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Review

A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade

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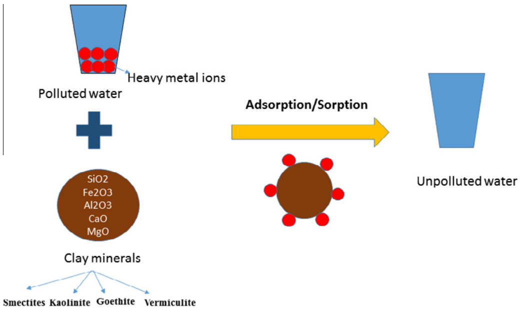
HIGHLIGHTS

- A detailed, informative and comprehensive review of clay minerals as successful adsorbent has been carried out.
- The chemical composition of various clay minerals is presented in this paper.
- An outline of classification of various clay minerals is successfully emphasized.
- Chemical, thermal, etc. modification were described and stated very carefully.
- An elaborated information about the adsorption behavior for various heavy metals.

GRAPHICAL ABSTRACT



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ABSTRACT

Adsorption has been proved to be the best process of water treatment because of its significant advantages. Clays and their minerals are abundant and cheap material successfully used for decades as an adsorbent for removing toxic heavy metals from aqueous solutions. Clays and their minerals, both in its natural and modified forms, effectively remove various heavy metals from aqueous solution, as extensively discussed in this review. This detailed review compiles thorough literature of current research over the last ten years (2006–2016) and highlights the key findings of adsorption studies that use clay minerals as an adsorbent. This review article presented an outline of the structure, classification, and chemical composition of various clay minerals, and a descriptive analysis of their adsorption behavior. The review confirmed that both natural and modified forms of clay minerals have excellent feasibility in removing different toxic aquatic metal pollutants. However, modification and further development of the synthesis of novel clay materials and their application to adsorb different environmental pollutants, which would enhance pollution control, is still needed.

Contents

1. Introduction 439
2. Properties and classification of clays 440
3. Structure of clays 441

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1385-8947/

4. Investigations of the adsorption properties of various clay minerals . . . 444
  4.1. Heavy metals removal by natural and modified clays . . . 444
    4.1.1. Natural clays . . . 444
    4.1.2. Modified forms . . . 445
  4.2. Heavy metal removal by the Smectite group . . . 446
    4.2.1. Montmorillonite . . . 446
    4.2.2. Smectite . . . 448
    4.2.3. Bentonite . . . 449
  4.3. Heavy metals removal by Kaolinite . . . 450
    4.3.1. Raw kaolinite . . . 450
    4.3.2. Modified kaolinite . . . 451
  4.4. Heavy metal removal by vermiculite . . . 452
  4.5. Heavy metal removal by goethite . . . 453
5. Summary, conclusion and future research . . . 456
  Acknowledgements . . . 456
  References . . . 456

1. Introduction

Environmental pollutants and their toxicity cause a major problem worldwide. New pollutants keep emerging and pose severe health and scientific challenges. Water pollution is one of the biggest environmental issue causing serious problems to living beings. The removal of various toxic substances from water and wastewater has been a core interest of many scientists and researchers around the globe over the past decades. Dyeing, battery, printing, mining, metallurgical engineering, electroplating, pigment, PVC stabilizers, nuclear power operations, electric appliances manufacturing, semiconductor, cosmetics, and so on belong to industries that generate various types of pollutants in wastewater effluent [1,2]. Therefore, the only solution is to remove them from the waste stream before they are discharged into the ecosystem. The removal of toxic organic and inorganic materials from industrial effluents is thus of great environmental interest. Heavy metals are a serious environmental problem because of their toxicity and abundance. Existence of heavy metals in aquatic environment has been known to cause various health problems to human beings and animals [3]. Heavy metals are the main group of inorganic pollutants and contaminate a large area of land due to its presence in sludge, fertilizers, pesticides, municipal waste, mines residues, and smelting industries [4]. Most heavy metals are known to be carcinogenic agents and may represent a serious threat to the living population because of their non-degradable, persistent, and accumulative nature [5–7]. Some heavy metals, however, are essential to life and play irreplaceable role in the human metabolic system like the functioning of critical enzyme sites, but it can harm the organism in excessive level [8]. Some other metals are xenobiotics i.e. they have no useful role in human physiology (and most other living organisms) and may cause disorders even at trace levels of exposure. Table 1 shows the permissible limits [9–13] while Table 2 shows the health effects and sources of various heavy metals [14–39]. To regulate the uncontrollable discharge of these hazardous pollutants in wastewater, novel and recent water treatment technologies are proposing globally. Several techniques like chemical precipitation, evaporation, solvent extraction, ion exchange, electrochemical treatment, and membrane filtration technologies, etc. have been used to remove these hazardous pollutants. However, these techniques are not suitable to use in the removal of low metal concentrations, which cause damage both to the environment and life. Adsorption process is a suitable technique for inorganic and organic pollutants removal from wastewater, because of the significant advantages like low-cost, availability, profitability, ease of operation, efficiency, and effectiveness than other techniques [40–45]. The process involves separation of a substance from one phase and its accumulation at another surface [46]. This technique is easy to operate and equally effective in the removal of toxic pollutants, even at low concentrations.

Clay, a small particle, found naturally on the surface of the earth composed mainly of silica, alumina, water and weathered rock [47]. Clay, a fine-grained natural raw material, is a matter of much attention due to its use as an effective adsorbent to trace heavy metal ions present in aqueous solution for more than a decade now. Clay has a property to show plasticity through a variable range of water content, which can harden when dried [48]. Clay evenly disperses and forms a slurry upon contacting with water, because water molecules are strongly attracted to clay mineral surfaces. Mixing of clay and water results in a mud form, which can mould into desired shape and dried to form a relatively rigid solid. Because of this property, pottery and the ceramics industries used

Table 1
Permissible limits of various toxic heavy metals in drinking water according to various standards.

	Permissible limit for drinking water (mg L^{-1})						
Metal	IS 10500 [9]	WHO [10]	USEPA [10,11]	EU Standard [11]	MEP, China [11]	CDW, Canada [12]	NHMRC, Australia [13]
Nickel	0.020	0.020	0.100	0.020	0.000	–	0.020
Lead	0.010	0.010	0.015	0.010	0.010	0.010	0.010
Zinc	5.000	3.000	5.000	–	–	5.000	–
Copper	0.050	2.000	1.300	2.000	1.000	1.000	2.000
Cadmium	0.003	0.003	0.005	0.005	0.005	0.005	0.002
Mercury	0.001	0.001	0.002	0.001	0.000	0.001	0.001
Arsenic	0.010	0.010	0.010	0.010	0.050	0.010	0.010
Chromium	0.050	0.050	0.100	0.050	0.050	0.050	0.050
Manganese	0.100	0.500	0.050	0.050	–	0.050	–
Iron	0.300	0.200	0.300	0.200	–	0.300	–

Table 2
Sources and health effects of various toxic metals.

Metal	Uses	Health effects	Sources (industry)	Sources (natural)
Nickel	Catalyst and battery manufacture, nickel coating, nickel stainless steel, catalyst and pigment [14,15]	Causes chronic bronchitis, reduced lung function, cancer of the lungs, intestinal cancer[10]	Electroplating, Ferrous and non-ferrous metal production, Smelting operations, thermal power plants, nickel–cadmium battery industries [15]	wind-blown dust, soil and dust volcanoes, sea salt, forest fires and vegetation [14,15]
Lead	Car batteries, pigments, lead crystal glass, radiation protection, architecture [16]	Carcinogenic, anaemia, abdominal, muscle and joint pains, kidney problems, and high blood pressure [10]	Lead acid batteries, paints, e-waste, smelting operations, coal- based thermal power plants, ceramics, bangle industry [16]	Sea and salt lake aerosols, forest fires and volcanic eruptions [17]
Zinc	Batteries, coating, compound, crops, diecasting alloys [18]	Stomach cramps, skin irritations, vomiting, nausea, respiratory disorders, anaemia and mental fever [19]	Smelting, electroplating, pig and poultry manures [18]	Surface water, soil and rock [18]
Copper	Electrical wiring, stoves, portable CD players, transmission wires, copper alloys and coins [20]	Stomach ache, irritation of nose, mouth, and eyes, headaches [21]	Mining, electroplating, smelting operations [20]	Wind-blown dust, decaying vegetation, forest fires and sea spray [20]
Cadmium	Electroplating of steel, nickel-cadmium batteries, cellular telephones, Laptop computers and camcorders [22]	Carcinogenic, causes lung fibrosis, dyspnoea [10], chronic lung disease and testicular degeneration [23]	Zinc smelting, waste batteries, e-waste, paint sludge, incinerations & fuel combustion [24]	Coal combustion, iron and steel production, phosphate fertilizer manufacture and use, and zinc production, volcanic activities and from anthropogenic sources [25]
Mercury	Batteries, fluorescent lights, felt production, thermometers and barometers [26]	Headache, abdominal pain and diarrhoea, paralysis, and gum inflammation, loosening of teeth, loss of appetite [10]	Chlor-alkali plants, thermal power plants [27]	Volcanoes, geologic deposits of mercury and volatilization from the ocean [27]
Arsenic	Rat poisons, bronzing, in forming special glass and preserve wood [28]	Carcinogenic, producing liver tumors, and gastrointestinal effects, diabetes [10]	Geogenic/natural processes, smelting operations, thermal power plants, fuel burning [29]	Earth's crust, ground water, geothermal processes, Volcanic action, mineral ore [29]
Chromium	Electroplating, stainless steel production, leather tanning, textile manufacturing and wood preservation [30]	Nasal and sinus cancers, kidney and liver damage, nasal and skin irritation, ulceration, eye irritation and damage [30]	Mining, industrial coolants, chromium salts manufacturing, leather tanning [30]	Rocks, animals, plants, soil and in volcanic dust and gases [30]
Manganese	Decolorise glass, oxidising agent, depolariser in dry cells, to form alloys [31]	Toxic and causes growth retardation, fever, sexual impotence, muscles fatigue, eye blindness [10]	Coal mining, production of dry battery cells, matches, fireworks, porcelain and glass-bonding materials [32,33]	Ocean spray, forest fires, vegetation, and volcanic activity [34,35]
Cobalt	Electroplating, magnet steels and stainless steels, paint pigments [36]	Lung effects such as asthma and pneumonia, Vomiting and nausea, Vision problems, Heart problems, Thyroid damage, hair loss, weight loss [37]	Sewage sludge, phosphate fertilizers, processing of cobalt alloys [38]	Erosion (wind-blown continental dusts), weathering of rocks and soil, seawater spray, volcanoes, forest fires, extraction by plants, continental and marine biogenic emissions [39]

to produce items like plates, cups, bowls, pipes, and children's toys etc. [49]. Variety of clays and clay minerals play an important role in the environment and used as an effective adsorbent material for the removal of toxic metal ions from water solution.

The use of clays as adsorbent have advantages upon many other commercially available adsorbents in terms of low-cost, an abundant availability, high specific surface area, excellent adsorption properties, non-toxic nature, and large potential for ion exchange [50]. Clays also contain exchangeable cations and anions held to the surface and for these reasons, the attention of scientists worldwide has been focused on using natural or modified clay materials as adsorbent for water treatment [51]. The most of the clay minerals are negatively charged and very effective and extensively used to adsorb metal cations from the solution; due to their high cation exchange capacity, high surface area, and pore volume. The uptake of heavy metals by clay minerals involves a series of complex adsorption mechanisms; such as direct bonding between metal cations with the surface of clay minerals, surface complexation, and ion exchange etc. [52]. In many studies, pre-treatment is required to enhance the adsorption capacity of clays and hence modified to increase metal uptake [53]. This pre-treatment enhances the surface area, pore volume, and number of present acid sites on the surface. Through this treatment or modification, the clay minerals become hydrophobic, organophilic, and it thus enhances the uptake of small non-ionic organic compounds [54]. Therefore, utilization of clays and its materials would solve disposal problem, and also access to less-expensive material in the wastewater treatment. Because of low production cost of clays, there is no need to regenerate them; which provide more advantages in using clays as an adsorbent. This paper presented a detailed and critical outline analysis of clays and clay minerals as successful, effective, result oriented, and low-cost adsorbent. This review paper has also adequately summarised their effect, adsorptive potential, compositions, and outcomes. The main goal of this review is to provide an elaborated information about the natural or modified forms of clay minerals and their excellent adsorption capacities for various toxic heavy metals from aqueous solution. This review paper presents the classification of various types of clay minerals and their importance for the removal of toxic contaminant removal from water sources. It also successfully emphasizes the clay and its modified forms as an excellent, environmentally friendly adsorbent.

2. Properties and classification of clays

The term "clay" applies to the materials having a particle size of less than 2 μm (25,400 μm = 1 in.), and also to the family of minerals having similar chemical compositions and common crystal structural characteristics [55]. Clay has a variety of physical characteristics such as plasticity, shrinkage under fire and under air-drying, fineness of grain, colour after firing, hardness, cohesion, and capacity of the surface to take decoration [56]. Clays are hydrous aluminosilicates which composed of mixtures of fine-grained clay minerals, crystals of other minerals, and metal oxides [57]. On the basis of such qualities, clays are variously divided into classes or groups such as smectites (montmorillonite, saponite), mica (illite), kaolinite, vermiculite, serpentine, pyrophyllite (talc), and sepiolite etc. [58]. It was Grim, in 1962, who first proposed the classification of clay minerals, which lead to the basis for outlining the nomenclature and the differences between various clay minerals [60]. According to Grim, important groups of clay minerals are kaolinite, montmorillonite, and illite. Almost, all clays composed of one or more members of these three groups [59]. Fig. 1 shows Grim's classification and lattice structure of clay minerals [59].

Clays and clay minerals have small particle size and complex porous structure with high specific surface area, which allows strong physical, chemical interactions with dissolved species. These interactions are due to the electrostatic repulsion, crystallinity, and adsorption or specific cation exchange reactions. The highly porous surface area that possesses attractive force suggests that the bonding power will also be high [59].

China clay, a primary, ancient, and purest clay, used first by the Chinese. Its main component is kaolinite, however, in addition it is a mixture of different minerals which frequently contains quartz, mica, feldspar, illite, and montmorillonite.

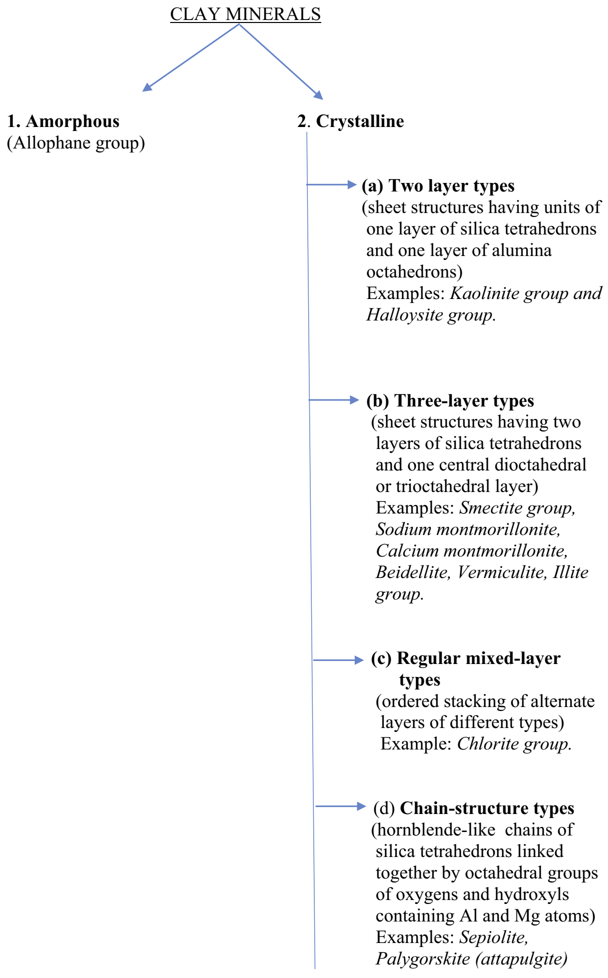


Fig. 1. Classification of clay minerals according to Grim (Grim, 1962).

Bentonite composed, mainly, of hydrous magnesium-calcium-aluminum silicate called montmorillonite, which is a clay mineral of the smectite group. It is highly colloidal and plastic clays composed of very fine particles, which produced by in situ devitrification of volcanic ash [61].

The term Montmorillonite is used both for a group of related clay minerals and for a specific member of that group [62]. Smectite is the mineral name given to this group of Na, Ca, Mg, Fe, and Li-A1 silicates. The mineral names in the smectite group which are most commonly used are Na-montmorillonite, Ca-montmorillonite, saponite (Mg), nontronite (Fe), and hectorite (Li) [63].

Illite, together with chlorite, is the main component of common clay and is present as an impurity in limestone [64]. Illite group includes hydrous micas, phengite, brammalite, celadonite, and glauconite (a green clay sand), which is formed by the decomposition of some micas and feldspars [60].

Ball clay, a fine-grained and highly plastic sedimentary clay, consists mainly of kaolinite, mica, and quartz with small amounts of organic matter and other minerals. This type of clay has the commercially values and white or near white firing characteristics [65]. Compared with primary china clay, the ball clay contains a remarkably high proportion of extremely fine particles. Ball clays were the coarsest, with 20–30% finer than 0.2 μm and 45–60% finer than 1 μm [65].

Table 3 shows the chemical composition of various types of natural clay minerals [66–101]. Results showed that they are mainly constituted of alumina and silica in major quantities, iron, calcium, magnesium oxide, and other elements in minor quantities. The loss on ignition values indicated that clay has lower carbonaceous matter and higher mineral matter contents [100]. Results clearly confirmed that clay and clay minerals have the superb potential to be used as an effective adsorbent in reducing the concentrations of various contaminants, especially heavy metals, in water and wastewater treatment because they are richly composed of silica, alumina, iron, calcium, and magnesium oxides.

3. Structure of clays

The structure, crystal chemistry, mineralogy, and surface chemistry of clays are responsible for their important role in natural environments; and their useful environmental and industrial applications. The pioneering work of Ross, in 1927 [102], Hendricks, in 1929 [103], Hendricks and Fry, in 1930 [104], and Pauling, in 1930 [105,106] introduced the crystallinity in the structures of clay minerals. The majority of the clay minerals, mainly composed of layers containing silica and alumina sheets, which belong to the class of layer silicates or phyllosilicates group. These groups can be subdivided according to the type of layer structure. Clays consist of a interconnected silicates sheet combined with a second sheet like grouping of metallic atoms, oxygen, and hydroxyl [107]. The basic structure units are divided into silica sheets and brucite or gibbsite sheets [108,109]. The 1:1 clay-mineral type consists of one tetrahedral sheet (Fig. 2a) and one octahedral sheet (Fig. 2b) [108].

Octahedrons consist two planes of hydroxyl ions between which lies a plane of magnesium or aluminum ions, which is typically coordinated by hydroxyl sheets octahedrally. These octahedrons are also arranged in a hexagonal pattern which called octahedral sheets [108].

The 2:1 (three layer) layer lattice silicates consist of two silica tetrahedral sheets between which is an octahedral sheet. The 2:1 clay minerals include the mica and smectite groups, which are the most abundant among the clay minerals. The serpentine and mica group is subdivided on the basis of dioctahedral and trioctahedral type [108].

Table 3
Chemical composition of various natural clay minerals.

Natural clays	Elemental composition (% weight)									References
	SiO_2	Fe_2O_3	Al_2O_3	TiO_2	Loss on ignition	CaO	NaO	K_2O	MgO	
Montmorillonite	65.34	2.38	12.89	0.52	8.06	0.24	0.53	1.54	0.95	[66]
Indigenous clay	46.22	0.68	38.40	–	13.47	0.86	–	–	0.37	[67]
Pure Smectite	50.08	6.00	17.40	–	20.31	0.28	1.39	0.84	3.95	[68]
Egyptian clay	50.65	4.61	30.31	1.65	–	0.27	0.16	–	0.20	[69]
Kaolinite clay	53.70	2.00	43.60	0.10	–	–	–	0.50	–	[70]
Illitic clay	62.72	5.58	14.34	0.82	–	7.27	1.01	3.59	1.82	[71]
Beidellite	58.08	2.96	29.92	0.22	–	0.63	1.85	0.22	5.48	[72]
Indian clay	48.12	2.48	34.54	0.40	12.44	0.83	–	–	0.50	[73]
Vermiculite	39.00	8.00	12.00	–	–	3.00	–	4.00	20.00	[74]
Kaolin	46.70	0.75	37.33	<0.01	13.68	<0.10	<0.10	0.93	<0.10	[75]
Nigerian clay	48.62	2.88	34.82	0.01	11.54	0.10	0.06	0.94	0.23	[76]
Ball clay	53.70	1.99	31.31	1.91	10.03	0.41	0.44	Nil	Nil	[77]
Landfill clay	42.35	13.36	16.06	–	–	22.51	1.56	2.50	1.68	[78]
Algerian clay	23.34	8.86	7.02	–	–	0.78	–	4.07	1.91	[79]
Tunisia clay	52.50	3.00	18.20	–	16.00	2.81	1.78	1.50	2.45	[80]
Burkina Faso clay	56.51	4.11	23.24	0.66	11.64	1.46	0.10	1.77	0.54	[81]
Sepiolite	55.21	0.15	0.43	0.05	19.21	0.20	0.10	0.15	24.26	[82]
Jebel Tajra clay	62.72	5.58	14.34	0.82	–	7.27	1.01	3.59	1.82	[70]
China clay	46.22	0.68	38.40	–	13.47	0.86	–	–	0.37	[66]
Palygorskite	56.50	3.63	7.87	0.05	19.84	0.20	0.07	0.28	10.81	[82]
Ugwuoba Clay	47.32	1.14	25.91	–	13.56	4.39	2.86	1.07	3.14	[83]
Attapulgite	58.38	–	9.50	0.56	–	0.40‘	–	–	12.10	[84]
Clinoptilolite	65.52	1.04	9.89	0.21	10.02	3.17	2.31	0.88	0.61	[85]
Hectorite	62.71	–	–	–	–	–	3.23	–	17.12	[86]
Petra clay	44.97	9.32	20.85	1.20	–	17.81	0.07	0.33	1.12	[87]
Dolomite	0.25	0.03	0.07	0.02	47.25	30.29	0.03	0.03	21.75	[82]
Bofe Clay	46.60	3.58	7.43	0.42	–	0.44	0.54	0.12	1.34	[88]
Halloysite	46.86	2.27	34.10	2.72	12.60	0.13	0.05	0.80	0.08	[89]
Chlorite	27.40	2.40	18.90	–	–	–	–	–	34.00	[90]
Mayo-Belwa clay	59.80	2.54	7.08	–	–	–	4.39	2.54	0.30	[91]
Red Clay	41.10	6.05	31.48	1.49	16.58	0.28	0.62	1.77	0.35	[92]
Leca	66.06	7.10	16.57	0.78	1.36	2.46	0.69	2.69	1.99	[93]
Bejoypur clay	72.09	1.01	18.69	1.02	–	0.10	0.11	0.61	0.14	[94]
Diatomite	72.00	5.80	11.40	–	–	1.50	7.20	–	–	[95]
Sarooj Clay	39.10	5.53	11.98	–	23.60	17.30	0.69	1.23	4.28	[96]
Caro Clay	53.35	0.99	30.33	1.23	11.35	0.09	0.13	2.06	0.47	[97]
Brazilian clay	59.57	11.31	22.28	1.03	–	0.72	0.01	2.83	2.25	[98]
Brown clay	51.10	4.45	15.57	0.13	–	10.57	0.17	3.42	0.86	[99]
Spent Bleaching Clay	45.00	5.10	10.90	–	16.60	15.00	0.94	1.09	4.03	[100]
Red mud clay	2.15	7.15	51.07	1.77	33.90	1.07	2.84	–	–	[101]

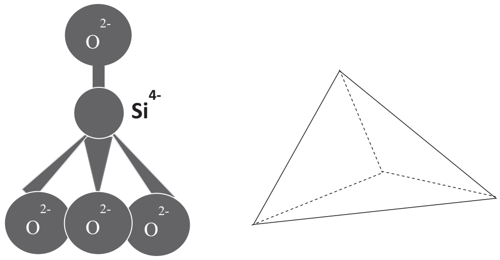


Fig. 2a. Silica sheets consist of SiO_4^{2-} tetrahedra connected at three corners forming a hexagonal network in the same direction which is called tetrahedral sheets (Weaver and Pollard, 1973).

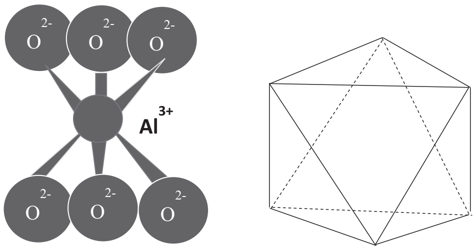
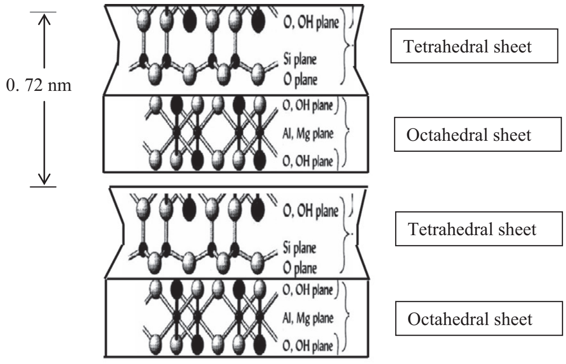


Fig. 2b. Octahedron consists central cation (Al^{3+}, Fe^{2+}, Mg^{2+}) surrounded by 6 oxygens (or hydroxyls) (Weaver and Pollard, 1973).

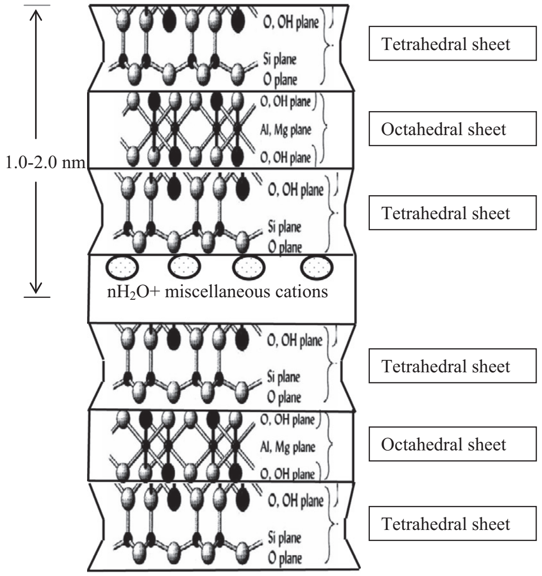
The structure of some most important clay minerals is briefly summarised as follows:

Kaolinite structure possesses great advantages in many processes, due to its high chemical stability, cation exchange capacity, and low expansion coefficient [109]. Kaolinite layers composed of one tetrahedral sheet linked to an octahedral sheet. Therefore, they classified as 1:1 type layer silicates. The structure of kaolinite is a tetrahedral silica sheet, alternating with an octahedral alumina sheet (Fig. 3). One layer of the mineral, consists an alumina octahedral sheet and a silica tetrahedral sheet, share a common plane of oxygen atoms and repeating layers of the mineral [110]. The bonding is so strong that there is no interlayer swelling and the strong bonding between Vander Waals forces and hydrogen bonds [111]. The tips of the silica tetrahedrons and the adjacent layers of the octahedral sheet arranged to form a common layer [112]. In the layer common to the octahedral and tetrahedral groups, two-thirds of the oxygen atoms are shared by the silicon and aluminum, and then they become O instead of OH. The charges within the structural unit are balanced. Analyses of many samples of kaolinite minerals have shown that there is very little substitution in the lattice [107].

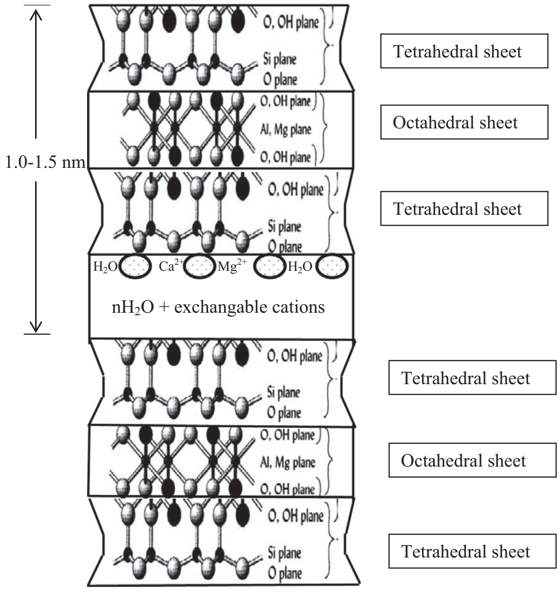
Montmorillonites (Smectite) have a 2:1 layer structure consist of an octahedral alumina sheet sandwiched between two opposing tetrahedral silica sheets [112]. (Fig. 3). The bonding between two silica sheets is very weak, which permits the water and



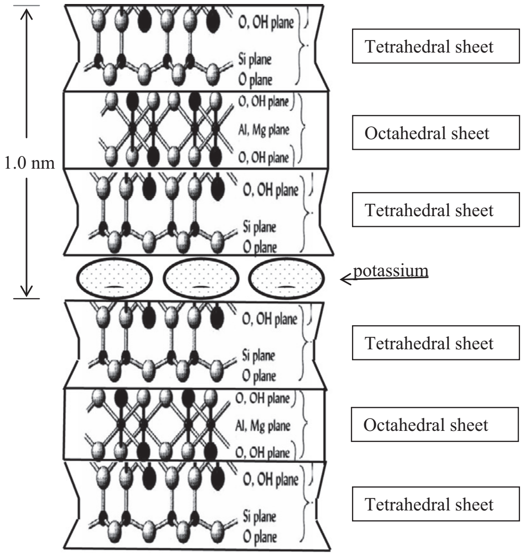
(a) Kaolinite (1:1)

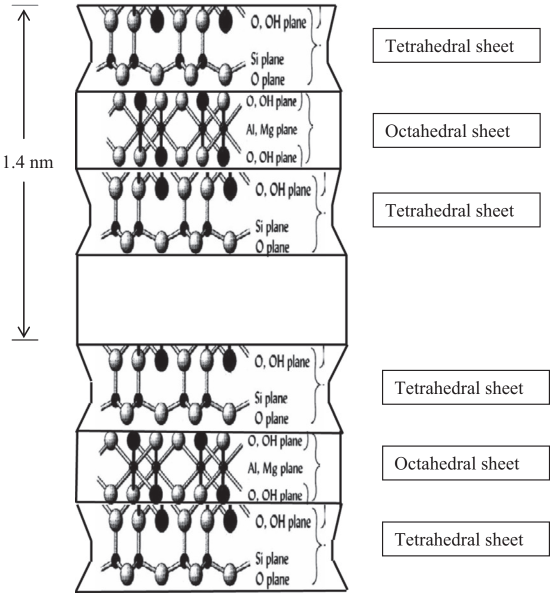


(b) Montmorillonite (Smectite)



(c) Vermiculite





(e) Chlorite

Fig. 3. Diagrammatic representation of crystal structures (a) Kaolinite (b) Montmorillonite (smectite) (c) Vermiculite (d) Illite (e) Chlorite.

exchangeable ions to enter. This leads to the development of swelling capacity [113].

Bentonite is typically considered by clay mineralogists as an impure ore clay that consists both the crystalline structure of montmorillonite and other additional crystalline structures [114].

Illites are also 2:1 type minerals, but the interlayers are bonded together with potassium ion (K^+) to satisfy the charge and lock the structure (Fig. 3). The balancing cation is, therefore, potassium (mainly or entirely), while charge deficiency from substitutions is at least twice that of smectites and close to the surface of the unit layer [110].

Vermiculites clays have a 2:1 structure with a medium shrink-swell capacity. Vermiculite has a high cation exchange capacity, in which the potassium ions K^+ interlayer of illite replaced mainly by magnesium Mg^{2+}. Vermiculite layered structure has pseudo-hexagonal cavities (made of six-membered tetrahedral rings), which are facing each other in adjacent tetrahedral layers (Fig. 3) [115].

The chlorites are a group of phyllosilicate minerals and its structure consist of a talc-like, regularly stacked, and negatively charged 2:1 layers (Fig. 3). Chlorites are usually trioctahedral with Mg^{2+}, Al^{3+}, Fe^{3+}, and Fe^{2+} on octahedral sites; in which a single and positively charged interlayer octahedral sheet connected by H-bonds. Tetrahedral cations are Si^{4+} and Al^{3+} (0.4–1.8 atoms per four tetrahedral positions). Si^{4+} can occasionally be substituted by Fe^{3+}, Zn^{2+}, Be^{2+}, or B^{3+} [112]. In chlorite, the trioctahedral mica-like layers alternate regularly with a hydroxide layer, giving a repeat distance of −1.42 nm. The charge deficiency in the mica-like layer is partly balanced by the positively charged hydroxide layer [116].

The important properties derived from clay mineral's composition, layered structure, size, exchangeable ions, and texture are the ability to exchange ions, plasticity, ability to hold ions, or water on the surface, high adsorbing capacity etc. These properties of clay minerals accumulate all types of toxic inorganic and organic molecules on its surfaces. Clays are very important sheet silicates that incorporate water into their atomic structure. The presence of water lubricates the sheets and makes clays easy to work in pottery industries.

4. Investigations of the adsorption properties of various clay minerals

The use of natural and modified clays as potential adsorbents in the removal of different toxic heavy metal ions from aqueous solutions have been studied immensely from the past many years. This review covers up the thorough literature of last ten years (2006–2016) undertaking the use of various natural clays and its modified form as adsorbents, for the uptake of toxic metals from aqueous solution. This paper represents literature review of investigations done in the last decade with different clay minerals, their ways of modification, and achieved results towards removal of various metal ions from aqueous solutions. This review is informative and useful to the researchers who want to use clay minerals for synthesis procedures and potential adsorbent.

4.1. Heavy metals removal by natural and modified clays

Various scientists conducted numerous studies to explore the adsorptive characteristics of clay in its natural and treated or modified form. The factors including initial solution pH, initial metal concentration, contact time, and adsorbent dosage etc. are crucial for heavy metal removal studies, as they can explain the adsorption processes.

4.1.1. Natural clays

Loads of many successful studies were conducted, for the removal of various heavy metal ions by natural clays. The properties and application of natural clay were recently investigated for the removal of copper Cu (II) from cachaça [117]. An equilibration time of 120 min for clay and 360 min for activated charcoal resulted in the removal of 68.7% and 98.3% of the copper. The pseudo-second-order kinetic behavior indicated that the main type of adsorption mechanism was the chemical reaction between the copper ions and the functional groups presented on the clay surface. The isotherms were studied in the wide range of copper concentrations of 0–2000 mg L^{-1} in this study. The results of Langmuir and Freundlich isotherm models found to adapt better to the Freundlich model. However a large number of adsorption systems, especially in solution, do not obey Freundlich isotherm model. From a critical point of view, an equilibration time of 120 min for clay resulted in the removal of 68.7% only, and thus needed improvement.

Recently, five samples of clay materials from Morocco have investigated for the removal of arsenic (V) from aqueous solution [118]. The effect of the pH on As (V) adsorption indicated that it was most favorable in the acidic pH range. However it had noticed for some clays, no significant adsorption was found in the whole studied pH range. Critically for some clays in this study, the sorption efficiency was too low. Therefore, it was not possible to determine the favorable isotherm models, which might be explained by its lower content of iron oxides. It might concluded that presence of iron oxide controlled the arsenic adsorption onto clay. Another study was also conducted to remove cadmium (II), lead (II), and chromium (VI) ions from wastewater on naturally occurring clay [119]. The kinetic rate constants (K_{ad}) indicated that the adsorption followed first order. The results confirmed that clay was a good adsorbent for the removal of these metals from wastewater. The magnitude of Langmuir and Freundlich constants at 30 °C also indicated good adsorption capacity.

Clays were strongly dependent on temperature, and the high temperature treatment of clays leads to destruct the crystalline structure of the clay minerals [120]. Several studies have reported the changes in properties of natural clay after thermal treatment at various heated temperatures. A multi technique was used to investigate the interaction of Cr (VI) species with pre-fired brick clay at 200 °C temperature [121]. It was found that Cr (VI) adsorption by fired brick clay was strongly dependent on the firing temperature as the maximum adsorption was found at 200 °C. The reducing agents such as organic materials containing carboxylic acid functional groups and Fe^{2+} ions reduced Cr (VI) to Cr (III), and firing process provided enhanced exposure of adsorption sites.

The adsorption abilities of three thermally treated natural clay soils, which differed in textural compositions, tested to remove Cr (VI) from aqueous solutions at different temperatures [122], and those with the highest Cr (VI) adsorption capacities then chosen for batch adsorption studies. The results indicated that the maximum Cr (VI) ion removal varied with the firing temperature. Removal efficiencies of some clay soils were found to increase in the firing temperature range of 200–400 °C and decreased at firing temperatures higher than 400 °C. In another study, one type of clay utilized to increase in removal efficiency up to a firing temperature of 500 °C and then reduced when fired at temperatures exceeding 500 °C. The kinetic studies conducted using the Weber and Morris equation showed that the adsorption mechanism involved intraparticle diffusion, but it was not the fully operative mechanism in the adsorption of Cr (VI) by the three clay soils.

Ball clay found to exhibit an excellent adsorption capacity toward Cd (II) ions [77]. It was found that the sample heated at 200 °C showed maximum adsorption capacity toward Cd (II) ions. The% adsorption decreased with increase in temperature (200–

1000 °C), which indicated that adsorption sites of Cd(II) on ball clay occurred on SiOH or Al–OH were lost at or above 800 °C, hence, there was a sharp decrease in the metal binding capacity of ball clay. In another investigation about equilibrium and thermodynamic studies of the removal of cadmium (II) by adsorption on an indigenous adsorbent China clay [67], displayed good efficiency of removal at 30 °C.

However some studies also confirm the opposite nature of clay (endothermic), like the maximum adsorption capacities of various Saudi clays increased with the temperature [123]. The study concluded that adsorption process of three types of natural Saudi clays to remove cobalt ions was an endothermic process.

Another investigation supported this result, in which spent activated clay (SAC), a natural waste, produced in Refinery Company, was first thermally treated by pressure steam treatment and then used as an adsorbent to remove Cr (VI). The study proved its beneficial use in wastewater treatment [124]. To investigate the effect of temperature on adsorption, experiments were conducted under lower isothermal conditions at 4–40 °C which differ from many studies. Results showed that the maximum adsorption capacities for Cr (VI) ranged from 0.743 to 1.422 mg/g for temperature between 4 and 40 °C under a condition of pH 2.0. It can be concluded that the rate of removal was found to speed up with decreasing pH and increasing temperature. The adsorption mechanism of this study was not attributed to ion exchange. It might be suggested that a weak surface complex reaction was the major mechanism responsible for the $HCrO_4$ adsorption.

The effect of pH is the most critical parameter that affects the adsorption process and is largely observed in heavy metal ion adsorption studies. The comparative study of heavy metal adsorption on raw Smectite rich clayey rock (AYD clay) by the two modes of adsorption (batch and column) showed that the column test result was better than that obtained by the batch test [125]. This study revealed that heavy metal adsorption increases with a decrease in the pH from 8.11 to 5.0. However, in another study, the opposite trend was observed in the removal of Cu (II) and Zn (II) from aqueous solutions by a natural clay, Cankiri bentonite [126]. In this study, the optimum pH values for copper and zinc removal were determined to be 7 and 8, respectively, because the highest removal efficiency of the copper and zinc adsorption by the natural clay was obtained at a pH level >6. This result is not obvious and, thus interesting as most studies proved that the adsorption of most heavy metals (Cu, Pb, Zn, and Cd etc.) decreased with the increase in pH above 6, due to the precipitation. Another example is the adsorption of Pb (II) ions by four samples of Tunisian clay in aqueous solution, using batch system. The results concluded that adsorption of Pb (II) ions increased with an increase in pH of the solution to a maximum around a neutral pH (7.0), and then decreased as the pH became more basic due to the precipitation of some Pb (II) ions. The results also indicated that cation exchange was the main adsorption mechanism for acid-activated clays [127]. Another use of various natural and modified kaolinite clays for the adsorption of Cr (VI) from water [128] confirmed that the adsorption was strongly dependent on the pH medium with Cr (VI) uptake increased from pH 1.0 to pH 7.0. However from the critical point of view, the kinetics tested by several models in this study, but it interactions did not follow a simple model. Cr (VI) adsorption on clays reached equilibrium in around 240 min but the kinetics of clay-Cr (VI) interactions was very complex.

4.1.2. Modified forms

Many forms of treatment can modify clay, with a goal to increase the adsorption capacity of the raw clay material. Heavy metal ions can be removed efficiently by various treatment methods. Many comparative studies have shown that the adsorption capacity of a clay surface is increased with modification or treatment.

Using the column method, not the batch method, the application of a cellulose-clay biopolymer composite for effective adsorption of chromium from industrial wastewater was discovered. The adsorption percentage was found to be a maximum (99.5%) with three replicate measurements when the amount of the adsorbent was in the range from 0.5 to 0.6 g. The mesoporous nature of this type of clay material was determined from the nitrogen adsorption isotherm study, and the adsorption process was in accordance with second order kinetics [129]. In another treatment method, a Japanese volcanic soil called Akadama clay was functionalized with metal salts ($FeCl_3$, $AlCl_3$, $CaCl_2$, $MgCl_2$, and $MnCl_2$) and was recently tested for Cr (VI) removal from an aqueous solution [130]. The adsorption showed little dependence on the pH of solutions ranging from 2 to 8. $FeCl_3$ was selected to be the most efficient activation agent.

Various parameters such as equilibrium isotherms, kinetics, and thermodynamic interactions were employed for the adsorption of iron oxide, Fe (III), from water by natural and acid activated clays [131]. This study demonstrated that the adsorption increased with pH until Fe (III) became insoluble at a pH level >4.0, and acid activation raised the adsorption capacity compared to untreated clay minerals. Fe (III) uptake continuously increased over time until 300 min; after 300 min, the increase was insignificant. However, in this study, the kinetics of the interactions were not found to be certain, and no definite kinetic mechanism could be proposed, but second order kinetics appeared to give a better description.

In a recent work, a new type of titanium pillared clay (Ti-PILC) impregnated with potassium iodine (KI) was synthesized to remove elemental mercury (Hg^0) [132]. Compared with the original clay or the KI-impregnated clay, the modified KI-impregnated Ti-PILC showed an excellent Hg^0 removal ability because of its larger BET surface area. It was found that the Hg^0 removal efficiency was enhanced with an increase in temperature. Natural and modified clay was successfully utilized for the removal of Mn (II) and Cd (II) from wastewater by a single metal system [66]. Sorption was rapid during the first 5 min, and equilibrium was attained within 60 min. Two distinct adsorption mechanisms were observed that might influence adsorption. During the first 5 min of interaction, a cation exchange mechanism occurred, but the second sorption mechanism could be related to the formation of inner-sphere surface complexes.

The results have shown that both Cd (II) and Mn (II) were totally retained from a 50 mg L^{-1} solution when K10 grafted with ammonium pyrrolidinedithiocarbamate (APDC) was used as an adsorbent.

Another study of Cr (VI) removal using batch studies was conducted by exploring the adsorptive properties of the natural red clay after modification by hexadecyltrimethylammonium bromide (HDTMA). The optimal pH range corresponding to the maximum adsorption of Cr (VI) on red clay was found to be 4–6.5 [133]. In this study, a model with distribution constants of the H_2CrO_4, $Cr_2O_7^{2-}$, $HCrO_4^-$, and CrO_4^{2-} species to the adsorbent phase was used for the first time in adsorption behavior evaluation. The optimal pH range corresponding to the maximum adsorption of Cr (VI) on red clay was 4–6.5. The contact time between the phases that is necessary to reach equilibrium was 300 min for Cr (VI).

However, numerous publications also present results that treatment or modification do not increase the adsorption properties. These confirm the applicability of clay in its natural raw form, not the modified form. Three types of local clays, Tabuk, Baha, and Khaiber, were tested for their abilities to adsorb Pb (II) from wastewater. The clays were then treated with hydrochloric acid to activate the adsorption sites within clay particles. Untreated Tabuk clay had the largest adsorption capacity, approximately

30 mg lead/g clay, in comparison with those of Baha and Khaiber clays. The adsorption of the acid-activated clays was not enhanced compared to those of the untreated clays [134]. Pottery glaze, a thin viscous liquid, consists of various clay minerals has been developed to have excellent adsorption of Cu (II) from aqueous solutions [135]. The effect of adsorbent treatment with a complexing agent like PAN [1-(2-pyridylazo)-2-naphthol] was also studied, and it was found that treatment did not show any increase in the adsorption.

The naturally occurring clays, in their raw forms, have shown excellent adsorption potential for the removal of heavy metals from aqueous solution. The adsorbed amount of targeted metals increased with the concentration of metals in most studies. The adsorption of most metals increased up to a pH value of 6 and then decreased above a pH value of 8 because of the formation of precipitates. The optimum pH value is 6 for most metals, but 4 for chromium. It was found that the adsorption was initially fast, and equilibrium was reached within the first several hours in most studies. In almost all cases, the percentage of adsorption increased with the increase in dose.

Clays were highly dependent on temperature, and several studies have reported the changes after thermal treatment. Adsorption was found to increase with the temperature up to some extent and then decreased at very high temperatures. The results confirmed both exothermic and endothermic processes. The modified forms of clays have also been widely used, and it can be observed from the results that the modifications increased the surface area and the adsorption capacity.

4.2. Heavy metal removal by the Smectite group

The name Smectite was suggested as a group name by the Clay Minerals Group of the Mineralogical Society of Great Britain for all clay minerals with an expanding lattice, e.g., montmorillonite, beidellite, nontronite, saponite, and bentonite [107]. The cation exchange capacity, specific surface area, and adsorption capacity of Smectites are considerably larger than those of other clay families [47]. The clay minerals present in this group differ mostly in their chemical content and formulas.

4.2.1. Montmorillonite

Montmorillonites (MMT), part of the smectitic clays, are abundantly present in nature. Montmorillonite is the special name given to a Smectite clay that was found in the Montmorillon area of France [136]. Given the large amount of modern literature and the best interests of science, the use of the montmorillonite name has been commonly used for Smectite and has been widely accepted [137].

The hydrophilic MMT micro-particles cannot be largely used as an adsorbent because water is absorbed in the interlayer regions between the silicate sheets. Chemically, montmorillonites have been treated or modified to increase the surface area for making highly porous composites. The modified forms of MMT in addition to treatment, physical, and adsorption detail investigations have been widely carried out.

Organo-modified montmorillonites (OMMT) have been widely used in polymer/clay nano-composites. Organically modified montmorillonite clay (OMHP-MMT) was used for the removal of Cu (II) as a function of solution pH, stirring time, common ion effects, eluent type, concentration, and volume [138]. It showed good removal efficiency and selectivity towards Cu (II) at a pH range of 3.0–8.0 with a stirring time of 10 min. The maximum removal efficiency (99.2 ± 0.9%) was obtained at pH 6.0. However, the introduction of Cu (II) as sulfate or nitrate instead of chloride had no influence on the removal process, indicating that the major role was a result of OMHP. The results concluded that OMHP-MMT was successfully applied to recover Cu (II) from different samples. In the advancement of organically modified montmorillonite clay and for the removal of copper, recent work was conducted in which organo-montmorillonites (OMts) were modified by a cationic surfactant and a zwitterionic surfactant [139]. The adsorption capacity of the zwitterionic surfactant (Z16) modified montmorillonite toward Cu (II) was comparable with that of raw montmorillonite. The results of this work may provide novel information for developing new effective adsorbents of heavy metals.

In contrast, organoclays have received limited interest as adsorbents of heavy metals primarily because the organic cations compete with metals for adsorption sites on the clay mineral surfaces. A study reported the adsorption of Pb (II) and Hg (II) by montmorillonites modified with natural organic cations [140]. In this study, the synthetic organic cations suppressed the adsorption of Pb (II) and Hg (II) because of the competition between organic cations and heavy metals for adsorption sites and lack of organic functional groups that are capable of interacting with heavy metals. These findings are consistent with the prior understanding of organic functional group-metal complexation reactions.

Several authors have extensively studied the preparation techniques and adsorption properties of aluminum-pillared clays. Carbon modified aluminum-pillared montmorillonite has shown good uptake of Cd (II) from an aqueous system. The Cd (II) adsorption followed a mechanism based on second-order kinetics. Adsorption of Cd (II) was low at a pH level <6.0, but uptake increased sharply at a pH level >6.0. This may be a result of the relatively low H^+ concentration on the clay surface as the surface became negatively charged at a higher pH; this could allow for strong bonds with Cd (II) [141]. Al_{13} pillared montmorillonites (AlPMts) were also prepared with different Al/clay ratios to remove Cd (II) and phosphate from an aqueous solution [142]. In the single adsorption system of this study, Cd (II) adsorption was not adsorbed very much, but in a simultaneous system, significantly enhanced Cd (II) adsorption was observed. This result suggested that the formation of surface complexes promoted the uptake of Cd (II). For both contaminants (Cd (II) and phosphate), the adsorption of one increased with the other one. However, in simultaneous studies, different results may also be observed. The adsorption and XPS results suggested that the formation of P-bridge ternary surface complexes were the possible adsorption mechanism for promoting uptake of Cd (II) and phosphate on AlPMt.

Removal of Pb (II) and Cd (II) from spiked water samples by adsorption onto clays (Kaolinite and Montmorillonite) was studied. Here, Pb (II) adsorbed exothermally, whereas Cd (II) was adsorbed endothermically [143]. In the case of clay-metal interactions, the amount of adsorbed per unit mass of clays decreased, whereas the extent of adsorption increased rapidly. Aluminum-pillared-layered montmorillonites (PILMs) also proved their potential as a sorbent in the removal of copper and cesium from aqueous solutions [144]. The Al/clay ratio appeared to have a significant effect on the sorption of copper on PILMs. With an increasing Al/clay ratio, the amount of sorbed copper increased. This indicated that the sorption of copper involved a specific group of high-affinity sites on the pillar surfaces. The study concluded that copper sorption should be driven by both a cation exchange mechanism and by complexation reactions with the pillar oxides.

An acid-activated montmorillonite-illite type of clay collected from the Gulbarga region of Karnataka, India was examined for removing Cu (II) and Zn (II) ions from industrial wastewater containing minor amounts of Pb (II) [145]. Critically, this study had difficulties in describing the adsorption of metal ions from wastewater because of the presence of several different components that caused interference and competition on adsorption sites.

Kaolinite and montmorillonite were modified with tetrabutylammonium (TBA) bromide followed by calcination and used for the adsorption of Fe (III), Co (II), and Ni (II) ions from aqueous solution [146]. However, in this study, the calcined TBA clay minerals have a lower adsorption capacity compared to the parent clay minerals at the same experimental conditions. The reaction of kaolinite with TBA decreased the adsorption of Fe (II) by 55%, Co (II) by 47%, and Ni (II) by 44%. Calcined TBA-montmorillonite had only 44, 41, and 42% of the adsorption capacity of the parent montmorillonite for Fe (III), Co (II), and Ni (II), respectively. These negative results may be because of the bulky TBA groups that block several negatively charged sites and most likely, also the pores.

Phosphate-modified montmorillonite (PMM) was used for the removal of Co^{2+}, Sr^{2+}, and Cs^{+} from an aqueous solution. The Freundlich model was the best for indicating the heterogeneous surface property of PMM [147]. Sorptions of Co^{2+} and Sr^{2+} were strongly dependent on the initial solution pH and endothermic, but Cs^{+} was not and was exothermic. The strongly pH-dependent sorption of Co^{2+} indicated that surface complexation was the main mechanism of Co^{2+} sorption onto PMM.

Possible use of montmorillonite modified with polyethyleneimine was investigated for the removal of Co (II) and Ni (II) metal ions from aqueous solutions [148]. The increased sorption of cobalt on the modified sorbent being studied (compared with the natural mineral) pointed to the binding of cobalt ions with amine groups attached to the sorbent. It was found that the employment of such a composite sorbent is promising for the purification of medium and highly mineralized wastewaters with a neutral value of pH.

Humic substances and clay minerals have been studied intensively because of their strong complexation and adsorption capacities. The adsorption and desorption of Ni (II) on Na-montmorillonite was studied using the batch technique under ambient conditions [149]. The effects of pH, ionic strength, fulvic acid, humic acid, and additional sequences were investigated. The results indicated that the adsorption of Ni^{2+} onto montmorillonite is strongly dependent on pH and ionic strength. It can be concluded from this study that montmorillonite is a suitable candidate for the pre-concentration and solidification of Ni^{2+} from large volumes of solutions. Humic acid was found to enhance the metal adsorption capacity of mineral surfaces. An investigation of the adsorption of lead (II) onto montmorillonite clay modified by humic acid under a fixed pH condition was also recently conducted [150]. The adsorption of Pb (II) onto humic acid was high; this might be the result of its strong affinity for carboxylic and phenolic groups of humic substances. The adsorption mechanism of Pb (II) might be the result of bridging between the adsorption sites on montmorillonite and HA molecules.

Some studies also confirmed that Ti-pillared montmorillonite is a promising adsorbent for As (III) and As (V) removal from arsenic-contaminated water. Arsenic adsorption onto Ti-pillared montmorillonite was carried out as a function of contact time, pH, temperature, coexisting ions, and ionic strength [151]. Only phosphate had a noticeable influence on the adsorption of arsenate, whereas the effect of other ions was negligible. The work confirmed that Ti-pillared montmorillonite is an effective adsorbent. In another work, a TiO_2 pillared montmorillonite (TiO_2/MMT) adsorbent was used to remove As (III) and As (V) from an aqueous solution. The adsorption kinetics, pH role, UV effect, and column experiments were investigated in this study [152]. The adsorption capacity increased quickly within the first 20 min, and the adsorption equilibrium was less than 1 h. It can be concluded from these results that TiO_2 exhibited MMT as an adsorbent with improved arsenic adsorption capacity.

Fe (II)–montmorillonite, an environmentally benign clay mineral, was recently efficiently used for the reduction of Cr (VI) in an aqueous solution [153]. The Cr (VI) reduction was rapid at an acidic pH and increased with temperature up to 50 °C. A complete reduction occurred in approximately 5 min at a pH range of 3–5. The adsorption–desorption kinetics of arsenate on a Fe (III)-modified montmorillonite (Fe-M) were studied at different arsenate concentrations, pH levels, and stirring rates [154]. Adsorption took place in a two-step mechanism, with an initial fast binding of arsenate to the Fe (III) species followed by a slower binding. It is clear from the study that arsenate adsorption is because of the presence of Fe (III) species that created favorable adsorption sites for arsenate species.

Cu (II)-bearing montmorillonite was assessed for Cd (II) adsorption [155]. The results showed that the adsorption capacity of Cu bearing MMT onto Cd was stronger than the MMT. The maximum adsorption (94%) was found at 20 min of shaking time using Cu-MMT as an adsorbent. Here, the treatment affected the adsorption to such a large extent (94%), but that is not the case in all treatment studies. A recent study investigated the adsorption of Cd^{2+} from an aqueous solution onto octadecane-betaine modified montmorillonite (BS-Mt) [156]. Here, in this study based on kinetic models, it was concluded that the maximum adsorption capacity of Cd^{2+} in aqueous solution was only slightly enhanced after modification.

Some other modified forms, such as Chitosan-montmorillonite (KSF-CTS) beads to remove Cu (II) [157] and iron-free synthetic montmorillonite to measure the Fe (II) uptake from aqueous solutions [158], were also prepared and successfully used as adsorbents. These results are highly promising and suggest that treatment technologies on this adsorbent can be applied for improved metal removal in wastewater streams.

Montmorillonite in its natural form also showed its applicability as a potential adsorbent for metal ion removal, as numerous publications have proved that MMT is a cheap, abundant, and locally available resource. If, as an adsorbent, the exchangeable cation is sodium, the specific mineral is sodium montmorillonite, and if it is calcium, it is calcium montmorillonite [60]. The effects of an anionic bio surfactant, rhamnolipid (RL), and pH on the adsorption and desorption of Cu (II) ions using Na-montmorillonite were investigated [159]. The adsorption process proceeded mainly through diffusion between the interlayers by the mechanism of ion exchange and specific adsorption. The addition of RL, however, did not cause an increase in the adsorbed amounts over the amounts adsorbed on the pure clay. The reason for this slightly lower capacity of RL modified clay was most likely the result of the partial occupation of the active sites through the adsorption of RL molecules onto the interlayer of clay and thus the reduction in the number of active sites for the adsorption of Cu^{2+} ions.

Antimony, because of its non-polar characteristic, is difficult to adsorb and is thus mostly toxic. However, the use of sodium montmorillonite (Na-MMT) successfully removed antimony acetate, $Sb(OAc)_3$, from an aqueous solution. The results showed that the corresponding data from adsorption experiments fitted fairly well to the Langmuir isotherm. The adsorption process appeared to be controlled by the chemical process in accordance with the pseudo-second-order reaction mechanism, and the adsorption fitted well to the intraparticle diffusion model up to 30 min, but diffusion was not the only rate controlling step [160].

Plutonium (Pu) can exist in four oxidation states and is highly toxic to the environment. Not many adsorbents have adsorbed Pu because of a wide array of factors, but a study was conducted that showed that Na-montmorillonite was successfully used for the adsorption of Pu contaminants from water [161]. Comparison between the rates of adsorption of Pu (V) to montmorillonite and a range of other minerals found that minerals containing significant Fe and Mn adsorbed Pu (V) faster than those that did not, highlighting the potential importance of minerals with redox couples in increasing the rate of Pu (V) removal from solution.

Competitive sorption among Cu (II), Pb (II), and Cr (VI) in a ternary system on Na-montmorillonite and the effect of varying concentrations of Al (III), Fe (III), Ca (II), and Mg (II) on the sorption of heavy metals were studied. The competitive sorption of Cu (II), Pb (II), and Cr (VI) in a ternary system on montmorillonite followed the sequence of Cr (VI) > Cu (II) > Pb (II) [162]. Moreover, the competition was weakened by the increase of pH, whereas it was intensified by the increase in heavy metal concentration. These findings are of fundamental significance for evaluating the mobility of heavy metals in polluted environments.

Recently, a study was conducted that aimed to reduce the water surface tension using prepared Na-MMT Nano gels (reactive amphiphilic montmorillonite) and to increase the adsorption water pollutants into clay galleries [163]. The data proved that the Na-MMT Nano gels reduced the surface tension of water and efficiently removed metal ions from water.

In another recent work, Na-montmorillonite and Ca-montmorillonite were used to remove Pb (II), Cu (II), Co (II), Cd (II), Zn (II), Ag (I), Hg (I), and Cr (VI) from an aqueous solution [164]. The Na-Mt was more effective for heavy metal adsorption than Ca-Mt and proved to be a potentially useful material for Pb (II), Cu (II), Co (II), Cd (II), Zn (II) removal from aqueous solutions. The role of ion exchange was the main mechanism for Ca-Mt, whereas both ion exchange and precipitation were the main mechanism for Na-Mt. The surface of sodium montmorillonite can also be modified, and a meticulous study revealed the intercalation of trioctylamine onto sodium montmorillonite for the adsorption of mercury as a tetrachloromercurate (II) anion [165]. The adsorption was facile in an acidic medium and a N_2 adsorption–desorption isotherm study confirmed the mesoporous nature of the adsorbent and thermodynamically favorable adsorption process of this study. The adsorption process was consistent with the mechanism involved in the electrostatic interaction between the tetrachloromercurate (II) anion and the protonated amine in the clay.

When used as calcium montmorillonite (Ca–montmorillonite), insights into the control and remediation of a variety of metal pollutants Hg^{2+}, Cr^{3+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Ba^{2+}, Ni^{2+}, Mn^{2+}, Cd^{2+}, Ba^{2+}, and Ag^{+} were studied [166]. It was observed in this study that Cr^{3+}, Pb^{2+}, and Cu^{2+} precipitate oxides or hydroxides at a pH level <5. As the alkalinity increased, the adsorption sites on the clay surface and the amphoteric crystal edges were deprotonated and readied to adsorb metal cations.

Ca–montmorillonite was also modified with humic acid, and the performance of the modified material with respect to the Cu (II), Cd (II), and Cr (III) ions from aqueous solutions was studied [167]. The IR spectra showed a shift in H–O–H band to a lower wave number indicated an increase in the interlayer water following Cd (II) accumulation in the interlayer space of montmorillonite.

The sorption process of mercury (II) on calcium-montmorillonite as a function of pH was also determined [168]. The sorption properties were determined by the fact that there was no precipitation at higher pH values. The sorption mechanism of neutral mercuric hydroxide species on the clay mineral demands further study.

In some other uses of raw montmorillonite, its adsorption behavior for copper and nickel removal [169] was determined. It can be assumed by the adsorption mechanism that the diffusion of the solute inside the clay was more important for the adsorption rate than the external mass transfer. The results supported by another study indicated that montmorillonite and sepiolite are good adsorbents for Cu (II) in aqueous solutions [170]. The results showed that the adsorption of Cu(II) increased rapidly over time (in the first 30 min) and reached saturation in approximately 120–240 min. Multi metal ions Cd (II), Co (II), Cu (II), Ni (II), and Pb (II) were also successfully removed using montmorillonite [171]. The results confirmed that, without citrate, montmorillonite showed higher Ni (II) adsorption [172]. The mechanisms of interaction between Cu (II) and ciprofloxacin (Cip) in the adsorption onto montmorillonite and kaolinite were also studied. It was found that Cip increased Cu (II) adsorption onto montmorillonite at a pH level <7.0, whereas it decreased the adsorption of Cu (II) onto kaolinite at pH levels ranging from 6.0 to 8.0 [173].

The raw form of montmorillonite has not been largely used as an adsorbent because of its hydrophilic nature. Its modified forms have been widely used, and it can be observed from the results that the modifications increased its surface area and adsorption capacity. The amount of adsorbed metals mostly increased with the concentration of targeted metals. The adsorption, in most of the studies, was strongly pH-dependent, suggesting the contribution of the surface complexation mechanism. Arsenic and copper adsorption, however, mostly decreased at a high pH, and a pH level of 6 was found to be optimum for these. It was found that the adsorption in most of the studies was initially fast, and equilibrium was reached within the first several hours. In most cases, percentage adsorption increased with the increase in dose.

4.2.2. Smectite

The X-ray diffraction patterns, chemical analyses, and refractive indices showed that the names Smectite and montmorillonite appear to be the same mineral [174]. This name Smectite was at one time widely used in the mineralogical texts from the 18th century [137]; however, some authors still use this name in their studies. Pure Smectite is found in nature and can be obtained by the purification of bentonites [107]. The structure, chemical composition, exchangeable ion type, and small crystal size of Smectite clays are responsible for several unique properties including a large chemically active surface area and a high cation exchange capacity [175]. Because of its high cation exchange capacities, it has been used to remove toxic metal ions from liquids in both raw and treated forms.

The effect of a new method of adsorption using membrane filtration to determine the maximum amount of lead adsorbed by Smectite clay was studied [176]. It was concluded that clay has a strong adsorption capacity for Pb (II) as the maximum interaction occurring with purified clay treated at a high concentration of lead. Pb (II) adsorption was achieved in two steps: the first reaction stage was controlled diffusion, and the second stage was controlled chemisorption. The increase of the clay adsorption capacity was mainly the result of the purification method introduced in this study.

The adsorption of Ni (II) ions from aqueous solution on Smectite from Sabga has been investigated [177]. The results showed that the amount of Ni (II) ions adsorbed increases with increased contact time and that equilibrium adsorption was reached in 15 min.

The efficiency of Smectite clay as an adsorbent was studied for its adsorption of Co (II) ions in the presence of four different electrolytes at three different ionic strengths [178]. The quantity of Co (II) adsorbed from the solution decreasing with increased ionic strength might be the result of the interference of electrolytes during adsorption. The reduction of Co (II) ion adsorption was related to the nature of ion pairs involving the dominant anion in the system. The adsorption of Co (II) was reduced to a greater degree when nitrate was the dominant anion in the solution instead of chloride. A similar trend was also observed in solutions containing calcium ions instead of sodium ions.

Recently, a series of aluminum and iron oxide modified Smectites was used for a comparative study of the effectiveness of heavy metal adsorption from water [179]. Except for Hg (II), the starting Smectites and the obtained materials displayed higher metal adsorption properties in comparison to that of carbon that is used as the reference in this study.

The adsorption of uranyl (VI) on two common edge surfaces of 2:1 Smectite clay minerals using standard periodic DFT models was recently studied [180]. Comparing uranyl species at various sites of these two types of surfaces, the authors found that the structural parameters of such adsorption complexes were essentially determined by the surface chemical groups forming the adsorption site, not by the type of the clay mineral.

In the treatment of Smectite clay, Guerra et al. collected original Brazilian Smectite-bearing clay samples, and [3-(2-aminoethylamino)propyl] trimethoxysilane was successfully anchored onto the pillared Smectite; then, new reactive sites were added in the clay surface through the presence of the NH groups in the agent intercalated chain that displayed the ability for lead adsorption [181]. The authors also used the original Smectite clay mineral to evaluate the adsorption of chromium (VI) ions after the compound 2-aminomethylpyridine (AMP) was anchored onto the Amazon Smectite surface by the heterogeneous route [182]. The energetic effects caused by metal cation adsorption were determined through calorimetric titrations.

The adsorption of Pb (II) ions onto Tunisian Smectite-rich clay in aqueous solution was studied [183]. The type of smectitic clay could adsorb Pb (II) via two different mechanisms: cation exchange and innersphere complex formations. A comparative study between sulfuric acid activated clay (AYDs) and powder activated carbon (PAC) for the adsorption of lead was also conducted. The results showed that sulfuric acid activated clay was more efficient than PAC. However, the thermic activation of AYD clay reduced the Pb (II) uptake as soon as the calcination temperature reached 200 °C; this may be attributed to the decrease in the surface area.

The adsorption of Pb (II), Zn (II), and Cd (II) in single and multi-element systems onto raw, acid-activated, and aluminum-pillared Tunisian Smectite was investigated [80]. The selected order of adsorption Pb (II) > Zn (II) > Cd (II) showed the importance of the competitive phenomenon onto clay material pore adsorption. However, the study failed to yield the Langmuir isotherm in the case of Pb (II), Zn (II) and Cd (II) on some samples that had less heterogeneity than other samples.

Smectite has been modified using hexadecyltrimethylammonium bromide in an amount of double cationic exchange capacity for the interchangeable sorption of phosphate (V) and lead (II) [184]. This alteration makes it possible to use organo-Smectite as a sorbent to remove anionic forms. Experimental data showed that lead was more likely to absorb on the organo-Smectite than on the organo-Smectite with previously adsorbed phosphate ions. It followed that the most effective use of the organo-Smectite is through the sorption of Pb cations and then PO_4 anions. This enables the removal of harmful lead and phosphorus compounds from wastewater and immobilizes them on the sorbent's surface.

The adsorption capacity of Smectite, with similar properties to Montmorillonite, was largely increased by various modifications. It was increased with the increase in concentration for almost all studies. The optimum pH for the adsorption of many metals was in the range of 5–6 after precipitation occurred. The reason for the low adsorption capacity with a high pH was the competition between the excess of H^+ ions in the medium and the positively charged cationic species presented in the solution. It was found in almost all studies that the adsorption was initially fast, and equilibrium was reached quickly. The percentage adsorption increased with increases in dose. This was an expected result because as the dose of adsorbent increases, the number of adsorbent sites increases; therefore, these amounts attach much more ions to their surfaces. It was also noted in some studies that adsorption became faster and increased with increasing temperature.

4.2.3. Bentonite

Bentonite and Montmorillonite have similar mineral properties [136]. Bentonite was originally named for Smectite clay found near Fort Benton, Wyoming [136]. Bentonite consists of nanometer scale Smectite clay minerals (mainly Montmorillonite) and micrometer scale macro-grains (mainly quartz) [136]. Bentonite, a naturally occurring clay mineral, is becoming a substitute for the use of expensive adsorption materials, such as active carbon, because of its availability, relatively low cost and high adsorption capacity towards various heavy metal ions. The chemically modified surfaces of bentonite have been widely investigated and play a very important part in applications because of their ion exchange reaction and high pore volume.

Several researchers have investigated the use of chitosan as an adsorbent for the removal of heavy metals from aqueous streams. The adsorption capacity can be enhanced by spreading chitosan on physical supports that can increase the accessibility of the metal binding sites. Bentonite was coated with chitosan (Chi) and its derivative, 3,4-dimethoxy-benzaldehyde (Chi/DMB), and the product was then used as an adsorbent for the removal of Cd (II) from aqueous solutions in a study [185]. The presence of imine groups resulting from chemical modification confirmed that Chi/DMB successfully coated on bentonite, increasing the accessibility of metal binding sites. Critically, the Chi/DMB/bentonite showed no significant pH dependence in the pH range of 2–9, but bentonite coated with chitosan revealed very intensive pH dependence that had a considerable effect on cadmium removal.

Cross-linked chitosan/bentonite composite (CCB) was prepared and characterized for the adsorption of hexavalent chromium [186]. The mechanism for the adsorption of Cr (VI) on CCB at pH 2 might include electrostatic interaction and chemical interaction between CCB and Cr (VI) ions. The weight loss of chitosan is higher than that of a CCB composite at high temperatures. Thus, the thermal stability of the CCB composite was improved because of the addition of clay particles (bentonite) to crosslinked chitosan.

Bentonite clay has been modified with a binary mixture of goethite and humic acid for the removal of Cu (II) and Cd (II) from aqueous solutions [187]. Pre-modification of bentonite clay with goethite and humic acid resulted in an increased cation exchange capacity by a binary mixture of goethite and humic acid reagents. The inner sphere complexation mechanism was suggested for the adsorption of both metal ions onto the modified adsorbents.

Various chemicals in the treatment process have also been incorporated into bentonite and resulted in the enhancement of heavy metal removal. Natural bentonite was chemically treated by hydrochloric, nitric, and phosphoric acids followed by washing with sodium hydroxide to enhance its adsorption capacity. The sample treated with hydrochloric acid followed by further treatment with NaOH showed the highest cation exchange capacity and was used for cobalt and zinc removal from aqueous solution [188]. It can be concluded that this chemical treatment leads to opening more macro and micro pores in the material; hence, more surfaces became available for adsorption and ion exchange.

Another chemical treatment, in addition to the equilibrium, kinetic, and thermodynamic aspects of copper ion adsorption from an aqueous solution using linear alkyl benzene sulfonate modified bentonite (organo-bentonite), was reported [189]. The modification of bentonite was performed via microwave heating with a concentration of LABORATORIES surfactant equivalent to 1.5 times that of the cation exchange capacity (CEC) of the raw bentonite. One of the possible adsorption mechanisms between Cu (II) ions and organo-bentonite involved the exchange of metal ions with H^+ ions.

To study the capacities of natural and organic bentonite samples to remove lead ions from an aqueous medium, the chemical modifications were conducted with a Brazilian bentonite sample; 3-aminopropyltrietoxisilane (APS) and 3,2-aminoethylaminopropyltrimetoxisilane (AEAPS), as the raw material and the intercalating agent, respectively, were used [190]. The adsorption processes of Pb^{2+} by adsorbent surfaces of the materials used in this work are exothermic. However, it is noted that the removal of Pb^{2+} by raw and natural bentonite surface materials was a principally complex phenomenon in the heterogeneous surfaces.

The adsorption properties of raw bentonite were further improved by modification with manganese oxide. The high performance exhibited by manganese oxide modified bentonite (MMB) was attributed to an increased surface area and a higher negative surface charge after modification and successfully traced Cu (II) from an aqueous solution [191]. The adsorption of Cu (II) onto the RB appeared to involve two distinct mechanisms: an ion exchange reaction and the formation of surface complexes. It can be concluded that bentonite, which has a high surface area, provided an efficient surface for manganese oxide, improving the metal adsorption capacity of bentonite.

In another newly studied work, the adsorption of Co (II), Cu (II), Ni (II), Pb (II), and Zn (II) by bentonite clay from a polycationic solution was investigated. In this study, bentonite clay achieved >99% removal efficiencies for metal species in acidic wastewaters. The sorption affinity varied in the following order: Co > Cu > Ni = Zn > Pb [192]. The interactions of bentonite clay and metal species showed a decrease in the base cations on the clay matrices, thus proving that ion exchange was also governing the removal of metal species. This comparative study proved that bentonite clay can increase the pH and effectively remove metal species from acidic and metalliferous wastewaters.

Amine and carboxylate functionalized bentonites were used as adsorbents of heavy metal ions Pb (II), Hg (II), and Cu (II) from aqueous solutions [193]. 3-Aminopropyl trimethoxysilane was grafted on sodium bentonite, and this amine functionalized bentonite was converted into carboxylate functionality by the reaction with succinic anhydride. Further research, however, is needed to determine the specific applications of the two adsorbents with respect to other pollutants and industrial wastewaters.

Pillaring and an acid activated process are used to improve clay properties. Bentonite clay from south Tunisian clay has been modified by several treatments such as aluminum pillaring, acid activation, and pillaring followed by acid activation that was then utilized for the adsorption of the chromium ions [194].

Aluminum-pillared and unpillared bentonite clays were prepared to evaluate the mechanism of thermodynamic and kinetic evaluations of some heavy metal ions [195]. The transformation of natural clay mineral into pillared clay was achieved using aluminum (0.1 M $Al(NO_3)_3 \cdot 9H_2O$) by slowly adding a basic solution of 0.2 M NaOH to the aluminum solution under constant stirring. However, in this study, the adsorption characteristics of Al-pillared bentonite clay followed a similar pattern as the unpillared sample.

A large-scale test was performed to investigate the thermal-hydro-mechanical behavior in the bentonite buffer using an experimental apparatus (KENTEX) to determine its adsorption property towards cesium and iodide ions using batch test and in-diffusion test methods [196]. The cesium ions were highly sorbed on the bentonite, and the experimental data fitted the Freundlich isotherm well. The iodide ions, on the contrary, were negligibly sorptive because of anion exclusion from the negative surface charge of the bentonite particles.

A nano ferrite bentonite clay composite (NFBC) of magnesium ferrite nanoparticles ($MgFe_2O_4$NPs) and bentonite is synthesized using the sol–gel method for the effective removal of Cr (VI) from water [197]. It is a blend of promising adsorptive and magnetic properties and can be easily separated from the solution by using a magnet or can be subsequently regenerated by washing with 0.1 N NaOH.

A comparative study of bentonite in its natural and modified form for the adsorption of Cu (II) has been conducted because of its strong adsorption capacity. The X-ray diffraction (XRD) spectra indicated that the Cu (II) adsorption onto the bentonite samples led to changes in unit cell dimensions and symmetry of the parent bentonites [198]. The results indicated that the mechanism of Cu (II) ion adsorption onto MMB perhaps involved an exchange reaction of Cu^{2+} with H^+ on the surface and surface complex formation. It is concluded that the adsorption of Cu (II) by the bentonite samples is a complex process controlled by a number of environmental variables; the adsorption occurred in two stages.

Bentonites disperse into colloidal particles and provide large surface areas per unit weight of clay that act as a medium to hold heavy metal ions. Sodium bentonite (Na-bentonite) has excellent water absorbing capacity. Chen et al. collected Na-bentonite from Gaomiaozi County, Inner Mongolia, China (herein called GMZ bentonite) and successfully utilized it for the removal of Cr(III) ions from aqueous solution [199]. They also studied the adsorption of La (III) onto GMZ bentonite [200] in which the adsorption mechanism involved outer-sphere surface complexes on the surface of bentonite or cation exchange between La (III) and bentonite on the ion exchange sites. The competitive adsorption of Na(I)/Cr(III) and Cr(III)/Cu(II) onto GMZ bentonite was also conducted [201]. The results confirmed that bentonite has a larger total adsorption amount of Cu (II) and Cr (III) in binary ions solution compared to that of single ion solutions. Recently, Na-bentonite was used to present a study on cadmium (II), copper (II), and lead (II) removal using adsorption [202]. The experimental results showed that ionic strength strongly affected the clay structure and cadmium removal but had little influence on the lead and copper removal. The results confirmed that tested Na-bentonite possesses a high capacity for the removal of Cd, Cu, and Pb.

The adsorption potential of natural and raw bentonite in the removal of Pb(II) ions [203], for the removal of Pb(II) and Cd(II) ions [204], Zn(II) ions [205,206], and Cu(II), Zn(II), and Co(II) [207] from aqueous solutions was also investigated. Recently, bentonite clay from west of Saudi Arabia was characterized and investigated for the adsorption of chromium and lead ions [208]. It was found that internal mass diffusion was the major rate controlling step for maximum removal of chromium and lead ions from wastewater.

The various modifications of bentonite increase the accessibility of metal binding sites, resulting in a more porous surface. It was found in most reported studies that increases in concentration resulted in increased adsorption. However, some studies also showed decreases with increases in concentration; these might be a result of the hydrolysis of metal cations with the subsequent release of protons. The optimum pH for adsorption of many metals was in the range of 5–6 after precipitation occurred. Only chromium marked a decrease with increasing pH, and 2 was found to be the optimum pH for it. It was found in almost all studies that the adsorption was initially fast, and equilibrium was reached in a few hours. This short time period required to attain equilibrium suggested an excellent affinity of the metal ions for these materials. The percentage adsorption increased with increase in dose. The effect of temperature resulted in increased adsorption with increasing temperature.

4.3. Heavy metals removal by Kaolinite

Kaolinite, a natural resource, has been widely used in its raw form to remove heavy metal ions despite its low cation exchange capacity. This behavior can also be formed by the modification of suitable treatment techniques.

4.3.1. Raw kaolinite

Kaolinite clay obtained from Longyan, China was investigated to remove heavy metal ions Pb (II), Cd (II), Ni (II), and Cu (II) from wastewater [70]. The removal was based on ion exchange and adsorption mechanisms; kaolinite had a relative low cation-exchange capacity. However, there was a significant reduction in the adsorption of Pb (II), Cd (II), Ni (II), and Cu (II) onto kaolinite clay when the electrolyte concentration varied from 0.01 to 0.1 M. It has been suggested that increasing the electrolyte concentration can cause the screening of surface negative charges by the electrolyte ions leading to a decrease in the adsorption of the metal ions [209]. Therefore, it may be concluded that the increasing ionic strength made the potential of the adsorbent surface less negative and thus would decrease metal ion adsorption.

The same decreased result in adsorption capacity with increasing electrolyte concentration was also noted in the uptake of trivalent chromium ions from aqueous solutions using kaolinite [210]. The study found that an increased concentration of electrolyte depressed the sorption of Cr (III). This was because ionic strength enters into electrical double layer calculations and affects the coulomb interactions between the charged surface and the sorbing ions through the number of counter ions in the diffuse double layer and the extent of co-ion exclusion.

Recently, the adsorption of Cu (II), Cd (II), and Zn (II) from one and two component systems on the raw and Na-form of kaolin was investigated under batch conditions. The identified homogeneous Langmuirian adsorption on raw kaolin changed after sodium saturation into a heterogenous one [211].

A study covered the synthesis and characterization of low-silica zeolite from calcined kaolin for the adsorption of Zn (II) ions from aqueous solution [212]. It was observed that 40 min was used as the period of contact time, and the sorbent dosage was optimized at 4 g for this study. The results suggested that the obtained zeolite could be converted to a beneficial product that will be used in future as an ion exchanger for removing heavy metals from wastewaters.

The local molecular structure of Cd adsorbed onto kaolinite was examined with X-ray absorption fine structure spectroscopy (XAFS) over a range of pH values and initial Cd solution concentrations [213]. The adsorption mechanism concluded that at pH levels from 4 to 7, Cd (II) was adsorbed as an inner-sphere complex at AlOH edge sites. It can be critically noted that the study failed to determine whether there was a change in the relative importance of Al versus Si edge sites with loading or whether the adsorption of Cd onto edge sites alters binding to other nearby sites or some other factor.

The synthesis of kaolinite at high temperatures is relatively well known, and some studies were conducted to observe the change in adsorption behavior after thermal treatment. The adsorption potential of the kaolinite clay for the removal of lead ions from aqueous solutions was tested [214]. An increase in the retention capacity with increasing temperature was measured. The measured adsorption kinetic data at different temperatures proved that not only intraparticle diffusion controlled the adsorption process but also surface adsorption contributed to the control of the rate of adsorption.

Metakaolinite was obtained from kaolinite obtained from clay soils from the South Western Region of Cameroon by heating 20 g of kaolinite at a heating rate with a temperature of 700 °C and was recently used as an adsorbent to study their adsorptive capacities on the removal of zinc (II) ions [215]. The adsorption mechanism confirmed that the physical and chemical adsorption processes controlled the zinc (II) ion uptake onto the two adsorbents. The quantity adsorbed decreased with an increased adsorbent dose because interactions between the material's particles increased with mass. Throughout this study, it was observed that metakaolinte was an excellent adsorbent compared to kaolinite.

The adsorptive behavior of As (V) ions with kaolinite, montmorillonite, and illite in an aqueous medium as a function of temperature was investigated. An increase in the adsorption temperature resulted in a decrease in the amount of adsorbed As (V) [216]. The results of the leaching study showed that kaolinite was a very active clay constituent regarding both As (V) adsorption and mobility.

The removal of Zn (II) ions from aqueous solution was studied using natural, thermally activated, and acid-activated kaolinite samples at different temperatures [217]. In this study, the Langmuir constants for natural kaolinite were found to be negative; for the other samples, the isotherm models gave a good fit.

Water has been successfully adsorbed onto clay minerals (Kaolinite, Illite, and Montmorillonite clays) as a function of relative humidity (RH) at room temperature (298 K). The application of BET and Freundlich adsorption models was explored to provide complementary multilayer adsorption analysis of water uptake on the clays in this study [218]. However, BET analysis failed to adequately describe the adsorption phenomena at RH values greater than 80%, 50%, and 70% RH for kaolinite, illite, and montmorillonite clays, respectively.

4.3.2. Modified kaolinite

The two stage batch adsorption of Pb (II) ions onto tripolyphosphate-modified kaolinite clay was optimized [219]. The mechanism of this study suggested that Pb (II) ion adsorption possibly took place at the negatively charged O-P-O sites. The presence of up to three negative charged sites per molecule of pentasodiumtripolyphosphate adsorbed onto the kaolinite clay may have contributed to raising the adsorption capacity of the TPP-modified adsorbent.

The competitive adsorptions of Cu (II), Cd (II), and Pb (II) on kaolinite-based clay in the absence and presence of humic acid has been interpreted by the modified Langmuir multisite models [220]. The mechanism of the study revealed that clay mineral in the presence of humic acid most likely behaved more like a chelating sorbent for heavy metal ions than a simple inorganic ion exchanger. The potential for application of sodium polyphosphate (SPP) modified kaolinite clay as an adsorbent for the removal of lead (II), zinc (II), and cadmium (II) ions from aqueous solutions was evaluated. The adsorption of lead, zinc, and cadmium onto SPP kaolinite clay at different temperatures showed an increase in the adsorption capacity with increasing temperature [221].

Modified kaolinite clay with 25% (w/w) aluminum sulfate and unmodified kaolin was used as an adsorbent to remove Pb (II) from an aqueous solution. The results showed that the amount of Pb (II) adsorbed onto modified kaolin (20 mg/g) was more than 4.5-fold than that adsorbed onto unmodified kaolin (4.2 mg/g) under the optimized condition [222].

A recent work addresses the study of adsorption properties of natural raw materials–siderite (S) and kaolin (K) as potential adsorbents of heavy metal cations. To enhance their adsorption capacity, a MnO_2 surface coating was used [223]. Because of the chemical precipitation of MnO_2 particles on the surface of natural samples, their values of specific surface area increased, pointing to enhanced adsorption properties. Nano magnetite (Fe_3O_4) and its composite with kaolinite were synthesized and tested for heavy metal (copper, lead, cadmium, chromium, and nickel) adsorption [224]. The adsorption capacity of the magnetic composite increased over time, and the adsorption increased with increasing pH.

The natural and raw form of kaolinite provided excellent results. In most reported studies, it has been reported that an increase in concentration resulted in an increase in adsorption. The adsorption increased with pH; because of precipitation, it decreased. The optimum pH for adsorption of many metals was in the range of 5–6. It was found, in almost all studies, that the adsorption was initially fast, and equilibrium was reached in a few hours. The percentage adsorption increased with increasing dose. The effect of temperature resulted in increased adsorption with increasing temperature. However, for arsenic adsorption, adsorption decreased with increasing temperature. A decrease in adsorption of metal ions with increasing ionic strength of electrolytes was also noted, implying that increasing ionic strength made the potential of the adsorbent surface less negative and resulted in decreased metal ion adsorption.

The treated and modified forms of kaolinite also pointed towards enhanced adsorption properties.

4.4. Heavy metal removal by vermiculite

Vermiculite in its natural raw form proved to be a potential adsorbent for the adsorption of various toxic metal ions. The potential of vermiculite was assessed for the adsorption of lead (II) from an aqueous solution [225]. The adsorption of Pb (II) was strongly affected by pH. A first order kinetics model best described the reaction rate mechanism, and the adsorption capacity calculated by the model was consistent with the actual measurement. The quantitative desorption of Pb (II) from vermiculite was found to be more than 40%, facilitating the sorption of metal by ion exchange.

It is important to assess the effects of ionic strength when studying the adsorption of metal ions onto clay minerals because the background salt may result in complex metals and compete for adsorption sites. The competitive adsorption behavior of some heavy metal ions such as Cr (III), Cu (II), Ni (II), and Co (II) by vermiculite pure clay mineral was studied [226]. The result showed competition between coexisting heavy metal cations for the same adsorption sites of an adsorbent. However, when a trivalent metal was added to the solution, it competitively replaced divalent ions that had been previously adsorbed onto the vermiculite pure clay mineral, resulting in the desorption of these metals into the solution. In another study, the adsorption behavior of vermiculite has been studied with respect to cadmium, copper, lead, manganese, nickel, and zinc as a function of pH and in the presence of different ligands. In general, the metal uptake onto the clay was hindered by the presence of strong complexing agents in solution and decreases with increasing complexation constants of the ligands, with the exception of cysteine and tiron [227]. The main adsorption mechanisms responsible for the retention of metal ions are sorption by a reaction with the planar sites and consequent formation of outer-sphere complexes and the introduction of metal ions in interlayers.

To compare the adsorption behaviors of Zn (II) and Cd (II) ions in different systems onto vermiculite from buffered and unbuffered aqueous solutions, a study showed that the use of buffer reagents had a strong and negative effect on the adsorption of metal ions [228]. The results obtained suggested that the use of buffer reagents had a negative effect on ion adsorption. Additionally, the experimental data obtained from both the buffered and unbuffered solutions could not be described by a single traditional adsorption isotherm because of the effect of the adsorbent concentration; hence, it can be concluded that the use of a buffer solution is not an effective measure for eliminating the effect of the adsorbent concentration. To evaluate the combined effects of ionic activity, pH, and contact time on the cadmium sorption in three different minerals (vermiculite, zeolite, and pumice), batch experiments were performed [74]. The percentage of cadmium sorption in zeolite and vermiculite did not depend on the cadmium concentration; in pumice, this percentage was positively correlated with the initial cadmium concentration. In a recent study, the single and competitive sorption of Pb (II), Cd (II), Cu (II), and Ni (II) ions onto vermiculite were studied [229]. The quaternary bio sorption experimental results revealed that severe competition exists between metal ions during sorption onto the vermiculite surface; it was inferred that the total metal uptake was distributed among four elements.

The effects of the presence of Ag (I), Ni (II), and Cd (II) ions on the adsorption of Pb (II) ions were investigated in terms of the equilibrium isotherm. Experimental results indicated that Pb (II) ions always favorably adsorbed on vermiculite over Ag (I), Ni (II), and Cd (II) ions [230]. The overall sorption of Pb (II) involved more than one mechanism, such as ion exchange, surface complexation, etc.

To examine the interactions between metal ions and vermiculite, the effect of temperature was conducted in several studies. The removal of cesium from a synthetic aqueous solution through adsorption onto vermiculite at five different temperatures has been investigated [231]. The experiments showed that adsorption equilibrium was reached within 24 h; this was very slow, and critically, it can be concluded that the study has not provided good results because the adsorption of cesium was a slow process. Additionally, the optimum temperature for this adsorption system (T = 75 °C) meant that vermiculite could only be used after thermal treatment at high temperatures.

The influence of temperature on the adsorption of copper on vermiculite and clinoptilolite was examined at three different temperatures (25, 50, and 75 °C) [232]. The comparison has also been made of Cu^{2+} adsorption with other adsorbents. Vermiculite could adsorb copper via two different mechanisms: cation exchange and formation of inner sphere complexes at the clay particle edges. From a critical point of view, the comparison presented in this study has not enabled an exact comparison because operating conditions of the experiment such as temperature, solution pH, and the number of mineral constituents were not same. Wu et al. also investigated the influence of temperature on the adsorption of Zn^{2+} and Cd^{2+} ions onto vermiculite [233]. They concluded that although temperature had a positive effect on the adsorption of Zn^{2+} and Cd^{2+} ions, its effect was statistically negligible over the range from 15 to 45 °C.

The results of several other studies also proved that pure clay mineral vermiculite is a promising adsorbent of different metal ions in aqueous solution [234–240]. Vermiculite was subjected to mechano-chemical treatment using a vibration mill. The mechano-chemical treatment led to a reduction in the particle size and a significant increase in the surface area. The mechano-chemical treatment of vermiculite resulted in a dramatic improvement in the lead (II) adsorption capacity [241].

Modified vermiculite was prepared in the form of a composite to increase its adsorption capacity towards heavy metal ions. The abilities of chitosan-g-poly (acrylic acid)/vermiculite (CTS-g-PAA/VMT) hydrogel composites to remove Pb (II) and Cd (II) ions from aqueous solutions were compared in a study. The adsorption processes were all relatively fast, and over 90% of the total adsorption was reached in approximately 3 min for both Pb(II) and Cd(II) adsorption at 303 K [242]. The adsorption mechanism of Pb (II) and Cd (II) ions by the composite seemed to involve ion exchange, chelation, electrostatic attraction, or adsorption.

Ethylamine modified vermiculite (Ethyl-VER) with a high specific surface area and excellent pore structure was prepared to remove cesium from an aqueous solution. The study found that the adsorption capacity of cesium in an aqueous solution was improved from 56.92 to 78.17 mg g^{-1} after modification [243]. Based on these results, it was concluded that Ethyl-VER, with good surface characteristics and high adsorption capacity, is a suitable adsorbent for cesium removal from aqueous solution.

The manganese oxide-modified vermiculite (Mn-MV) was prepared from raw vermiculite (RV) and was chemically and morphologically characterized before and after silver adsorption. The adsorption surface of RV was increased approximately 10 times after the modification because of the increase in negative charge onto the sorbent surface [244].

A novel approach to prepare adsorbents for Hg (II) uptake from aqueous media based on the grafting of dimercaprol (BAL) containing thiol and hydroxyl groups onto the natural montmorillonite and vermiculite was investigated [245]. The results showed that BAL was successful grafted on montmorillonite and vermiculite surfaces provided plentiful adsorption sites as chelating ligands. The mechanisms of Hg (II) adsorption on these samples could be further explained by ion exchange and electrostatic attraction for Vm and Mt and the formation of complexes for BAL-Vm and BAL-Mt.

It was found in the most reported studies of vermiculite as an adsorbent that an increase in concentration resulted in an increase in adsorption. The adsorption of metal ions on vermiculite decreases with decreasing pH and increasing ionic strength. The optimum pH for adsorption of many metals was in the range of 5–7. It was found to be 9 for cesium because the excess amount of OH^- ions caused a strong attraction between these sites and positively charged Cs ions. In almost all studies, the adsorption was initially fast, and equilibrium was reached in a few hours. The percentage adsorption increased with increasing dose. Increases in temperature caused an increase in the mobility of the ion indicated in the endothermic process. A small increase in heavy metal uptake was also noted with decreased particle size. A small clay particle size seems to be the most suitable to adsorb heavy metals in continuous column systems. The modified forms of vermiculite had a positive effect in the adsorption process and were successfully utilized.

4.5. Heavy metal removal by goethite

Accurate model studies are important for environmental risk assessment and have been used to quantify the adsorption of various heavy metals onto goethite.

The first successful and systematic prediction of the competitive interactions of As (III, V) on goethite using extended triple layer model (ETLM) has been published [246]. Magnesium and calcium significantly enhanced As (V) adsorption at higher pH values, whereas they had little effect on As (III) adsorption. The enhanced adsorption of As (V), however, could not be predicted by the ETLM. Critically, further studies are necessary to identify ternary complexes, particularly at high pH levels.

The adsorption of Cu (II), Zn (II), Cd (II), and Pb (II) onto goethite was enhanced in the presence of sulfate [247]. The metal adsorption onto a pure goethite in SO_4-rich waters was accurately described by the DLM model used in this study. However, when this effect was observed for ferrihydrite, it was not predicted by the diffuse layer model (DLM).

Depending on the pH and Cu^{2+} loading, the binding of Cu ions to the solid phase was enhanced or reduced by the presence of fulvic acid (FA) [248]. A surface complexation model, the Ligand and Charge Distribution (LCD) model, was used to describe Cu binding to the mixture of goethite and FA, but with Ca^{2+}, the LCD model has not resulted in good agreement with experimental results.

In a recent study, a charge distribution multisite surface complexation model (CD-MUSIC) for the adsorption of chromate onto goethite was carefully developed. The results showed that the adsorption of Cr (VI) was minimally influenced by ionic strength, suggesting that an inner-sphere complexation mechanism was involved, and the model developed in this study was applicable for various conditions [249]. The model used in this study is a useful supplement for the surface complexation model database for oxyanions onto goethite surfaces.

A surface sites-species model was used to quantify the adsorption of fluoride and As (V) onto goethite as a function of pH and surface loading [250]. Fluoride and As (V) uptake by goethite decreased with increasing pH at the same surface loading; however, ionic strength had a slight influence on their adsorption. This model can satisfactorily predict their adsorption characteristics with several adsorption constants.

In another study, surface complexation modelling was addressed in Ni (II) and Zn (II) adsorption and competition on goethite surfaces. Adsorption competition was predicted using bidentate surface species with parameters calibrated using single adsorbate data [251].

The determination of the effect of ionic strength in water quality is important. The sorption of As (V) on two commercial iron oxides (hematite and goethite) was studied as a function of ionic strength [252]. The sorption experiments for iron oxides showed that there was no effect of ionic strength on arsenate adsorption, suggesting the formation of an inner sphere surface complex. The formation of colloid particles during goethite dissolution in the alkaline condition decreased the number of surface sites, resulting in decreasing arsenate adsorption.

A novel goethite/silica nanocomposite was tested to be an efficient adsorbent for the removal of As (V) [253]. The adsorption capacity did not change significantly with increasing ionic strength. However, to assess the practical applicability of this adsorbent, further study is needed.

To provide a better understanding of As (V) and Cd transport and useful information on their remediation strategies, their sorption behaviors on goethite were studied by batch experiments [254]. The formation of co-precipitates decreased the mobility of Cd but increased the mobility of As (V) because less As (V) was sorbed on goethite through surface complexation.

A study investigated the influence of low molar mass organic acids, acetic acid, tartaric acid, and citric acid on Cd (II) and Pb (II) adsorption by goethite and montmorillonite [255]. The effects of the acid concentrations on Cd (II) and Pb (II) adsorption were more obvious on goethite than montmorillonite. In the goethite system, Cd (II) adsorption was additionally increased by citric acid and tartaric acid than by acetic acid at low acid concentrations.

The adsorption of both antimony, Sb (III) and Sb (V) onto goethite was studied as a function of pH and Sb concentration [256]. Antimony (III) strongly adsorbed on goethite over a wide pH range (3–12); however, at higher ionic strength, the desorption of Sb (V) was shifted to lower pH values most likely because of the formation of ion pairs $KSb(OH)_6^\circ$. The weak pH-dependence of the rate coefficients suggested that the adsorbed Sb (III) was oxidized by O_2 and that the coordination of Sb (III) to the surface increased the electron density of the Sb atom that enhanced the oxidation process.

An attempt was made to elucidate the mechanism of arsenic (V) adsorption on goethite synthesized from the oxidation of ferrous carbonate [257]. The optimum adsorption pH was found to be 5.0. The value of activation energy, *Ea*, suggested that the initial phase adsorption is diffusion controlled, whereas the latter part is controlled via chemically controlled processes. Though the concept of this variation of *Ea* is not theoretically accepted, the results of this study eventually supported the theory of surface complex formation.

A study was successfully conducted to better understand the temperature changes in the surface acidity of goethite and to evaluate the effect of increasing temperature on the adsorption of arsenate [258]. The adsorption of arsenate onto the goethite surface was exothermic and thus became weaker with increasing temperature. The increase of adsorption efficiency for As along the temperature gradient may serve well as an additional process to prevent ecosystem contamination by As-rich water seepage from geothermal energy generation facilities.

A study reported the adsorption of arsenate, As (V), on goethite and oil-coated goethite at experimental conditions chosen to mimic settings of wastewater released into marine and freshwater

Table 4
Maximum adsorption capacities of various clay minerals towards different adsorbates.

Adsorbent	Adsorbate	Adsorption capacity, qm (mg/g)	References
	Cadmium (II)		
Ball Clay		27.27	[77]
Beidellite		42.00–45.60	[72]
Bentonite methylene bis-acrylamide		416.67	[265]
Hydroxyapatite		142.85	[266]
Kaolinite		6.80	[267]
Montmorillonite		30.70	[267]
Bentonite		11.20	[66]
Montmorillonite		6.30	[66]
Na-Bentonite		30.00	[268]
Kaolinite		11.00	[269]
Ca–montmorillonite with humic acid		14.14	[167]
Sepiolite		5.69	[270]
Attapulgite		10.57	[270]
Smectite		971.00	[271]
Loess modified clay		7.08	[272]
Goethite		29.15	[252]
Illitic Clay		11.25	[273]
Unmodified Kaolinite		12.58	[274]
NTB-modified Kaolinite		44.05	[274]
Pure Smectite		3.87	[68]
Kaolin		41.84	[275]
Smectite		22.17	[276]
	Copper (II)		
ZrO-Montmorillonite		7.10	[277]
Na-bentonite		17.87	[278]
Na-montmorillonite		33.33	[279]
Bentonite polyacromide composite		11.36	[280]
Geothite modified bentonite		9.90	[187]
Humic acid modified bentonite		10.33	[187]
Montmorillonite-Illite		30.99	[145]
Montmorillonite		17.88	[281]
Natural clay		44.84	[67]
Kaolinite		10.78	[269]
Goethite		37.25	[263]
Montmorillonite		13.27	[169]
Functionalised bentonite		45.80	[193]
Kaolinite		4.42	[282]
Mauritanian clays		47.60	[283]
Ca–montmorillonite with humic acid		12.63	[167]
Palygorskite		2.35	[284]
Spent activated clay		10.90	[285]
Pure montmorillonite		33.60	[159]
Modified montmorillonite		48.30	[159]
Montmorillonite		7.61	[169]
Immobilized bentonite		54.07	[286]
Clinoptilolite		13.60	[287]
Siderite		19.80	[223]
Smectite		42.43	[276]
Pottery Glaze		5.78	[135]
	Chromium (III)/(VI)		
Modified Vermiculite		87.72	[288]
Kaolin		11.60	[128]
Ca-montmorillonite with humic acid		12.44	[289]
Alkyl ammonium surfactant-bentonite		8.36	[290]
Spent activated clay		1.42	[124]
Bentonite		4.68	[194]
Bentonite		48.83	[291]
Organo-Bentonite		8.08	[292]
Ball Clay		3.6	[75]
Kaolinite		0.57	[293]
Illite		0.27	[293]
Sepiolite		27.05	[294]
Treated clay		8.77	[123]
Bentonite		13.79	[295]
Micelle-Clay		2.84	[296]
Polyaniline/Montmorillonite composite		308.60	[297]
Natural sepiolite		37.00	[298]
Acid-activated sepiolite		60.00	[298]
Modified Na-montmorillonite		23.69	[299]
Brazilian smectite		97.23	[182]
Escherichia coli supported on kaolin		2.10	[300]
Turkish vermiculite		87.70	[236]
Fe^{2+} modified vermiculite		87.72	[288]
Cellulose-montmorillonite composite		22.20	[129]
GMZ bentonite		40.50	[199]
	Lead (II)		
Ehandiagu clay		0.45	[301]
Sodic-Montmorillonite		121.95	[302]
Jordanian Kaolinite		13.32	[303]
Polyphosphate-modified kaolinite clay		25.13	[221]
Kaolinite		11.50	[267]
Montmorillonite		31.10	[267]
Kaolinite		7.75	[282]
Turkish Illitic clay		238.98	[273]
Smectite		49.56	[276]
Saudi Arabian clays		30.00	[134]
Modified kaolinite clay		82.65	[304]
Goethite		109.20	[263]
Clinoptilolite		27.70	[305]
Tetraborate modified Kaolinite clay		42.92	[274]
Beidellite		24.4	[72]
Clay–PMEA composite		81.02	[306]
Amine functionalised bentonite		110.00	[193]
Tunisian Smectite		75.35	[80]
PVA-modified Kaolinite clay		36.23	[307]
Treated bentonite		110.00	[204]
Bentonite Clay		51.19	[295]
Agbani clay		0.82	[308]
Smectite		3.13	[309]
	Manganese (II)		
Natural clay		11.36	[310]
Montmorillonite		4.80	[66]
Bentonite		6.00	[66]
Kaolinite		0.44	[269]
Kaolinite		149.25	[311]
Bentonite		94.34	[311]
Gabon clay		12.41	[312]
Clinoptilolite		0.07	[313]
Diatomite-perlite composite		100	[314]
Mangolian Clinoptilolite		6.11	[315]
Sepiolite		22.90	[294]
Montmorillonite		16.20	[166]
Sulfuric treated kaolin		1.41	[316]
Bentonite		12.41	[317]
	Mercury (II)		
AEPE-montmorillonite		46.10	[318]
AEPE-hectorite		54.70	[318]
Natural clay		9.70	[319]
Aluminium pillared clay		49.75	[319]
4-aminoantipyrine immobilized bentonite		52.90	[320]
Polymer/organosmectite composites		157.30	[321]
Perlite		0.35	[322]
Amine functionalised bentonite		102.70	[193]
Carboxylate functionalised bentonite		113.00	[193]
Montmorillonite		385.50	[166]
Laterite		3.33	[323]
HMAS Clinoptilolite		20.65	[324]

(*continued on next page*)

Table 4 (*continued*)

Adsorbent	Adsorbate	Adsorption capacity, qm (mg/g)	References
	Zinc(II)		
Natural Bentonite		21.09	[205]
Polyphosphate-modified kaolinite clay		22.83	[221]
Kaolin		250.00	[325]
Montmorillonite		154.60	[166]
Clinoptilolite		0.01	[313]
Kaolinite		4.95	[282]
Turkish clinoptilolite		8.21	[326]
Bentonite		68.49	[327]
Serbian natural clinoptilolite		12.00	[328]
Ca-clinoptilolite		43.09	[329]
Vermiculite		2.64	[330]
Composite E20 bentonite		29.67	[331]
Composite A85 bentonite		14.1	[331]
Bentonite		98.04	[332]
Smectite		42.37	[277]
Sulphate modified bentonite		104.17	[332]
Calcareous Clay		10.96	[333]
Natural clay		80.64	[67]
Kaolinite		4.95	[282]
Chemically treated clay		15.22	[188]
Ca-bentonite		149.00	[334]
Gray clay		12.50	[335]
Brazilian Bentonite		5.09	[336]
	Cobalt(II)		
Fe_3O_4/bentonite nanocomposite		18.76	[337]
Bentonite/Zeolite mixture		2.73	[338]
Kaolinite		11.00	[339]
ZrO-Kaolinite		0.15	[340]
Smectite		6.68	[177]
Attapulgite		138.17	[84]
Bentonite		0.91	[207]
Kaolinite		9.00	[269]
TBA- kaolinite		106.21	[146]
Saudi activated bentonite		7.30	[313]
Goethite		86.60	[263]
Al-pillared bentonite clay		38.61	[341]
Natural Bentonite		25.80	[342]
Chemically treated bentonite		138.10	[189]
	Nickel(II)		
Palygorskite clay		33.40	[343]
NPP-modified bentonite		30.30	[344]
Humic acid immobilized amine polyacrylamide bentonite		2.80	[345]
Bofe bentonite		1.91	[88]
ZrO-kaolinite		8.40	[340]
TBA-kaolinite		15.23	[146]
Chitosan immobilized bentonite		18.70	[346]
Hectorite Clay		28.90	[347]
Montmorillonite		11.20	[267]
Kaolinite		2.10	[267]
Montmorillonite K10		0.90	[348]
Kaolinite		140.84	[70]
Bentonite		92.59	[311]
Montmorillonite		12.88	[169]
Clinoptilolite		1.69	[349]
Sepiolite		2.23	[350]
Clinoptilolite		13.03	[305]
Na-bentonite		13.96	[278]
Ca-bentonite		6.30	[268]
Smectite		6.68	[177]
Sericite		44.00	[351]
Chitosan-clay composite		32.36	[352]
Ca-montmorillonite		4.84	[166]

bodies from oil fields [259]. It was found that the adsorption of As (V) was significantly reduced when goethite is coated with oil. The adsorption mechanism suggested that the mineral surface area remained the main controlling adsorption variable. The results of the study suggested that oil-covered goethite significantly reduced the adsorption of As (V); this points to a potentially significant indirect effect of oil on the cycling of As (V) and other oxyanions in oil-polluted waters.

Goethite, in the form of biogenic goethite, has a high specific surface area and great capacity for the adsorption of many contaminants and hence used the adsorption of Cr^{3+} and Cr (VI) in a study [260]. However, the investigations of SEM/EDS and TEM/EDS indicated that the two ions did not homogeneously adsorb on goethite because of the different microstructures of goethite, indicating that the microstructure of goethite has a great effect on the adsorption.

The adsorption of germanium on goethite was studied at 25 °C in batch reactors as a function of pH, germanium concentration in solution, and solid/solution ratio. The percentage of adsorbed Ge increased with pH at a pH level <9, reached a maximum at a pH level of 9, and slightly decreased when the pH was further increased to 11 [261].

To improve the understanding of how the goethite crystal structure is affected by the incorporation of metals, an investigation was conducted that focused on the incorporation of multiple metals, e.g., Cr, Zn, Cd, and Pb [262]. The results revealed that Cr and Cd had significant positive effects on their mutual incorporation and on the incorporation of Pb in the goethite structure. On the contrary, Zn limited the incorporation of Cr, Cd, and Pb in the goethite structure. Critically, the present study demonstrated that the results from single-metal substituted goethite may not be applied to the natural environment where multiple elements may be associated with goethite.

Goethite was synthesized at pH 3.0, and its cation adsorption behavior was studied for Pb (II), Cd (II), Cu (II), and Co (II) from single and binary aqueous solutions [263]. The Pb (II) loading capacity increased in the presence of Cd (II) or Co (II), whereas it decreased in the presence of Cu (II) in the studied range of concentration variations.

A study also reported the existing competitive adsorption between arsenate and citrate on goethite [264]. It was found that the mechanism of adsorption of arsenate and citrate onto goethite in the presence of one another involved not only competition for binding sites, but cooperation between the two species at the water goethite interface as well.

Several model studies have been used to quantify the adsorption of heavy metals onto goethite for environmental risk assessments. These models can satisfactorily predict the adsorption characteristics of heavy metals onto goethite, as successfully reported in studies. The results showed that the model developed in the studies was applicable for various conditions. The adsorption of metal ions (copper and cadmium) on vermiculite increased with increasing pH; the optimum pH for adsorption of these metals was 6. However, for chromium and arsenic, opposite trends have been observed. The adsorption of these metals decreased with increasing pH, and pH 3 was found to be the optimum pH for adsorption. Ionic strength showed a slight influence on the adsorption of arsenic, and in many cases, it decreased the adsorption. These might be because of the formation of colloids in alkaline pH conditions. The adsorption on goethite was also highly dependent on time and concentration.

Table 4 gives the maximum adsorption capacities of heavy metals conducted on various forms of clays.

For the sake of comparison and to describe the approximate comparative studies on the adsorptive performance of various clay materials with each other, Table 5 shows the maximum adsorption capacities of clay minerals. Based on a comparative study between the maximum adsorption capacities of various clay minerals towards different adsorbates, it can be stated that treated bentonite performed better in the adsorption of cadmium than others. Montmorillonite, in its modified form, showed better adsorption for chromium and mercury in comparison to the others. Kaolin is

Table 5
Maximum adsorptive performance (comparatively) of clay minerals towards different metal ions.

Adsorbate	Adsorbent	Maximum adsorption capacity, qm (mg/g)	Reference
Cadmium (II)	Smectite	971.00	[271]
Chromium (III/VI)	Polyaniline/ Montmorillonite composite	308.60	[297]
Mercury (II)	Montmorillonite	385.50	[166]
Cobalt (II)	Chemically treated bentonite	138.10	[188]
Copper (II)	Immobilized bentonite	54.07	[286]
Zinc (II)	Kaolinite	250.00	[325]
Lead (II)	Illitic clay	238.98	[273]
Nickel (II)	Kaolinite	140.84	[70]
Manganese (II)	Kaolinite	149.25	[311]

better for the adsorption of zinc, nickel, and lead; goethite related studies showed excellent arsenic adsorption. Finally, it can be concluded that the Smectite group (Smectite, MMT, and bentonite), in its treated form, is the optimal group to adsorb several metal ions.

5. Summary, conclusion and future research

Clay minerals have space between their layers, which is the main reason they adsorb toxic metals that are present in water molecules. Most of the clays can swell and increase the space between their layers to accommodate the adsorbed water and ionic species [353]. Many clay adsorbents have been extensively investigated to minimize the use of expensive adsorbents. In most of the reported works, adsorption experiments were conducted by the batch technique to report the maximum adsorption capacities towards targeted pollutants, confirming their applicability and selectivity. Adsorption is one of the most important processes of metal uptake with several properties that take place at the mineral-solute interface. The performance of clay materials and the adsorption process in the reported studies have been verified by examining the effect of various factors such as pH, contact time, initial concentration, temperature, dosage, etc. To determine the adsorption rate, mechanism, and efficiency of clay materials in removing toxic metals from aqueous solution, the parameters of adsorption isotherms, kinetics, thermodynamics, etc., have been demonstrated. Desorption and regeneration studies have been implied by various researchers in the reported studies to determine the application, recovery and reuse of clay adsorbents. To characterize the material, several instrumentation methods such as FTIR, SEM, TEM, XRD, TGA, etc., were used in almost all of the reported studies. Many clay materials have shown their excellent potential for the removal of metal pollutants without any modifications, but in many studies, their removal capacities can be improved through certain chemical modifications as discussed in this review. The adsorption properties, thus, also depend on the extent of chemical treatment, activation, and modification of the adsorbent. The use of nanotechnology to address water problems is a promising application to solve technical problems in removing water pollutants. Nano clays are now in use because they are a natural nanosize material that occurs in the clay fraction of soil; they are a mixture of layered mineral silicates. Nano clay composites such as organically modified montmorillonites or organoclays, polymer-clay nanocomposites, etc., are an attractive class of hybrid organic-inorganic nanomaterials. Nano clay is a matter of an increased interest in research and development around the globe based on their capacity for selective adsorption of molecules and to solve water problems.

Clay, an inexpensive, locally available, and effective adsorbent material, will undoubtedly offer numerous promising benefits in future. The enormous surface area, excellent adsorption capacity, uniqueness, surface charge, richness, physical and physiochemical properties impart tremendous importance to the clay minerals and can be demonstrated in future research. The clay minerals as an adsorbent have usually been studied with regards primarily to adsorbates such as cadmium, copper, lead, zinc, chromium (VI), nickel, etc., and there is comparatively less information in the presented report on the adsorption of inorganic pollutants such as mercury, cobalt, manganese, chromium (III), etc. Another important area to investigate is the interactions between clays and organic pollutants, pesticides, herbicides, radioactive metals, etc. However, clay minerals have shown the applicability to remove metal pollutants; chemical and physical interactions of clays with different varieties of pollutants with the same broad significance can offer further scope. In clay mineralogy, new and improved instrumentation has contributed significantly and advanced new areas of research and is thus needed in this rapid pace of scientific achievement for many new lines of investigation. The synthesis of novel clay materials based on nanotechnology for environmental aspects is one of the future research trends of clay minerals that is likely to be investigated more extensively. Advanced efforts to develop analytical methods for the determination of more accurate, convenient, and reliable quantitative mineral analysis are likely to be made. Further modification and design of Nano clays, metal oxide-delaminated and pillared clays, chemically treated clay mineral surfaces, and composite clay structures will provide potential future applications in water remediation. Hopefully, the reviewed scheme will be sufficiently informative to provide new developments.

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