

Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review

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Abstract

The feasibility of using two important and common clay minerals, kaolinite and montmorillonite, as adsorbents for removal of toxic heavy metals has been reviewed. A good number of works have been reported where the modifications of these natural clays were done to carry the adsorption of metals from aqueous solutions. The modification was predominantly done by pillaring with various polyoxy cations of Zr^{4+} , Al^{3+} , Si^{4+} , Ti^{4+} , Fe^{3+} , Cr^{3+} or Ga^{3+} , etc. Preparation of pillared clays with quaternary ammonium cations, namely, tetramethylammonium-, tetramethylphosphonium- and trimethyl-phenylammonium-, N' -didodecyl- N , N' -tetramethylethanediammonium, etc, are also common. Moreover, the acid treatment of clays often boosted their adsorption capacities. The adsorption of toxic metals, viz., As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Zn, etc., have been studied predominantly. Montmorillonite and its modified forms have much higher metal adsorption capacity compared to that of kaolinite as well as modified-kaolinite.

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Keywords: Kaolinite; Montmorillonite; Modified clay; Heavy metals; Adsorption

Contents

1. Introduction	115
1.1. Clays in the environment	115
1.2. Structural features	115
1.3. Modified clays	116
1.3.1. Intercalation and pillaring	116
1.3.2. Acid activation	117
2. Heavy metal removal by adsorption	117
2.1. Arsenic	118
2.2. Cadmium	118
2.3. Chromium	120
2.4. Cobalt	121
2.5. Copper	122
2.6. Iron	124
2.7. Lead	125
2.8. Manganese	126
2.9. Nickel	127
2.10. Zinc	129
3. Cost comparison of clays with common adsorbents	129

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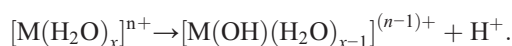
4. Conclusions	130
Acknowledgements	130
References	130

1. Introduction

1.1. Clays in the environment

Clays are hydrous aluminosilicates broadly defined as those minerals that make up the colloid fraction ($<2\ \mu$) of soils, sediments, rocks and water [1] and may be composed of mixtures of fine grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate and metal oxides. Usually the term clay is used for materials that become plastic when mixed with a small amount of water. Clays play an important role in the environment by acting as a natural scavenger of pollutants by taking up cations and anions either through ion exchange or adsorption or both. Thus, clays invariably contain exchangeable cations and anions held to the surface. The prominent cations and anions found on clay surface are Ca^{2+} , Mg^{2+} , H^+ , K^+ , NH_4^+ , Na^+ , and SO_4^{2-} , Cl^- , PO_4^{3-} , NO_3^- . These ions can be exchanged with other ions relatively easily without affecting the clay mineral structure.

Large specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), etc., have made the clays excellent adsorbent materials. Both Brönsted and Lewis type of acidity in clays [2] has boosted the adsorption capacity of clay minerals to a great extent. The Brönsted acidity arises from H^+ ions on the surface, formed by dissociation of water molecules of hydrated exchangeable metal cations on the surface:



The Brönsted acidity may also arise if there is a net negative charge on the surface due to the substitution of Si^{4+} by Al^{3+} in some of the tetrahedral positions and the resultant charge is balanced by H_3O^+ cations. The Lewis acidity arises from exposed trivalent cations, mostly Al^{3+} at the edges, or Al^{3+} arising from rupture of $\text{Si}-\text{O}-\text{Al}$ bonds, or through dehydroxylation of some Brönsted acid sites.

The edges and the faces of clay particles can adsorb anions, cations, non-ionic and polar contaminants from natural water. The contaminants accumulate on clay surface leading to their immobilization through the processes of ion exchange, coordination, or ion–dipole interactions. Sometimes the pollutants can be held through H-bonding, van der Waals interactions or hydrophobic bonding arising from either strong or weak interactions. The strength of the interactions is determined by various structural and other features of the clay mineral. van Olphen [3] has cited several types of active sites in clays, viz., (i) Brönsted acid or proton donor sites, created by interactions of adsorbed or interlayer water molecules, (ii) Lewis acid or electron acceptor sites occurring due to dehydroxylation, (iii) Oxidizing sites, due to

the presence of some cations (e.g. Fe^{3+}) in octahedral positions or due to adsorbed oxygen on surfaces, (iv) Reducing sites produced due to the presence of some cations (e.g. Fe^{2+}), and (v) Surface hydroxyl groups, mostly found in the edges, bound to Si, Al or other octahedral cations.

1.2. Structural features

The structural features of the clays are well established. Kaolinite has a 1:1 layer structure, first suggested by Pauling [4], with the basic unit consisting of a tetrahedral sheet of SiO_4 and an octahedral sheet with Al^{+3} as the octahedral cation. Both the sheets combine to form a common layer such that the tips of the silica tetrahedra point towards the octahedral layer. The tetrahedral layer is inverted over the octahedral layer with the apical 'O' atoms being shared by the two layers (Fig. 1). In the layer common to the octahedral and tetrahedral sheets, two-thirds of the O-atoms are shared between Si and Al atoms. The remaining one-third of the sites in this layer consists of hydroxyl groups coordinated to the octahedral Al atoms alone. Two-thirds of the possible positions in the octahedral sheet are filled with Al and the remaining one-third of the sites is vacant. The Al-atoms are placed in such a manner that any two Al-atoms are separated by two hydroxyl groups — one above and one below; making a hexagonal distribution in a single plane in the centre of the octahedral sheet. The hydroxyl groups are placed directly against the centres of oxygen-hexagons of the basal plane of the tetrahedral layer [5].

Kaolinite, $(\text{Si}_4)^{\text{IV}}(\text{Al}_4)^{\text{VI}}\text{O}_{10}(\text{OH})_8$, has the theoretical composition of SiO_2 46.54%, Al_2O_3 39.50%, H_2O 13.96% expressed in terms of the oxides. The formula indicates that there is no substitution of Si^{4+} with Al^{3+} in the tetrahedral layer and no substitution of Al^{3+} with other ions (e.g., Mg^{2+} , Zn^{2+} , Fe^{2+} , Ca^{2+} ,

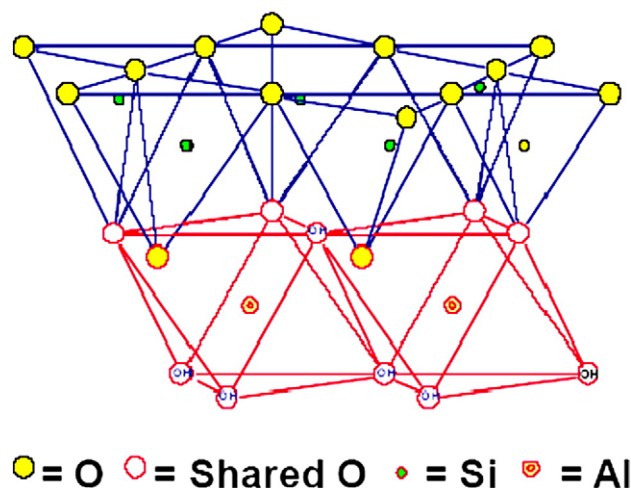


Fig. 1. Structure of kaolinite.

Na^+ or K^+) in the octahedral layer. Thus, the net layer charge of kaolinite is: $[4 (+4)] + [4 (+3)] + [10 (-2)] + [8 (-1)] = 0$, but in nature, kaolinite has a small net negative charge arising from broken edges on the clay crystals. This negative charge, although small, is responsible for the surface not being completely inert. Some workers have also reported substitution of octahedral Al^{3+} with Fe^{2+} and/or Ti^{4+} in kaolinite [6].

Though kaolinite is the least reactive clay [7], its high pH dependency enhances or inhibits the adsorption of metals according to the pH of the environment [8]. The metal adsorption is usually accompanied by the release of hydrogen (H^+) ions from the edge sites of the mineral. Adsorption may also take place on the flat exposed planes of the silica and the alumina sheets [9]. The structure of kaolinite would be affected by adsorption of heavy metals, but the effects are likely to be determined by the mode of use of kaolinite. The displacement of H^+ ions and the adsorption of the cations of Pb(II) , Zn(II) or Cd(II) could create swelling, internal stress, flocculation, a decrease in shear strength and an increase in hydraulic conductivity and compressibility. In addition, the substitution of H^+ ions for metal ions could influence the van der Waals forces within the kaolinite structure. Changes in these properties indicate the creation of empty spaces in the clay structure. Similar spaces could also be produced if the adsorption of metal ions produces a reduction in the van der Waals forces between the elements in kaolinite, but it is not certain exactly how these forces are affected [10].

The structure of montmorillonite was given by Marshall [11]. Montmorillonite is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. The tetrahedral and octahedral sheets combine in such a way that the tips of the tetrahedra of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer (Fig. 2). The atoms in this layer, which are common to both sheets, become oxygen instead of hydroxyl. It is thus referred to as a three-layered clay mineral with T–O–T layers making up the structural unit.

The silica–alumina–silica units are continuous in the ‘a’ and ‘b’ crystallographic directions and are stacked one above the other in the ‘c’ direction. In the stacking of these units, oxygen layers of

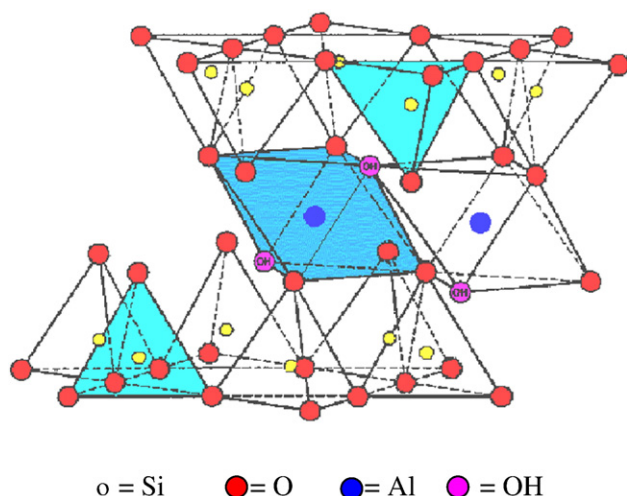


Fig. 2. Structure of montmorillonite.

each unit are adjacent to oxygen of the neighbouring units. This causes a very weak bond and an excellent cleavage between the units. The outstanding feature of this clay structure is that water and other polar molecules can enter between the layers causing the lattice to expand in the ‘c’ direction. Thus, the ‘c’ axis dimension in montmorillonite varies from a minimum value of 9.6 Å when there is no polar molecules between the unit layers and above. The ‘c’ axis spacing also varies with the nature of the interlayer cations present between the silicate layers.

The formula for montmorillonite is $(\text{Si}_{7.8}\text{Al}_{0.2})^{\text{IV}}(\text{Al}_{3.4}\text{Mg}_{0.6})^{\text{VI}}\text{O}_{20}(\text{OH})_4$ and the theoretical composition without the interlayer material is SiO_2 , 66.7%, Al_2O_3 , 28.3%, H_2O , 5%. The above formula indicates that there is substitution of Si^{4+} by Al^{3+} in the tetrahedral layer and of Al^{3+} by Mg^{2+} in the octahedral layer. Thus, the net layer charge of montmorillonite is: $[7.8 (+4)] + [0.2 (+3)] + [3.4 (+3)] + [0.6 (+2)] + [20 (-2)] + [4 (-1)] = -0.8$ charge/unit cell. The resulting negative net charge is balanced by exchangeable cations adsorbed between the unit layers and around their edges.

Montmorillonite is a clay mineral with substantial isomorphic substitution. Exchangeable cations in the 2:1 layers balance the negative charges generated by isomorphic substitution. The uptake kinetics of cation exchange is fast and the cations such as Na^+ and Ca^{2+} form outer-sphere surface complexes, which are easily exchanged with solute ions by varying the cationic composition of the solution. In addition to cation exchange there is a pH-dependent uptake of metals on montmorillonite. In this adsorption process, adsorbate ions are bound to the clay surface by sharing one or several ligands (generally oxygen) with adsorbent cations as isolated complexes. With increasing pH or adsorbate cation concentration, metal precipitation can occur [12]. In the montmorillonite structure, interlayer swelling occurs when it is exposed to water. The swelling procedure depends on valences and atomic radii of the exchangeable cations. Al and Si atoms exposed to the crystallite edges are partially hydrolyzed to silanol (SiOH) and aluminol (AlOH) groups. These unsaturated edge sites are much more reactive than the saturated basal sites [13]. In montmorillonite, adsorption can occur both at the edge sites, which leads to inner-sphere metal complexes, and at the planar (internal) sites of the clay mineral, which results in outer-sphere metal complexes [14].

1.3. Modified clays

There have been various attempts to improve the quality and characteristics of the clays by modifying them with different techniques. Two of the common techniques in this regard are intercalation and pillaring, and acid activation.

1.3.1. Intercalation and pillaring

Intercalation is the insertion of a guest species in the interlayer region of a clay mineral with preservation of the layered structure [15,16]. The material obtained is called intercalated clay. XRD measurements show that intercalation increases the spacing between adjacent layers.

Pillaring of clay minerals by various inorganic as well as organic compounds [16] is well known. In pillared clays, the

two-dimensional silicate layers of thickness of about 1 nm are kept apart by ceramic oxides with a dimension of nano- to subnano-metre sizes [17]. The pillaring process is generally presented as a way of increasing the accessibility of the clay layers, but an alternative viewpoint is that it stabilizes ‘oxide’ particles of nanometre dimension that prevent aggregation by interaction with the layers. The surface groups exposed by these ultradispersed ‘oxides’ probably play a key role in determining the promising adsorptive and catalytic properties of pillared clays [18].

Clays pillared with metal oxides are of great importance because of their high thermal stability, high surface area, and intrinsic catalytic activity. These materials are usually prepared by ion-exchanging cations in the interlayer region of swelling clays with bulky alkylammonium ions, polynuclear complex ions bearing inorganic ligands (hydroxo ligand, chloro ligand), large metal complex ions bearing organic ligands, etc. The intercalated species are capable of preventing the collapse of the interlayer spaces, propping open the layers as pillars, and forming interlayer space. On heating, the intercalated inorganic species are converted to metal oxide clusters, generating a stable microporous structure with a high surface area.

Burch and Warburton [19] introduced Zr-tetramers from fresh zirconyl chloride solution into montmorillonite. Ohtsuka et al. [20] have shown that the zirconium species exist in a number of polynuclear ionic species in zirconium oxychloride solution and pillaring can give three kinds of microporous clays with 7-, 12-, and 14-Å interlayer spacings. The major species in zirconium oxychloride solutions at room temperature has been shown as the zirconium tetramer, $[\text{Zr}_4(\text{OH})_{8+x}(\text{H}_2\text{O})_{16-x}]^{(8-x)+}$, giving the intercalation compound with a 7 Å interlayer spacing. Upon hydrolytic polymerization of the zirconium tetramer in solution, highly polymerized zirconium species are generated that can provide the intercalation compounds with 12 or 14 Å interlayer spacings. The two polymeric species forming the intercalates with 12 and 14 Å interlayer spacing are composed of three-dimensionally polymerized clusters based upon the tetramer. Pereira et al. [21] prepared pillared Zr-montmorillonite in a similar way. Other than Zr^{4+} , the polycations, namely, Al^{3+} , Si^{4+} , Ti^{4+} , Fe^{3+} , Cr^{3+} or Ga^{3+} etc. have also been used as inorganic pillar [17,18,22–25]. Preparation of pillared montmorillonite with quaternary ammonium cations (QACs) of the form $[(\text{CH}_3)_3\text{NR}]^+$ or $[(\text{CH}_3)_3\text{NR}_2]^+$, namely TMA (tetramethylammonium), TMP (tetramethylphosphonium) and TMPA (trimethyl-phenylammonium) cations has also been reported [26,27]. Preparation of N, N'-didodecyl-N, N'-tetramethylethanediammonium (DEDMA) montmorillonite has been reported recently [28].

A pillared clay is distinguished from an ordinary intercalate by virtue of intracrystalline porosity made possible by the lateral separation of the intercalated guest molecules. In fact, the intercalated clays undergo calcination at a moderately high temperature (such as 773 K) in order to transform the polyoxocations to metal oxidic particles cross-linked to the clay lamellae, thus preventing the collapse of the interlayer space and generating a stable porous structure [24].

1.3.2. Acid activation

Treatments of clay minerals with inorganic acids of rather high concentration and usually at high temperature are known as acid activation. Acid treatments of clay minerals are an important control over mineral weathering and genesis [29,30]. Such treatments can often replace exchangeable cations with H^+ ions and Al^{3+} and other cations escape out of both tetrahedral and octahedral sites, leaving SiO_4 groups largely intact [31]. This process generally increases the surface area and acidity of the clay minerals [32], along with the elimination of several mineral impurities and partial dissolution of the external layers. The change of surface area and porous structure of the clays due to acid treatment depends on the particular clay mineral, and also on other clay minerals and non-clay minerals present, and the overall chemical composition, the type of cations between the layers, the type of the acid, the process temperature and the process period, and other environmental factors [33].

The depopulation of the octahedral layer of montmorillonite has been reported as leading to different levels of structural decomposition depending on individual resistance to acid attack of the initial clay minerals [34]. On acid attack, the crystalline structure of kaolinite is transformed thermally to amorphous metakaolin and the octahedral Al^{3+} ions are preferentially released from the clay structure leading to formation of additional Al–OH and Si–OH bonds, without changing the original mineral structure [7]. It has been reported that acid activation followed by thermal treatment increases the adsorption capacity to a good extent [35]. Due to complex changes of clay minerals in acid environments, their surface properties are also modified [36]. Christidis et al. [37] have reported that treatment of bentonite with hydrochloric acid leads to an increase of surface area of the raw clays by as much as five times. The increase may be caused by production of finely dispersed silicon oxide from destruction of mineral structures, removal of amorphous Al or silica components, plugging surface pores or interlamellar spaces, formation of cracks and voids in the surface [36]. After acid attack, the number of weakly acidic surface functional groups is observed to increase while the number of groups of stronger acidic character shows decreases [38].

2. Heavy metal removal by adsorption

The metals of major environmental concern today are arsenic, cadmium, chromium, cobalt, copper, lead, manganese, mercury, nickel and zinc. A few familiar methods in practice for removal of these and other metals are chemical precipitation, ion exchange, solvent extraction, reverse osmosis, adsorption, etc. Reverse osmosis, although very effective, is a cost-prohibitive process as the membranes get easily spoiled requiring frequent replacement. Chemical precipitation is not very suitable when the pollutants are present in trace amounts and also a large amount of sludge is produced. Ion exchange is expensive and sophisticated. Solvent extraction or electrolytic processes are also available but they are considered to be cost-effective only for more concentrated solutions. The process of adsorption has become one of the preferred methods for removal of toxic contaminants from water as it has been found to be very effective, economical, versatile and

simple [39]. Adsorption has the additional advantages of applicability at very low concentrations, suitability for using batch and continuous processes, ease of operation, little sludge generation, possibility of regeneration and reuse, and low capital cost [40]. The processes have acquired global importance for minimization of the problem of contamination of water and air, and these processes have become a significant addition to Green Chemistry endeavours.

Mondal et al. [41] have recently reviewed arsenic remediation techniques like precipitation with alum, iron, Fe/Mn, lime softening, reverse osmosis, electro-dialysis, ion exchange, adsorption on activated alumina/carbon, etc. and compared the techniques with respect to their efficiencies. Recent developments in various arsenic removal techniques including modifications and advances in conventional techniques have also been reviewed. Arsenic remediation by the adsorption process has also been reviewed by Mohan and Pittman [42]. Arsenic adsorption on commercially available carbons and other low-cost adsorbents was surveyed and critically reviewed by these authors. The adsorption efficiencies of the different types of adsorbents for arsenic were compared and the adsorption behaviour in presence of various impurities was discussed. Low-cost adsorbents, viz., treated slags, carbons developed from agricultural waste, biosorbents (immobilized biomass, orange juice residue), goethite and commercial adsorbents like resins, gels, silica, etc. were found to have excellent ability for arsenic removal, sometimes superior to commercial adsorbents. Gerente et al. [43] have presented value-added applications of chitin and chitosan as highly potent materials to remove metal ions from wastewaters. Developments in chitosan research with particular interests for scavenging and recovering metal ions have been highlighted in this work. The current status of adsorption research for a variety of metals by geomedia ranging from individual minerals to sediments and soils has been reviewed in a recent volume edited by Jenne [44]. The different adsorption mechanisms and the factors affecting the uptake of metals have been reviewed with respect to the effects of selected anions, competition among metals, pH, metal concentration, loading, variable metal adsorption capacity, ionic strength, etc. A variety of adsorption models have been briefly introduced with a view to extend the laboratory studies to field.

Technical feasibility of using various low-cost adsorbents for heavy metal removal from contaminated water has also been reviewed earlier [45]. Some of the materials reviewed were commercial activated carbon, various inexpensive materials such as chitosan, zeolites, clay, peat moss, fly ash, coal, aluminium oxide, waste slurry, etc. The activities of these adsorbents for treating effluents contaminated with Cd(II), Co(II), Cr(III), Cr(VI), Cu(II), Fe(II), Hg(II), Ni(II), Pb(II), Zn(II), etc. were discussed and compared. The adsorption capacities of the adsorbents varied, depending on the characteristics of the individual adsorbents, the extent of chemical modifications, and the concentration of adsorbate.

Clays and their modified forms have received wide attention recently for use as adsorbents of metal ions from aqueous medium because of their easy availability and comparatively less cost. Results obtained with respect to heavy metal removal by clays, kaolinite and montmorillonite in particular, are reviewed below.

2.1. Arsenic

Adsorption of As(III) or As(V) in the form of anions in aqueous solution has not been much investigated by the clay scientist. However, in one of the notable works, kaolinite intercalated with hexadecyltrimethylammonium ions [46] has been tried as an effective adsorbent for arsenate. The interactions have yielded a Langmuir adsorption capacity and adsorption affinity of 7.0 mmol kg^{-1} and 6.0 L mmol^{-1} respectively ($r^2=0.998$). It is shown that arsenate is retained by the intercalated kaolinite by an ion exchange mechanism.

Various other adsorbents have, however, been used for removal of As(III) and As(V) from aqueous solution. Say et al. [47] used fungus *Penicillium purpurogenum* for As(III) adsorption with the adsorption capacity of 35.6 mg g^{-1} . Orange juice residue has also been found to be effective with maximum adsorption capacity for As(V) and As(III) of 9.4 and 9.1 mmol kg^{-1} at optimum pH values of 3.1 and 10.0, respectively [48]. Polymetallic sea nodules on the other hand had adsorption capacities of 0.31 and 10.2 mg g^{-1} [49] for As(III) and As(V) respectively. Gupta et al. [50] have even tried oxide-coated and uncoated sand for adsorption of As(III). The oxide-coated sand was the more effective one with adsorption capacity of $28.57 \text{ } \mu\text{g g}^{-1}$ compared to the uncoated sand (capacity $5.63 \text{ } \mu\text{g g}^{-1}$).

2.2. Cadmium

Sen Gupta and Bhattacharyya [51] used kaolinite, montmorillonite along with their poly(oxo zirconium) and tetrabutylammonium derivatives and also the activated forms of kaolinite and montmorillonite [52] for Cd(II) removal from water. The adsorption of Cd(II) was influenced by pH of the aqueous medium and the amount adsorbed increased with gradually decreasing acidity. By increasing the solution pH from 1.0 to 10.0, the extent of adsorption increased from 4.3 to 29.5% for kaolinite, 4.1 to 27.6% for ZrO-kaolinite, 4.2 to 28.0% for TBA-kaolinite, 10.1 to 39.1% for acid-activated kaolinite, 74.7 to 94.5% for montmorillonite, 39.6 to 64.8% for ZrO-montmorillonite, 57.7 to 81.0% for TBA-montmorillonite and 82.5 to 99.3% for acid-activated montmorillonite.

Usually montmorillonite has a very large adsorption capacity compared to that of kaolinite, the values may be as much as three times or more. This can be seen from some of the values available in the literature for Cd(II) adsorption on clays (Table 1). Thus, while the Langmuir monolayer capacity varies between 3.0 (kaolinite) and 11.4 mg g^{-1} (acid-activated kaolinite) for kaolinite, the same values for montmorillonite are from 26.2 (Na-bentonite) to 33.2 mg g^{-1} (acid-activated montmorillonite). Acid activation and pillaring do not change the adsorption capacity to a very large extent.

Na- and Ca-exchanged bentonites have also been used for removal of Cd(II) from aqueous solutions and the results closely follow the Langmuir model of adsorption [53]. The adsorption capacity of Ca-bentonite was found to be lower than that of Na-bentonite (Table 1), as Ca-bentonite possesses lower H^+ adsorption capacity implying less metal hydroxide precipitation. The lower cation exchange capacity (CEC) and the higher

Table 1

Adsorption capacities of clays and some other adsorbents for Cd(II) (units of Langmuir capacity and Freundlich capacity are mg g^{-1} and $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ respectively)

	Adsorbent	Langmuir capacity	Freundlich capacity	References
Clay adsorbents	Kaolinite	9.9	0.5	[51]
	ZrO-kaolinite	9.7	0.4	
	TBA-kaolinite	9.8	0.5	
	Montmorillonite	32.7	8.6	[52]
	ZrO-montmorillonite	27.7	2.5	
	TBA-montmorillonite	30.0	4.4	
	Acid-activated kaolinite	11.4	0.8	[53]
	Acid-activated montmorillonite	33.2	12.9	
	Na-bentonite	26.2	–	
	Ca-bentonite	7.3	–	[54]
	Kaolin	3.0	–	
	Bentonite	9.3	–	
Other adsorbents	Low-grade phosphate	7.5	1.7	[58]
	Red mud	10.6	–	[60]
	Bagasse fly ash	2.0	1.3	[61]
	Juniper fiber	9.2	–	[62]
	Base-treated juniper fiber	29.5	–	

charge of Ca^{2+} may also be responsible for the decreased retention. The process, favoured by increasing pH, has been found to be very rapid with >95% uptake in 30 min. The adsorption of Cd(II) on kaolinite and bentonite has been reported by Ulmanu et al. [54].

Cd(II) adsorption has been investigated on hydroxy-aluminium-pillared montmorillonite as well as unpillared montmorillonite [55]. The experimental data follow the Freundlich equation very well ($R^2=0.98$ to 0.99) with adsorption capacities of 3775.5 and $507.0 \mu\text{M}^{1-n} \text{kg}^{-1} \text{L}^n$ for unpillared and pillared clays, respectively. Pillared montmorillonite has a lower uptake of Cd(II) than the unpillared montmorillonite at all concentrations at $\sim\text{pH } 6$, but the uptake increases as the medium turns towards alkaline.

Cd(II)-clay interactions took place through sufficiently strong endothermic interactions accompanied by thermodynamically favorable entropy and Gibbs energy changes [51]. The mean enthalpy values for kaolinite-Cd(II) and montmorillonite-Cd(II) interactions vary respectively from 25.0 to 35.2 kJ mol^{-1} and 13.8 to 40.2 kJ mol^{-1} (Table 2). The corresponding mean adsorption entropy values vary in the range of 66.3 to $96.1 \text{ J K}^{-1} \text{ mol}^{-1}$ and 43.4 to $147.5 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively for adsorption of Cd(II) on kaolinites and montmorillonites.

The influence of temperature (from 283 to 343 K) on adsorption of Cd(II) on kaolinite has been investigated by Angove et al. [56]. The adsorption isotherms follow Langmuir model at all temperatures ($\text{pH } 5.5$). From the values of thermodynamic parameters, these authors have also shown the process of adsorption of Cd(II) on clays to be endothermic driven by an entropy increase.

Although acid activation does not have much influence on the Langmuir monolayer capacity of the clays and the modified clays, an increase in the overall adsorption of Cd(II) has been observed [52]. At 303 K , 1 g of kaolinite can adsorb 15.9 mg of Cd(II) from an aqueous solution containing 50 mg Cd(II)/L . This value increases to 21.4 mg for the acid-activated kaolinite. Under the same set of experimental conditions, 1 g of

montmorillonite and acid-activated montmorillonite can adsorb 86.4 and 92.1 mg of Cd(II). The influence of amount of clay and initial Cd(II) concentration on adsorption of Cd(II) is shown in Fig. 3.

A few of the adsorbents used for Cd(II) removal from water are shown in Table 1. Adsorption of Cd(II) on perlite followed the Freundlich isotherm model, where a value of 0.6 mg g^{-1} was obtained as the adsorption capacity [57]. Kandah [58] used low-grade phosphate for Cd(II) adsorption where both Freundlich and Langmuir adsorption models were applied for data analysis. The Freundlich adsorption capacity and the Langmuir adsorption capacity were obtained as 1.7 and 7.5 mg g^{-1} , respectively. The adsorption characteristics of Cd(II) on river bed sediments had been investigated by Jain and Sharma [59]. For the sediment fraction of $0-75 \mu\text{m}$, q_m and K_f were measured as 5.0 mg g^{-1} and 0.043 mg g^{-1} respectively, but the values changed to 5.9 mg g^{-1} and 0.034 mg g^{-1} respectively when the sediment fraction of $210-250 \mu\text{m}$ was used. The adsorption of Cd(II) on red mud fitted Langmuir isotherm model having a maximum adsorption capacity of 10.57 mg g^{-1} [60]. Gupta et al. [61] used bagasse fly ash (a sugar industry

Table 2

Thermodynamic data for adsorption of Cd(II) on clays (clay 2 g/L , Cd(II) $10, 20, 30, 40, 50 \text{ mg/L}$, $\text{pH } 5.5$, time 240 min ; units of ΔH , ΔS and ΔG are kJ mol^{-1} , $\text{J K}^{-1} \text{ mol}^{-1}$ and kJ mol^{-1} respectively)

Clay adsorbents	ΔH	ΔS	$-\Delta G$			Reference
			303 K	308 K	313 K	
Kaolinite	25.0	66.3	20.0	20.4	20.7	[51]
ZrO-kaolinite	35.2	96.1	29.1	29.6	30.0	
TBA-kaolinite	31.1	85.9	25.9	26.4	26.9	
Montmorillonite	40.2	147.5	44.6	45.4	46.1	[52]
ZrO-montmorillonite	13.8	43.4	13.1	13.4	13.6	
TBA-montmorillonite	19.3	68.2	20.7	21.0	21.3	
Acid-activated kaolinite	8.6	14.3	4.3	4.4	4.5	
Acid-activated montmorillonite	25.0	107.3	32.5	33.0	33.6	

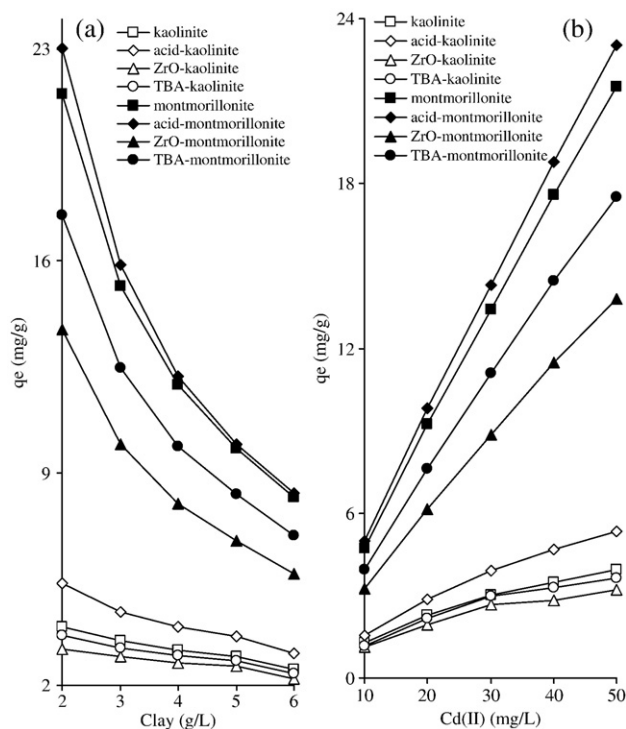


Fig. 3. Adsorption of Cd(II) on natural and modified kaolinite and montmorillonite at 303 K (a) Influence of clay amount on amount of Cd(II) adsorbed per unit mass of clays (Cd(III) 50 mg/L, pH 4.6, time 240 min), (b) Influence of initial concentration on amount of Cd(II) adsorbed per unit mass of clays (clay 2 g/L, pH 4.6, time 240 min) [51,52].

waste) for removal of Cd(II) and the process followed the Langmuir model better than the Freundlich model. It was reported that in the temperature range of 30 to 50 °C, the values of K_F , q_m and b varied from 1.20 to 1.26, 1.24 to 2.00 mg g⁻¹ and 5.67 to 7.14 respectively. Min et al. [62] used juniper fiber (a small-diameter underutilized lignocellulosic material) along with its base-treated forms for adsorption of Cd(II). The base treatment enhanced the Cd(II) uptake and the Langmuir adsorption capacity increased from 9.2 mg g⁻¹ (untreated fiber) to 29.5 mg g⁻¹ (treated fiber).

2.3. Chromium

The removal of Cr(III) and Cr(VI) by bentonite was reported by Khan et al. [63]. Cr(III) adsorption at pH 3.5 (at 303 K) was almost instantaneous, but at pH 2.0, the uptake of Cr(VI) was very rapid. Alvarez-Ayuso and Garcia-Sanchez [53] have used Na-exchanged bentonite and Ca-exchanged bentonite for the removal of Cr(III) from aqueous solution with the Langmuir adsorption capacities of 49.8 mg g⁻¹ and 44.4 mg g⁻¹ respectively. There is reduced Cr(III) adsorption at low pHs, but adsorption increases at higher pHs, which could be due to metal hydroxide precipitation helping Cr(III) retention by the clay. A very similar pH-dependence has also been observed with respect to adsorption of Cr(VI) on kaolinite, acid-activated kaolinite, ZrO-kaolinite and TBA-kaolinite by Bhattacharyya and Sen Gupta [64]. Adsorption peaks around pH 7.0 with

declining trends on both sides of this pH (Table 3). It is suggested that formation of hydroxyl complexes of chromium, Cr(OH)₃, at pH > 7.0 is likely to hinder the diffusion of Cr(VI) ions to the clay surface and therefore, reduction in adsorption is observed.

The adsorption of Cr(III) on ion-exchanged bentonites [53] is observed to be in excess of the cation exchange capacity (CEC) of the clays and since this could not be attributed to broken bonds alone at the edges of the clay minerals, some other factors like precipitation of hydroxide, etc. might have been working simultaneously.

The interactions of Cr(VI) is fast initially, but the equilibrium is reached only after an appreciable length of time. Thus, although maximum adsorption of Cr(VI) is attained within 40 min, the equilibrium could be attained only after 240 min [64]. As the interaction time increases from 40 to 240 min, Cr(VI) adsorption changes from 16.1 to 24.3% for kaolinite, 24.1 to 31.9% for acid-activated kaolinite, 13.8 to 22.3% for ZrO-kaolinite and 12.9 to 21.5% for TBA-kaolinite (Clay 2 g/L, Cr(VI) 50 mg/L). At equilibrium, kaolinite, acid-activated kaolinite, ZrO-kaolinite and TBA-kaolinite retain 23.3, 31.9, 22.2 and 21.5% of Cr(VI), respectively. The equilibrium adsorption capacity is similar except for the acid-activated kaolinite. This is also reflected in the Langmuir monolayer capacity values of 11.6, 13.9, 10.9 and 10.6 mg g⁻¹ for kaolinite, acid-activated kaolinite, ZrO-kaolinite and TBA-kaolinite, respectively (Table 4). Fig. 4 shows how the four clay adsorbents differ from one another with respect to the amount of Cr(VI) adsorbed per unit mass.

Khan et al. [63] have found that Cr(III) is exothermically adsorbed on bentonite, but Cr(VI)-bentonite interactions are endothermic. The spontaneity of the adsorption process is ensured by decreasing Gibbs energy. The adsorption enthalpy has been measured at -51.9 and +5.6 kJ mol⁻¹ for Cr(III) and Cr(VI) respectively. The corresponding adsorption entropy is -0.15 and +0.02 J K⁻¹ mol⁻¹. Similar observations have been made by Bhattacharyya and Sen Gupta [64] by showing Cr(VI)-kaolinites interactions to be endothermic with an increase in entropy and decrease in Gibbs energy (Table 5). Acid activation

Table 3

Influence of pH on Cr(VI) adsorption by kaolinite and modified kaolinite (clay 2 g/L, Cr(VI) 50 mg/L, time 240 min, temperature 303 K) [64]

pH	Kaolinite		Acid-activated kaolinite		ZrO-kaolinite		TBA-kaolinite	
	%	q_e (mg g ⁻¹)	%	q_e (mg g ⁻¹)	%	q_e (mg g ⁻¹)	%	q_e (mg g ⁻¹)
1.0	12.1	3.6	19.3	5.5	10.2	3.1	9.1	2.8
2.0	14.6	3.7	22.2	5.6	12.7	3.2	11.4	2.9
3.0	19.7	4.9	27.1	6.8	17.6	4.4	16.6	4.2
4.0	22.7	5.7	30.3	7.6	20.5	5.1	22.7	4.9
5.0	25.9	6.5	33.3	8.3	23.6	5.9	25.5	5.7
6.0	28.8	7.2	36.0	9.0	26.5	6.6	28.4	6.4
7.0	31.9	8.0	39.2	9.8	29.3	7.3	25.6	7.1
8.0	29.4	7.0	36.5	8.5	26.1	6.2	22.0	6.0
9.0	26.3	6.7	33.6	8.4	22.8	5.7	19.0	5.5
10.0	23.0	5.8	30.1	7.5	19.3	4.8	19.1	4.6

Table 4

Adsorption capacities of clays and some other adsorbents for Cr(III)/Cr(VI) (units of Langmuir capacity is mg g^{-1})

	Adsorbents	Langmuir capacity		Reference
		Cr(III)	Cr(VI)	
Clay adsorbents	Na-bentonite	49.8	–	[53]
	Ca-bentonite	44.4	–	
	Kaolinite	–	11.6	[64]
	Acid-activated kaolinite	–	13.9	
	ZrO-kaolinite	–	10.9	
	TBA-kaolinite	–	10.6	
Other adsorbents	Wool	–	41.2	[65]
	Saw dust	–	15.8	
	Almond shell	–	1.6	
	Coal	–	6.8	
	Cactus	–	7.1	[66]
	Coconut shell carbon (CSC)	–	2.2	
	CSC-oxidised with H_2SO_4	–	4.1	
	CSC-oxidised with HNO_3	–	10.9	
	Commercial activated carbon (CAC)	–	4.7	[67]
	CAC-oxidised with H_2SO_4	–	8.9	
	CAC-oxidised with HNO_3	–	10.4	
	Fly ash	–	1.4	
	Al impregnated fly ash	–	1.8	
	Fe-impregnated fly ash	–	1.7	

increases the mean enthalpy and mean entropy compared to the parent kaolinite as well as the ZrO- and TBA-derivatives.

Similar ranges of adsorption coefficients for Cr(III)/Cr(VI) on various adsorbents are common in literature (Table 4). Dakiky et al. [65] used low-cost adsorbents such as wool, olive

Table 5

Thermodynamic parameters for Cr(VI) adsorption on kaolinite and modified kaolinite (clay 2 g/L, Cr(VI) 10, 20, 30, 40, 50 mg/L , time 240 min, units of ΔH , ΔS and ΔG are kJ mol^{-1} , $\text{J K}^{-1} \text{mol}^{-1}$ and kJ mol^{-1} respectively) [64]

Clay adsorbents	ΔH	ΔS	$-\Delta G$		
			303 K	308 K	313 K
Kaolinite	30.4	88.4	26.8	27.2	27.6
Acid-activated kaolinite	63.9	198.1	59.9	60.9	61.9
ZrO-kaolinite	30.5	87.8	26.5	27.0	27.5
TBA-kaolinite	32.1	92.5	28.0	28.4	28.9

cake, sawdust, pine needles, almond, coal and cactus at 303 K and pH 2.0 for adsorption of Cr(VI) and reported q_m values from 6.78 to 41.15 mg g^{-1} and K_f from 0.094 to 2.23 L g^{-1} . Babel and Kurniawan [66] studied Cr(VI) adsorption on coconut shell charcoal and commercial activated carbon (modified with oxidizing agents and chitosan) and reported the q_m , b , R_L and k_f values in the range of 2.18 to 10.88, 0.209 to 0.149, 0.161 to 0.217 and 0.61 to 1.84 respectively. The adsorption of Cr(VI) on fly ash (FA) and Al- and Fe-impregnated fly ash received attention of Banerjee et al. [67] and the materials were shown to have Langmuir adsorption capacities of 1.379, 1.820, and 1.667 mg g^{-1} , respectively. Removal of Cr(III) by ion-exchange resins, namely, Amberjet 1200H, Amberjet 1500H and Amberlite IRN97H showed adsorption capacities of 84.04, 188.67 and 58.14 mg g^{-1} , respectively [68].

2.4. Cobalt

The influence of temperature (283 to 343 K) on adsorption of Co(II) on kaolinite was studied by Angove et al. [56] who found that the experimental data fit the Langmuir model at all temperatures. The use of raw kaolin for removing Co(II) from aqueous solution [69] has yielded Langmuir monolayer capacities of 1.5 mg g^{-1} at 313 K. Bhattacharyya and Sen Gupta [70] have obtained a similar Langmuir adsorption capacity value of 11.2 mg g^{-1} for kaolinite, but the values for acid-activated kaolinite, montmorillonite and acid-activated montmorillonite (12.1, 28.6 and 29.7 mg g^{-1} respectively) are substantially large. A comparison of Langmuir adsorption capacities of kaolinite and montmorillonite with that of acid-activated kaolinite and acid-activated montmorillonite is given in Table 6. Acid activation of the clays has been found to have a positive influence on their adsorption capacities.

Yavuz et al. [69] have proposed first order kinetics with rate coefficients of $2.4 \times 10^{-3} \text{ min}^{-1}$ at 298 K and $3.8 \times 10^{-3} \text{ min}^{-1}$ at 313 K for Co(II)-kaolinite interactions. In a more detailed study, Bhattacharyya and Sen Gupta [70] have tested a number of models, starting from Lagergren first order kinetics to second order model, Elovich equation, intra-particle diffusion mechanism and liquid film diffusion model for Co(II)-clay interactions and have observed that the second order model gives the best fit with the experimental results. The second order rate coefficient has values of 2.5×10^{-2} , 2.5×10^{-2} , 4.6×10^{-2} , $5.4 \times 10^{-2} \text{ g mg}^{-1} \text{ min}^{-1}$ respectively for Co(II) interactions with kaolinite, acid-activated kaolinite, montmorillonite and acid-

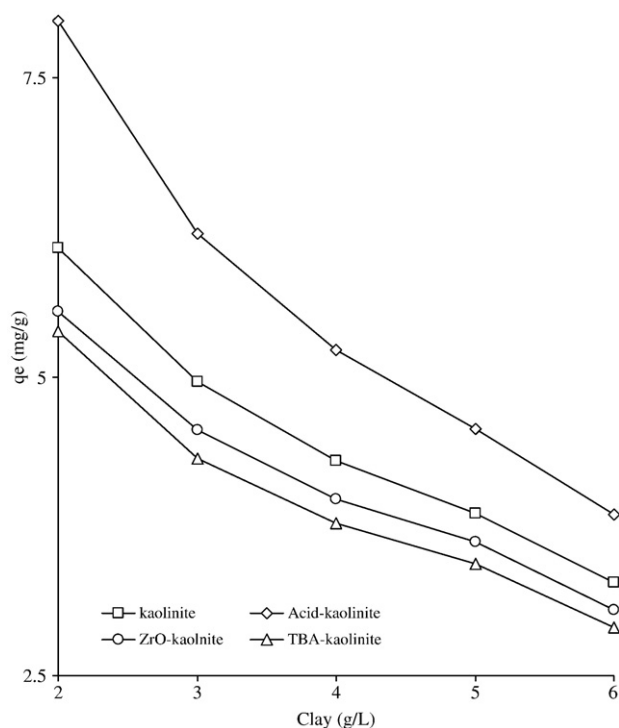


Fig. 4. Influence of adsorbent amount on adsorption of Cr(VI) on natural and modified kaolinite at 303 K (initial Cr(VI) 50 mg/L , pH 4.6, time 240 min) [64].

Table 6

Adsorption capacities of clays and some other adsorbents for Co(II) (units of Langmuir capacity and Freundlich capacity are mg g^{-1} and $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ respectively)

	Adsorbents	Equilibrium time (min)	Langmuir capacity	Freundlich capacity	Reference
Clay adsorbents	Raw kaolinite	120	1.5	–	[69]
	Kaolinite	240	11.2	1.1	[70]
	Acid-activated kaolinite		12.1	1.5	
	Montmorillonite		28.6	4.6	
	Acid-activated Montmorillonite		29.7	6.0	
Other adsorbents	Mg-pellets	–	15.8	–	[71]
	Cation-exchange resin	200	–	75.6	[72]

activated montmorillonite. It is also observed that at low surface coverages, equilibrium is reached within 240 min.

For a fixed amount of clay, adsorption is not only dependent on the initial Co(II) concentration (Fig. 5), but is also influenced by pH of the aqueous solution in the range of 1.0 to 8.0 [70]. However, the experiments could not be carried out beyond pH 8.0 as the solubility of Co(II) rapidly decreases resulting in separation by precipitation.

Thermodynamically, Co(II)-kaolinite interactions have been found to be endothermic [69,70] accompanied by entropy increase (Table 7). This has also been found to be true for adsorption on acid-activated kaolinite, but in case of montmorillonite and acid-activated montmorillonite, the interactions are exothermic [70]. The endothermic interactions are supported by considerable entropy increase indicating an increased state of randomness at the solid-solution interface following adsorption. These are most likely to be due to structural changes and adjustments in the adsorbate as well as the adsorbent as the adsorption proceeds. The structural changes arise from the release of ions like H^+ and K^+ from the clay surface into the solution and also from partial de-solvation of the metal ions. Since stability is associated with an ordered arrangement, it is obvious that Co(II) ions are in a much more chaotic distribution in aqueous solution than when they are adsorbed on montmorillonite or acid-activated montmorillonite.

Use of adsorbents like Mg pellets has also been reported for Co(II) removal from water [71] and the adsorption capacity has been found to be 15.8 mg g^{-1} . Rengaraj et al. [72] used IRN77 cation-exchange resin for Co(II) adsorption with the Freundlich adsorption capacity, K_f of 75.63 (Table 6).

2.5. Copper

Adsorption of Cu(II) on raw kaolinite has been shown to follow Langmuir isotherm with a maximum adsorption capacity of 11.0 mg g^{-1} [69]. The retention of Cu(II) on Na-bentonite and Ca-bentonite was favoured by increase of pH with maximum Langmuir capacities of 30.0 and 7.7 mg g^{-1} , respectively [53]. Lin and Juang [73] tried to modify the adsorptive properties of montmorillonite by introducing sodium dodecylsulfate before adsorbing Cu(II) and adsorption increased with the solution pH. However, Langmuir adsorption capacity of 0.02 mg g^{-1} for the modified montmorillonite did not show significant increase in the number of adsorption sites. De Leon et al. [74] have found a Langmuir monolayer adsorption capacity of 110.0 mg g^{-1} for

adsorption of Cu(II) on a 1:10 phenanthroline-grafted Brazilian bentonite. Zeng and Jiang [75] tried to modify bentonite and montmorillonite with incorporation of various polymeric species like Fe/Al, HDTMA (hexadecyltrimethylammonium ions), and Fe/Al-HDTMA for finding suitable adsorbents for Cu(II), and found that the Freundlich adsorption capacities were in the order of raw clay without treatment > Fe/Al-HDTMA modified clay > HDTMA modified clay > raw clay after pretreatment > Fe/Al modified clay. The modified clays had a maximum uptake $\sim 110 \text{ mg g}^{-1}$ for Cu(II), which was almost 10 times more compared to the untreated bentonite.

Cu(II) adsorption on natural kaolinite is sensitive to the variation of pH over the range 2.0–6.0 [76]. At pH 2.0, the maximum removal efficiency was 38.46%, whereas at pH 6.0, the removal efficiency increased to 75.27%. The relative variation of the removal efficiency in the pH range 2.0–6.0 was 95.7%. As the adsorbent concentration increased from 0.25 to 5.0 g/L, the equilibrium adsorption capacity decreased from

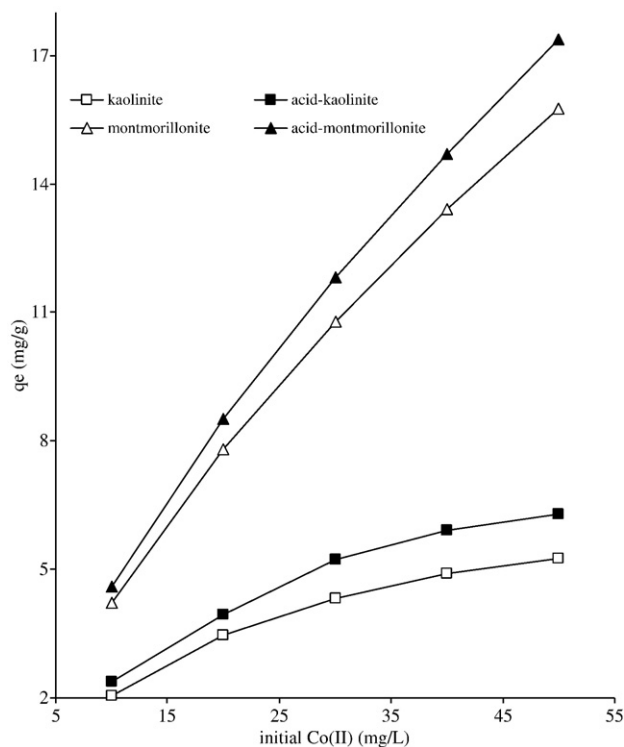


Fig. 5. Influence of initial concentration of Co(II) on natural and acid-activated kaolinite and montmorillonite at 303 K (Clay 2 g/L, pH 5.8, time 240 min) [70].

Table 7

Thermodynamic parameters for Co(II) adsorption on clays (units of ΔH , ΔS and $-\Delta G$ is kJ mol^{-1} , $\text{J K}^{-1} \text{mol}^{-1}$ and kJ mol^{-1} respectively)

Clay adsorbents	ΔH	ΔS	$-\Delta G$				Reference
			298 K	303 K	308 K	313 K	
Raw kaolinite	21.5	5.4	5.5	—	—	4.6	[69]
Kaolinite	15.3	37.7	—	11.4	11.6	11.8	[70]
Acid-activated kaolinite	16.6	44.1	—	13.3	13.6	13.8	
Montmorillonite	−15.1	−47.1	—	14.3	14.5	14.7	
Acid-activated Montmorillonite	−19.9	−59.3	—	17.9	18.2	18.5	

30.39 to 5.98 mg g^{-1} . However, the relative adsorption efficiency increased from 18.9 to 74.8%. In the temperature range of 293 to 313 K, the Langmuir adsorption capacities varied between 14.89 to 16.99 mg g^{-1} .

Adsorption of Cu(II) has been studied on kaolinite, montmorillonite, ZrO-kaolinite, ZrO-montmorillonite, TBA-kaolinite, TBA-montmorillonite [77], acid-activated kaolinite and acid-activated montmorillonite [78]. Cu(II) ions were taken up by the clays as pH was increased, the only limiting factor being the precipitation of Cu(II) as the hydroxide at $\text{pH} > 6.0$. The acid-activation boosted Cu(II) uptake in both kaolinite and montmorillonite as the acid treatment increased surface area and pore volume, however the adsorption declined for ZrO- and TBA-derivatives of both kaolinite and montmorillonite (Fig. 6). Kaolinite and acid-activated kaolinite could remove 15.5 and 18.9% Cu(II) (3.9 and 4.7 mg g^{-1}) but ZrO-kaolinite and TBA-kaolinite could remove only 10.5 and 11.2% Cu(II) (Clay 2 g/L ,

Cu(II) 50 mg/L) respectively. The results for montmorillonite, acid-activated montmorillonite, ZrO-montmorillonite and TBA-montmorillonite were 83.8% (21.0 mg g^{-1}), 87.5% (21.9 mg g^{-1}), 21.1% (5.3 mg g^{-1}) and 60.3% (15.1 mg g^{-1}) respectively under identical conditions (Clay 2 g/L , Cu(II) 50 mg/L). Similar variations were also observed for the Langmuir capacities (Table 8).

The interactions of Cu(II) with clays were rather slow requiring from 120 min [69] to 360 min [77,78]. Alvarez-Ayuso and Garcia-Sanchez [53] have found the uptake of Cu(II) on ion-exchanged bentonites to be very rapid with more than 95% of the uptake taking place within 30 min. Cu(II) adsorption on natural kaolinite [76] has also been shown to be very fast with equilibrium attaining in ~ 60 min. Adsorption of Cu(II) ions onto a 1:10 phenanthroline-grafted Brazilian bentonite was also reported to be very rapid by De Leon et al. [74] with most of the adsorption process occurring within 5 min and no more uptake after 10 min of interaction.

The clay–Cu(II) interactions have been shown to follow a second order mechanism with rate coefficients of 9.5×10^{-2} (kaolinite), 14.4×10^{-2} (ZrO-kaolinite), 14.4×10^{-2} (TBA-kaolinite), 15.4×10^{-2} (montmorillonite), 7.78×10^{-2} (ZrO-montmorillonite), 14.4×10^{-2} (TBA-montmorillonite), 12.0×10^{-2} (acid-activated kaolinite) and 15.9×10^{-2} (acid-activated montmorillonite) $\text{g mg}^{-1} \text{min}^{-1}$ [77,78]. Lin and Juang [73] have

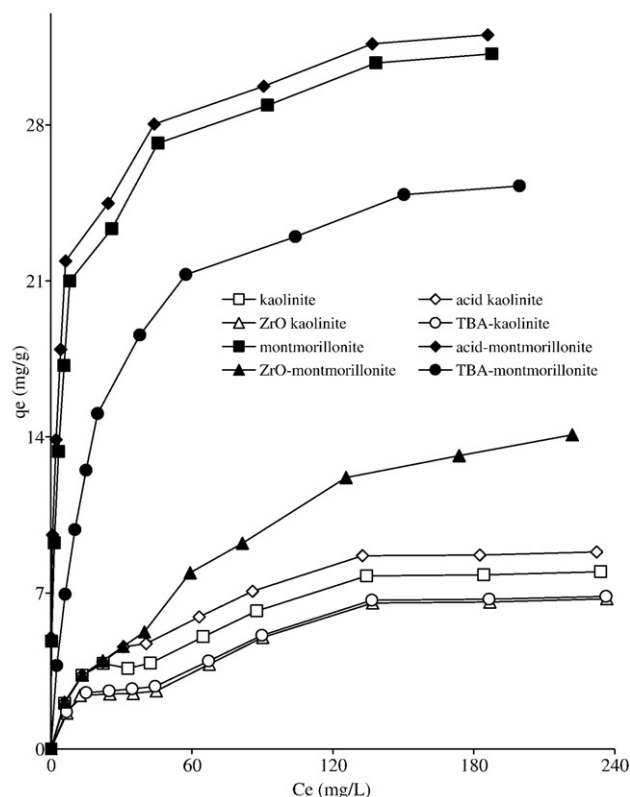


Fig. 6. Plots of q_e vs C_e for Cu(II) adsorbed on natural and modified kaolinite and montmorillonite at 303 K (clay 2 g/L , Cu(II) 10, 20, 30, 40, 50, 75, 100, 150, 200, 250 mg/L , $\text{pH} 5.7$, time 360 min) [77,78].

Table 8

Adsorption capacities of clays and some other adsorbents for Cu(II) (units of Langmuir capacity and Freundlich capacity are mg g^{-1} and $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ respectively)

	Adsorbents	Langmuir capacity	Freundlich capacity	Reference
Clay adsorbents	Raw kaolinite	11.0	—	[69]
	Na-bentonite	30.0	—	[53]
	Ca-bentonite	7.7	—	
	Sodium dodecylsulfate-montmorillonite	0.02	—	[73]
	Kaolinite	4.4	1.1	[77]
	ZrO-kaolinite	3.0	0.7	
	TBA-kaolinite	3.2	0.8	
	Montmorillonite	25.5	9.2	
	ZrO-Montmorillonite	7.1	0.8	
	TBA-Montmorillonite	27.3	3.4	
Other adsorbents	Acid-activated kaolinite	5.6	1.3	[78]
	Acid-activated montmorillonite	28.0	12.4	
	Tree fern	7.6	—	[82]
	Electric furnace slag	39.2	1.1	[83]
	Red mud	19.7	—	[85]
	Spirogyra species	133.3	—	[86]

Table 9
Thermodynamic data for Cu(II) on clays (ΔH and ΔS in mg g^{-1} , kJ mol^{-1} and $\text{J K}^{-1} \text{mol}^{-1}$ respectively)

Clay adsorbents	ΔH	ΔS	Reference
Raw kaolinite	39.5	11.7	[69]
Na-bentonite	—	—	[53]
Ca-bentonite	—	—	
Sodium dodecylsulfate-montmorillonite	7.1	9.1	[73]
Kaolinite	30.7	86.8	[77]
ZrO-kaolinite	50.5	148.3	
TBA-kaolinite	49.8	148.8	
Montmorillonite	50.7	180.7	
ZrO-Montmorillonite	35.9	105.3	
TBA-Montmorillonite	29.2	96.5	
Acid-activated kaolinite	32.7	94.9	[78]
Acid-activated montmorillonite	45.8	267.6	

however proposed a pseudo-first order kinetics with a rate coefficient of $3.14 \times 10^{-3} \text{ min}^{-1}$ at 298 K. Wang et al. [76] proposed second order kinetics for adsorption of Cu(II) on natural kaolinite with the rate coefficient varying from 0.238 to $0.399 \text{ g mg}^{-1} \text{ min}^{-1}$ in the temperature range of 293 to 313 K.

Cu(II)-kaolinite interactions have endothermic nature with adsorption enthalpy of $+39.5 \text{ kJ mol}^{-1}$ driven by an entropy gain of $+11.7 \text{ J K}^{-1} \text{mol}^{-1}$ [69]. Adsorption on sodium dodecylsulfate-montmorillonite was also endothermic in nature with enthalpy of $+7.05 \text{ kJ mol}^{-1}$ and entropy of $+9.09 \text{ J K}^{-1} \text{mol}^{-1}$ (Table 9). The decrease in Gibbs energy of $-9.66 \text{ kJ mol}^{-1}$ [73] makes the interactions spontaneous. Bhattacharyya and Sen Gupta [77,78] have also observed an endothermic path for Cu(II) adsorption on kaolinite, montmorillonite and their modified forms. For an adsorbent amount of 2 g/L, adsorption increases from 15.4% (3.9 mg g^{-1}) to 24.7% (6.2 mg g^{-1}) for kaolinite, 18.9% (4.7 mg g^{-1}) to 28.1% (7.0 mg g^{-1}) for acid-activated kaolinite, 10.4% (2.6 mg g^{-1}) to 20.5% (5.1 mg g^{-1}) for ZrO-kaolinite, 11.2% (2.8 mg g^{-1}) to 21.3% (5.3 mg g^{-1}) for TBA-kaolinite, 83.9% (21.0 mg g^{-1}) to 89.3% (22.3 mg g^{-1}) for montmorillonite, 87.5% (21.9 mg g^{-1}) to 92.7% (23.2 mg g^{-1}) for acid-activated montmorillonite, 21.0% (5.3 mg g^{-1}) to 32.6% (8.2 mg g^{-1}) for ZrO-montmorillonite and 60.2% (15.1 mg g^{-1}) to 68.0% (17.0 mg g^{-1}) for TBA-montmorillonite, as the temperature increased from 303 to 313 K. The endothermic enthalpy change varies significantly for kaolinite and montmorillonite, but acid treatment results in minor variations (kaolinite $\sim 30.7 \text{ kJ mol}^{-1}$, acid-activated kaolinite $\sim 32.7 \text{ kJ mol}^{-1}$ and montmorillonite $\sim 50.7 \text{ kJ mol}^{-1}$, acid-activated montmorillonite $\sim 45.8 \text{ kJ mol}^{-1}$). Endothermic adsorption of Cu(II) on natural kaolinite has also been shown by other workers [76]. Doula et al. [79] have, however, observed earlier that Cu(II) interactions with Ca-kaolinite were exothermic in nature.

Strawn et al. [80] have reported adsorption of Cu(II) by smectites (montmorillonite and bedellite) as a function of varying ionic strength and pH. The X-ray adsorption fine structure (XAFS) and electron paramagnetic resonance (EPR) spectroscopic experiments on Cu(II) adsorbed on clays have revealed that Cu–Cu linkages in the multinuclear complexes were 2.65 Å apart having a coordination number near one.

A good number of adsorbents have been used for Cu(II) removal from water (Table 8). Pan et al. [81] used two types of sewage sludge ash and reported Langmuir monolayer capacity, q_m of 3.282 and 4.139 mg g^{-1} . Ho et al. [82] have found q_m of 7.58 mg g^{-1} for adsorption of Cu(II) on tree fern. Both Freundlich and Langmuir models were applied for the uptake of Cu(II) on electric furnace slag [83] and for a temperature range of 293 to 313 K, the coefficients, K_f and q_m , varied from 0.44 to $1.09 \text{ mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$ and 32.68 to 39.22 mg g^{-1} , respectively. The adsorption intensity and adsorption capacity of Cu(II) uptake on silico-antimonate ion exchanger was found as 0.82 and 0.44 mmol g^{-1} , respectively [84]. The maximum adsorption capacity for Cu(II) on red mud was observed as 19.72 mg g^{-1} [85]. Gupta et al. [86] used *Spirogyra* species for removal of Cu(II) with the maximum adsorption capacity of 133.3 mg g^{-1} .

2.6. Iron

Adsorption of Fe on clays has not received much attention. Recently, Bhattacharyya and Sen Gupta [87] investigated the removal of Fe(III) on kaolinite, montmorillonite and their acid-activated forms. The adsorption experiments were confined to $\text{pH} \leq 4.0$ to avoid precipitation of Fe(III)-hydroxide. In the pH range of 1.0 to 4.0, adsorption increased from 17.0 to 30.0% (kaolinite), 20.6 to 34.8% (acid-activated kaolinite), 59.6 to 75.8% (montmorillonite) and 66.0 to 79.3% (acid-activated montmorillonite). With the amount of clay varying from 2 to 6 g/L, Fe(III) adsorption increased from 23.8 to 39.5% for kaolinite, 28.1 to 44.9% for acid-activated kaolinite, 66.2 to

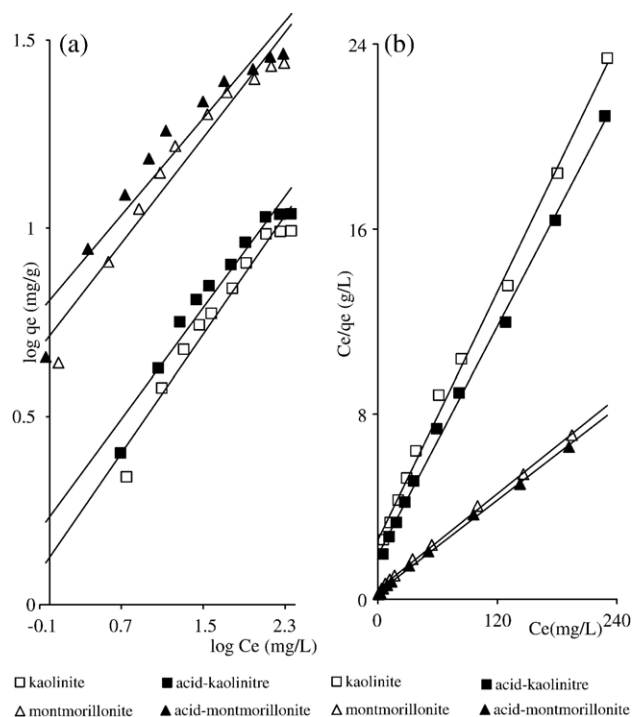


Fig. 7. (a) Freundlich plots and (b) Langmuir plots for Fe(III) adsorbed on clays at 303 K (clay 2 g/L, Fe(III) 10, 20, 30, 40, 50, 75, 100, 150, 200, 250 mg/L, pH 3.0, time 300 min) [87].

81.9% for montmorillonite, and 72.7 to 87.8% for acid-activated montmorillonite (Fe(III) 50 mg/L). Acid activation thus modifies the surfaces of the clays sufficiently to enhance adsorption capacity. The interactions produced good Freundlich and Langmuir isotherm plots (Fig. 7). The relevant adsorption coefficients (e.g. Langmuir capacity has values of 11.2, 28.9, 12.1, and 30.0 mg g⁻¹ for kaolinite, montmorillonite, acid-activated kaolinite and acid-acid-activated montmorillonite) show that both kaolinite and montmorillonite, and their acid-activated forms have good potential to be used for treating Fe-rich water (Table 10).

After being considerably fast initially, the Fe(III)-clay interactions slow down and reach equilibrium at about 300 min. The initial rapid uptake is most likely to take place at the active sites on the surface, but as the surface sites get saturated with Fe(III), the ions slowly diffuse into the interior resulting in a gradual approach towards equilibrium. When the kinetics of the interactions is worked out, it is observed that the experimental data can be best explained with a second-order mechanism. It is further seen that whether the clays are treated with acid or not, the mechanism of Fe(III) adsorption remains the same and consequently, the rate coefficients increase only marginally after acid activation (Table 11). Obviously the adsorptive strength of the Fe(III)-adsorption sites increase by some extent following acid treatment and the clay surface now has a stronger affinity towards Fe(III).

Clay surfaces take up Fe(III) exothermically (the mean adsorption enthalpy, ΔH lies between -27.6 and -42.2 kJ mol⁻¹) accompanied by considerable decreases in Gibbs energy and entropy of the system (Table 11). The clay-Fe(III) adsorption complex is thus more stable than either the clay or Fe(III) ions in aqueous medium in isolation indicating formation of moderately strong bonding between Fe(III) ions and clay adsorbents leading to a decrease in the overall energy of the system.

Fe(III) removal from aqueous solution by adsorption has received only scant attention (Table 10). From his experiments on adsorption of Fe(III) on granular activated carbon, Kim [88] has reported adsorption isotherms giving good fit of the Freundlich equation ($r^2=0.9468$) with values of adsorption capacity (K_F) and adsorption intensity (n) as 0.108 and 0.423. Nassar [89] used maize cobs for adsorption of Fe(III) from aqueous solution with the Langmuir adsorption capacity and

Table 10

Adsorption capacities of clays and some other adsorbents for Fe(III) (Langmuir capacity and Freundlich capacity are mg g⁻¹ and mg^{1-1/n} L^{1/n} g⁻¹ respectively)

Adsorbents		Langmuir capacity	Freundlich capacity	Reference
Clay adsorbents	Kaolinite	11.2	1.3	[87]
	Acid-activated kaolinite	12.1	1.7	
	Montmorillonite	28.9	5.2	
	Acid-activated montmorillonite	30.0	6.4	
Other adsorbents	Granular activated carbon	—	0.1	[88]
	Maize cobs	2.5	0.1	

Table 11

Second order rate coefficient and thermodynamic data for Fe(III) on clays (clay 2 g/L, Fe(III) 10, 20, 30, 40, 50 mg/L, pH 3.0, time 300 min, units of ΔH , ΔS and ΔG are kJ mol⁻¹, J K⁻¹ mol⁻¹ and kJ mol⁻¹ respectively) [87]

Clay adsorbents	Rate coefficient ($k_2 \times 10^2$)	$-\Delta H$	$-\Delta S$	$-\Delta G$		
				303 K	308 K	313 K
Kaolinite	4.7	33.9	123.7	37.5	38.0	38.7
Acid-activated kaolinite	7.4	28.7	104.5	31.7	32.2	32.7
Montmorillonite	7.0	27.6	86.6	26.2	26.7	27.1
Acid-activated montmorillonite	7.2	42.2	131.8	39.9	40.6	41.2

Freundlich adsorption capacity were of 2.53 mg g⁻¹ and 0.104 L g⁻¹, respectively.

2.7. Lead

In one of the earlier studies, Naseem and Tahir [90] have reported that a good uptake of Pb(II) by bentonite from aqueous solution (20 mg of Pb(II) per 1 g of clay at pH 3.4). The adsorption increases from 30 to 94.5% with an increase in pH of the solution from 1.4 to 3.4 and decreases to 40% at pH 5.0. The Langmuir adsorption capacity for Pb(II)-bentonite interactions has been shown to be 52.6 mg g⁻¹.

A group of clay adsorbents [91,92] have been tested for their utility in removing Pb(II) from aqueous solutions. At equilibrium time of 180 min, the adsorption capacities of the clays for Pb(II) (clay 2 g/L, Pb(II) 50 mg/L, temperature 303 K) are:

Adsorbent	Kaolinite	Montmorillonite
Parent clay	20.9% (5.2 mg g ⁻¹)	86.5% (21.6 mg g ⁻¹)
After acid-activation	25.1% (6.3 mg g ⁻¹)	90.7% (22.7 mg g ⁻¹)
Introduction of TBA-	12.6% (3.2 mg g ⁻¹)	42.9% (10.7 mg g ⁻¹)
Introduction of ZrO-	17.5% (4.4 mg g ⁻¹)	67.6% (16.9 mg g ⁻¹)

The isotherm plots (q_e vs C_e) for Pb(II) adsorption on clay adsorbents are shown in Fig. 8. The Langmuir adsorption capacities obtained from these plots vary from 9.4 mg g⁻¹ (TBA-kaolinite) to 12.1 mg g⁻¹ (acid-activated kaolinite) for kaolinites and from 22.2 mg g⁻¹ (TBA-montmorillonite) to 34.0 mg g⁻¹ (acid-activated montmorillonite) for montmorillonites (Table 12). Acid-activation has been observed to increase the Langmuir capacity only marginally, but introduction of both ZrO- and TBA-groups had the effect of reducing the adsorption capacity of montmorillonite sufficiently. In case of kaolinite, the decrease was not so spectacular.

Naseem and Tahir [90] reported >96% Pb(II) uptake in bentonite within 10 min of interactions. Maximum adsorption of Pb(II) on kaolinite, montmorillonite and their modified forms was reported within 40 min [91,92] but equilibrium was attained only after ~180 min. These authors have found that a second order mechanism is more viable and the second order rate coefficient has values of 1.5×10^{-2} to 11.3×10^{-2} g mg⁻¹ min⁻¹ (Table 13). The rate coefficient for montmorillonite is about 2.5 times the corresponding value for kaolinite. Acid activation has resulted in increasing the rate coefficient from 3.5×10^{-2} g mg⁻¹ min⁻¹ (kaolinite) to 4.1×10^{-2} g mg⁻¹ min⁻¹,

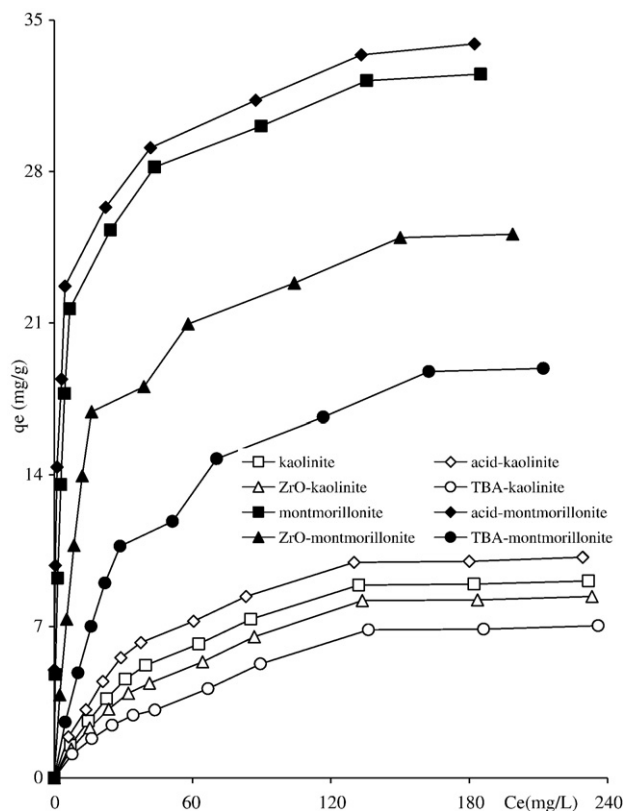


Fig. 8. Plots of q_e vs C_e for Pb(II) adsorbed on natural and modified kaolinite and montmorillonite at 303 K (clay 2 g/L, Pb(II) 10, 20, 30, 40, 50, 75, 100, 150, 200, 250 mg/L, pH 5.7, time 180 min) [91,92].

but the influence was more prominent for montmorillonite, increasing from 8.4×10^{-2} to 11.2×10^{-2} g mg $^{-1}$ min $^{-1}$ after acid activation. The affinity of the acid-activated montmorillonite towards Pb(II) is definitely much more and the interactions take place rapidly compared to those in case of non-activated clays, and even activated kaolinite.

Pb(II)-clay interactions are strongly exothermic (Table 13). Thus, the adsorption of Pb(II) on all the clay adsorbents decreased with increasing temperature as an increased supply of heat energy resulted in enhanced desorption [91,92].

The mean adsorption enthalpy of -58.9 kJ mol $^{-1}$ for kaolinite decreased to -31.5 kJ mol $^{-1}$ on acid activation, which showed that Pb(II) ions were held more strongly to kaolinite surface than the acid-treated surface. The situation is different for montmorillonite, now the acid-activated surface was the one which held Pb(II) ions more strongly (ΔH values -75.5 kJ mol $^{-1}$ and -83.4 kJ mol $^{-1}$ respectively for montmorillonite before and after acid-activation). Spontaneity of the adsorption process is supported by the decrease in Gibbs energy from (i) -63.5 to -65.6 kJ mol $^{-1}$ for kaolinite, (ii) -74.6 to -77.1 kJ mol $^{-1}$ for ZrO-kaolinite, (iii) -119.6 to -121.6 kJ mol $^{-1}$ for TBA-kaolinite, (iv) -35.2 to -36.4 kJ mol $^{-1}$ for acid-activated kaolinite, (v) -71.4 to -73.8 kJ mol $^{-1}$ for montmorillonite, (vi) -40.4 to -41.7 kJ mol $^{-1}$ for ZrO-montmorillonite, (vii) -43.7 to -45.2 kJ mol $^{-1}$ for TBA-montmorillonite and (viii) -78.3 to -80.9 kJ mol $^{-1}$ for acid-activated montmorillonite in the temperature range of 303 to 313 K.

Adsorption of Pb(II) on bentonite is, however, shown to be endothermic in nature in the temperature range of 298 to 323 K [90]. By changing the Pb(II) concentration from 100 μ g/ml to 200 μ g/ml, the adsorption enthalpy and entropy changed from 33.7 to 69.6 kJ mol $^{-1}$ and 0.18 to 0.29 kJ K $^{-1}$ mol $^{-1}$, respectively (Table 14).

Different types of adsorbents have been tested for removal of Pb(II) (Table 12). Taty-Costodes et al. [93] used sawdust for Pb(II) adsorption with the Langmuir adsorption capacity of 8.45 to 22.22 mg g $^{-1}$. Curkovic et al. [83] used electric furnace slag for Pb(II) uptake and K_f and q_m varied from 0.57 to 1.82 mg $^{1-1/n}$ L $^{1/n}$ g $^{-1}$ and 33.78 to 37.04 mg g $^{-1}$, respectively for a temperature range 293 to 313 K. Langmuir adsorption capacities of Pb(II) on silica and grafted silica was reported as 0.019 mmol g $^{-1}$ and 0.184 mmol g $^{-1}$, respectively [94]. Adsorption of Pb(II) on tannin was found to have the adsorption capacities from 57.5 to 114.9 mg g $^{-1}$ in the pH range of 3.0 to 4.2 [95]. Bhatnagar et al. [96] carried out a comparative study of adsorption of Pb(II) on adsorbents prepared from several industrial wastes, namely, fertilizer industry waste (carbon slurry) and steel plant wastes (blast furnace slag, dust, and sludge). The adsorption of Pb(II) has been found in the order: blast furnace sludge (227 mg g $^{-1}$) > blast furnace dust (142 mg g $^{-1}$) > blast furnace slag (125 mg g $^{-1}$) > carbonaceous adsorbent (25 mg g $^{-1}$). The adsorption of Pb(II) on nonylthiourea-coated Fe $_3$ O $_4$ nanoparticles exhibits a maximum loading capacity of 8.1 mg g $^{-1}$ within 30 min [97].

2.8. Manganese

Raw kaolinite could remove Mn(II) from aqueous solution [69] with Langmuir monolayer capacity of 0.446 and 0.461 mg

Table 12

Adsorption capacities of clays and some other adsorbents for Pb(II) (units of Langmuir capacity and Freundlich capacity are mg $^{1-1/n}$ L $^{1/n}$ g $^{-1}$ and mg g $^{-1}$ respectively)

	Adsorbents	Langmuir capacity	Freundlich capacity	Reference
Kaolinite	Without treatment	11.2	0.7	[91,92]
	Acid-activated	12.1	1.0	
	ZrO-pillared	10.7	0.6	
	TBA-pillared	9.4	0.4	
Montmorillonite	Without treatment	33.0	8.9	[91,92]
	Acid-activated	34.0	11.3	
	ZrO-pillared	26.6	4.2	
	TBA-pillared	22.2	1.6	
Other adsorbents	Saw dust	22.2	—	[93]
	Electric furnace slag	37.1	1.8	
	Blast furnace sludge	227.0	—	[96]
	Blast furnace dust	142.0	—	
	Blast furnace slag	125.0	—	[97]
	Carbonaceous adsorbent	25.0	—	
	Nonylthiourea coated Fe $_3$ O $_4$	8.1	—	

Table 13

Second order rate coefficient and thermodynamic data for Pb(II) on clays (Clay 2 g/L, Pb(II) 10, 20 30, 40, 50 mg/L, time 180 min, pH 5.7, temperature 303 K, units of rate constant, ΔH , ΔS and $-\Delta G$ is $\text{g mg}^{-1} \text{min}^{-1}$, kJ mol^{-1} , $\text{J K}^{-1} \text{mol}^{-1}$ and kJ mol^{-1} respectively)

Clay adsorbents	Rate coefficient ($k_2 \times 10^2$)	$-\Delta H$	$-\Delta S$	$-\Delta G$			Reference
				303 K	308 K	313 K	
Kaolinite	3.4	58.9	209.7	63.5	64.6	65.6	[91]
ZrO-kaolinite	1.5	69.9	246.4	74.6	75.8	77.1	
TBA-kaolinite	2.1	388.8	117.7	119.6	121.6	121.6	
Montmorillonite	8.4	75.5	235.9	71.4	72.5	73.8	
ZrO-montmorillonite	7.9	41.0	133.4	40.4	41.0	41.7	
TBA-montmorillonite	6.4	41.2	144.5	43.7	44.5	45.2	[92]
Acid-activated kaolinite	4.1	31.5	116.4	35.2	35.8	36.4	
Acid-activated montmorillonite	11.3	83.4	258.7	78.3	79.6	80.9	

g^{-1} at 298 and 313 K, respectively. The kinetics followed Lagergren first order mechanism with rate coefficient of 1.20×10^{-3} and $1.90 \times 10^{-3} \text{ min}^{-1}$ at 298 and 313 K, respectively. The interactions were endothermic in nature with adsorption enthalpy, $\Delta H = 36.73 \text{ kJ mol}^{-1}$. The process has been driven by entropy increase with $\Delta S = 0.101 \text{ kJ mol}^{-1}$.

Mn(II) adsorption from water has not been studied much. Nassar [89] used maize cobs for uptake of Mn(II) from aqueous solution with the Langmuir adsorption capacity of 2.29 mg g^{-1} and Freundlich adsorption capacity of 0.132 L g^{-1} , respectively.

2.9. Nickel

The adsorption of Ni(II) on Ca-bentonite and Na-bentonite was reported by Alvarez-Ayuso and Garcia-Sanchez [53]. The Langmuir adsorption capacities were 6.3 mg g^{-1} and 24.2 mg g^{-1} , respectively for Ca-bentonite and Na-bentonite (Table 15). The low adsorption capacity of Ca-clay was related to its lower H^+ adsorption capacity, which implied less metal hydroxide precipitation. The low value of cation exchange capacity and the higher charge of Ca^{2+} may also have contributed to decreased retention. Yavuz et al. [69] have obtained an adsorption capacity of 2.8 mg g^{-1} for Ni(II) on kaolinite.

In a recent work, Ni(II) adsorption in aqueous medium has been reported on kaolinite, ZrO-kaolinite, TBA-kaolinite, montmorillonite, ZrO-montmorillonite, TBA-montmorillonite [98], acid-activated kaolinite and acid-activated montmorillonite [78]. The adsorption is found to increase as the alkalinity increases, although the experiments have to be stopped at $\text{pH} > 8.0$ due to precipitation of the metals. In the pH range of 1.0 to 8.0, the adsorption increases as follows:

Clay adsorbents	pH	
	1.0	8.0
Kaolinite	11.3% (2.0 mg g^{-1})	27.3% (6.8 mg g^{-1})
Acid-activated kaolinite	13.1% (3.3 mg g^{-1})	34.2% (8.3 mg g^{-1})
ZrO-kaolinite	13.1% (3.3 mg g^{-1})	34.2% (8.3 mg g^{-1})
TBA-kaolinite	3.4% (0.9 mg g^{-1})	15.4% (3.9 mg g^{-1})
Montmorillonite	50.1% (12.5 mg g^{-1})	71.1% (17.8 mg g^{-1})
Acid-activated montmorillonite	56.3% (14.1 mg g^{-1})	77.6% (19.4 mg g^{-1})
ZrO-montmorillonite	17.7% (4.4 mg g^{-1})	38.6% (9.7 mg g^{-1})
TBA-montmorillonite	17.1% (4.3 mg g^{-1})	33.1% (8.6 mg g^{-1})

Acid activation of kaolinite and montmorillonite has been found to enhance adsorption of Ni(II). While kaolinite and montmorillonite (2 g/L) take up Ni(II) to the extent of 5.2 and 15.7 mg g^{-1} respectively, the acid-activated forms adsorb 6.4 and 17.3 mg g^{-1} . The Langmuir capacity varied from 8.4 mg g^{-1} (TBA-kaolinite) to 11.9 mg g^{-1} (acid-activated kaolinite) and from 19.7 mg g^{-1} (TBA-montmorillonite) to 29.5 mg g^{-1} (acid-activated montmorillonite) (Table 15).

Various authors have reported different rates of Ni(II)-clay interactions. For example, Alvarez-Ayuso and Garcia-Sanchez [53] have shown the interactions to be very rapid Ni(II) on Ca-bentonite and Na-bentonite) with 95% or more of the extent of the interactions being completed within 30 min. Yavuz et al. [69], on the other hand, have reported an equilibrium time of 120 min for Ni(II)-raw kaolinite interactions. An equilibrium time of 180 min has recently been reported for Ni(II) on kaolinite, montmorillonite and their modified forms [78,98]. These variations could be attributed to differences in environmental conditions, exact nature and composition of the clay, and other factors. A detailed analysis of the kinetics by applying various models (Lagergren pseudo first order, second order, Elovich equation, intra-particle and Liquid film diffusion), have led to proposing the second order kinetics as the most suitable. The rate coefficient has values of 2.2×10^{-2} , 3.6×10^{-2} , 1.3×10^{-2} , 2.5×10^{-2} , 5.3×10^{-2} , 2.6×10^{-2} and 2.5×10^{-2} , $5.5 \times 10^{-2} \text{ g mg}^{-1} \text{min}^{-1}$, for kaolinite, ZrO-kaolinite, TBA-kaolinite, acid-activated kaolinite, montmorillonite, ZrO-montmorillonite, TBA-montmorillonite, and acid-activated montmorillonite, respectively.

Ni(II) adsorption on clays decreased in the temperature interval of 303 to 313 K (Fig. 9) showing the exothermic nature of the interactions [78,98]. The exothermic enthalpy varies from -24.0 to $-43.1 \text{ kJ mol}^{-1}$ for kaolinites and from

Table 14

Thermodynamic data for Pb(II) on bentonite (units of ΔH , ΔS and ΔG are kJ mol^{-1} , $\text{kJ K}^{-1} \text{mol}^{-1}$ and kJ mol^{-1} respectively) [90]

Pb(II) ($\mu\text{g/ml}$)	ΔH	ΔS	$-\Delta G$			
			298 K	303 K	313 K	323 K
100	33.7	0.18	56.7	54.9	53.2	52.3
150	67.4	0.28	91.6	88.7	85.9	84.5
200	69.6	0.29	93.2	90.3	87.4	86.0

Table 15

Adsorption capacities of clays and some other adsorbents for Ni(II) (units of Langmuir capacity and Freundlich capacity are mg g^{-1} and $\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$ respectively)

	Adsorbents	Equilibrium time (min)	Langmuir capacity	Freundlich capacity	Reference
Clay adsorbents	Raw kaolinite	120	2.8	—	[69]
	Ca-bentonite	120	6.3	—	[53]
	Na-bentonite		24.2	—	
	Kaolinite	180	10.4	1.1	[98]
	ZrO-kaolinite		8.8	0.8	
	TBA-kaolinite		8.4	0.5	
	Montmorillonite		28.4	4.5	
	ZrO-montmorillonite		22.0	1.3	
	TBA-montmorillonite		19.7	1.2	
	Acid-activated kaolinite	180	11.9	1.5	[78]
Other adsorbents	Acid-activated montmorillonite		29.5	6.0	
	Bagasse fly ash	80	1.1	0.9	[61]
	Peat	—	28.3	5.3	[100]
	Granular activated carbon	200	6.5	—	[101]
	Modified granular activated carbon		7.0	—	
	Protonated yeast (<i>Saccharomyces cerevisiae</i>)	60	11.4	—	[102]

–33.7 to –56.9 kJ mol^{-1} for montmorillonites. The corresponding entropy varies from –112.3 to –160.5 $\text{J K}^{-1} \text{mol}^{-1}$ for kaolinites and –121.9 to –181.9 $\text{J K}^{-1} \text{mol}^{-1}$ for montmorillonites (Table 16). Endothermic interactions were also observed by Yavuz et al. [69] when Ni(II) was adsorbed on raw kaolinite in the temperature range 298 to 313 K and an adsorption enthalpy of +37.3 kJ mol^{-1} , was computed.

The adsorption of Ni(II) on various adsorbents is reported in the literature (Table 15). Gupta et al. [61] used bagasse fly ash (a

sugar industry waste) for removal of Ni(II) from wastewater, and in the temperature range 30 to 50 °C, the values of K_f , q_m and b varied from 0.90 to 1.17, 1.12 to 1.70 mg g^{-1} and 6.42 to 8.66 respectively. The uptake of Ni(II) on two different Turkish fly ashes (Afsin-Elbistan and Seyitomer) were studied [99] through Freundlich and Langmuir isotherms. One of the fly ash samples showed q_m , and b in the range of 0.480 to 0.987 mg g^{-1} and 0.721 to 2.092 L mg^{-1} respectively in the pH range of 6.0 to 8.0. The other fly ash had q_m and b in the range of 0.060 to 1.160 mg g^{-1} and 1.435 to 3.124 L mg^{-1} respectively in the pH range of 5.0 to 8.0. Adsorption kinetics for Ni(II) on silico-antimonate was studied and found to follow the Freundlich isotherm over the entire range of bulk concentration of the metal ions. The adsorption intensity and the adsorption capacity values were found to be 0.73 and 0.93 mmol g^{-1} respectively [84]. Chen et al. [100] used peat for Ni(II) removal with q_m of 28.26 mg g^{-1} ($R=0.999$) and K_f of 5.321 L g^{-1} ($R=0.962$). Chemically treated granular activated carbon (modified with potassium bromate) was used for uptake of Ni(II) from aqueous solution by Satapathy and Natarajan [101]. The modified activated carbon showed a significant improvement in the adsorption of Ni(II) compared to the raw granular activated carbon. The Langmuir

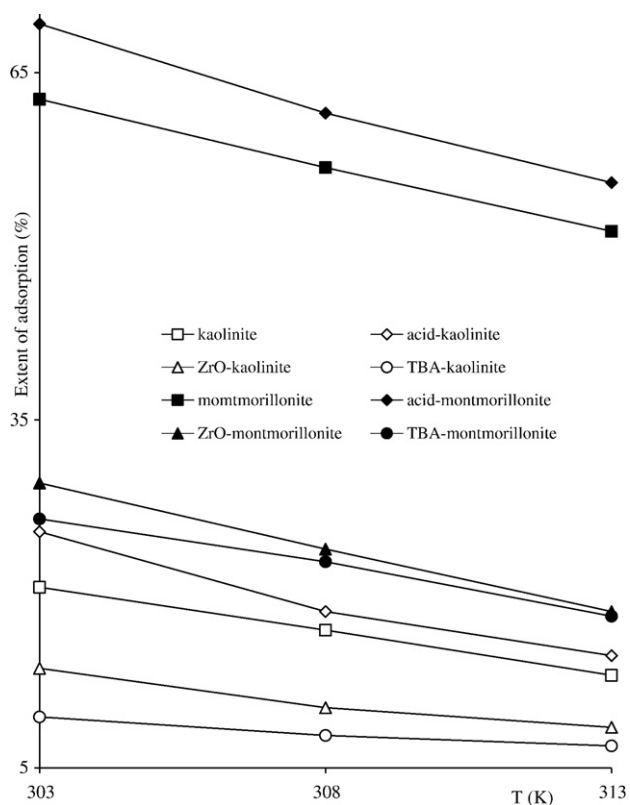


Fig. 9. Influence of temperature on extent of adsorption (%) of Ni(II) (Clay 2 g/L, Ni(II) 50 mg/L, pH 5.7, time 180 min) [78,98].

Table 16

Thermodynamic data for Ni(II) on clays (clay 2 g/L, Ni(II) 10, 20, 30, 40, 50 mg/L, pH 5.7, time 180 min, units of ΔH , ΔS and ΔG are kJ mol^{-1} , $\text{J K}^{-1} \text{mol}^{-1}$ and kJ mol^{-1} respectively)

Clay adsorbents	$-\Delta H$	$-\Delta S$	$-\Delta G$			Reference
			303 K	308 K	313 K	
Kaolinite	37.9	118.2	41.9	42.6	43.3	[98]
ZrO-kaolinite	41.3	152.9	46.4	47.1	47.9	
TBA-kaolinite	24.0	112.3	34.0	34.6	35.2	
Montmorillonite	45.1	146.4	44.4	45.1	45.9	
ZrO-montmorillonite	37.7	133.8	40.6	41.2	41.9	
TBA-montmorillonite	33.7	121.9	36.9	37.5	37.7	
Acid-activated kaolinite	43.1	160.5	48.1	49.5	50.3	[78]
Acid-activated montmorillonite	56.9	181.9	55.0	55.8	56.9	

Table 17

Adsorption capacities of clays and some other adsorbents for Zn(II) (Freundlich capacity (k_f), Langmuir capacity (q_m) and Langmuir intensity (b) in L g^{-1} , mg g^{-1} and L mg^{-1} respectively)

Adsorbents		Temperature (K)	Freundlich coefficient		Langmuir coefficient		Reference
			k_f	$1/n$	q_m	b	
Clay adsorbents	Bentonite	293	8.4	0.2	52.9	0.01	[103]
		313	3.8	0.4	53.1	0.01	
		353	2.3	0.5	25.8	0.08	
Other adsorbents	Na-bentonite	—	—	—	23.1	—	[53]
	Ca-bentonite	—	—	—	5.8	—	
	SBA-15	298	—	—	7.2	—	[104]
	Turkish fly ash	293	—	—	1.2	1.39	[99]
		—	—	—	0.4	1.35	
	Rice bran	303	—	—	14.2	0.01	[107]
		313	—	—	14.8	0.02	
323		—	—	18.3	0.02		

adsorption capacity was found as 2.86 mg g^{-1} , 6.53 mg g^{-1} and 7.03 mg g^{-1} respectively for untreated GAC and two modified activated carbons. Biosorption of Ni(II) ions by deactivated protonated yeast (*Saccharomyces cerevisiae*) yielded a maximum Langmuir adsorption capacity of 11.4 mg g^{-1} at a pH ~ 6.75 [102].

2.10. Zinc

Mellah and Chegrouche [103] used natural bentonite for uptake of Zn(II) from aqueous solution. The process was favoured by high values of initial Zn(II) concentration and decreased particle size of clay adsorbent. The agitation speed influenced the interactions and was pronounced at the onset of the process. After ~15 min, the amount of Zn(II) adsorbed was higher for 200 than 500 rpm. It was likely that more particles were broken at 500 rpm or/and the suspension was not homogeneous at 500 rpm. In the temperature range of 293 to 353 K, Freundlich adsorption capacity varied between 2.3 to 8.4 L g^{-1} and Langmuir monolayer adsorption capacity varied between 25.8 to 52.9 mg g^{-1} (Table 17).

The uptake of Zn(II) on Na-bentonite and Ca-bentonite was investigated by Alvarez-Ayuso and Garcia-Sanchez [53]. The interactions were followed by Langmuir isotherm with maximum monolayer adsorption capacity of 23.1 mg g^{-1} for Na-bentonite whereas only 5.8 mg g^{-1} for Ca-bentonite. The adsorption of Zn(II) on sodium dodecylsulfate-montmorillonite [73] was influenced by solution pH and by increasing pH, the number of negatively charged sites increases, which favours adsorption of Zn(II). The Langmuir adsorption capacity was $202.9 \text{ mmol kg}^{-1}$.

Uptake on ion-exchanged bentonite occurred very rapidly with >95% completed in 30 min [53]. Adsorption of Zn(II) on modified clay [73] was rapid during the first 10 min and the equilibrium was attained within 120 min. A pseudo-first-order mechanism was proposed with a rate coefficient of $6.64 \times 10^{-4} \text{ min}^{-1}$ at 298 K.

Lin and Juang [73] carried out adsorption of Zn(II) on montmorillonite treated with sodium dodecylsulfate in the temperature range of 298 to 328 K. The adsorption enthalpy and entropy were computed as $+7.39 \text{ kJ mol}^{-1}$ and $+6.39 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. The positive entropy change was due to the

fixation of ions on the exchange sites of the randomly distributed surfactant species. The change in free energy (ΔG) was $-9.17 \text{ kJ mol}^{-1}$ and the negative value conformed to the spontaneity of the interactions, perhaps because the surfactant molecules have more affinity toward the metal ions. However, Mellah and Chegrouche [103] reported exothermic nature of Zn(II)–bentonite interactions in the temperature range of 293 to 353 K.

A number of adsorbents have been used for removal of Zn(II) (Table 17). Mesoporous silicate SBA-15 has a high adsorption capacity of 7.23 mg g^{-1} at pH 2.7 [104]. Bayat [99] compared two different Turkish fly ashes for their ability to remove Zn(II) from aqueous solution. The fly ash with high calcium content was found to be a better adsorbent with Langmuir adsorption capacity varying from 0.251 to 1.194 mg g^{-1} in the pH range of 3.0 to 6.0. The Langmuir adsorption capacity of the other fly ash varied from 0.071 to 0.356 mg g^{-1} in the same pH range. The removal of Zn(II) on red mud [105] and on bagasse fly ash [106] were almost complete at low concentrations, while the uptake were 60–65% at higher concentrations with 10 g/L of adsorbent. Wang et al. [107] used rice bran for Zn(II) adsorption with Langmuir capacities of 14.17 mg g^{-1} (303 K), 14.84 mg g^{-1} (313 K) and 18.31 mg g^{-1} (323 K) indicating an endothermic process of adsorption.

3. Cost comparison of clays with common adsorbents

When the prices of a number of common adsorbents are compared, as shown below, clays appear to be among the cheapest being in the same range as zeolites. Some cost addition will of course be required if any treatment like acid-activation is to be done.

Types of adsorbent	Price (US \$ kg^{-1})	Reference
Clay	0.04–0.12	[108]
Commercial activated carbon (CAC)	20–22.00	[45]
Zeolite	15.43	
Spheroidal cellulose	1.07	
Lignin	0.06	
Chitosan	15.43	[109]

(continued on next page)

Zeolites	0.03–0.12	[110]
Clinoptilolite	0.03–0.12	[111]
Chabazite	0.03–0.12	
Peat	0.023	[112]
Coconut shell charcoal (CSC)	0.34	[66]
Nitric acid oxidized CSC	0.34	
Nitric acid oxidized CAC	1.37	
Sphagnum moss peat	0.02	[113]
CAC type Filtrasorb-400	20–22	[114]
Perlite	1.50	[57]

4. Conclusions

Clays have been good adsorbents because of existence of several types of active sites on the surface, which include Bronsted and Lewis acid sites, and ion exchange sites. The edge hydroxyl groups have been particularly active for various types of interactions. Although kaolinite has a net zero layer charge, small negative charge at the broken edges has been responsible for the activity. Montmorillonite, on the other hand, has a net negative charge of 0.8 unit per unit cell and this has been responsible for giving superior activity to montmorillonite as an adsorbent. The activity however depends on many other environmental factors such as pH, temperature, etc. Modification of clays by pillaring and acid activation has considerable influence on the structural properties, very often enhancing their adsorption capacities, but the reverse trends are also observed.

Clays and modified clays have been found particularly useful for adsorption of heavy metals. Clays have received attention as scavengers of As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, Zn in their ionic forms from aqueous medium. The adsorption capacities vary from metal to metal and also depend on the type of clay used. When a comparison is made with other low-cost adsorbents, the clays have been found to be either better or equivalent in adsorption capacity. Environmental factors like pH do have effects on the adsorption capacity as also the case with other adsorbents. The results also show how and why clays can be effectively used as a liner in water treatment plants.

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