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Chapter

Sorption of Heavy Metals on Clay Minerals and Oxides: A Review

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Abstract

Sorption of heavy metals plays a vital role in controlling environmental pollution. Here, we reviewed the sorption of heavy metals such as Ni, Co, Cu, Zn, V, Pb, Hg, In, As, Cd, Cr, Ga, Cs, Mn, V, Eu, Mo, Th, TI and Cr on metal oxides and clay minerals. The mechanism of association between these ions and the host minerals, and the factors controlling their sorption are discussed in detail. Both chemical and empirical methods of describing sorption mechanism are discussed. The sorption processes depend on the pH, metal concentration, ionic strength, temperature, time, adsorbent dosage, type of ion, surface area, type of adsorbent modification and nature of adsorbent. The review confirmed that both metal oxides and clay have capability of sequestering heavy metals, however, combination of both metal oxides and modified clay have enhanced capability of removing heavy metals from aqueous solution. These inorganic adsorbents have the regeneration and recycling potentials and can be used to remediate and sequester economic metals for commercial purposes, however, this needs future investigation.

Keywords: sorption, adsorption, heavy metals, remediation, oxides, clay minerals

1. Introduction

Heavy metal pollution is an environmental problem that has harmful effect on both aquatic and terrestrial environment. These metals are released to the environment through activities such as mining, electroplating and manufacturing of paper and pesticides in form of mine tailings or effluents [1]. They have ability to complex with minerals to form inorganic ligands with variable solubility and acid–base potentials, thus, making their remediation from contaminated land/soil a major concern [2, 3].

Pollution arising from heavy metals poses serious health problems to both human beings and animals [1]. *For example,* low concentration of cadmium in human being can lead to 'Itai-Itai' disease, lungs cancer, and kidney and liver problems [4, 5]. Ingestion of water contaminated with high level of Cr can cause ulcer, skin inflammation and pulmonary congestion [6, 7]. Health problems associated with ingestion or inhaling of nickel dust are diarrhoea, renal oedema, nausea, chest pain, pulmonary fibrosis and gastrointestinal ache. Excess of lead in the environment can lead to mental retardation, kidney and nervous disease, cancer [8, 9]. The Cu^{2+} is the most toxic form of copper [10], and health problems

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associated with copper are anaemia, headache, kidney damage and death [11, 12]. Large amount of zinc in human body can result to anaemia, fever, vomiting and skin inflammation [13]. Mercury ingestion can lead to damaging of reproductive and respiratory system, kidney and brain [14]. Also, health problem associated with arsenic are gastrointestinal problems, cancer, diabetes, and liver tumours [15]. Large concentration of Mn causes retardation of growth, infertility, fever, eye blindness and muscles [15]. Consumption of water with high concentration of cobalt can lead to heart problems, asthma, damage of thyroid, pneumonia, hair and weight loss, nausea and vomiting, [16]. Depending on the route and length of exposure to vanadium, it can lead to immunological, genetoxic, developmental, reproductive and systemic problems and even death [17]. Exposure to indium via respiration can lead to lung disease, kidney and lungs damage [18, 19]. Long term exposure of gallium may damage the kidney, liver, lungs and bone marrow [20]. Health effects of molybdenum are headache, weight loss, joint or muscle ache, diarrhoea, kidney and liver problems [21]. Exposure to radioactive caesium can lead to cells damage, cancer, diarrhoea, vomiting, nausea and mental abnormality in babies [22]. Exposure to thorium workers can cause lung and liver disease, cancer, liver diseases and death at large exposure [23].

Clay minerals and metal oxides are formed from weathering of primary minerals [24]. These minerals have high surface area and can absorb heavy metals from aqueous and natural environments [25]. Clay minerals, bentonite, sepiolite and palygorskite have been used extensively to remove heavy metals from wastewater and agricultural soil, and the mechanisms of remediation are sorption, precipitation and liming [26]. Heavy metal polluted water is mostly remediated using ion-exchange, adsorption and mechanism [27]. Even though, clay minerals have adsorption affinity for heavy metals, e.g. Cu and Zn, their roles are not significant when compared to iron oxides (e.g. goethite), manganese oxides (e.g. birnessite) and organic materials on a unit mass basis [28]. Comparison of the adsorption potentials of deep sea minerals such as clay minerals, Mn-oxides, Fe-oxides, calcite and apatite reveal that Mn and Fe oxides and oxyhydroxides are crucial phases for scavenging heavy metals [29] Lead readily sorbs on all phases but has greatest affinity for carbonate fluorapatite, however, Caesium (Cs) has affinity for illite [29]. In sea water, hydrated cations such as Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Ba^{2+}, $MnCl^{+}$ and $PbCl^{+}$ have strong affinity for Mn-oxide while HVO_4^{2-}, MoO_4^{2-}, $PbCO_3$ and $HAsO_4^{2-}$ preferentially adsorb onto Fe oxyhydroxide [29].

Sorption techniques have the ability to remove these contaminants via adsorption onto sorbents. However, the type of sorbent to be used for remediation depends on the sorption capacity, sorption pH and distribution coefficient of the contaminant [30]. The review on the sorption of Ni(II) adsorbents indicates that bisorbents are the most effective for removal of the ion from aqueous solution [31]. In addition, Pb and Cd be successfully immobilised with wide range of low cost materials such as metal oxides, animal manure, apatite, lime, biosolids, and biochar [32]. However, the review on the adsorption capabilities of low-cost sorbents such as agricultural waste, household wastes, industrial by-products and sludge indicates that even though these material has great adsorption potentials their particle size, surface area, contact time, initial concentration of ion, adoption dose are not stated by the researchers [33]. This poses great limitation for the use of these adsorbents for remediation. Further review of the sorption of nickel, copper, lead, cadmium, caesium, chromium, europium and thorium on both natural and synthetic materials reveal that more studies on multi-component sorption of these metals are required [34]. Therefore, synthetizing effective and low cost adsorbent that can be recycled for removal of contaminants from aqueous environment will be of high interest

[34]. Similarly, synthesising and discovering new novel methods of using modified clay for environmental remediation is required metals [25].

To this end, this paper presents the review the sorption of heavy metals such as Ni, Co, Cu, Zn, V, Pb, Hg, In, As, Cd, Cr, Ga, Cs, Mn, Eu, Mo, Th, TI and Cr on both natural and synthetic metal oxides and clay minerals for soil and water remediation. The main aim of this review is to summarise the adsorption mechanism and recent remediation method of single and multicomponent system of these toxic metals using clay minerals and metal oxides. In addition, the advantages of reusability these adsorbents after remediation are discussed.

2. Adsorption mechanism and models

2.1 Adsorption mechanism

The interactions between metallic ions and mineral surfaces in any environment allow the sorption of ions to the solid surface, thereby decreasing the concentration of ions in the aqueous phases below the solubility limits of the solid phase [35]. Determination of partitioning of heavy metals among the solid phase and accurately predicting their mobility in natural environment requires adequate knowledge of the chemical process such as ion exchange, adsorption, surface precipitation, coprecipitation and mineralisation, that govern sorption mechanism [36]. For example, cobalt sorbs to goethite through surface complexation, surface precipitate and structural incorporation depending on the concentration and sorption duration [37].

Surfaces of substances (oxides, organic and inorganic) have surface functional groups or hydroxyl groups of solute ligands [38]. These functional groups are dominant in natural environments as oxides of Al, Fe and Si and in aqueous solution. The surface charge of metallic oxy-hydroxides, phosphate and carbonates is formed through ionisation of surface groups [39]. The pH of surface oxide and oxyhydroxides changes due to adsorption of protons or ions from solution [40]. Thus, the surface charge set up potential differences between the sorbent and sorbate, thereby influencing the approach of ions towards the surfaces [40]. Consequently, surface hydroxyl groups are responsible for complexation on metal oxides, oxyhydroxides, hydroxides and aluminosilicates. The type of surface functional group influences the sequence of the adsorption reaction, variation in adsorption solution chemistry, electrical properties of the interface and the adsorption ability [41]. The reaction of metals and oxygen atoms at the surface results in the formation of hydroxyl groups (OH^-), which are taken as part of the surface instead of solution. The surface hydroxyl is amphoteric (i.e. they can either accept a proton or donate a proton) as shown below:

$$\equiv S\text{–}OH + H^+ \rightleftharpoons \equiv S\text{–}OH_2^+ \quad (1)$$

$$\equiv S\text{–}OH \rightleftharpoons \equiv S\text{–}O^- + H^+ \quad (2)$$

Adsorption of metal to the surface takes place via substitution of surface protons (H^+) to form inner sphere complexes:

$$\equiv S\text{–}OH + M^{Z+} \rightarrow \equiv S\text{–}O\text{–}M^{Z-1} + H^+ \quad (3)$$

$$2{\equiv}S{-}OH + M^{Z+} \rightarrow (\equiv S{-}O)_2 M^{Z-1} + 2H^+ \quad (4)$$

$$2{\equiv}S{-}OH + M^{Z+} \rightarrow (\equiv S{-}O)_2 M^{Z-1} \quad (5)$$

The surface oxygen, ΞSO$^-$ may attract ions from bulk solution to form outer sphere complexes [42]:

$$\equiv S{-}O^- + M(H_2O)_6^{2+} \rightarrow \equiv S{-}O^-.....(H_2O)_6 M^{2+} \quad (6)$$

Bidentate ligands (Lewis bases, e.g. Cl^-, OH^-, H_2O, NH_3^+) are sorbed to the surface by the replacement of the surface hydroxyl group (ΞSOH) as follows:

$$\equiv S{-}OH + L^- \rightarrow \equiv S{-}L + H_2O \quad (7)$$

Adsorbed ligands can also take up another metal while metals already adsorbed can attach themselves to another ligand [43].

$$\equiv S{-}L + M^{Z+} \rightarrow \equiv S{-}L{-}M^{Z+1} \quad (8)$$

$$\equiv S{-}O{-}M^{Z-1} + L^- \rightarrow \equiv S{-}O{-}M{-}L^{Z-2} \quad (9)$$

2.2 Adsorption and Kinetic models

An adsorption isotherm is a relationship between the amount adsorbed and the concentration of the adsorbate at a constant temperature [39]. Both empirical and chemical models are used in describing the adsorption reaction. The former model uses mathematical expressions to interpret adsorption (e.g. Freundlich isotherm, Langmuir isotherm and distribution coefficient) whereas the latter uses a molecular approach to calculate equilibrium constants (e.g. constant capacitance model, triple layer models) [44]. Langmuir isotherm is based on the assumption that only one monolayer is formed during reaction, presence of equivalent sites, immobility of adsorbate and absence of adsorbate-adsorbent interaction [39]. The difference between Langmuir isotherm and Freundlich is that Langmuir isotherm considers maximum sorption whereas Freundlich considers infinity site [39]. However, adsorption isotherms are of limited application when modelling because of the complex and variability of natural environment with heavy metal and existence of sorbents with pH dependent surface charges [39]. Therefore, application of surface complexation models that can integrate both the experimental data and the electrostatic interaction between the ion and the oxide surface is required for modelling the mobility sorption of heavy metal. Computer models such as MINTEQ, FITEQL EQLFOR, HYDRAQL and SOILCHEM can calculate both equilibrium speciation and constants [44–46].

Adsorption kinetic model is used to investigate sorption mechanism as well as the rate controlling steps in a batch reaction [34]. Kinetic studies is carried out in a way to vary the initial concentration of adsorbate, temperature, time, sorbent dosage, particle size, pH, type of sorbent and sorbate [34]. It is a continuous measurement of experimental data until equilibrium is attained. The result is tested using kinetic equations to determine the best fit, which will give a better understanding of the sorption mechanism. The adsorption isotherms

Isotherm equations	Kinetic equations
$q_e = \frac{RT}{b}\ln(aC_e)$ Temkin	$\frac{dq}{dt} = k(q_e - q)^2$ Pseudo-second-order model
$\theta = \frac{K_{ad}[M]}{1+K_{ad}[M]}$ Langmuir	$\frac{dq}{dt} = k(q_e - q)$ Lagergren model
$\theta = K_{ad}[M]^n$ Freundlich	$\frac{dq}{dt} = \alpha \exp(-\beta q)$ Elovich model
$q_e = q_{\max} \exp\left(-\left(\frac{RT\ln\left(\frac{C_e}{C_s}\right)}{\beta E_0}\right)^2\right)$ Dubinin-Radushkevich	$\frac{dq}{dt} = k_1 C - K_2 C_s$ Bhattacharya and Venkobachar model
$q_e = q_{\max}\frac{BC_e}{q_{\max}(C_e - C_s)[(1+B-1)(C_e/C_s)]}$ Brunauer, Emmett and Teller (BET)	$\frac{dq}{dt} = k_{sorp}C(q_e - q) - k_{des}q$ Adam-Bohart-Thomas
$\log\frac{\theta}{C_0} = \log K_{FH} + n_{FH}\ \log(1-\theta)$ Halsey	
$q_e = \frac{K_{RP}C_e}{1+a_{RP}C_e^{\beta}}$ Redlich-Paterson	
$q_e = q_{\max}\frac{(K_s C_e)^{\gamma}}{(1+(K_s C_e)^{\gamma})}$ Sip	
$q_e = q_{\max}\frac{b_T C_e}{\left(1+(b_T C_e)^{nT}\right)^{1/n_T}}$ Toth	

θ = fraction of surface coverage; [M] = concentration of ion; Ce = concentration at equilibrium; Cs = solubility of adsorbate at a particular temperature; q_{max} = saturated monolayer sorption capacity; qe = the amount of solute adsorbed at equilibrium; q = the amount of solute adsorbed at any given time 't' #; C = the concentrations of sorbate in solution at any given time 't'; Cs = the concentrations of sorbate in sorbent at any time 't'.

Table 1.
Adsorption isotherm and kinetic model equations.

and kinetics commonly used are listed in **Table 1**. In addition, most of the adsorption of ions on clays and oxides are best described by Langmuir, Dubinin-Radushkevich and Freundlich isotherm models and Pseudo-second-order kinetic model [47–53].

Better understanding of sorption mechanism is done using technologies and spectroscopy studies such as Attenuated Total Reflection Infrared [37, 54], Fourier Transform Infrared (FTIR) spectroscopy, extend X-ray absorption fine structure spectroscopy (EXAFS) [55–57], powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and Electron paramagnetic resonance (EPR) [58]. Spectroscopic studies show that copper, nickel, zinc and cobalt bind to Mn(IV) vacancy sites in birnessite to form inner-sphere surface complexes via interlayer triple-corner-sharing or enter the vacancy site to become part of the structure [56]. ATR-FTIR is very useful in distinguishing the outer-sphere and inner-sphere complexes on minerals. Yoon et al., determined of the types and structures of the adsorption complexes formed by oxalate at boehmite (γ-AlOOH)/water and corundum (α-Al_2O_3)/water interfaces using in situ ATR-FTIR spectroscopy and quantum chemical [54]. Their findings suggest that the adsorption mechanism involves loss of protons from aqueous species during ligand-exchange reaction and is useful clue on the transport mechanism and removal of toxic elements in natural water.

3. Investigations of the sorption properties of clay and metal oxides

Clay minerals, e.g. montmorillonite, illite, and kaolinite, are known to have ability of adsorbing heavy metals in their inter layers through ion exchange reaction [25]. They generally have high sorption and expansion properties and are widely

used for removal of contaminants from aqueous solution [25]. Their specific roles for adsorption of heavy metals from aqueous solutions and natural environments are discussed below. These adsorbents and the metals they are capable of removing from aqueous solution are summarised in **Table 2**.

Metals	Adsorbents	Temperature (°C)	Concentration	Optimum recovery pH	Time for maximum adsorption	References
Zn(II) Cu(II) Mn(II) Cd(II) Pb(II) Ni(II)	Montmorillonite	25–26.85	500 mg/L	6–8	180 min	[47, 62, 63]
U(VI) Th (IV)	Jordanian Bentonite	25	100 mg/L	3	18 h	[49]
Cu(II) Ag(I)	Verde-lodo bentonite	Cu: 60 Ag: 20	1.2429 mmol/L	<4.5	2 days	[75]
Th (IV)	Activated bentonite					[76]
In(II)	Chitosan-coated bentonite	25	70 mg/L	4.0	300 min	[77]
Cs(II)	Mixture of iron pillared Layered montmorillonite (80%) and goethite (20%)	15	13.3 mg/L	7.3.	30 min	[50]
Cu(II) Cs(II)	Aluminium-pillared-layered montmorillonites	—	100 mg/L	For Cu 4.0–6.0 and For Cs 3.0–8.0	1.5 h	[51]
Cr (VI))	Magnetite nanoparticles	25	50 mg/L	3.0	3 h	[53]
Mn(II) Ni(II) Cu(II)	Hexagonal birnessite	25	143 mg/L	7–8	24 h–22 days	[55] [100]
Pb(II) Cu(II) Zn(II) Cd(II)	Hexagonal birnessite Hydrous Mn-oxide (HMO)-coated clay	25	2801 mg/L	4.5 to ~5.5	24 h–2 weeks	[101] [102]
Hg(II) Cr(III) Pb(II) Cu(II) Zn(II) Ba(II) Ni(II) Mn(II) Cd(II) Ba(II) Ag(I)	Ca-montmorillonite	—	1 N	4.8	16 h	[64]

Metals	Adsorbents	Temperature (°C)	Concentration	Optimum recovery pH	Time for maximum adsorption	References
Eu(III)	Na-montmorillonite	25	1×10^{-3} mol/L	~ 7	8 days	[65]
Cd(II)	Heated ball clay Combination of montmorillonite and humic acid	30	50 mg/L	8 8.5	18 h 24 h	[68] [111] [112]
Pb(II) Cd(II) Ni(II) Cu(II)	Kaolinite	30	160 mg/L	7	30 min	[69]
Cd(II) Co(II) Cu(II) Pb(II) Ni(II) Cr(VI)	Acid-activated form kaolinite	30	250 mg/L	Co and Ni: pH 7.8 Cu and Pb: Ph 5.8 Cd: Ph 10, Cr: pH 7	40–240 min	[70] [71]
Cs(II)	Clay soil with predominantly illite as clay mineral	25	4 mg/L	8	16 h	[72] [73]
TI(I)	Illite	25	8.39×10^{-6} mol/L	7.18	6 days	[74]
Pb(II) Cu(II) Ni(II)	Synthetic magnesium-aluminium layered double hydroxides modified palygorskite	18–40	500 mg/L	5.0	4.0, 8.0, and 20.0 min, for Pb(II), Cu(II) and Ni(II), respectively	[84]
Pb(II)	Palygorskite-iron oxide nanocomposite	25			12 h	[85]
As(III) Cd(II) Cr(III) Cu(II) Hg(II) Ni(II) Pb(II)	Fe-oxide modified smectites (montmorillonite and saponite)	25	100 μg/L	pH 5	2 h	[88]
Ga (III) V(V) Co(II) Ni(II)	Goethite	20–25	10–58 mg/L	pH 7	24 h	[38] [93] [94] [98]
Cu(II) Zn(II) Cd(II) Pb(II)	Amine-magnetic Fe-oxide	30	1.0 mmol/L	6	60 min	[103]
Ni(II)	Mixture of goethite, humic acid and kaolinite	30	100 mg/L	5.5	2 h	[104]

Table 2.
Summary of metals, potential adsorbents and experimental parameters.

3.1 Montmorillonite clay

The sorption ability of montmorillonite and its remediation potential for nickel and copper from polluted water was investigated by [47]. In their study, sorption rate follows pseudo-second-order rate model and the adsorption model fits to Langmuir model. Also, the point of zero charge (PZC) for the aqueous solution containing both metal at different ionic strengths 0.01 and 0.001 M KCl, is pH 3.4 ± 0.2 [47]. In contrast, the sorption of cadmium, chromium and lead (II) from wastewater on clay follow 1st order kinetics and can be modelled with both Freundlich and Langmuir model [59]. This study reveals that clay has the capability of removing these metals from aqueous solution at low temperature. In another study, the adsorption of Pb on clay from Tunisia reached maximum at pH 7 and declined above pH 7 due to formation of Pb precipitates, and the mechanism of adsorption via ion exchange [60]. Similarly, sorption of Cu(II) and Ni(II) onto white montmorillonite from obtained Kahramanmaras show increased adsorption with increasing amount of the initial amount of adsorbent, pH and temperature. The white montmorillonite shows more affinity for Cu(II) with 100% adsorption compared to Ni(II) [61]. In another study, sorption of Ni(II) on montmorillonite is influence by the presence of copper in a bi-metal aqueous solution with distortion of the shape of the adsorption isotherm whereas the presence of nickel has negligible effect on the sorption of copper [58]. EPR and XAS analyses of adsorption data reveal that both copper form inner-sphere complexes at pH 8 in both single-metal and binary metal system. However, nickel in single metal system forms inner-sphere complex at pH 8 but in binary-solute systems, it forms Ni phyllosilicate co-precipitate/alpha-$Ni(OH)_2$(s) precipitate at pH 8.0 [58]. In another study, the sorption of Ni(II) and Mn(II) on montmorillonite from Ugwuoba, Nigeria, reveals 90% removal of these ions from solution containing 500 mg/L at pH 6.0 with maximum adsorption capacity of 166.67 mg/g for nickel and 142.86 mg/g for manganese [62]. Acid treated montmorillonite has enhance adsorption ability for heavy metals (Zn, Cu, Mn, Cd, Pb, Ni), depending on the initial metal concentration [63].

Similarly, the adsorption of mercury, chromium, lead, copper, zinc, barium, nickel, manganese, cadmium, silver on Ca-montmorillonite from single metal solutions followed second-order at greater rate compared to montmorillonite [64]. Copper, lead and chromium forms surface precipitation with montmorillonite whereas mercury, zinc, barium, nickel manganese, cadmium and silver sorb onto montmorillonite via adsorption and ion exchange to form both inner and outer sphere complex at the silanol and aluminol site [64]. However, sorption of bi-metal solution of these metals is better described with Langmuir isotherm model [64]. In another study, Europium (III) sorbs on Na-montmorillonite to form an outer-sphere complex at the exchange site as well as inner-sphere surface complexes at the 'aluminol' and 'silanol' edge sites [65]. In another study, heavy metals such as Hg(II), Cr(III), Pb(II), Cu(II), Zn(II), Ba(II), Ni(II), Mn(II), Cd(II), Ba(II) and Ag (I) in a single metal system adsorbs more on Ca-montmorillonite compared to Na-montmorillonite [66]. The adsorption selective sequence is Hg(II) > Zn(II) > Ba (II) > Cd(II) > Ni(II) > Mn(II). However, Na-Montmorillonite is more effective for removal of Pb(II), Cu(II), Co(II), Cd(II) and Zn(II) from aqueous solution than Ca-Montmorillonite [66]. In general, montmorillonite clay and its modified form has stronger adsorption capacity for arsenic, cadmium, chromium, cobalt, lead, iron, manganese, nickel and zinc than kaolinite and its modified form [67].

3.2 Kaolinite

Adsorption of Cd, Cu, Ni, Zn, Pb and Cr with Ball clay (kaolinite with high plasticity) at 30°C indicates that it sorbs more ion compared to Ca-montmorillonite,

illite, kaolinite and Kaolin, and has the higher affinity for cd relative to other metals [68]. The sorption was at the maximum at pH 6 and 100% adsorption of 50 mg/L Cd. The sorption rate follows pseudo-first-order kinetics whereas the Langmuir model is used to describe the isotherm model [68]. Similarly, Pb(II), Cd(II), Ni(II) and Cu(II) sorption on kaolinitic clay from Longyan, China, show maximum sorption in 30 min and reduction of Pb concentration from 160.00 to 8.00 mg/L [69]. Another study found that adsorption of Cd(II), Co(II), Cu(II), Pb(II) and Ni(II) onto Acid treated kaolinite have great potential for removal these metals from aqueous solution compared to untreated kaolinite [70]. However, the use of natural and modified kaolinite clays for the removal of Cr(VI) for contaminated water is pH dependent and the adsorption increases from pH 1–2 at equilibration time of 240 min [71].

3.3 Illite

The adsorption of Caesium on clay made up of predominately of illite in the presence of small amount of organic matter and Fe-Oxide indicate that presence of organic matter play significant role for Cs uptake. The adsorption is described by Freundlich [48]. Maximum sorption of Caesium on to clay soil occurs at pH 8 and ambient temperature [72]. Comparative study of Cs sorption on illite, montmorillonite and kaolinite show that Cs is most reactive and has strong affinity for illite compared to other clay [73]. The sorption data was successfully modelled with 1-pK Diffuse layer model [73]. In another study, thallium is found to associate with illite in natural environment and sorption studies reveal that TI(I) sorbs more onto illite than smectite [74]. The affinity for TI follows this sequence: MnO_2 > illite > smectite = ferrihydrite > = Al_2O_3 = goethite > SiO_2. However, in presence of Rb, Cs, Ti adsorption to illite is less [74].

3.4 Bentonite

Removal of silver and copper in a binary solution containing the two ions with Verde-lodo bentonite reveals that the adsorbent has high adsorption affinity for copper than silver [75]. Cu adsorption on Verde-lodo bentonite is more at an elevated temperature and attained adsorption capacity of 0.110 mmol/g at 60°C, whereas silver attained 0.090 mmol/g at 20°C [75]. In another study, adsorption of indium on chitosan-coated bentonite is best described by Langmuir isotherm whereas the adsorption kinetics fits the pseudo second order [76]. Thorium (IV) sorption onto activated bentonite depends on temperature, pH, ionic strength, and type of anion and the adsorption kinetics can be described by pseudo-second-order model [77]. The activated bentonite is effective for removal of thorium (IV) and associates with it via surface complexation [77]. In the another study, bentonite was effectively used to remove thorium (IV) at pH 3, equilibration time of 18 h and 25°C and adsorption was fitted to Freundlich, Langmuir and Dubinin-Radushkevich isotherm models. Desorption experiment shows that thorium (IV) is best recovered with 1.0 M HNO_3 [49]. However, the use of bentonite for sorption of heavy metals has some negative effect. This is because increase in concentration of heavy metals such as zinc, lead and copper results to decrease in liquid limit, swelling potential, swelling pressure and free swelling of bentonite but increases its hydraulic conductivity due to sorption of heavy metal in the double layer structure [78].

3.5 Natural clay

Competitive adsorption and desorption cadmium, chromium, copper, lead and zinc on natural clay show difference in the optimum maximum pH of adsorption

and metal affinity for single and multi-element adsorption [79]. The adsorption sequence for single metal sorption is Cr > Pb > Cu > Cd > Zn whereas Cr > Cu > Pb > Cd > Zn is the obtained sequence in the multicomponent system. The study also notes that the initial pH determines the solubility and removal of heavy metal in competitive multi element scenario [79]. In both the single and multielement adsorption, about 90–100% metal uptake expect Zn was achieved at pH 2–12 [79]. In another study, sorption of Cd, Cu, Pb, and Zn with concentration of 10 mmol/L on clay minerals, Fe rich clay minerals, clay-Fe oxide, Fe-oxyhydroxides, and calcite at both alkaline and acidic condition show that cadmium and zinc are adsorbed in acidic media by clay minerals whereas copper and lead sorb more at alkaline meda [80]. Sorption of Pb(II), Cd(II), Cu(II) and Zn(II) on clay obtained from Aleg formation, Tunisia that has surface area of 71 m^2/g indicate adsorption sequence of Pb(II) > Cu(II) > Zn(II) > Cd(II) and capacity of 131.58 mg/g in single metal systems and less than 50.10 mg/g for multi-metal [81]. Another study found that Cd(II) adsorption is effective for clay samples heated at 200°C, however, above 200°C adsorption decreases as a result of loss of SiOH or Al–OH binding sites [68]. Similarly, clay from china shows to be effective for removal of Cd at 30°C [82]. In addition, investigation for the temperature and pH effect on Cr (VI) adsorption reveal that sorption rate increases with increasing temperature and decreasing pH for concentration range of 0.743–1.422 mg/g [83].

3.6 Palygorskite

Synthetic magnesium-aluminium layered double hydroxides modified palygorskite shows high adsorption capacity for of Pb(II), Cu(II) and Ni(II) in the aqueous solution with initial concentration of 100 mg/L at pH 5.0 [84]. The reaction fit into Langmuir isotherm and the pseudo-second-order kinetic model [84]. In another study, the use of synthetic palygorskite-Fe oxide nanocomposite removal of Pb(II) from aqueous solution with initial 20–500 mg/L Pb indicates that the adsorbent has maximum Pb(II) adsorption capacity of 26.6 mg/g at 5 g/L adsorbent 150 min^{-1} stirring speed, and 25°C [85]. The adsorption data best fitted to the Langmuir isotherm model and pseudo-second-order kinetic model [85].

3.7 Modified clay

Montmorillonite clay modified with tetramethylammonium cations show enhances adsorption capacity for copper compared with unmodified montmorillonite, and removed up to 99.4% Cu(II) from aqueous solution with adsorption capacity of 925.93 mg/g [86]. Another study found that modification of clay minerals with hexadecylammonium bromide (HDTMA) is effective for attenuation of As(III) and As(V) in the presence of Cd(II), Cu(II) and Mn(II) and anions such as glycine, iminodiacetic acid, ethylenediaminetetraacetic acid disodium salt, oxalic acid, phosphate and sulfate [87]. In contrast, Fe-oxide modified smectites (montmorillonite and saponite) have the best adsorption capacity for removal of As (III), Cd(II), Cr(III), Cu(II), Hg(II), Ni(II), Pb(II) and Zn(II) from aqueous solution with at concentration of 10–100 ppb [88]. Mercury is sequestered in Al pillared Clay from Aleg formation, Tunisia at pH 3.2 and 240 min equilibration time [89]. The adsorption fit to Langmuir model with adsorption capacities 49.75 mg/g whereas the adsorption kinetics fits to pseudo-second-order kinetic. The adsorption reaction is exothermic [89]. Another study found that Indium sorbs readily on montmorillonite Metosol modified with di(2-ethylhexyl) phosphoric acid with kinetics that follow pseudo-first- and pseudo-second-order models [89]. Sorption of copper and caesium on Al-pillared montmorillonites follow a pseudo-first-order equation and pH of sorption 4.0–6.0 for copper and 3.0–8.0 for caesium [51].

Caesium sorption is best described with Langmuir model while copper fits the Freundlich isotherm model [51]. Sorption of Cs onto Fe-pillared montmorillonite, goethite and their mixture show that optimum sorption pH range is 5–9 and 93% removal of Cs occurred with the mixture of 20% goethite with Fe-pillared montmorillonite. The sorption process is exothermic and follows pseudo-first-order kinetics and can be described with Dubinin-Radushkevich, Freundlich and Langmuir models [50]. Also, combination of Al-pillared montmorillonite and Fe_3O_4 an MMT/Fe3O4 removes Cs from contaminated soil and water and can be recycled efficiently, and can be applied for the remediation of Cs contaminated land. The adsorption follow pseudo-second-order kinetics and Freundlich isotherm model [52]. In addition, maximum adsorption of Cr(IV) from aqueous solution was achieved by using clay heated at 200 to 400°C [91]. The heating process increased the exposure of the adsorptive site and the adsorptive capabilities [91].

3.8 Metal oxides

The Fe^{3+} oxides and Mn-oxides such as goethite, magnetite and birnessite are usually used in sorption studies of heavy metals and anions because of its simple synthesis in the laboratory [40, 92]. These metal oxides act as hosts for toxic trace elements with valences of +2, +3 and +5 [92]. The potential use of these minerals and their mixtures for remediation of contaminated land are reviewed below.

3.8.1 Goethite

Gallium adsorbs on to goethite to form Ga hexa-coordinated >FeOGa (OH)(2)(0) surface complexes at both acid and alkaline pH and exhibit the same isotope fractionation [93]. In another study, vanadium (V) adsorbs onto goethite to form bidentate corner-sharing complex from initial solution of 2.5 and 25 mg/L at pH 1.5 to 12 [94]. Mononuclear V(V) complexes are present at 25 ppm whereas both mononuclear and polynuclear V(V) complexes exist at 25 mg//solution species form [94]. In another study, at concentration < 10 mg/L and pH 7, cobalt sorbs on goethite at pH 7 to form bidentate edge and corner complexes but form surface precipitates, bidentate edge and corner complexes from 10 to 58 mg/L and pH 7.5 [37]. With ageing, Co sorption on goethite is irreversible depending on the initial concentration [37]. In addition, sorption of Pb, Hg, Cd, Zn, Cu, Ni, Co, Mn, Cr and Al on goethite from solution 10^{-6} M was achieved in 2 h and 20°C, but different pH [94]. The pH of 50% sorbed metals (pH 50) ranges from 2.81 for Hg to 6.45 for Mn [95]. The adsorption of Cu(II) with initial concentration of 25 mg/L onto goethite, haematite and lepidocrocite from pH 2–7 reveal that at pH of total metal sorption is 6 for goethite, 6.2 for haematite and 6.8 for lepidocrocite [56]. In same study, EXAFS spectra show that Cu(II) adsorbs these Fe-(hydr)oxides to form two or three bidentate edge sharing, corner sharing and tridentate complexes [56]. Adsorption of Ni, Zn, and Ca onto the goethite reveal that goethite has stronger affinity for Ni and Zn compared to Ca, however, in no observable competition occur in Ni–Ca and Zn–Ca bi-metal systems [96]. The adsorption is well described with single-site Langmuir model [96]. In another study, indium with concentration of 6–29 μg/L was immobilised form acid mine drainage by raising it pH to 8 and subsequent sorption onto iron oxide [97]. In addition, up to 100 mg/L Ni sorbs onto goethite at pH 8, 25°C and equilibration time of 21 days [98].

3.8.2 Birnessite

Mn(II) forms edge-sharing complex with birnessite whereas Ni(II) forms triple corner-sharing complexes at pH 6.5–7.5, however, the addition of Mn(II) in

Ni(II)-birnessite suspension at pH 6.5 results to formation of edge-sharing Ni(II) complexes due to site competition [99]. However, at pH 7.5, the presence of Mn(II) results to transformation of birnessite into feitknechtite that encourages sorption and incorporation of Ni(II) from solution [99]. This suggests that alteration of birnessite can influence the solubility of nickel in anaerobic environment [98]. In another study, hexagonal birnessite (δ-MnO_2) was used to sorb Cu(II) containing 143, 77 and 32 mg/L at pH 1–9 [100]. At pH 3, 100% adsorption results to about 5, 2.5 and 1% of copper in the adsorbate [100]. However, EXFAS characterisation of adsorbates at pH 4 reveals that Cu forms by inner-sphere complexation whereas at pH 8, it associates with birnessite via structurally incorporation [100]. Sorption of Zn onto synthetic δ-MnO_2 from an initial solution containing 2000 mg/L of Zn occurs at pH $\sim$ 1 and at maximum pH $\sim$5 [101]. However, desorption reaction indicates the Zn sorption is reversible and EXFAS show that it form inner-sphere surface complexes at high pH [101]. Similarly, removal of Pb from solution containing 810, 1782, 2801 mg/L occur at pH $\sim$5.5 pH and equilibration time of 2 weeks, thus indication high sorption capacity of birnessite for Pb [101]. Also, desorption experiment show that the sorption is reversible at pH $\sim$1 [101]. In another study, sorption of Pb(II), Cu(II), Zn(II), Cd(II) onto hexagonal birnessite was carried out at pH 4.5 and characterised with powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The result of the study indicates that sorption capacity of biressinte for these metals follow this sequence: $Pb^{2+} \gg Cu^{2+} > Zn^{2+} > Cd^{2+}$ but Pb sorption is up to 3.9 times more than other metals [102].

3.8.3 Magnetite

Synthetic magnetite nano particles was used to remove Hexavalent chromium (Cr(VI)) from synthetic wastewater containing 0 to 50 mg/L Cr(IV) at pH 3.0 and 30°C.Up to 72% of Cr was removed via adsorption and the isotherm fitted to Freundlich model [53]. In addition, rapid sorption of Cu(II), Zn(II), Cd(II), Pb(II) and Ni(II) on synthetic Amine-magnetic Fe-oxide is influenced by pH, ionic strength and the complexation of amino groups [101]. Maximum adsorption occur at pH 6, ionic strength of 1.0 mmol/L NaCl and duration of 60 min and are best described with Pseudo-second-order kinetic model, Langmuir model [101]. The adsorption affinity of the adsorbent follow this sequence Pb(II) > Cu(II) > Zn (II) > Cd(II) > Ni(II) [103].

3.9 Mixture of oxide, clay and/or other materials

Mixture of goethite, humic acid and kaolinite are good adsorbents for lead, cadmium, zinc, nickel and copper and the adsorption is better described with Langmuir and Freundlich isotherm model [104]. However, in a five metal ion system (Quinary), the adsorption of lead, cadmium and nickel are affected negatively by the presence of zinc and copper whereas the presence of lead, cadmium and nickel has synergistic effect on the sorption of zinc and copper [104]. Another study found that low-cost adsorbent Algeria clay that is composed of predominantly montmorillonite and kaolinite has the capacity of adsorbing Cu(II) at pH of 6.5 and 20°C with maximum adsorption capacity of 12.22 mg/g [105]. However, treated Algeria clay under similar condition as the untreated clay has adsorption capacity of 15.40 mg/g [105]. The process of adsorption was spontaneous and exothermic [105]. Sorption of copper (II) ion on palygorskite and sepiolite is enhanced at elevated temperature [106]. The adsorption reactions are endothermically driven but sepiolite sorbs copper spontaneously and has more copper retention capacity compared to palygorskite [106]. In another study, combination of montmorillonite

and ZnO show high capacity for adsorption of Pb and Cu from aqueous solution at wide range of pH [107]. The kinetic of the adsorption reaction follow pseudo-second-order whereas the adsorption isotherm is described by Langmuir isotherm [107]. Arsenic adsorption on goethite, amorphous Fe-hydroxide, and Ti(IV)-Fe (III)-Al(III)-pillared bentonite, clay pillared with titanium (IV), iron (III), and aluminium (III) reveal that amorphous Fe-hydroxide has highest adsorption capacity for arsenate and arsenite [108]. Arsenic is stable at pH 7 and is mobilised at pH 4 and 10 but mostly at acidic condition. Mn- oxides, amorphous iron oxides and clay minerals sequester up to 61% of arsenic [109].

Combination of montmorillonite and humic acid in the ratio of 100:3 is efficient for removal of cadmium at pH 8.5 and contact time of 24 h with adsorption capacity of 18.96 mg/g for cadmium [110]. Another study reveal that the adsorption and desorption of cadmium and copper from montmorillonite, allophane, kaolinite, halloysite reveal that sericite has the highest ability for Cd sorption, however, montmorillonite showed greatest retention for Cd [111]. In addition, all clay types has sorption ability for copper with pH of 50% metal sorbed lower than pH of 50% metal sorbed for cadmium sorption [111]. In another study, the removal of Cu and Zn from aqueous solution by Al-montmorillonite, goethite, kaolinite and their mixtures at room temperature and pH 4 reveal that adsorption is via inner and outer sphere complexation [112]. However, mixing of different mineral for sorption of Cu and Zn retards their removal and decreases the exchange of proton and acid/base potential of the reactive sites [112]. The sorption of Zn onto hydrous Mn-oxide (HMO)-coated clay reveals that the affinity the HMO-coated montmorillonite was greater than that of uncoated montmorillonite, and possess linear isotherm at pH 5–6 [113]. X-ray absorption spectroscopy (XAS) reveal reduction of first shell distance at surface loading of 10^{-3} mol and pH 5–7 due to higher electrostatic attraction [113]. In another study, sorption of copper, zinc and lead on soil composed of clay minerals (smectites and vermiculites), carbonates and Fe-oxide show that Copper and lead has higher sorption capacity and retention compared to Zn [114]. Clay minerals adsorbs more metals than other phases, however, for lead, similar capacity was obtained for Fe-oxides [114]. The presence of carbonate in alkaline condition increases the amount of metal uptake, and the mixture of clay minerals and Fe-oxide enhanced adsorption of the metals [114]. Competitive sorption and desorption of Cd, Cr, Cu, Ni, Pb and Zn by iron oxide, Mn oxides, kaolinite, vermiculite and mica from initial solution of 100 mg/L show that kaolinite and mica has strong affinity and retention capability for cd; vermiculite, Cu and Zn; iron oxide and Mn-oxide, Pb [115]. Kaolinite has low retention capability for Cu whereas vermiculite and Mn oxide has greatest retention capability of all the metal [115].

In another study, the effect of increase surface area of clay minerals (kaolinite, montmorillonite and illite) through coating with Fe-oxide, organic matter and Al-oxides for adsorption of heavy metals indicate that coating clay increases the surface area of clay minerals with expectation of Aluminium oxide coated montmorillonite and organic matter coated 2:1 phyllosilicates [116]. Another study found that, both amorphous hydrous manganese oxide (HMO) and HMO-coated montmorillonite sorbs Ni and Pb to form inner-sphere complexes with Ni coordinating to vacant site of Mn-oxide structure and Pb forming bidentate corner-sharing complexes [117]. In addition, another study reveal that montmorillonite clay coated with amorphous (hydrous manganese oxide (HMO), birnessite and pyrolusite has the same surface properties as the coated oxide, however, the surface area of the coated Montmorillonite increases whereas the while the pore size distribution decreased. The HMO- and birnessite-coated clay still retained their pH (point of net zero charge (pnzc)) of 2.8 and 3.1, respectively, [118].

3.10 Advantages of using metal oxides and clays for remediation

The use of clay minerals and oxides is more effective than using other materials for remediation of heavy metals from the environment. From example, the use of sepioloite is better for remediation of Cd compared to $Ca(OH)_2$ [119]. In addition, clay minerals and oxides can be recycled and regenerated for additional remediation use. For example, synthetic palygorskite-Fe oxide exhibited the capability of removing Pb and three cycles reusable potential and retains it magnetic properties for the removal of the heavy metals [85]. Recovery of metals from sorbents can increase the life cycle and long term remediation cost [120]. The estimated zinc that will accumulate in composite substrate in Force Crag Mine is will amount to €7600 in 10 years, however, removal of this substrate after its exhaustion will cost more than €0.8 M whereas recycling the substrate through acid washing is estimated to cost €155,000 [120]. Similarly, oxides and clay minerals can be recycled and reused for remediation of the contaminant. In addition, these sorbents can be used to remediate economic heavy/rare earth metals for commercial and industrial purposes, however, this requires further investigation.

4. Conclusion

Oxides and clay minerals have large surface areas and can sorb heavy metals via adsorption and ion exchange, respectively. Sorption of these toxic metals on oxides and clay minerals reduce their concentration and mobility in aqueous solution and natural environment. This review confirms that sorption is highly dependent on pH, equilibration time, initial concentration of adsorbate, type of adsorbent, temperature, type of adsorbent modification and surface area. In addition, most of the adsorption of ions on clays and oxides are best described by Langmuir models and Pseudo-second-order model. Most remediation techniques employ the use of permeable reactive barriers (PBRs) to react the contaminant from groundwater. These barriers can be Fe-oxides, montmorillonite, Mn oxide-coated montmorillonite, Fe-oxide-coated montmorillonite [121]. The review confirmed that both metal oxides and clay have capability of sequestering heavy metals, however, combination of both metal oxides and modified clay have enhanced capability of removing heavy metals from aqueous solution. These inorganic adsorbents has the regeneration and recycling potentials and can be used to remediate and sequester economic metals for commercial purposes, however, this needs future investigation.

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