al
ratios. Chemical conditioning with saturated NaCl solution resulted in the
exchange of tightly bound K$^+$ and Ca^{2+} cations from the zeolitic lattice and
removal of fine dust particles, making the channel apertures more easily   35
accessible for incoming metal cations. Pretreatment of clinoptilolite with
four different chemicals, namely NaCl, KCl, HCl and CaCl$_2$ has been carried
out by Gedik and Imamoglu.[93] The results of this study reveal that pre-
treatment with NaCl can be adopted as an efficient way to obtain the
monoionic form of clinoptilolite, which shows more than 2-fold enhance-   40
ment in the metal removal capacity compared with that of the as-
received form.

Alkaline Ca-bentonite (ACB) was utilized in the study by Zhang *et al.* by
treating raw bentonite clay with calcium hydroxide as a cheap sorbent to
remove zinc(II) ions.[94] The ACB sorbent displayed a monolayer sorption   45
capacity 2-times greater than raw bentonite and a more effective

performance in terms of shorter equilibrium time and broader pH range for
metal removal. In this study, adsorption (cation exchange and fixation) and
formation of Zn precipitates on the outer surface were the two main
mechanisms for Zn(II) removal using ACB sorbent over a pH range of 1–7.
The adsorbed Zn^{2+} ions were found to intercalate between the clay layers,
causing structural changes and generation of micropores in the sorbent wall.

In another work, Dimirkou conditioned natural clinoptilolite using an
$Fe(NO_3)_3$ solution under strong basic conditions to prepare a fully iron ex-
changed form of clinoptilolite, designated as a Clin-Fe-oxide system.[95] The
hardness as well as the concentrations of alkali and alkali earth metal cat-
ions of the Clin-Fe-oxide system dramatically dropped after Fe conditioning,
nevertheless the Si to Al ratio of the clay system remained intact compared
with the respective ratio of the parent clay. The synthesized Clin-Fe-oxide
system contains high iron concentrations, exceeding the practical and the-
oretical cation-exchange capacity of the parent clay, characterizing the 'over-
exchanged' feature. The non-crystalline iron clusters (as −Fe−OH) deposited
in the zeolite channels and on the external sites give rise to the Clin-Fe
system higher specific surface area as well as extra-framework positions for
Zn(II)-exchange through outer-sphere complexation.

Abu-Eishah synthesized a chemically modified local clay (termed Sarooj
clay) by saturating the solid phase with 0.01 M $NaNO_3$ solution.[96] The Na-
saturated clay was employed to sorb three heavy metal ions, namely Zn^{2+},
Cd^{2+} and Pb^{2+}, and showed an effective performance due to its higher
surface properties, including BET surface area, specific micropore surface
area, external surface area and total pore volume. During chemical treat-
ment, more than half of the interlayer Ca^{2+} cations were exchanged with
Na^+ ions, while other metal cations (in the oxide forms) such as Al_2O_3,
Fe_2O_3, MgO and K_2O were increased. From several of the previous studies
discussed earlier, it can be concluded that the final monoionic and near-
monoionic nature of the clays was found to enhance their effective exchange
capacity and performance in ion-exchange applications, including heavy
metals sorption. Recently, surface modification processes of clays and clay
minerals have been switched to pillaring, grafting or intercalation techni-
ques because they are simpler, and provide cost and energy savings.

11.3.3   Pillaring, Grafting and Intercalation Techniques

Many studies are currently interested in functionalizing the surface chem-
istry of clays and clay minerals through pillaring, grafting and intercalation
techniques rather than conventional thermal and chemical activation pro-
cesses, due to the simpler procedures, cost reduction in respect of prepar-
ation of adsorbents and energy saving. Generally, all these techniques aim to
increase the adsorption potential of clays/clay minerals for removing heavy
metal ions either by increasing the specific surface area and/or tailoring the
chemical nature of the mineral surface so that particular metal species can
be selectively sorbed. The modified clays/clay minerals are well defined as

organoclays in which the organofunctionalization is normally used to introduce basic groups on anchored pendant chains.[97,98] Typical examples of guest molecules that have been used for the surface modification processes are long-chain ionic surfactants [*e.g.*, cetyltrimethylammonium bromide (CTAB), lauryl alkyl sulfate (LAS), sodium dodecyl sulfate (SDS), cetylpyridinium bromide (CPBr), tetramethylammonium bromide (TMAB), phenyl trimethylammonium bromide (PTMAB) and hexadecyltrimethyl ammonium (HDTMA)], metal salts that are Lewis acids (*e.g.*, $FeSO_4$, $NaNO_3$, NaCl and $ZnCl_2$), amino acids or polypeptides, chelating agents (*e.g.*, chitosan, chitin, citric acid, succinic acid and organosilanes) and metallic/composite oxides (*e.g.*, Al_2O_3, Fe_2O_3, Fe_3O_4, TiO_2, ZnO, MnO_2, SiO_2 and $MnFe_2O_4$).

Nowadays, pillared clays (PILCs) have become a well-known class of porous materials with properties exceeding those of zeolitic clays. The pillaring of clays and clay minerals involves intercalation of bulky inorganic and organic clusters, such as polynuclear complex inorganic ligands (*e.g.*, hydroxo and chloro ligands), large metal complex ions with organic ligands and polyhydroxy cations (*e.g.*, $AlCl_3 \cdot 6H_2O$, $ZrOCl_2 \cdot 8H_2O$ and hydroxyl zirconium) to exchange interlayer cations. Upon high-temperature treatment (calcination), the intercalated polyoxycations convert into their metal oxide forms, which expand the internal pores and create a solid with a stable two-dimensional microporous structure and large surface area. Some important factors in the clay pillarings include the size and amount of pillars and their configuration in the interlayer space, which are highly sensitive to the clay characteristics (*e.g.*, the layer charge and its location) and hydrolysis conditions under which the polyoxycations are formed.[99,100] The resulting pillared clays also inherit properties specific to the chemical nature of the pillaring species, in addition to their improved permanent porosity. Karamanis *et al.* studied the application of Al-pillared montmorillonite for the fast uptake of strontium and caesium ions from aqueous solutions.[101] In the study of Bhattacharyya and Gupta,[102] kaolinite and montmorillonite pillared with polyoxo-Zr ions were used for the removal of Fe(III), Co(II) and Ni(II) ions in single batch systems. After the pillaring and calcination processes, the exchange capacity of clays substantially fell due to dehydroxylation and interlayering of positively charged cations. Accordingly, the sorption capacity of pillared clays was lower compared with the parent clays, possibly due to the blockade of negatively charged adsorption sites and probably some pore networks by bulky polyoxycations.

The surface modification of clays and clay minerals with cationic surfactants involves both a cation-exchange process and the bonding of a hydrophobic moiety in the clay layers. In this regard, the concentration of the loaded surfactant crucially determines the types of adsorptive layer formed. Cationic surfactants can form two types of adsorptive layers: monolayers and bilayer/patchy bilayers.[103,104] At low loading levels, surfactant cations eventually create an adsorptive monolayer, while at higher loading levels, the formation of a bilayer, patchy bilayer or bilayer with a

paraffin-type structure may take place. In the study by Atia, commercial bentonite was loaded with cetylpyridinium bromide to prepare organo-bentonite for sorbing chromate and molybdenum oxyanions from water.[105] From this study, the configuration of surfactant cations in the interlayer space of the clay depends on the amount of surfactant adsorbed and is a CEC-function. The formation of a surfactant monolayer was observed when the amount of surfactant in the interlayer space slightly exceeds the CEC, while a bilayer and a bilayer with a paraffin-type arrangement are formed when the adsorbed amount of surfactant cations were lower than twice and several-fold higher than the CEC, respectively.

The results of the study conducted by Ouellet-Plamondon *et al.* demonstrated that Al-pillared and quaternary ammonium cation (QAC)-intercalated bentonites could be potential sorbents with adsorption capacities of mg g^{-1} and mg g^{-1} toward Pb(II) ion.[106] The amounts of Pb adsorbed by Al-pillared bentonites were higher than those for untreated bentonite. Faghihian and Kabiri-Tadi modified natural clinoptilolite using three different chemicals, namely NaNO$_3$, KNO$_3$ and Ca(NO$_3$)$_2$ to prepare Na, K and Ca-exchanged forms of zeolitic clays.[107] The adsorptive properties of natural and cation-exchanged clinoptilolite to treat Zr-bearing aqueous effluents were contrasted and higher effectiveness for the latter adsorbent was found under identical conditions. Chemical modification of kaolin and montmorillonite with tetrabutylammonium bromide (TBAB) has been carried out to effectively sorb Cu(II), Ni(II) and Co(II) metal cations.[108] However, an intercalation process following calcination resulted in the decreasing adsorption capacity due to the blockade of some parts of the surface pores and negatively charged sites by bulky ammonium cations. The intercalation of Algerian halloysites with saturated sodium acetate solution has been conducted by Mellouk *et al.*[109] In their study, the intercalation process causes the basal spacing of halloysite to increase from 7.6 to 10.1 Å and the specific surface area from 58 to 884 m^2 g^{-1}, of which the increase in basal spacing was found to be unaffected with an increase in contact time during the modification process. The CH$_3$COONa intercalated halloysite was used thereafter for removing Cu^{2+} ions and shows a maximum uptake capacity of 52.3 mg g^{-1}.

Silane coupling agents are a family of organosilicon monomers with the general structure of R–SiX$_3$ where R and X refer to the organo-functional group attached to silicon and hydrolysable alkoxy groups are typically methoxy (−OCH$_3$) or ethoxy (−OC$_2$H$_5$), respectively.[110] This coupling agent has found many applications related to uses involving site-specific interactions because of its capability of providing chemical bonding between an organic and an inorganic material. In the case of surface modification of clays/clay minerals, the organosilanes (*e.g.*, organosiloxanes and organo-chlorosilanes) are attached to the clay edge sites through condensation reactions between surface hydroxyl groups (−Si−OH or −Al−OH) and the chloro or alkoxy groups of the organosilane.[111–113] Dogan *et al.* functionalized sepiolite with [3-(2-aminoethylamino)propyl]trimethoxysilane for the preconcentration of six metal ions from aqueous solutions namely Co^{2+},

Cu^{2+}, Mn^{2+}, Zn^{2+}, Fe^{3+} and Cd^{2+}.[114] The functionalized material was characterized using FT-IR, XRD and zeta potential measurements to investigate its surface and electrokinetic properties. It was revealed from their study that the anchored pendant chains contain basic nitrogen active sites that facilitate the uptake of metal ions. The intercalated clays exhibit different sorption characteristics, including higher selectivity and sorption capacity.

A low cost chemical sensor for detecting various toxic heavy metals was prepared from sepiolite grafted with 3-aminopropyltriethoxysilane (3-APT).[115] The grafted sepiolite clays acquire basic amino centres that are favourable for retaining more metal cations. The specific adsorption of metal cations onto the grafted sepiolite imparts more positive charges and shifts the isoelectric point (iep) of the modified clay to higher pH. The following sequence of metal adsorptivity onto the grafted sepiolite surface (Fe > Mn > Co > Cd > Zn > Cu > Ni) may reflect that basic amino centres preferentially sorb hard cations such as iron and manganese.

Three different intercalation methods of montmorillonite with aluminium hydroxypolycation and cetyltrimethylammonium bromide (CTAB) have been performed by Hu and Luo.[116] Based on the combined characterization analyses, including X-ray diffraction analysis, Fourier transform infrared and zeta potential measurements, it was found that the modifying agent had either entered the interlayer spaces or sorbed onto the external surface of the clay. Furthermore, they also studied the intercalation orders of surfactant agents for batch adsorption process of hexavalent chromium. Modification of various clay minerals such as zeolite, bentonite, exfoliated vermiculite and attapulgite using a cationic surfactant (hexadecylammonium bromide) to sorb hexavalent chromium ions was studied by Thanos *et al.*[117] The results show that the intercalation of cationic surfactant expands the lamellar space and changes the negative zeta values of clays to positive, which are favourable for the adsorption of chromate anions. The maximum adsorption capacity followed the order of vermiculite (27.06 mg g^{-1}) > bentonite (24.16 mg g^{-1}) > attapulgite (15.25 mg g^{-1}) > zeolite (13.22 mg g^{-1}). The intercalated clays also exhibit a different thermal stability compared with untreated clays.

The potency of Na-montmorillonite intercalated with a long-chain amine (*i.e.*, dodecylamine) has been evaluated by Kumar *et al.*[118] They observed a significant enhancement on the sorption capacity of dodecylamine-intercalated clay due to the presence of protonated amine and surface silanol groups as well as changes on the surface properties of the modified clay to organophilic. A series of characterizations, including infrared spectroscopy and X-ray diffraction, revealed that the organic bound to *via*, which makes them an effective charged adsorbent to remove anion species, such as hydrogentetraoxochromate(VI) ions.

The application of bentonite modified with a commercial alkyl ammonium surfactant known as Arquad$^{®}$ 2HT-75 for the removal of hexavalent chromium ions was studied by Sarkar *et al.*[119] The results obtained indicated

that the organoclays loaded with higher amounts of surfactant exhibited a
more ordered structure and a remarkable increase in the sorption capacity.
The maximum monolayer Cr(VI) adsorption of 14.64 and 8.51 mg g^{-1} at 37 °C
was obtained by loading the clay with surfactant to clay mass ratios of 4.75 : 1
and 2.38 : 1, respectively. Modified bentonites have also proved their worth
for the remediation of water polluted by antimony ions from aqueous so-
lutions. Polyvinyl alcohol (PVA) modified kaolinite was also employed to
remove Pb^{2+} ions in a two-stage counter-current batch adsorber design.[120]
Although PVA-modified kaolinite had lower specific surface area and ex-
change capacity, it showed higher adsorptivity toward Pb^{2+} ions due to more
active sorption sites donated from the deprotonation of hydroxyl group of
PVA species. In another study, the functionalizing of 2 : 1 clay minerals (*i.e.*,
vermiculite and montmorillonite) with an amino acid [*e.g.*, cysteine,
H$_2$NCH(CH$_2$SH)CO$_2$H] has been undertaken by Malferrari *et al.*[121] They de-
scribed the modification to the structure of clay minerals addressing the
sorption behaviour of Cd(II) ions onto both untreated and treated clays.

Chelating agents or natural polysaccharide materials have also now been
widely used to modify surface characteristics of clays, with the aim of ren-
dering the clay surface to be more hydrophobic or hydrophilic, at will, de-
pending on the chelating functionalities and, more importantly, to improve
the selectivity and sorption capacity of the sorbents towards specific metal
ions. Moreover, the incorporation of clays/clay minerals into polymeric
networks can strengthen the swelling properties, gel strength and reduce the
production costs of the corresponding adsorbents. Some common func-
tionality inserted into the clays/clay minerals platelets are amine (−NH$_2$) and
hydroxyl (−OH) groups. Natural polymer materials with high amino or hy-
droxyl contents have been found to possess good sorption capacity for many
heavy metal ions through surface complexation with these active surface
groups. Chitosan, a hydrophilic and cationic polymer product of chitin has
been used as a chelating agent of zeolite to prepare a chitosan–zeolite
composite adsorbent with a weak basic nature.[122] The optimum pH for Cu(II)
sorption using a chitosan–zeolite composite was 3, when electrostatic ions
were sorbed onto the solid surface by forming electrostatic attractions.

Similar work employing chitosan to prepare a magnetically separable
composite adsorbent was taken by Chen *et al.*[123] The composite adsorbent,
termed chitosan–montmorillonite–Fe$_3$O$_4$ microspheres, showed a notable
maximum sorption capacity of 74.2 mg g^{-1} towards Cr(VI) at low pH. In this
study, the separation of composite microspheres from metal solution after
the adsorption process was easily performed with the aid of an external
magnetic force. Natural Wyoming montmorillonite embedded with different
chelating functional groups (*e.g.*, −NH$_2$, −COOH, −SH and −CS$_2$) from
ammonium organic derivatives was tested for the removal of Pb^{2+}, Cd^{2+} and
Zn^{2+} ions from aqueous solutions by Sathi *et al.*[124] When compared with the
unmodified montmorillonite, the resulting organoclays showed consider-
able improvement in terms of sorbing selectivity and metal loading capacity.
The insertion of four guest organic functionalities into the lamellar space of

clay minerals causes the increase in organophilicity and the presence   1
of more negatively charged ligands from the intercalated organics. Abou-
El-Sherbini and Hassanien immobilized Na-montmorillonite clay with a
2-oxyhydrazino-*N*-(2-methylen-yl-hydroxyphenyl)pyridinium (OHMP) hydra-
zone derivative chelating agent to remove copper ions from spiked   5
natural water and granite samples.[125] The intercalated clay possessed
good chemical tolerance in acids, bases and common ionic species such as
Na^+, K^+, Ca^{2+}, Cl^- or SO_4^{2-} as well as good removal efficiency towards $Cu(\text{II})$
ions (119 meq per 100 g) at pH 6. They also found that the grafted MMT-clay
also found potential application for the treatment of real contaminated   10
effluent.

The possibility to use natural chitin–bentonite biocomposites for re-
moving toxic chromium(VI) ions in batch mode was conducted by Saravanan
et al.[126] The results showed that the prepared biocomposite materials were
able to sorb more than 80% Cr(VI) ions at pH 4 with fast uptake in the initial   15
30 min and the sorption tends to slow after 45 min. From this study, one can
conclude that the negatively charged nitrogen or oxygen ligands of chitin
macromolecules serve as ancillary sites that are responsible for chelating
higher amounts of metal ions.

The preparations of clays/clay minerals modified with metallic/composite   20
oxides have gained increasing awareness because they are specifically
functional for sorbing different heavy metal ions. The following are several
reasons for employing metal/composite oxides to modify clays/clay minerals:
(1) the surface groups of metal/composite are amphoteric in nature and can
function as an acid or a base, depending on the suspension pH; (2) metal/   25
composite oxides have relatively high surface energy and reaction activity
stemming from the large specific surface area; and (3) favourable physical
AQ:10 and chemical properties such as swelling ability, stiffness, and. Despite
these advantages, most metallic/composite oxides possess low durability and
mechanical strength so they often aggregate due to lack of dispersibility,   30
which reduces the specific surface area and effectiveness to sorb pollutants
in aqueous suspensions.

The aggregated metal oxides also possess difficulties in the separation
process after the metal sorption. To address this challenging issue, various
immobilization techniques are being developed for improving stability and   35
dispersibility of metal/composite oxides and one of the convenient, cost-
effective methods is by loading with clays and clay minerals as a support
material. Among the metal oxides, iron (Fe) oxides and manganese oxide are
the two most widely used because they have high affinity towards metal ions,
large surface area and microporous structure. Clays/clay minerals pillared   40
with metal oxides exhibit superior structural and chemical properties, such
as high thermal stability, large surface area, intrinsic catalytic activity and
significant sorption capacity over a wide pH range. For example, kaolin
loaded nanoscale zero-valent iron, nZVI (size < 100 nm), was synthesized
and tested in the removal process of Pb(II) ions from aqueous solution.[127]   45
Kaolin-loaded nZVI showed higher specific surface area than untreated

kaolin (26.11 $m^2 g^{-1}$ *versus* 3.67 $m^2 g^{-1}$), which may be ascribed to the kaolin
support preventing agglomeration of iron particles and therefore presenting
a higher specific surface area of available iron to the aqueous phase. The
removal percentage of nearly 100% was observed for kaolin-supported nZVI,
while those of nZVI and kaolin are only 15.8 and 8.6%, respectively. This
observation is in good agreement with the study by Uzum *et al.* for Cu(ɪɪ) and
Co(ɪɪ) removal using Turkey kaolinite-supported nZVI.[128]

According to the study carried out by Sari and Tuzen, the surface area of
MnO_2-modified vermiculite increased about 10-fold from 0.84 to 8.42 $m^2 g^{-1}$
after the modification process.[129] The MnO_2-modified vermiculite also
demonstrated higher sorption capacity than the parent vermiculite (46.2
versus 69.2 $mg g^{-1}$). The optimum concentration of MnO_2 deposited onto
the clay surface ranged between 0.2 and 0.3 $g g^{-1}$ while at higher loading
concentrations, the adsorption efficiency levels off due to obstructed
micropores, which reduced the number of active adsorption sites.

Manganese oxide coated zeolite has been tested for the removal of Mn^{2+}
ions in a batch adsorption system.[130] The coating of manganese oxide on the
surface of zeolitic clay provides more available sites for the sorption of Mn(ɪɪ)
ions at suspension pHs higher than the point of zero charge of the sorbent.
The MnO_2 species bound on the zeolite surface (mainly as vernadite) are also
responsible zeolite is much higher compared to untreated zeolite for re-
moving metal ions. The interfacial reactions of surface hydroxyl groups are
also responsible for the enhanced sorption process of metal cations. Similar
results were obtained by Eren for the removal of copper ions using MnO_2-
modified bentonite.[131] After modification, the maximum sorption capacity
of raw bentonite was enhanced significantly from 42.41 to 105.38 $mg g^{-1}$.
Incorporation of manganese oxide was evidence of increasing the specific
surface area and the resultant surface charge of raw bentonite giving rise to
effective removal of Cu(ɪɪ) ions.

In another study, the preparation of low-cost ceramisite consisting of
three raw materials, namely sintering bentonite, hematite powder (Fe_2O_3)
and activated carbon, and its adsorption performance towards zinc and lead
metals, has been tested by Yuan and Liu.[132] The presence of fine hematite
particles on the outer surface of the ceramisite composite were found to
react and enhance the removal percentage while the increase of activated
carbon dosage led to decreasing bulk density. The maximum removal cap-
acity of ceramisite was found to be 17.5 $mg g^{-1}$ for Pb^{2+} ions and 7.4 $mg g^{-1}$
for Zn^{2+} ions at pH 5. Additionally, the chemical reaction between the hy-
droxyl group and heavy metal ions occurred during metals removal, forming
new prismatic and spherical crystalline grains containing Pb(ɪɪ) and Zn(ɪɪ),
respectively, that accumulated and piled up onto the surface of the
adsorbent.

Therefore, it can be concluded that the incorporation of metal/composite
oxides enhances removal efficiency due to the increase in the surface area
and negative surface charge associated with the formation of deprotonated
oxides on the sorbent surface.

11.4 Isotherms, Kinetics and Thermodynamics Evaluation of Heavy Metals Sorption onto Clays and Clay Minerals

Considering the sorption process of heavy metal ions onto the surface of clays and clay minerals, some crucial information such as adsorption equilibria, kinetics and thermodynamics are of great importance for reliable prediction of adsorption parameters and behaviour, effective design of the sorption system and optimization of the sorption mechanism pathways. Given this, adsorption isotherms are invaluable for the adsorption studies because they describe the equilibrium relationship of adsorbate concentration in the bulk liquid phase (*i.e.*, aqueous solution) and in the solid phase (*i.e.*, adsorbent surface) at a constant temperature and pH. Adsorption equilibrium is established when an adsorbate-containing phase has been in contact with the adsorbent for sufficient time, with both the adsorption and desorption rates being equal.[133] This knowledge is not only indispensable for the process design and optimization, but also in understanding the adsorption kinetics and thermodynamics of single and multicomponent systems. Typically, the mathematical models describing such phenomenon are usually depicted by graphically expressing the solute concentration in the solid phase (q_e, mg g^{-1} or mmol g^{-1}) against its residual concentration in the liquid phase (C_e, mg L^{-1} or mmol L^{-1}).

Over the years, a wide variety of empirical and semi-empirical adsorption equations have been widely used to correlate experimental isotherm data of various adsorbate–adsorbent pairs, including heavy metal ions. The earliest model to be known was introduced by Langmuir in 1918 to address the adsorption of gases onto planar surfaces of mica, glass and platinum, based on the kinetic principle.[134] He developed an empirical adsorption equation based on the three assumptions as follows:[135]

a. Adsorption is limited to monolayer surface coverage (the adsorbed layer is one molecule in thickness) without further adsorption can take place on the occupied sites.
b. The adsorbate molecules can only accommodate one localized site without lateral interactions between the adsorbed species, even on the neighbouring sites.
c. The surface of the solid is ideal with definite localized sites that are identical in terms of adsorption heat and affinity.

Graphically, a Langmuir isotherm is characterized by a plateau curve, which means that no further adsorption and desorption can take place when the saturation point is established. This isotherm equation describes Henry's law behaviour when the solute concentration in the liquid phase is fairly low; on other hand, at a high-end concentration, the saturation point of adsorption will be established and the Langmuir isotherm model equals the maximum

sorption capacity for a given solid (q_{max}, mg g^{-1} or mmol g^{-1}) or characterizes the monolayer surface coverage. The essential characteristic of a Langmuir equation can be characterized with a dimensionless equilibrium constant called the separation factor (R_L), as defined by Weber and Chakravorti:[136]

$$R_L = (1 + K_L \cdot C_0)^{-1} \qquad (11.5)$$

Various R_L values indicate the types of adsorption to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The applications of this isotherm model have found reasonable success for correlating various heavy metal–clay sorption systems[15,16,18,80–89] with favourable adsorption nature and can be implied as the platform and most useful isotherm model for describing physical and chemical adsorption phenomena, both in gas and liquid phases.

The Freundlich equation is another adsorption isotherm model that has been frequently used to describe non-ideal and reversible adsorption phenomena,[137] specifically for complex solids with non-uniform distribution in terms of adsorption energy and affinity, such as activated carbons or molecular sieves. In this isotherm perspective, the amount of adsorbate retained in the solid phase continually rises with increasing concentration in the bulk solution, which means that infinite adsorption can take place on the solid surface. Generally, a Freundlich isotherm gives accurate predictions in the intermediate range of adsorption equilibrium data, typically at moderate solute concentrations. In some cases, the favourability of the adsorption process can also be evaluated from the Freundlich empirical constant, called the intensity factor (n_F), in which the characteristic of the adsorption process is poor ($n_F < 1$), moderately difficult ($1 < n_F < 2$), feasible ($2 < n_F < 10$) and approaching a rectangular or non-reversible isotherm when n_F value is larger than 10, respectively.[135] However, this model is criticized due to the lack of a fundamental thermodynamic basis and not approaching Henry's law at the vanishing concentration and saturation adsorption limit at high-end concentrations. The same as for the Langmuir isotherm model, the successful applications of Freundlich isotherms have been reported in many sorption studies involving heavy metal ions and clays/clay minerals, apart from the limitation and lack of fundamental thermodynamics in this model.

In the past few years, much effort has been paid to formulating various empirical or semi-empirical adsorption equations, either to overcome some drawbacks in the predecessor equations (*e.g.*, Langmuir and Freundlich equations) or to propose new adsorption models featuring adequate fundamental kinetics and thermodynamics as well as satisfactory agreement over a wide range of concentrations. Some examples are Hill, Temkin, Flory–Huggins, Dubinin–Radushkevich, Langmuir–Freundlich or Sips, Toth, Redlich–Peterson and Brunauer–Emmett–Teller adsorption equations.[138] Table 11.5 presents several studies with successful applications of the two-parameter or three-parameter adsorption equations mentioned here for describing liquid phase adsorption behaviour for heavy metal–clays/clay mineral systems.

Table 11.5 Several two-parameter and three-parameter isotherm models used for liquid phase heavy metals adsorption equilibria correlation.

Isotherm models	Mathematical form	Adsorption parameters	Systems	References
Langmuir	$q_e = q_m \dfrac{K_L C_e}{1 + K_L C_e}$	q_m = maximum adsorption capacity (mg g^{-1} or mmol g^{-1})	Sarooj clay – Zn(II) Sarooj clay – Cd(II) Sarooj clay – Pb(II)	96
		K_L = Langmuir adsorption affinity (L mg^{-1} or L mmol^{-1})	VSco – Ni(II) VPum – Ni(II)	73
			Kaolinite – Cu(II)	80
			CPBr/bentonite – Cr(VI) CPBr/bentonite – Mo(VI)	105
			TBA/kaolinite – Co(II) TBA/montmorillonite – Co(II)	108
			Smectite – Pb(II)	88
			Clinoptilolite – Zn(II)	92
			Functionalized sepiolite – Co(II) Functionalized sepiolite – Mn(II)	114
			Tunisian clay – Pb(II)	85
			Na-exchanged clinoptilolite – Ag(I)	91
			Spent bleaching earth – Pb(II)	89
			Halloysite – Cu(II)	109
			Attalpugite – Cr(VI)	117
			Diatomite – Th(IV)	82
			Chitosan/zeolite – Cu(II)	122
			MnO$_2$-coated zeolite – Mn(II)	130
			Chitosan/montmorillonite – Cr(VI)	123
			Organo montmorillonite – Cr(VI)	118

			Alkaline Ca-bentonite – Zn(II)	94
			Polyvinyl-modified kaolin – Pb(II)	120
			Expanded perlite – Hg(II)	71
			Palygorskite – Pb(II)	70
			Organobentonite – Cr(VI)	119
Freundlich	$q_e = K_F \times C_e^{1/n}$	K_F = Freundlich adsorption affinity (mg g^{-1})(L mg^{-1})$^{1/n}$ or (mmol g^{-1})(L mmol^{-1})$^{1/n}$	Bentonite – U(VI)	27
			Clinoptilolite – Zn(II)	92
			Na-exchanged clinoptilolite – Ag(I)	91
		n = dimensionless intensity factor characterizing the surface heterogeneity degree	Spent bleaching earth – Pb(II)	89
			Halloysite – Cu(II)	109
			Attalpugite – Cr(VI)	117
			Diatomite – Th(IV)	82
			Chitosan/zeolite – Cu(II)	122
			MnO$_2$-coated zeolite – Mn(II)	130
			Chitosan/montmorillonite – Cr(VI)	123
			Organo montmorillonite – Cr (VI)	118
			Alkaline Ca-bentonite – Zn(II)	94
			Chitin/bentonite – Cr(VI)	126
			Palygorskite – Cd(II)	81
			Boron-containing clay – Ni(II)	75
			Kaolinite – Cu(II)	80
Dubinin–Radushkevich (D–R)	$q_e = q_m - \exp(\beta\varepsilon^2)$	q_m = the maximum adsorption capacity (mg g^{-1} or mmol g^{-1})	Organo montmorillonite – Cr(VI)	118
			Diatomite – Th(IV)	82
		β = the Dubinin–Radushkevich constant of adsorption energy (mol^2 kJ^{-2})	Attalpugite – Cr(VI)	117
			Sepiolite – U(VI)	87
			Perlite – Pb (II)	
			Dolomite – Pb(II)	
			Unye clay – Cu(II)	68

Table 11.5 (*Continued*)

Isotherm models	Mathematical form	Adsorption parameters	Systems	References
		ε = the Dubinin–Radushkevich constant of the Polanyi potential, with ε equal to $RT \times \ln[1/(1 + C_e)]$		131
Redlich–Peterson (R–P)	$q_e = \dfrac{K_1 C_e}{1 + K_2 C_e^b}$	K_1, K_2 = Redlich–Peterson isotherm constants, in (mg g^{-1}) or (mmol g^{-1}) and $(\text{mg g}^{-1})^b$ or $(\text{mmol g}^{-1})^b$ b = Redlich–Peterson isotherm exponent which lies between 0 and 1	Chitosan/zeolite – Cu(II) Halloysite – Cu(II) Organo montmorillonite – Cr(VI)	122 109 118
Temkin	$q_e = \dfrac{RT}{b} \ln A + \dfrac{RT}{b} \ln C_e$	A = Temkin isotherm constant of adsorption affinity $(\text{L mg}^{-1}$ or $\text{L mmol}^{-1})$ b = Temkin isotherm constant of heat of sorption (kJ mol^{-1})	Organo montmorillonite – Cr(VI) Diatomite – Th(IV)	118 82
Flory–Huggins (FH)	$\log \dfrac{\Theta}{C_i} = \ln K_{FH}$ $+ n_{FH} \log(1 - \Theta)$	K_{FH} = Flory–Huggins adsorption equilibrium constant n_{FH} = the Flory–Huggins model exponent Θ = the degree of surface coverage, expresses as $1 - C_e/C_i$	Diatomite – Th(IV)	82
Elovich	$\ln\left(\dfrac{q_e}{C_e}\right) = \ln(K_e q_m) - \dfrac{q_e}{q_m}$	K_E = Elovich adsorption equilibrium constant $(\text{L mg}^{-1}$ or $\text{L mmol}^{-1})$ q_m = the maximum adsorption capacity $(\text{mg g}^{-1}$ or $\text{mmol g}^{-1})$	Organo montmorillonite – Cr(VI)	118

Considering the adsorption parameters associated with solute adsorptivity and maximum sorption capacity of a given solid, several environmental factors such as temperature and initial solute concentration all play crucially important roles. Generally speaking, the adsorptivity of solute molecules towards the adsorbent surface increases with increasing temperature because of the greater magnitude of kinetic energy in the system, which allows the solute molecules to move around faster and it is then easier to sorb onto the solid surface. The increasing adsorption affinity of heavy metal cations towards the solid surface with increasing temperature can be found in several studies. Moreover, the increasing amount of metal ions adsorbed at higher temperature may reveal that chemisorption is the dominant mechanism by forming chemical bonding between positive and negative charge clusters. Among the well-known adsorption models, Langmuir and Freundlich are the two most popular equations used for the correlation of liquid phase equilibrium data in many heavy metal–clay systems. These two isotherm equations have found reasonable success and correlations of copper adsorption isotherm data onto clays has been studied by and *et al*.

Adsorption kinetics is also one of the most crucial factors for the effective design of sorption systems since it predicts the rates of adsorption and desorption of pollutants in a given solid/solution system. The overall sorption rate may be mainly controlled by any or a few of the following steps:[139] (1) transport of solute in the bulk solution; (2) diffusion of solute across the so-called liquid film surrounding the solid particles; (3) diffusion of solute in the liquid contained in the pores of the solid particles and along the pore walls (intraparticle diffusion); and (4) adsorption and desorption of solute on/from the solid surface. In this context, some extensively used mathematical models for describing the kinetics of sorption for a particular system are pseudo-first order (Lagergren), pseudo-second order, intraparticle diffusion and the Elovich equations. These formulae have usually been associated with surface reaction kinetics as the rate-controlling step and offer some advantages, such as compactness and simplicity with few computer resources required to solve the rate equations. The common procedure used to verify whether the best kinetic models are suitable to fit experimental data is through best-fit either using linear or non-linear regression techniques.

11.5   Conclusions

Clays and clay minerals are promising low-cost materials for the cost-effective and efficient remediation of synthetic and real waste effluents contaminated by toxic heavy metal ions. Considering several previous studies dealing with the adsorption of heavy metal ions using clays and clay minerals, the following conclusions can be deduced:

a. The layer characteristics with structural negative charge and the surface chemical nature of natural clays and clay minerals are both

suitable for the effective removal of cationic pollutant species such as heavy metal ions.

b. The edge hydroxyl groups, namely silanol and aluminol, are pH-dependent and are important in the sorption of metal cations by providing negatively charged ligands at high pH.

c. Thermal activation of clays and clay minerals is essentially effective for increasing the surface area by removing and impurities as well as only remains intact. Extreme activation temperature causes structural distortion and amorphization of the solid, which means the adsorptive removal of the solid decreases.

d. Chemical activation with inorganic acids (*e.g.*, HCl and H_2SO_4) can improve the sorption capacity of clays/clay minerals considerably by introducing additional centres that are active for metal ions binding and also.

e. Surface modification of clays/clay minerals through pillaring, grafting or intercalation techniques can be employed in an effective way.

Uncited Reference

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