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Review

Removal of heavy metals from water sources in the developing world using low-cost materials: A review

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HIGHLIGHTS

- Removal of heavy metals on adsorption was reviewed in water sources.
- Low-cost materials were reviewed in the developing world.
- Various adsorption mechanisms for heavy metals were discussed.

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ABSTRACT

Heavy metal contamination is a growing concern in the developing world. Inadequate water and wastewater treatment, coupled with increased industrial activity, have led to increased heavy metal contamination in rivers, lakes, and other water sources in developing countries. However, common methods for removing heavy metals from water sources, including membrane filtration, activated carbon adsorption, and electrocoagulation, are not feasible for developing countries. As a result, a significant amount of research has been conducted on low-cost adsorbents to evaluate their ability to remove heavy metals. In this review article, we summarize the current state of research on the removal of heavy metals with an emphasis on low-cost adsorbents that are feasible in the context of the developing world. This review evaluates the use of adsorbents from four major categories: agricultural waste; naturally-occurring soil and mineral deposits; aquatic and terrestrial biomass; and other locally-available waste materials. Along with a summary of the use of these adsorbents in the removal of heavy metals, this article provides a summary of the influence of various water-quality parameters on heavy metals and these adsorbents. The proposed adsorption mechanisms for heavy metal removal are also discussed.
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1. Introduction

Freshwater is a basic requirement for humans and wildlife. The availability of clean drinking water is critical for maintaining a healthy life. However, while global water demand increases annually, various forms of pollution have compromised potential water sources (UN-Water, 2018). Moreover, researchers have found that the impacts of climate change, such as higher temperatures and changes to the water cycle, will also exacerbate these water issues and potentially result in increased flooding, more severe droughts, and enhanced toxicity of chemical contaminants in the environment (Milly et al., 2002; Noyes et al., 2009; Xi et al., 2017). Polluted water sources can be harmful to humans due to potential exposure to pathogens or toxic chemicals via irrigation of plants with contaminated water, the consumption of toxins in aquatic organisms, or the use of contaminated surface water for recreational purposes (*e.g.*, swimming) (Schwarzenbach et al., 2010). However, for the majority of individuals living in the developing world, human health is most commonly affected by the direct consumption of contaminated water.

In developing countries, the impact of increased pollution is particularly problematic because these populations do not have the resources to effectively treat contaminated water or access to clean drinking water systems that can supply water to their homes. The World Health Organization (WHO) estimates that 844 million people do not have a basic drinking water source and that 230 million people spend more than 30 min/d collecting water from an improved water source, which may include piped water, boreholes, protected wells and springs, rainwater, and packaged/delivered water (WHO, 2017a,b). The inability for people in developing countries to have consistent access to an improved drinking water source increases the likelihood of water-related diseases. According to WHO estimates, approximately 1.6 million people die every year from preventable water-related diseases, such as diarrhea, and 90% of these deaths are children under 5 years of age (Pandit and Kumar, 2015). In the developing world, drinking water contamination due to microbial agents (*e.g.*, bacteria and viruses) represents the greatest threat to human health. However, the proliferation of heavy metals in drinking water sources is also a growing concern. Table 1 provides the characteristics of common heavy metals found in the developing world.

In recent years, industrial and urban activities have increased throughout the developing world, which has subsequently contributed to increased heavy metal pollution. The release of contaminated wastewater from various industries, including coal-fired power plants (Demirak et al., 2006) and mining (Archundia et al., 2017), along with waste recycling and solid waste disposal activities (Herat and Agamuthu, 2012; Olafisoye et al., 2013; Perkins et al., 2014; Wu et al., 2015), represents a major source of pollution, while emissions from vehicles and other urban activities also contribute to it (Pandey and Pandey, 2009; Prasse et al., 2012). According to the United Nations, an estimated 80% of all industrial and municipal wastewater in the developing world is released to the environment without any prior treatment (UN-Water, 2018). Moreover, additional contributions to water pollution include polluted urban stormwater runoff, agricultural runoff, and rainwater transport into potential drinking water sources (Kambole, 2003; Lye, 2009). Heavy metals are of particular concern due to their toxic and carcinogenic nature, along with their documented harmful effects to human health (Chakraborty et al., 2013; Gleason et al., 2016; Jarup, 2003; Schwartzbord et al., 2013). Heavy metal pollution is also a concern because many of the drinking water treatment techniques used in the developing world, including chlorination, boiling, and solar disinfection, are ineffective at removing heavy metals (De Kwaadsteniet et al., 2013).

When considering the impact of heavy metals in the developing world, numerous review papers have investigated the prevalence of heavy metals in drinking water sources in several developing countries (Chowdhury et al., 2016; Emmanuel et al., 2009; Rahman et al., 2009; Rossiter et al., 2010), along with the human health hazards associated with heavy metal contamination (Amadia et al., 2017; Holecy and Mousavi, 2012; Jarup, 2003; Odongo et al., 2016).

Table 1
Characteristics of common heavy metals.

Heavy metal	Human health effects	Common sources	Maximum Contaminant Level	
			USEPA[a]	*WHO*[b]
Arsenic (As)	Skin damage Circulatory system issues	Naturally-occurring Electronics production	0.010 mg L^{-1}	0.010 mg L^{-1}
Cadmium (Cd)	Kidney damage Carcinogenic	Naturally-occurring Various chemical industries	0.005 mg L^{-1}	0.003 mg L^{-1}
Chromium (Cr)	Allergic dermatitis Diarrhea, nausea, and vomiting	Naturally-occurring Steel manufacturing	0.1 mg L^{-1}	0.05 mg L^{-1}
Copper (Cu)	Gastrointestinal issues Liver or kidney damage	Naturally-occurring Household plumbing systems	1.3 mg L^{-1}	2.0 mg L^{-1}
Lead (Pb)	Kidney damage Reduced neural development	Lead-based products Household plumbing systems	0.0 mg L^{-1}	0.01 mg L^{-1}
Mercury (Hg)	Kidney damage Nervous system damage	Fossil fuel combustion Electronics industries	0.002 mg L^{-1}	0.006 mg L^{-1}

[a] Values established by the United States Environmental Protection Agency (USEPA, 2019).
[b] Values established by the World Health Organization (WHO, 2017a,b).

Many researchers have conducted detailed studies on the heavy metal contamination of water sources in specific developing countries, including China (Cao et al., 2015; Li et al., 2014; Qu et al., 2012; Xu et al., 2017; Zou et al., 2015), India (Awasthi et al., 2016a, 2016b; Pandey and Pandey, 2009; Ramasamy et al., 2017; Sridhar et al., 2017), Bangladesh (Gleason et al., 2016; Islam et al., 2015b; Linderholm et al., 2011; Nahar et al., 2014; Wang et al., 2016), Ethiopia (Prasse et al., 2012; Yohannes et al., 2013), Pakistan (Bhowmik et al., 2015; Nawab et al., 2016, 2017; Rasheed et al., 2017; Rehman et al., 2008), and various other developing countries (Archundia et al., 2017; Belabed et al., 2017; Nweke and Sanders, 2009; Tarras-Wahlberg and Nguyen, 2008). Moreover, due to the well-documented impacts of heavy metals to human health, a significant amount of research has been conducted on methods of removing heavy metals from drinking water sources, as well as municipal wastewater, industrial wastewater, and other water sources. Many recent review articles highlight treatment methods and technologies that achieve high removal efficiencies for heavy metals and are currently being explored for use in many developed countries, such as membrane filtration (Kim et al., 2018), electrocoagulation (Al-Qodah and Al-Shannag, 2017; Bazrafshan et al., 2015), microbial remediation (Ayangbenro and Babalola, 2017; Li and Tao, 2015), activated carbon adsorption (Li et al., 2018a; Renu et al., 2017), carbon nanotechnology (Peng et al., 2017; Sherlala et al., 2018; Xu et al., 2018), and various modified adsorbents (Jiang et al., 2018; Sajida et al., 2018; Zare et al., 2018). However, these technologies are not feasible or cost-effective in the context of the developing world. To treat water in the developing world, proposed technologies must be easy to obtain, constructed by local workers with limited education, and have low operating and maintenance costs.

Therefore, in this review paper, we focus on the use of low-cost, often locally-available, materials that do not require additional energy input or modifications to remove heavy metals from water sources. While providing an exhaustive review of the studies conducted in the developing world regarding heavy metal removal is challenging, the objective of this review paper is to examine the major categories of materials that would be most readily available and utilized in the context of the developing world. The materials investigated in this review are divided into four broad categories: agricultural waste, which includes various types of residual waste from nuts (*e.g.*, peanut, cashew, pistachio, *etc.*), along with fruit and vegetable waste materials (*e.g.*, rice straw, corn, orange, banana peels, lemons, beets, grapefruit, *etc.*); naturally-occurring soil and mineral deposits; aquatic and terrestrial biomass (*e.g.*, seaweeds, water hyacinth, trees, *etc.*); and other waste materials that are commonly found in developing countries (*e.g.*, tea waste, local seashells, industrial by-products, *etc.*). We examined the removal of various heavy metals using these materials and surveyed the proposed removal mechanisms associated with these materials. To date, few review papers have surveyed the use of low-cost materials for the removal of heavy metals from water. The most recent review was published over approximately a decade ago (Babel and Kurniawan, 2003; Kurniawan et al., 2006).

2. Effect of water quality characteristics on heavy metal removal

When investigating the removal of heavy metals, it is important to evaluate the behavior of the heavy metals, along with the characteristics of the adsorbent, under varying water quality conditions. Among the most important water quality parameters related to heavy metal removal are pH, temperature, the presence of natural organic matter (NOM), and ionic strength. While heavy metal contamination is most often associated with industrial wastewater, in the developing world, heavy metals have been detected in various water sources, including domestic wastewater effluent (Emmanuel et al., 2009; Khatib et al., 2012), groundwater (Armah, 2014; Emmanuel et al., 2009; Kumarasinghe et al., 2017; Sridhar et al., 2017; Wang and Mulligan, 2006), rivers (Islam et al., 2015a, 2015b; Mohiuddin et al., 2011; Mwanamoki et al., 2015) and lakes (Archundia et al., 2017; Xu et al., 2017; Yohannes et al., 2013). These water sources have varying water quality characteristics, which ultimately influence the ability of an adsorbent to effectively remove heavy metal contamination from them. The following sections describe the chemical characteristics of heavy metals and the effects of water quality on heavy metals and their removal.

2.1. Chemical characteristics of heavy metals

Heavy metals typically enter the environment through various industrial activities, agricultural practices, and improper waste disposal (Chowdhury et al., 2016). Heavy metals are particularly problematic because of their persistence in the environment. Heavy metals are non-biodegradable and accumulate in humans and animals as they are exposed through the consumption of contaminated food and water. While humans, along with all living organisms, need varying amounts of heavy metals, such as iron, zinc, copper, and chromium, for proper growth and development, these metals can be toxic when consumed at elevated concentrations (Tchobanoglous et al., 2003). Table 2 provides the chemical properties of common heavy metals found in the environment.

Table 2
Chemical properties of heavy metals.

Heavy metal	Molecular weight (g mol^{-1})	Oxidation state(s)[a]	Van der Waals radius (10^{-12} m)	Electronegativity (Pauling Scale)	Log K_{OW}
Arsenic	74.9	−3, + **3**, + **5**	119	2.18	NA
Cadmium	112.4	+2	158	1.69	3.86 ± 0.36[b]
Chromium	52.0	0, +2, + **3**, + **6**	200	1.66	NA
Cobalt	58.9	−1, 0, + **2**, +3	200	1.88	NA
Copper	63.5	+1, + **2**	140	1.90	NA
Lead	207.2	**+2**, +4	202	2.33	4.02 ± 0.28[b]
Manganese	54.9	−1, 0, + **2**, +3, +4, +6, +7	205	1.55	3.98 ± 0.25[b]
Mercury	200.6	+1, + **2**	155	2.00	0.62[c]
Nickel	58.7	0, + **2**, +3	163	1.91	NA
Zinc	65.4	+2	139	1.65	NA

NA = not available.
[a] Bold values represent the most common oxidation state(s) for the heavy metal.
[b] Values determined experimentally by (Sakultantimetha et al., 2009).
[c] Values provided by Michigan Department of Environmental Quality.

2.2. Effect of pH

The pH of the water source has a significant impact on the presence of heavy metals and their characteristics. The speciation of heavy metals in aqueous solution is highly dependent on the pH. At neutral to low pH values, heavy metals generally exist in their cationic state and tend to be more soluble and mobile in water sources. As the pH rises, complexes begin to form with hydroxides and other anions that may be present in the water. Along with these effects of the heavy metals, pH can also affect the surface charge of the adsorbent, the concentration of ions on the functional groups of the adsorbent, and the ionization state of the adsorbent (Taşar et al., 2014).

Several studies have demonstrated the influence of pH on heavy metal speciation and removal. For example, the stability and mobility of copper have both been shown to increase with decreasing pH (Kumpiene et al., 2008). However, as the pH increases, the heavy metals form complexes with hydroxide ions, thus affecting the oxidation state of the heavy metal. In many cases, as the pH increases above neutral, the heavy metals form solids, which precipitate out of the water. The oxidation state for chromium, for example, has been shown to change from Cr(III), its more stable form, to Cr(VI), its more toxic form, as the pH increases (Pantsar-Kallio et al., 2001). Moreover, a wide variety of chromium species with various charges, such as H_2CrO_4, $HCrO_4^-$, Cr_2O_7, and CrO_4^{2-}, can be observed at different pH values (Sari and Tuzen, 2008). In the case of lead, lower pH values increase the concentration of free lead ions in the water source, while increased pH values lead to immobilization, primarily due to precipitation (Kumpiene et al., 2008).

Moreover, when evaluating the removal of heavy metals by adsorption, water sources with low pH values (<4.0) have high concentrations of H^+ ions, which often interfere with the interactions between soluble metal ions and adsorbent surfaces by competing for adsorption sites, thus reducing overall heavy metal removal (Al-Anber and Matouq, 2008; Chen et al., 2010; Li et al., 2018b; Thirumavalavan et al., 2010). However, when the pH increases, adsorption often increases as the surface of the adsorbent becomes more negatively charged and interacts more readily with the positively-charged heavy metals (Krishnani et al., 2008; Leyva-Ramos et al., 2005; Tan et al., 2010; Vimala and Das, 2009). This phenomenon has been observed using a wide variety of adsorbents. The removal of the majority of heavy metal ions by adsorption is minimal at low pH values (<3) (Bozbas and Boz, 2016; Rao and Khan, 2009; Taşar et al., 2014; Zhu et al., 2009). Meanwhile, as the pH increases, heavy metal removal increases as the concentration of H^+ ions is reduced and more adsorption sites become available (Qi and Aldrich, 2008; Taşar et al., 2014; Zhu et al., 2009). One notable exception is the removal of chromium, which exists in anionic species as the pH increases (*e.g.*, $HCrO_4^-$, CrO_4^{2-}). In this instance, adsorption has been shown to decrease as the pH of the solution increases. This is due to the electrostatic repulsion resulting from negative surface charges on the adsorbent, which inhibits the adsorption of anionic species (Ahmad et al., 2017; Georgieva et al., 2015).

Overall, when considering the behavior and potential removal of heavy metals, pH is a significant parameter that affects the behavior and removal of heavy metals. From the published research that was reviewed, the general consensus is that low pH values (<4) have been shown to hinder the adsorption of heavy metals, while pH values between 5 and 7 have been shown to be the most effective. In the context of the developing world, the pH of the water source to be treated should be maintained at neutral levels to maximize heavy metal adsorption.

2.3. Effect of temperature

Temperature is another important parameter that should be considered when evaluating the behavior of heavy metals and their subsequent removal. Many of the mechanisms that have been identified for the removal of heavy metals are enhanced at higher temperatures, including surface complexation reactions and various forms of ion exchange (Chen et al., 2010). For instance, in a previous study, the removal of Ni(II) using tea waste increased by approximately 22% when the temperature was increased from 25 to 60 °C, which was attributed to the increased mobility of the heavy metals, as well as the increased number of adsorption sites due to bond rupturing (Malkoc and Nuhoglu, 2005). In another study, increased removal of Cr(VI) using pistachio hull waste was achieved by increasing the temperature from 5 to 40 °C, which was attributed to the possible development of additional adsorption sites on the surface of the adsorbent (Moussavi and Barikbin, 2010). Another study found that the adsorption of Cu(II) onto hazelnut shells increased with increased temperature, which was attributed to the potential increased pore size of the shells and the increased kinetic energy of the Cu(II) ions, which facilitated more contact with the adsorbent (Demirbas et al., 2009). Along with increased adsorption, the adsorption process has also been shown to proceed more quickly at higher temperatures, due to the increased driving force of diffusion across the boundary layer and an increased diffusion rate within the adsorbent (Weng et al., 2014).

However, in many cases, increased temperatures have resulted in a decrease in the removal of heavy metals. For instance, in one study, the removal of total chromium by red algae was reduced from 90 to 78% with increasing temperature, possibly due to the tendency for ions to remain in the aqueous phase (Sari and Tuzen, 2008). Moreover, several researchers have reported a reduction in the removal of heavy metals such as Pb(II) and Ni(II) with increasing temperature, which was attributed to decreased surface activity (Senthil Kumar et al., 2011; SenthilKumar et al., 2011; Taşar et al., 2014). A study that investigated the adsorption of Cr(III) and Cu(II) onto peanut shells reported increased removal as the temperature rose to 50 °C, then a decrease when the temperature increased to 60 °C. This outcome was possibly due to potential damage to the adsorption sites on the peanut shells (Witek-Krowiak et al., 2011). In another study that evaluated the removal of Cd(II) using olive cake, the adsorption capacity of the olive cake decreased by 32% when the temperature was raised from 28 to 45 °C (Al-Anber and Matouq, 2008). Therefore, when assessing the effects of temperature on the removal of heavy metals, each adsorbent and the corresponding metal ion must be evaluated specifically to determine the overall impact of temperature changes on the adsorption process.

2.4. Effect of ionic strength

The ionic strength of the water source has also been shown to have an effect on heavy metals and the ability to remove them. The presence of chloride can lead to the formation of neutral or negatively-charged heavy metal-chloride complexes that are soluble and difficult to remove (Ferraz and Lourenco, 2000). This phenomenon was observed by Villaescusa et al. (2004), who reported a significant decrease in the removal efficiency of Cu(II) and Ni(II) as the ionic strength increased, due to the increased formation of heavy metal-chloride complexes that had a low affinity for adsorption. Researchers who studied the behavior of trace metals in an estuary also observed a strong correlation between increased salinity and increased concentration of dissolved metals, particularly copper, cadmium, and zinc (Wang et al., 2017).

When interactions between heavy metals and other surfaces are

strongly influenced by electrostatic forces, increased ionic strength in a solution can have a significant effect on the behavior and removal of heavy metals. Based on theories related to surface chemistry, an electric double layer decreases with increasing ionic strength influencing electrostatic interactions, which leads to reduced adsorption of heavy metals as the ionic strength increases (Onyancha et al., 2008). For example, Zhang (2011) investigated the effects of ionic strength on the removal of heavy metals, including Cu(II), Pb(II), and Zn(II), by dairy manure compost and reported that the overall removal of heavy metals decreased as the ionic strength increased (Zhang, 2011).

However, other studies have demonstrated that heavy metal removal increases with ionic strength. Yang et al. (2016) reported that the removal of As(III) and Ni(II) increased by approximately 25% as the ionic strength of the solution increased from 0.01 to 1.0 M Cl^-, due to the involvement of inner-sphere surface complexation. Moreover, a study on the adsorption of Co(II) and Cu(II) onto crab shell particles demonstrated increased removal of 2–5% when the ionic strength of the solution was increased by adding competing ions, such as Na^+ and K^+ (Vijayaraghavan et al., 2006).

2.5. Effect of NOM

NOM is commonly understood to consist of humic and fulvic acids that are derived from the decomposition of plant and animal matter (Merdy et al., 2006). NOM is a complex array of organic acids and is highly reactive with heavy metals. Interactions can occur between NOM and heavy metals, which can alter the reactivity of the heavy metals in the environment and affect their mobility, bioavailability, and toxicity (Merdy et al., 2006). The specific impact of NOM on heavy metals can be difficult to ascertain, primarily due to the wide array of additional factors that contribute to the manner in which NOM affects heavy metals, including pH, the humification of the specific NOM, and the oxidation state of the heavy metal (Kumpiene et al., 2008). In many instances, the acidic nature of the NOM allows them to interact with heavy metals through various mechanisms, including ion exchange, chelation, and surface adsorption (Reuter and Perdue, 1977).

For example, arsenic has been found to form complexes with both humic and fulvic acids, which may contribute to increased arsenic immobilization (Wang and Mulligan, 2006). Metals, such as copper and zinc, also form complexes with NOM (Wang et al., 2017). Du et al. (2011) reported that the presence of organic matter slightly enhances the removal of Cd(II), Pb(II), and Zn(II) by mollusk shells. Moreover, research has shown that the presence of NOM can reduce chromium from its toxic, hexavalent form, Cr(VI), to its less harmful, more stable form, Cr(III) (Kumpiene et al., 2008). However, NOM can reduce arsenic from its less toxic form, As(V), to its more toxic and mobile form, As(III) (Kumpiene et al., 2008). These studies demonstrate that NOM can often unpredictably affect the removal of heavy metals and complicate the identification of the prevailing mechanisms associated with heavy metal removal.

3. Removal of heavy metals using low-cost materials

3.1. Agricultural waste

The use of agricultural waste to remove heavy metals has been widely investigated by researchers in both developed and developing countries. When considering the removal of heavy metals in the context of a developing country, agricultural waste often represents a source of abundant, effective adsorbents to implement into water treatment processes. For example, dairy manure compost is a unique material that has been shown to effectively remove heavy metals by achieving maximum adsorption capacities of 15.5, 27.2, and 95.3 mg g^{-1} for Zn(II), Cu(II), and Pb(II), respectively (Zhang, 2011).

Residual waste materials from rice are a prevalent form of agricultural waste that are produced in large volumes, particularly in the developing world. These types of waste include rice bran, rice straw, and rice husk. These waste materials have been shown to effectively remove heavy metals from aqueous solutions. For instance, rice straw and rice bran have been shown to remove Cu(II) with maximum adsorption capacities of 18.4 and 21.0 mg g^{-1}, respectively (Singha and Das, 2013). Several studies have demonstrated the ability of rice husk to remove heavy metals from water sources. A study of the removal efficiencies of nine different heavy metals using rice husk observed maximum adsorption capacities ranging from 5.5 to 58.1 mg g^{-1}, with the values increasing in the following order: Ni(II) < Zn(II) ≈ Cd(II) ≈ Mn(II) ≈ Co(II) < Cu(II) ≈ Hg(II) < Pb(II) (Krishnani et al., 2008). Another study on the removal of Cu(II) using rice husks reported a maximum adsorption capacity of 17.9 mg g^{-1} (Singha and Das, 2013). In a study on the use of rice husks for the adsorption of Cr(VI), significant removal (>95%) only occurred in the case of low pH (<3.0), primarily due to the speciation of the Cr(VI) ions (Georgieva et al., 2015). Bansal et al. (2009) evaluated the removal of Cr(VI) using rice husk and achieved a maximum adsorption capacity of 8.5 mg g^{-1}; they also found that treating rice husk with formaldehyde enhanced removal by approximately 23%. Another study used phosphate-treated rice husk to evaluate the removal of Cd(II) from wastewater and achieved a high maximum adsorption capacity (103 mg g^{-1} at 20 °C) (Ajmal et al., 2003).

Residuals from peanuts were also found to be an effective adsorbent for the removal of heavy metals. A maximum adsorption capacity of 39 mg g^{-1} was achieved for the removal of Pb(II) using peanut shells; significant removal was observed at various temperatures and pH conditions (Taşar et al., 2014). Peanut shells were also shown to remove Cr(VI) at low pH values, achieving a maximum adsorption capacity of 4.3 mg g^{-1} (Ahmad et al., 2017). Moreover, researchers achieved effective removal of Cr(III) and Cu(II) using peanut shells with maximum adsorption capacities of 27.9 and 25.4 mg g^{-1}, respectively (Witek-Krowiak et al., 2011). Researchers also observed significant heavy metal removal with peanut husks, achieving maximum adsorption capacities of 7.7, 10.2, and 29.1 mg g^{-1} for Cr(III), Cu(II), and Pb(II), respectively (Li et al., 2007). Peanut hull, which is an abundant agricultural by-product, has also been shown to remove Cu(II) with a maximum adsorption capacity of 21.3 mg g^{-1} (Zhu et al., 2009).

Wastes from other nuts have also been shown to remove heavy metals from different water sources. Several studies have investigated the ability of cashew nut shells to remove heavy metals from aqueous solutions. When evaluating the removal of Cu(II), researchers achieved significant removal (>85%) and a maximum adsorption capacity of 20 mg g^{-1} with cashew nut shells (SenthilKumar et al., 2011). Another study evaluated the removal of Ni(II) using cashew nut shells and achieved 60–75% and a maximum adsorption capacity of 18.9 mg g^{-1} (Senthil Kumar et al., 2011). The removal of these heavy metals using cashew nut shells has been attributed primarily to its high surface area, which allows for significant number of active sites for adsorption to occur (Senthil Kumar et al., 2011; SenthilKumar et al., 2011). Pistachio hull waste also demonstrated significant removal (>98%) of Cr(VI) from various water sources, achieving a maximum adsorption capacity of 116.3 mg g^{-1} (Moussavi and Barikbin, 2010). The high adsorption capacity of Cr(VI) by pistachio hull waste was attributed to the electrostatic attraction, as well as binding to various functional groups on the surface of the adsorbent (Moussavi and Barikbin,

2010). Another study investigated the use of pecan shells to remove Cu(II), Pb(II), and Zn(II) by utilizing a variety of modification techniques to enhance removal, including acid, steam, and carbon dioxide activation (Bansode et al., 2003). In this study, Pb(II) was removed at the highest rate, followed by Cu(II) and Zn(II), for each type of modified pecan shell, with maximum adsorption observed for acid-activated pecan shells (Bansode et al., 2003). Almond shells also demonstrated approximately 20–40% removal of Cr(VI) when adjusting the pH and the adsorbent dose in the solution (Dakiky et al., 2002). Hazelnut shells also demonstrated effective removal of Cu(II), achieving a maximum adsorption capacity of 58.3 mg g^{-1} (Demirbas et al., 2009). Groundnut shells were also used as an adsorbent in the removal of heavy metals. Shukla and Pai (2005) achieved maximum adsorption capacities of 4.9, 8.05, and 11.0 mg g^{-1} for Cu(II), Ni(II), and Zn(II), respectively, with groundnut shells (Shukla and Pai, 2005). These adsorption capacities were also enhanced by 40–70% with chemical modifications to the groundnut shells using reactive dye (Shukla and Pai, 2005).

Various fruit wastes have been shown to effectively remove heavy metals from aqueous solutions. For instance, lemon peel was shown to effectively remove Zn(II), Pb(II), Cd(II), Cu(II), and Ni(II), achieving maximum adsorption capacities of 27.9, 37.9, 54.6, 71.0, and 80.0 mg g^{-1}, respectively (Thirumavalavan et al., 2010). Orange peel also demonstrated effective heavy metal removal in a variety of studies. Ajmal et al. (2000) achieved significant removal of Ni(II) (97.5%) with orange peel, along with lower removal efficiencies of Cu(II), Pb(II), Zn(II), and Cr(VI). Thirumavalavan et al. (2010) investigated the adsorption of Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II) with orange peel and demonstrated significant removal, achieving maximum adsorption capacities of 41.8, 63.3, 81.3, 27.1, and 24.1 mg g^{-1}, respectively. Another study demonstrated similar removal of Pb(II) using orange peel, achieving a maximum adsorption capacity of 27.9 mg g^{-1} (Abdelhafez and Li, 2016). Annadurai et al. (2002) also achieved much lower removal of five different heavy metals using orange peel with maximum adsorption capacities ranging from 1.9 to 7.8 mg g^{-1} in the following order of adsorption: Pb(II) > Ni(II) > Zn(II) > Cu(II) > Co(II). Significant removal of Cd(II), Cu(II), Pb(II), and Ni(II) was also achieved with chemically-modified orange peel with maximum adsorption capacities of 293, 289, 476, and 162 mg g^{-1}, respectively (Feng et al., 2009, 2011). Banana peel also exhibited varying degrees of heavy metal removal in aqueous solution. Thirumavalavan et al. (2010) demonstrated significant removal of a variety of heavy metals, achieving maximum adsorption capacities of 21.9, 25.9, 34.1, 52.4, and 54.4 mg g^{-1} for Zn(II), Pb(II), Cd(II), Cu(II), and Ni(II), respectively. A study conducted by DeMessie et al. (2015) achieved a maximum adsorption capacity of 7.4 mg g^{-1} for Cu(II) using banana peel, which increased to 38.3 and 38.4 mg g^{-1} after the banana peel was pyrolyzed at 500 °C and 600 °C, respectively. Another study observed relatively low removal for several heavy metals using banana peel, achieving maximum adsorption capacities ranging from 2.6 to 7.9 mg g^{-1} in the following order of adsorption: Pb(II) > Ni(II) > Zn(II) > Cu(II) > Co(II) (Annadurai et al., 2002). Grapefruit peel was also found to be an effective adsorbent for the removal of Cd(II) and Ni(II) from aqueous solution, achieving maximum adsorption capacities of 42.1 and 46.1 mg g^{-1}, respectively (Torab-Mostaedi et al., 2013). The adsorption onto the grapefruit peel was attributed to the ion-exchange mechanism and, to a lesser extent, complexation with –OH functional groups (Torab-Mostaedi et al., 2013). Grape stalk wastes have also demonstrated the ability to remove heavy metals, achieving maximum adsorption capacities of 10.1 and 10.6 mg g^{-1} achieved for Cu(II) and Ni(II), respectively (Villaescusa et al., 2004).

Other types of vegetable waste have been shown to remove heavy metals from water source. Mushroom residues were shown to be effective in the removal of heavy metals. Based on an evaluation of four different types of mushroom residues, removal efficiencies for Cu(II), Zn(II), and Hg(II) ranged from 39.7% to 81.7% (Li et al., 2018b). Another study investigated the removal of Cd(II) and Pb(II) using three different mushrooms and achieved maximum adsorption capacities of 35.0 and 33.8 mg g^{-1}, respectively (Vimala and Das, 2009). Corncob was also shown to remove heavy metals from aqueous solutions. When investigating its removal of Cd(II), researchers achieved a maximum adsorption capacity of 5.1 mg g^{-1}, along with a 4–10 fold increase in removal when the corncob was chemically modified using nitric and citric acid (Leyva-Ramos et al., 2005). Moreover, corncob successfully removed Pb(II), with a maximum adsorption capacity of 16.2 mg g^{-1} (Tan et al., 2010). The adsorption capacity for the removal of Pb(II) using corncob increased significantly (43.4 mg g^{-1}) when the corncob was treated with sodium hydroxide (Tan et al., 2010). A summary of selected studies evaluating the ability of agricultural wastes to remove heavy metals can be found in Table 3. Several comprehensive review papers that discuss the removal of heavy metals, along with other inorganic and organic contaminants, using agricultural waste products as adsorbents have been published (Dai et al., 2018; Mo et al., 2018; Nguyen et al., 2013; Sulyman et al., 2017).

3.2. Naturally-occurring soil and mineral deposits

Numerous studies have investigated whether soil and other mineral deposits can remove heavy metals from aqueous solutions. Natural soil and mineral deposits are heterogeneous and thus have varying degrees of affinity for heavy metals and other harmful constituents. The variability in their affinity for heavy metals is often attributed to the solubility (K_{sp}) of the heavy metal, which may result in the precipitation of metal carbonates and hydroxides, along with other physical and chemical properties, such as charge density, electronegativity, and the hydrolysis constant (pK_H) of the heavy metal (Appel et al., 2008). When considering the economic and technological constraints of a developing country, the use of soils and other natural materials may be an ideal and effective way of removing heavy metals from aqueous solution.

For example, Appel et al. (2008) investigated three different soils from Puerto Rico with respect to their ability to remove Pb(II) and Cd(II). Each soil removed Pb(II) and Cd(II), achieving maximum adsorption capacities ranging from 4.1 to 6.7 and 1.6–3.5 mg g^{-1} for Pb(II) and Cd(II), respectively. Kul and Koyuncu (2010) also evaluated the removal of Pb(II) using native and activated bentonite. A maximum adsorption capacity of 19.2 mg g^{-1} was achieved in the case of native bentonite, while the activated bentonite was much less effective at removing Pb(II) ($q_{max} = 1.7$ mg g^{-1}) (Kul and Koyuncu, 2010). Tang et al. (2009) evaluated the removal of Pb(II) using natural kaolin and observed significant adsorption, achieving a maximum adsorption capacity of 165.1 mg g^{-1}. The high adsorption capacity of kaolin was attributed to interactions between Pb(II) and the carbonate in the natural kaolin, along with the consistently negative charge of the surface of the kaolin particles, which were independent of pH (Tang et al., 2009). Qin et al. (2006) investigated the removal of Cd(II), Cu(II), and Pb(II) using two types of peat. For each type of peat, Pb(II) was the most favorably adsorbed heavy metal, followed by Cd(II) and Cu(II), with maximum adsorption capacities ranging from 88.7 to 118.7, 32.0–50.2, and 25.4–31.4 mg g^{-1} for Pb(II), Cd(II), and Cu(II), respectively. These levels of heavy metal removal by peat have been attributed to the presence of polar functional groups, such as carboxylic, hydroxylic, and phenolic groups, which can all contribute to heavy metal adsorption (Qin et al., 2006).

Tiede et al. (2007) investigated the use of mineral deposits containing manganese-oxyhydroxides as filter material to remove

Table 3
Removal of heavy metals by various agricultural waste products.

Adsorbent	Heavy metal	Surface area (m^2 g^{-1})	C_0 (mg L^{-1})	q_{max} (mg g^{-1})	Reference
A. Hypogea (peanut) shells	Chromium (VI)	1.8	0–40	4.3	Ahmad et al. (2017)
Almond	Chromium (VI)	N.R.	20-1000	10.2	Dakiky et al. (2002)
Apple residues	Copper (II)	N.R.	30	10.8	Lee and Yang (1997)
Banana peel	Cadmium (II)	1.3	100–800	34.1	Thirumavalavan et al. (2010)
	Cobalt (II)	N.R.	5–25	2.6	Annadurai et al. (2002)
	Copper (II)	1.3	100–800	52.4	Thirumavalavan et al. (2010)
	Copper (II)	N.R.	5–25	4.8	Annadurai et al. (2002)
	Copper (II)	38.49	10–30	7.4	DeMessie et al. (2015)
	Lead (II)	1.3	100–800	25.9	Thirumavalavan et al. (2010)
	Lead (II)	N.R.	5–25	7.9	Annadurai et al. (2002)
	Nickel (II)	1.3	100–800	54.4	Thirumavalavan et al. (2010)
	Nickel (II)	N.R.	5–25	6.9	Annadurai et al. (2002)
	Zinc (II)	1.3	100–800	21.9	Thirumavalavan et al. (2010)
	Zinc (II)	N.R.	5–25	5.8	Annadurai et al. (2002)
Cashew nut shells	Copper (II)	395	10–50	20.0	SenthilKumar et al. (2011)
	Nickel (II)	395	10–50	18.9	Senthil Kumar et al. (2011)
Coconut shells	Chromium (VI)	0.5	54.5	18.7	Singha and Das (2011)
	Copper (II)	N.R.	5–300	19.9	Singha and Das (2013)
Coconut-shell biochar	Cadmium (II)	212	100-2000	3.5	Paranavithana et al. (2016)
	Lead (II)	212	100-2000	13.4	Paranavithana et al. (2016)
Corncob	Cadmium (II)	<5	5–120	5.1	Leyva-Ramos et al. (2005)
	Lead (II)	N.R.	20.7–414	16.2	Tan et al. (2010)
Dairy manure compost	Copper (II)	N.R.	31.8	27.2	Zhang (2011)
	Lead (II)	N.R.	103.6	95.3	Zhang (2011)
	Zinc (II)	N.R.	32.7	15.5	Zhang (2011)
Grapefruit peel	Cadmium (II)	N.R.	50	42.1	Torab-Mostaedi et al. (2013)
	Nickel (II)	N.R.	50	46.1	Torab-Mostaedi et al. (2013)
Grape stalks	Copper (II)	N.R.	15.3–153	10.1	Villaescusa et al. (2004)
	Nickel (II)	N.R.	14.1–141	10.6	Villaescusa et al. (2004)
Groundnut shells	Copper (II)	N.R	73–465	4.5	Shukla and Pai (2005)
	Nickel (II)	N.R.	107–554	3.8	Shukla and Pai (2005)
	Zinc (II)	N.R.	38–244	7.6	Shukla and Pai (2005)
Hazelnut shells	Copper (II)	441.2	25–200	58.3	Demirbas et al. (2009)
Lemon peel	Cadmium (II)	1.3	100–800	54.6	Thirumavalavan et al. (2010)
	Copper (II)	1.3	100–800	70.9	Thirumavalavan et al. (2010)
	Lead (II)	1.3	100–800	37.9	Thirumavalavan et al. (2010)
	Nickel (II)	1.3	100–800	80.0	Thirumavalavan et al. (2010)
	Zinc (II)	1.3	100–800	27.9	Thirumavalavan et al. (2010)
Orange peel	Cadmium (II)	N.R.	50–1200	293	Feng et al. (2011)
	Cadmium (II)	2.0	100–800	41.8	Thirumavalavan et al. (2010)
	Cobalt (II)	N.R.	5–25	1.8	Annadurai et al. (2002)
	Copper (II)	N.R.	5–25	3.7	Annadurai et al. (2002)
	Copper (II)	2.0	100–800	63.3	Thirumavalavan et al. (2010)
	Lead (II)	N.R.	5–25	7.8	Annadurai et al. (2002)
	Lead (II)	N.R.	50-1200	476	Feng et al. (2011)
	Lead (II)	0.21	57	27.9	Abdelhafez and Li (2016)
	Lead (II)	2.0	100–800	27.1	Thirumavalavan et al. (2010)
	Nickel (II)	N.R.	5–25	6.0	Annadurai et al. (2002)
	Nickel (II)	N.R.	50-1200	162	Feng et al. (2011)
	Nickel (II)	2.0	100–800	81.3	Thirumavalavan et al. (2010)
	Zinc (II)	N.R.	5–25	5.3	Annadurai et al. (2002)
	Zinc (II)	2.0	100–800	24.1	Thirumavalavan et al. (2010)
Peanut shells	Chromium (III)	N.R.	10-1000	27.9	Witek-Krowiak et al. (2011)
	Copper (II)	N.R.	10-1000	25.4	Witek-Krowiak et al. (2011)
	Lead (II)	0.84	100–350	39.0	Taşar et al. (2014)
Peanut hull	Copper (II)	N.R.	10–400	21.3	Zhu et al. (2009)
Peanut husk	Chromium (III)	N.R.	0–50	7.7	Li et al. (2007)
	Copper (II)	N.R.	0–50	10.2	Li et al. (2007)
	Lead (II)	N.R.	0–50	29.1	Li et al. (2007)
Pistachio hull waste	Chromium (VI)	1.04	50–200	116	Moussavi and Barikbin (2010)
Rice bran	Chromium (VI)	0.1	54.5	12.3	Singha and Das (2011)
	Copper (II)	N.R.	5–300	21.0	Singha and Das (2013)
Rice husk	Cadmium (II)	N.R.	50–200	16.6	Krishnani et al. (2008)
	Chromium (VI)	0.5	54.5	11.4	Singha and Das (2011)
	Chromium (VI)	N.R.	100	8.5	Bansal et al. (2009)
	Cobalt (II)	N.R.	50–200	9.6	Krishnani et al. (2008)
	Copper (II)	N.R.	5–300	17.9	Singha and Das (2013)
	Copper (II)	N.R.	50–200	10.9	Krishnani et al. (2008)
	Lead (II)	N.R.	50–200	58.0	Krishnani et al. (2008)
	Mercury (II)	N.R.	50–200	36.1	Krishnani et al. (2008)
	Nickel (II)	N.R.	50–200	5.5	Krishnani et al. (2008)
	Zinc (II)	N.R.	50–200	8.1	Krishnani et al. (2008)
Rice straw	Chromium (VI)	1.2	54.5	12.2	Singha and Das (2011)
	Copper (II)	N.R.	5–300	18.4	Singha and Das (2013)

Table 3 (*continued*)

Adsorbent	Heavy metal	Surface area (m^2 g^{-1})	C_0 (mg L^{-1})	q_{max} (mg g^{-1})	Reference
S. Lychnophera Hance	Cadmium (II)	N.R.	0.25–1.0	27.1	Liu et al. (2006)
Sugar beet pulp	Copper (II)	N.R.	25–250	28.5	Aksu and Isoglu (2005)
Sugar cane bagasse	Cadmium (II)	0.49	10–30	0.96	Moubarik and Grimi (2015)
	Lead (II)	92.3	57	87.0	Abdelhafez and Li (2016)

Cd(II), Ni(II), and Zn(II) from drinking water. Using these deposits, the researchers achieved maximum adsorption capacities of 10.4, 14.2, and 32.0 mg g^{-1} for Ni(II), Zn(II), and Cd(II), respectively. Elouear et al. (2008) evaluated the removal of Cd(II), Cu(II), Pb(II), and Zn(II) using phosphate rock obtained from Tunisian ores. In their study, the phosphate rock achieved maximum adsorption capacities ranging from 8.5 to 12.8 mg g^{-1}, with the following order of adsorption: Pb(II) > Cd(II) > Cu(II) > Zn(II). The authors also reported that phosphate rock that was activated with sodium hydroxide and nitric acid solution achieved a 25–50% higher adsorption capacity than untreated phosphate rock (Elouear et al., 2008).

Several comprehensive review papers on the removal of heavy metals using soil and other natural remediation techniques have been published. Derakhshan Derakhshan Nejad et al., 2018 reviewed the use of various types of soil amendments, including mud, phosphate rock, and other soil materials, to remove heavy metals from water sources. Kumpiene et al. (2008) also reviewed the use of amendments to remediate heavy metal contamination in soil. Many of these amendments include various soils and other minerals that serve to immobilize heavy metals and reduce their toxicity. Furthermore, Wang and Mulligan (2006) extensively documented and reviewed natural processes for removing arsenic, which include naturally-occurring iron and manganese oxides, clays, and natural organic matter (Wang and Mulligan, 2006). Jimenez-Castaneda and Medina (2017) reviewed the use of zeolites and clays to remove heavy metals from water sources with an emphasis on the impact of the application of surfactants to enhance overall performance (Jimenez-Castaneda and Medina, 2017). With continuously growing interest in the use of abundant, locally-available soils, minerals, and other natural organic material to remove heavy metals, research in this area is anticipated to continue, particularly as developing countries seek less-expensive methods of addressing heavy metal contamination. Table 4 summarizes selected studies that highlight the ability of naturally-occurring soil and mineral deposits to remove heavy metals.

3.3. Aquatic and terrestrial biomass

Various forms of trees, plants, and other terrestrial and aquatic materials that are plentiful in developing countries have also been considered for bioremediation. For example, *Moringa oleifera* (MO) has received significant attention due to its potential ability to remove heavy metals. MO is a tropical, drought-tolerant tree that has been evaluated for its water and wastewater treatment capabilities (Shan et al., 2017). MO exhibits high removal (>90%) of a wide variety of heavy metals, including Cd(II), Fe(II), Cr(III), Zn(II), and Cu(II) from water and wastewater (Kansal and Kumari, 2014; Shan et al., 2017). However, a recent study showed that MO is not effective at removing Pb(II) from wastewater (Shan et al., 2017). Along with the removal of heavy metals, researchers have reported that the use of MO does not have a significant effect on the characteristics of the source water (*e.g.*, pH, ionic strength) (Shan et al., 2017). Several removal mechanisms have been proposed for MO, including adsorption, charge neutralization, complexation, and interparticle bridging (Kansal and Kumari, 2014).

Tree fern is another plant-based material that is effective at removing heavy metals. An equilibrium isotherm study conducted by Ho et al. (2002) found that tree ferns native to Taiwan effectively removed Zn(II), Cu(II), and Pb(II), achieving maximum adsorption capacities of 7.6, 10.6, and 39.8 mg g^{-1}, respectively. These adsorption capacities were attributed to the cellulose-based structure of the tree fern, which is negatively charged and exhibits a strong affinity for metal cations (Ho et al., 2002).

Table 4
Removal of heavy metals by naturally-occurring soil and mineral deposits.

Adsorbent	Heavy metal	Surface area (m^2 g^{-1})	C_0 (mg L^{-1})	q_{max} (mg g^{-1})	Reference
Bentonite	Lead (II)	72.0	5–25	19.2	Kul and Koyuncu (2010)
Kaolin	Lead (II)	8.0	80–320	165	Tang et al. (2009)
Mn-oxyhydroxide mineral	Cadmium (II)	143	0–225	32.0	Tiede et al. (2007)
	Nickel (II)	143	0–117	10.4	Tiede et al. (2007)
	Zinc (II)	143	0–131	14.2	Tiede et al. (2007)
Peat (Danish)	Cadmium (II)	13.3	225	50.2	Qin et al. (2006)
	Copper (II)	13.3	127	34.1	Qin et al. (2006)
	Lead (II)	13.3	414	119	Qin et al. (2006)
Peat (Heilongjiang)	Cadmium (II)	9.7	225	32.0	Qin et al. (2006)
	Copper (II)	9.7	127	25.4	Qin et al. (2006)
	Lead (II)	9.7	414	88.7	Qin et al. (2006)
Phosphate rock	Cadmium (II)	13.5	10–500	10.5	Elouear et al. (2008)
	Copper (II)	13.5	10–500	10.0	Elouear et al. (2008)
	Lead (II)	13.5	10–500	12.8	Elouear et al. (2008)
	Zinc (II)	13.5	10–500	8.5	Elouear et al. (2008)
Soil (Entisols)	Cadmium (II)	28.5	100-2000	3.4	Paranavithana et al. (2016)
	Lead (II)	28.5	100-2000	9.3	Paranavithana et al. (2016)
Soil (Mollisols)	Cadmium (II)	17.3	134.9	3.0	Appel et al. (2008)
	Lead (II)	17.3	248.6	5.7	Appel et al. (2008)
Soil (Oxisols)	Cadmium (II)	41.9	134.9	1.6	Appel et al. (2008)
	Lead (II)	41.9	248.6	4.1	Appel et al. (2008)
Soil (Ultisols)	Cadmium (II)	37.8	134.9	3.5	Appel et al. (2008)
	Lead (II)	37.8	248.6	6.7	Appel et al. (2008)
Zeolite (Clinoptilolite)	Arsenic (V)	1.6	5–300	0.36	Krauklis et al. (2017)

In a study on the adsorption capacity of *Lagerstroemia speciosa*, a tree that is native to India, on Cr(VI), the use of the tree was investigated in its native form and a maximum adsorption capacity of 20.4 mg g^{-1} was achieved (Srivastava et al., 2015). The use of leaves from the *Cinnamomum camphora* tree exhibited the effective removal of Pb(II), achieving adsorption capacities ranging from 74.1 to 75.8 mg g^{-1} (Chen et al., 2010). Moreover, the leaves from the *Cassia Fistula* tree removed Cr(VI), with a maximum adsorption capacity of 4.5 mg g^{-1} (Ahmad et al., 2017).

Sawdust is another material that has been frequently investigated for its adsorptive qualities. Several studies have demonstrated effective removal of heavy metals using sawdust from a variety of trees. Maple sawdust has achieved high removal (>80%) of Cr(VI) (Yu et al., 2003), while beech sawdust effectively removed Cu(II), Ni(II), Cd(II), and Zn(II) (Bozic et al., 2009). Moreover, sawdust from poplar and linden trees also exhibited varying degrees of removal of Zn(II), Ni(II), Cd(II), Cu(II), and Mn(II) (Bozic et al., 2009). Another study that investigated the removal of heavy metals using sawdust from poplar trees achieved adsorption capacities of 5.5, 6.6, and 21.1 mg g^{-1} for Cr(III), Cu(II), and Pb(II), respectively (Li et al., 2007). Along with these results, sawdust from teakwood also achieved maximum adsorption capacities of 4.9, 8.05, and 11.0 mg g^{-1} for Cu(II), Ni(II), and Zn(II), respectively (Shukla and Pai, 2005). These adsorption capacities were enhanced by 40–70% with chemical modifications to the sawdust using reactive dye (Shukla and Pai, 2005). Sawdust from the Indian jujube tree achieved a maximum adsorption capacity of 3.7 mg g^{-1} for Cr(VI) (Ahmad et al., 2017). Meanwhile, sawdust taken from Palestinian trees also demonstrated approximately 20–60% removal of Cr(VI) when the pH and adsorbent dose in the solution was adjusted (Dakiky et al., 2002).

Lignin is another commonly researched biomass material that has been used to remove heavy metals from water. Lignin is a natural polymer that is found in the cell walls of plants and makes them rigid and woody. Lignin is the primary binding agent for fibrous plant components and typically comprises 16–33% of plant biomass, and more than 50 million tons have been produced by paper industries throughout the world (Guo et al., 2008; Wu et al., 2008). Studies have shown that lignin is an effective adsorbent for the removal of heavy metals. In an extensive study by Guo et al. (2008), lignin obtained as a waste product from the paper industry achieved effective removal of several heavy metals, including Pb(II), Cu(II), Zn(II), and Ni(II). Other studies have reported the effective removal of chromium and cadmium using lignin (Liang et al., 2013; Wu et al., 2008). Researchers have stated that the removal of heavy metals using lignin is facilitated by the presence of carboxylic and phenolic functional groups, which interact strongly with heavy metals and potentially serve as ideal sites for heavy metal adsorption (Guo et al., 2008). Along with these specific studies, several review papers have been published on the adsorption of heavy metals using lignin and other lignocellulosic materials (Ge and Li, 2018; Neris et al., 2019).

Aquatic biomass, such as seaweed and algae, has also been shown to effectively remove heavy metals from a variety of water sources. For example, two freshwater algae, *S. Condensata* and *R. Hieroglyphicum*, have been shown to effectively remove Cr(III) from industrial wastewater, achieving maximum adsorption capacities of 14.8 and 12.5 mg g^{-1}, respectively (Onyancha et al., 2008). In another study, an artificially-cultured marine algae, *U. pinnatifida*, demonstrated effective removal of Ni(II) and Cu(II), achieving maximum adsorption capacities of 29.9 and 78.9 mg g^{-1}, respectively. Moreover, Romera et al. (2008) conducted an extensive study of the removal of Cd(II), Ni(II), and Zn(II) using brown (*A. nodosum*), red (*C. crispus*), and green (*C. vermialara*) algae in a variety of combinations and systems. In each instance, effective removal of each heavy metal (>90%) was achieved, even when they were examined in different combinations. The effective removal (>90%) of chromium by a red algae species (*C. Virgatum*), with a maximum adsorption capacity (26.5 mg g^{-1}), was achieved at a pH of 1.5, which would not occur consistently among the types of water sources that are typically found to contain chromium (Sari and Tuzen, 2008). A study of the removal of Cd(II) using brown, red, and green seaweeds showed a wide range of adsorption capacities based on the type of seaweed used. The maximum adsorption capacities ranged from 17.9 to 82.9 mg g^{-1}, with brown seaweeds being the most effective, followed by green and red seaweeds (Hashim and Chu, 2004).

A study that investigated the use of *S. polyrhiza*, a freshwater macrophyte, to remove Cu(II), Mn(II), and Zn(II) demonstrated maximum adsorption capacities of 52.6, 35.7, and 28.5 mg g^{-1}, respectively (Meitei and Prasad, 2014). Moreover, various aquatic weeds, including water lilies and mangrove leaves, have been shown to remove chromium, with adsorption capacities ranging from 6.1 to 7.2 mg g^{-1} for Cr(III) and 1.7–5.1 mg g^{-1} for Cr(VI) (Elangovan et al., 2008). Neem leaves and hyacinth roots have also been shown to remove Cu(II), with maximum adsorption capacities of 17.5 and 21.8 mg g^{-1}, respectively (Singha and Das, 2013).

In many instances, modifications and various treatments have been investigated to enhance the removal of heavy metals by biomass. For example, when removing Cu(II) and Ni(II), the adsorption capacities of *U. pinnatifida* increased by 10 mg g^{-1} after being washed with a 0.2 M $CaCl_2$ solution for 24 h (Chen et al., 2008). The removal efficiency of Cr(VI) by various aquatic weeds increased after being washed with a 4 N solution of H_2SO_4. However, the removal of Cr(III) by these aquatic weeds was reduced after being washed with 4 N solutions of H_2SO_4 and NaOH (Elangovan et al., 2008). A summary of selected studies evaluating the ability of aquatic and terrestrial biomass to remove heavy metals is provided in Table 5.

3.4. Other locally-available waste material

A significant amount of research has been conducted to evaluate the effectiveness of locally-available waste material to remove heavy metals from aqueous solutions. Due to variation in local environments, energy sources, agricultural practices, and cultures, different types of waste may be produced in excess of others. For example, approximately 857,000 tons of tea is produced annually in India (Wasewar et al., 2009), which leads to an inordinate amount of tea waste. Moreover, countries that produce a significant amount of energy from coal, such as India and China, must deal with a large amount of waste products from the combustion process, such as coal ash.

Several researchers have investigated the adsorptive capabilities of tea waste over the last two decades. Tea waste has been shown to effectively remove a wide variety of heavy metals. Malkoc and Nuhoglu (2005) achieved a maximum adsorption capacity of 18.4 mg g^{-1} for Ni(II) using tea waste (Malkoc and Nuhoglu, 2005). Wasewar et al. (2009) also reported significant removal of Zn(II) (>98%) using tea waste. Other researchers have modified tea waste with the objective of increasing its heavy metal removal efficiency. Weng et al. (2014) investigated various modification methods, including acid and base washing, steam, and ultrasound, to enhance the removal of Cu(II) using black tea waste. With each method, the removal of Cu(II) increased compared to untreated adsorbent, achieving maximum adsorption with base-treated black tea waste (Weng et al., 2014). The increased removal obtained using these modification techniques has been attributed to the changes induced in the physical and chemical properties of the adsorbent, such as increased surface area and porosity, along with the higher

Table 5
Removal of heavy metals by aquatic and terrestrial biomass.

Adsorbent	Heavy metal	Surface area (m^2 g^{-1})	C_0 (mg L^{-1})	q_{max} (mg g^{-1})	Reference
A. Bisporus (mushroom)	Cadmium (II)	NA	10–100	29.7	Vimala and Das (2009)
	Lead (II)	NA	10–100	33.8	Vimala and Das (2009)
A. Nodosum (brown algae)	Cadmium (II)	NA	10–150	69.7	Romera et al. (2008)
	Nickel (II)	NA	10–150	35.2	Romera et al. (2008)
	Zinc (II)	NA	10–150	41.2	Romera et al. (2008)
A. Polytricha (mushroom)	Copper (II)	NA	10–100	6.6	Li et al. (2018b)
	Mercury (II)	NA	10–100	6.0	Li et al. (2018b)
	Zinc (II)	NA	10–100	6.1	Li et al. (2018b)
Beech sawdust	Copper (II)	NA	5–200	4.5	Bozic et al. (2013)
	Nickel (II)	NA	5–200	4.0	Bozic et al. (2013)
	Zinc (II)	NA	5–200	2.0	Bozic et al. (2013)
C. Crispus (red algae)	Cadmium (II)	NA	10–150	65.2	Romera et al. (2008)
	Nickel (II)	NA	10–150	35.2	Romera et al. (2008)
	Zinc (II)	NA	10–150	42.5	Romera et al. (2008)
C. Fistula leaves	Chromium (VI)	1.1	0–40	4.5	Ahmad et al. (2017)
C. Indica (mushroom)	Cadmium (II)	NA	10–100	24.1	Vimala and Das (2009)
	Lead (II)	NA	10–100	23.4	Vimala and Das (2009)
C. Vermilara (green algae)	Cadmium (II)	NA	10–150	21.4	Romera et al. (2008)
	Nickel (II)	NA	10–150	12.9	Romera et al. (2008)
	Zinc (II)	NA	10–150	21.6	Romera et al. (2008)
F. Velutipes (mushroom)	Copper (II)	NA	10–100	7.2	Li et al. (2018b)
	Mercury (II)	NA	10–100	7.9	Li et al. (2018b)
	Zinc (II)	NA	10–100	6.3	Li et al. (2018b)
Green taro	Chromium (III)	NA	10–150	6.1	Elangovan et al. (2008)
	Chromium (VI)	NA	10–150	1.4	Elangovan et al. (2008)
H. Splendens (moss)	Cadmium (II)	NA	10–400	32.5	Sari et al. (2008)
	Chromium (III)	NA	10–400	42.1	Sari et al. (2008)
Hyacinth roots	Chromium (VI)	5.8	54.5	15.3	Singha and Das (2011)
	Copper (II)	NA	5–300	21.8	Singha and Das (2013)
Juniper bark	Cadmium (II)	NA	29.2	8.6	Shin et al. (2007)
Juniper wood	Cadmium (II)	NA	29.2	3.2	Abdolali et al. (2016)
L. speciosa bark	Chromium (VI)	0.4	5–30	24.4	Srivastava et al. (2015)
Lignin	Cadmium (II)	21.7	23–281	25.4	Guo et al. (2008)
	Chromium (III)	21.7	5–130	18.0	Wu et al. (2008)
	Copper (II)	21.7	13–159	22.9	Guo et al. (2008)
	Lead (II)	21.7	41–518	89.5	Guo et al. (2008)
	Nickel (II)	21.7	12–147	6.0	Guo et al. (2008)
	Zinc (II)	21.7	13–164	11.3	Guo et al. (2008)
Loess	Zinc (II)	24.1	10–700	216	Tang et al. (2008)
Mangrove leaves	Chromium (III)	NA	10–150	6.5	Elangovan et al. (2008)
	Chromium (VI)	NA	10–150	5.7	Elangovan et al. (2008)
Meranti sawdust	Chromium (III)	<0.6	1–200	37.9	Rafatullah et al. (2009)
	Copper (II)	<0.6	1–200	32.1	Rafatullah et al. (2009)
	Lead (II)	<0.6	1–200	34.2	Rafatullah et al. (2009)
	Nickel (II)	<0.6	1–200	36.0	Rafatullah et al. (2009)
Neem leaves	Chromium (VI)	0.6	54.5	16.0	Singha and Das (2011)
	Copper (II)	NA	5–300	17.5	Singha and Das (2013)
P. Eryngii (mushroom)	Copper (II)	NA	10–100	3.4	Li et al. (2018b)
	Mercury (II)	NA	10–100	2.8	Li et al. (2018b)
	Zinc (II)	NA	10–100	2.9	Li et al. (2018b)
P. Platypus (mushroom)	Cadmium (II)	NA	10–100	35.0	Vimala and Das (2009)
	Lead (II)	NA	10–100	27.1	Vimala and Das (2009)
P. Ostreatus (mushroom)	Copper (II)	NA	10–100	4.5	Li et al. (2018b)
	Mercury (II)	NA	10–100	3.4	Li et al. (2018b)
	Zinc (II)	NA	10–100	5.1	Li et al. (2018b)
Pine cone biochar	Arsenic	6.6	0.05–0.2	0.006	Van Vinh et al. (2015)
Pine needles	Chromium (VI)	NA	20-1000	21.5	Dakiky et al. (2002)
Poplar sawdust	Chromium (III)	NA	0–50	5.5	Li et al. (2007)
	Copper (II)	NA	0–50	6.6	Li et al. (2007)
	Lead (II)	NA	0–50	21.1	Li et al. (2007)
Reed mat	Chromium (III)	NA	10–150	7.2	Elangovan et al. (2008)
	Chromium (VI)	NA	10–150	1.7	Elangovan et al. (2008)
S. Lychnophera Hance	Cadmium (II)	NA	0.25–1.0	27.1	Liu et al. (2006)
	Lead (II)	NA	0.25–1.0	27.1	Liu et al. (2006)
Sawdust	Chromium (VI)	NA	20-1000	15.8	Dakiky et al. (2002)
Teakwood sawdust	Copper (II)	NA	73–465	4.9	Shukla and Pai (2005)
	Nickel (II)	NA	107–554	8.1	Shukla and Pai (2005)
	Zinc (II)	NA	38–244	11.0	Shukla and Pai (2005)
Tree fern	Copper (II)	1.59	30–150	10.6	Ho et al. (2002)
	Lead (II)	6.4	30–150	39.8	Ho et al. (2002)
	Zinc (II)	1.2	30–150	7.58	Abdolali et al. (2016)
Water hyacinth	Chromium (III)	NA	10–150	6.6	Elangovan et al. (2008)
	Chromium (VI)	NA	10–150	0.3	Elangovan et al. (2008)

(*continued on next page*)

Table 5 (*continued*)

Adsorbent	Heavy metal	Surface area (m^2 g^{-1})	C_0 (mg L^{-1})	q_{max} (mg g^{-1})	Reference
Water lily	Chromium (III)	NA	10–150	6.1	Elangovan et al. (2008)
	Chromium (VI)	NA	10–150	5.1	Elangovan et al. (2008)
Z. Mauritiana sawdust	Chromium (VI)	1.5	0–40	3.7	Ahmad et al. (2017)

NA = not available.

number of functional groups (Weng et al., 2014). Yang et al. (2016) also reported that base-treated green tea waste improved the adsorption of heavy metals, specifically As(III) and Ni(II). They observed that the use of base treatment via immersion in a 0.05-M solution of $Ca(OH)_2$ increased the number of –OH and amine functional groups on the surface of the green tea waste, which contributed to the increased As(III) and Ni(II) removal (Yang et al., 2016). A comprehensive review of the extensive use of tea waste for the removal of heavy metals and other contaminants was carried out by Hussain et al. (2018).

Coal ash, which is an abundant by-product of fossil fuel combustion, has also been shown to remove heavy metals from aqueous solution. Attari et al. (2017) showed that coal fly ash could remove up to 95% of Hg(II) from industrial wastewater. Another study that examined the removal of Cr(III), Pb(II), and Zn(II) using coal fly ash achieved maximum adsorption capacities of 22.7, 45.3, and 17.7 mg g^{-1}, which was attributed to electrostatic attraction between the heavy metals and the charged surface of the adsorbent (Papandreou et al., 2011). Several review articles have been published on the effectiveness of coal ash as an adsorbent (Ge et al., 2018; Rashidi and Yusup, 2016; Wang and Wu, 2006).

Shells from various aquatic species have been shown to effectively remove heavy metals from aqueous solutions. Shells from the mollusk *Anadara inaequivalvis* (*A. inaequivalvis*), which are primarily found in the Adriatic, Aegean, and Black Seas, effectively removed Cu(II) and Pb(II), achieving maximum adsorption capacities of 330.2 and 621.1 mg g^{-1}, respectively (Bozbas and Boz, 2016). Razor clam shells demonstrated significant removal of Cd(II), Pb(II), and Zn(II), achieving maximum adsorption capacities of 501.3, 656.8, and 553.3 mg g^{-1}, respectively (Du et al., 2011). Moreover, oyster shells achieved effective removal of Cd(II), Pb(II), and Zn(II), achieving maximum adsorption capacities of 118.0, 1,591, and 564.4 mg g^{-1}, respectively (Du et al., 2011). Crab shell particles have also been shown to remove Co(II) and Cu(II), achieving maximum adsorption capacities of 322.6 and 243.9 mg g^{-1}, respectively (Vijayaraghavan et al., 2006).

Various other locally-available waste materials have been evaluated for their ability to remove heavy metals from aqueous solutions. Boonamnuayvitaya et al. (2004) investigated the adsorptive capabilities of coffee residues for removing various heavy metals, including Cd(II), Cu(II), Ni(II), Pb(II), and Zn(II). In this study, coffee residues were mixed with clay and achieved maximum adsorption capacities ranging from 11.0 to 39.5 mg g^{-1} for five heavy metals in the following order of adsorption: Cd(II) > Cu(II) > Pb(II) > Zn(II) > Ni(II) (Boonamnuayvitaya et al., 2004). Meunier et al. (2003) evaluated the adsorptive capabilities of cocoa shells by determining the removal efficiency for a wide variety of heavy metals in a multi-solute solution, including Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Mn(II), Ni(II), Pb(II), and Zn(II). This study found maximum adsorption capacities that were relatively low ($\leq$1.1 mg g^{-1}) compared to other adsorbents with the following order of adsorption: Pb(II) > Cr(III) > Cd(II) ≈ Cu(II) ≈ Fe(III) > Zn(II) ≈ Co(II) > Mn(II) ≈ Ni(II) (Meunier et al., 2003). Neem oil cake, which is waste matter extracted from the fruit of the Neem (*A. Indica*) plant, has been shown to effectively remove Cu(II) and Cd(II). Researchers demonstrated maximum adsorption capacities of 9.4 and 11.8 mg g^{-1} for Cu(II) and Cd(II), respectively (Rao and Khan, 2009). Tobacco dust has also been shown to remove heavy metals from aqueous solutions. Qi and Aldrich (2008) investigated the use of tobacco dust to remove Pb(II), Cu(II), Cd(II), Zn(II), and Ni(II) and achieved maximum adsorption capacities of ranging from 24.5 to 39.6 mg g^{-1} with the following order of adsorption: Pb(II) > Cu(II) > Cd(II) > Ni(II) ≈ Zn(II) (Qi and Aldrich, 2008). The removal of heavy metals by tobacco dust was attributed to strong surface acidity exhibited by the tobacco dust and its negative surface charge across a wide pH range, which contributed to the removal of the heavy metals (Qi and Aldrich, 2008). A study investigating the removal of Cd(II) using olive cake, which is a waste product of olive oil production, demonstrated effective removal, achieving a maximum adsorption capacity of 65.4 mg g^{-1} (Al-Anber and Matouq, 2008). Dakiky et al. (2002) has also investigated a wide variety of locally-available materials in Palestine, including olive cake, cactus leaves, coal, and wool, for their ability to remove Cr(VI). In this study, the highest adsorption capacity was achieved with wool (41.2 mg g^{-1}), followed by olive cake (33.4 mg g^{-1}), cactus

Table 6
Removal of heavy metals by various locally-available waste materials.

Adsorbent	Heavy metal	Surface area (m^2 g^{-1})	C_0 (mg L^{-1})	q_{max} (mg g^{-1})	Reference
A. inaequivalvis shells	Copper (II)	1.82	20–100	330	Bozbas and Boz (2016)
	Lead (II)	1.82	20–100	621	Bozbas and Boz (2016)
Black tea waste	Cadmium (II)	192	5–100	13.8	Mohammed (2012)
	Cobalt (II)	192	5–100	12.2	Mohammed (2012)
	Copper (II)	2.04	N.R.	43.2	Weng et al. (2014)
	Zinc (II)	192	5–100	12.2	Mohammed (2012)
Cactus leaves	Chromium (VI)	NA	20-1000	7.1	Dakiky et al. (2002)
Coal	Chromium (VI)	NA.	20-1000	6.8	Dakiky et al. (2002)
Coal fly ash	Cadmium (II)	10.2	20–80	19.0	Papandreou et al. (2007)
	Chromium (III)	20	10–200	22.7	Papandreou et al. (2011)
	Copper (II)	10.2	20–80	20.9	Papandreou et al. (2007)
	Lead (II)	20	10–400	45.3	Papandreou et al. (2011)
	Mercury (II)	NA	10	0.4	Attari et al. (2017)
	Zinc (II)	20	10–200	17.7	Papandreou et al. (2011)
Cocoa shells	Cadmium (II)	NA	28.1	0.18	Meunier et al. (2003)
	Chromium (III)	NA	13.0	0.2	Meunier et al. (2003)
	Cobalt (II)	NA	14.7	0.2	Meunier et al. (2003)

Table 6 (*continued*)

Adsorbent	Heavy metal	Surface area (m^2 g^{-1})	C_0 (mg L^{-1})	q_{max} (mg g^{-1})	Reference
	Copper (II)	NA	15.9	0.5	Meunier et al. (2003)
	Iron (III)	NA	14.0	1.1	Meunier et al. (2003)
	Manganese (II)	NA	13.7	0.1	Meunier et al. (2003)
	Nickel (II)	NA	14.7	0.2	Meunier et al. (2003)
	Lead (II)	NA	51.8	5.2	Meunier et al. (2003)
	Zinc (II)	NA	16.3	0.001	Meunier et al. (2003)
Coffee residues	Cadmium (II)	6.48	25–250	39.5	Boonamnuayvitaya et al. (2004)
	Copper (II)	6.48	25–250	31.2	Boonamnuayvitaya et al. (2004)
	Nickel (II)	6.48	25–250	11.0	Boonamnuayvitaya et al. (2004)
	Lead (II)	6.48	25–250	19.5	Boonamnuayvitaya et al. (2004)
	Zinc (II)	6.48	25–250	13.4	Boonamnuayvitaya et al. (2004)
Crab shell particles	Cobalt (II)	NA	500-2000	323	Vijayaraghavan et al. (2006)
	Copper (II)	NA	500-2000	244	Vijayaraghavan et al. (2006)
Green tea waste	Arsenic (III)	0.75	7–23	0.4	Yang et al. (2016)
	Nickel (II)	0.75	7–23	0.3	Yang et al. (2016)
Neem oil cake	Cadmium (II)	NA	10–100	11.8	Rao and Khan (2009)
	Copper (II)	NA	10–100	9.4	Rao and Khan (2009)
Olive cake	Cadmium (II)	NA	100	65.4	Al-Anber and Matouq (2008)
	Chromium (VI)	NA	20-1000	33.4	Dakiky et al. (2002)
Olive stone	Cadmium (II)	0.38	10–30	0.93	Moubarik and Grimi (2015)
Oyster shells	Cadmium (II)	NA	0–300	118	Du et al. (2011)
	Lead (II)	NA	0–500	1591	Du et al. (2011)
	Zinc (II)	NA	0–300	564	Du et al. (2011)
Razor clam shells	Cadmium (II)	NA	0–300	501	Du et al. (2011)
	Lead (II)	NA	0–500	657	Du et al. (2011)
	Zinc (II)	NA	0–300	553	Du et al. (2011)
Tea Waste	Nickel (II)	0.39	50–300	18.4	Malkoc and Nuhoglu (2005)
	Zinc (II)	1.3	25–200	8.9	Wasewar et al. (2009)
Tobacco dust	Cadmium (II)	NA	0–50	29.6	Qi and Aldrich (2008)
	Copper (II)	NA	0–50	36.0	Qi and Aldrich (2008)
	Lead (II)	NA	0–50	39.6	Qi and Aldrich (2008)
	Nickel (II)	NA	0–50	25.1	Qi and Aldrich (2008)
	Zinc (II)	NA	0–50	24.5	(Qi and Aldrich,2008)
Wool	Chromium (VI)	NA	20-1000	41.2	Dakiky et al. (2002)

NA = not available.

leaves (7.1 mg g^{-1}), and coal (6.8 mg g^{-1}) (Dakiky et al., 2002). The effectiveness of the wool in the removal of Cr(VI) was attributed to its loose structure, which allowed for multi-layered adsorption to occur, while the other adsorbents were more compact, resulting in reduced adsorption (Dakiky et al., 2002). A summary of selected studies evaluating the ability of locally-available wastes to remove heavy metals can be found in Table 6.

4. Proposed mechanisms for heavy metal removal

When examining the ability of these low-cost adsorbents to remove heavy metals in the context of the developing world, adsorption has received the most attention as a removal method. With interactions between heavy metals and various materials, adsorption typically occurs in two different ways: surface

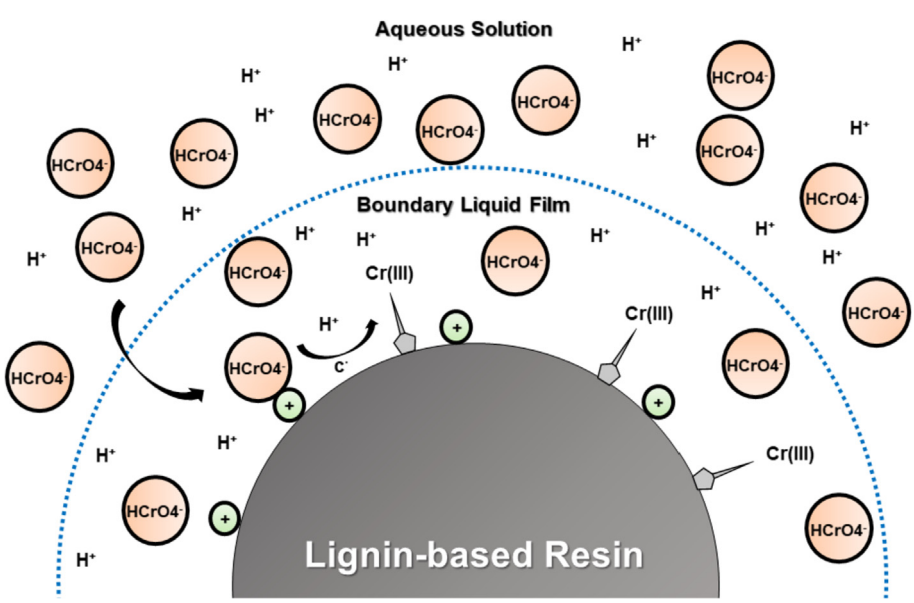

Fig. 1. Cr(VI) adsorption via surface adsorption (Liang et al., 2013).

adsorption and interstitial adsorption. During surface adsorption, heavy metal ions migrate by diffusion from the aqueous solution to the surface of the adsorbent, which contains an opposite surface charge. Then, once the heavy metal ions have passed through the boundary layer, they attach to the surface of the adsorbent and are subsequently removed from the solution. This type of adsorption is often achieved by Van Der Waals forces, dipole interactions, or hydrogen binding (Sulyman et al., 2017). Fig. 1 illustrates this type of adsorption.

During interstitial adsorption, heavy metal ions diffuse towards the adsorbent. However, the ions enter the pores of the adsorbent and adsorb to the surfaces on the interior of the material. This type of adsorption occurs most frequently with microporous adsorbents. Fig. 2 illustrates this type of adsorption. Several adsorption mechanisms have been proposed for the removal of heavy metals. Several researchers have suggested that ion exchange between the adsorbent and metal ions is the dominant mechanism, based on the activation energies of the reactions (Chen et al., 2010) and the consistent adsorption capacities across various water quality conditions (Bozic et al., 2009). For example, researchers have found that compounds with phenol groups are able to replace protons with metal ions, which is quickly followed by a decrease in pH, according to the following chemical formula (Bozic et al., 2009):

$$Me^{2+} + 2(\text{-ROH}) = Me(\text{-RO})_2 + 2H^+$$

Fig. 3 shows an illustration of this proposed mechanism.

A review by Dai et al. (2018) described the ion exchange mechanism of heavy metal removal and suggested that the removal of heavy metals using these adsorbents is facilitated by carboxyl and hydroxyl groups, which are attached by a divalent heavy metal ion via two pairs of electrons and subsequently release two Na^+ and/or H^+ ions into the solution. This mechanism is illustrated in Fig. 4. The pH of the solution plays a significant role in the ion-exchange mechanism. Several researchers have reported decreased adsorption at lower pH values (Taşar et al., 2014; Witek-Krowiak et al., 2011), which has been attributed to the increase in H^+ ions, which compete with aqueous heavy metal ions for adsorption sites (Bozic et al., 2009; Demirbas et al., 2009; Rafatullah et al., 2009; Vijayaraghavan et al., 2006).

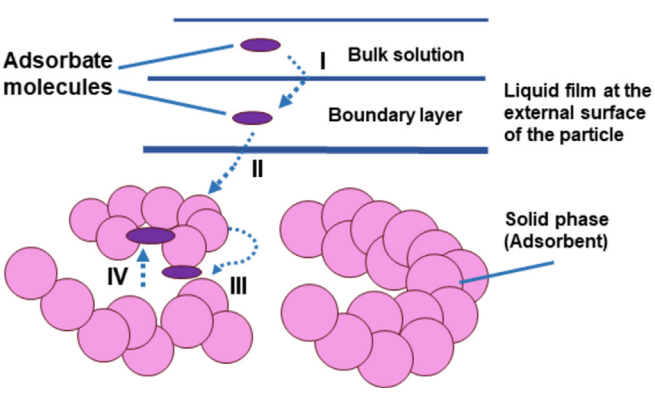

Fig. 2. Heavy metal removal via interstitial adsorption (Sulyman et al., 2017).

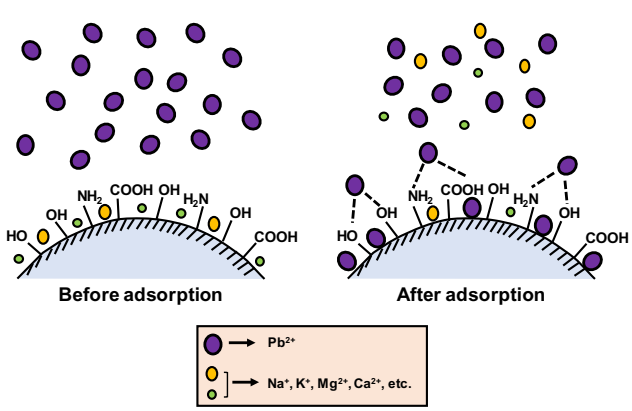

Fig. 3. Ion exchange removal mechanism (Chen et al., 2010).

Electrostatic forces have also been identified as a contributing factor to the adsorption of heavy metals. The presence of electrostatic forces is heavily dependent on the pH. Lower pH values contribute to the protonation of the various functional groups associated with the adsorption of heavy metals, which results in an overall positive charge on the adsorbent (Onyancha et al., 2008). As a result, electrostatic repulsion occurs, preventing the adsorption of positively charged heavy metal ions (Thirumavalavan et al., 2010). Conversely, electrostatic repulsion decreases with increasing pH, which is evident due to the increase in the adsorption of heavy metals (Rao and Khan, 2009). The influence of electrostatic forces during adsorption can be clearly seen when evaluating the removal efficiency of the adsorbent relative to the pH value that represents the point of zero charge (pH_{PZC}) of the adsorbent. The pH_{PZC} is the pH value at which the surface charge of the adsorbent is neutral (Singha and Das, 2013). The surface charge of the adsorbent is positive when the pH of the solution is less than the pH_{PZC}, while its surface charge is negative when the pH of the solution is greater that the pH_{PZC}. As a result, the removal of heavy metals, particularly those that exist in cationic form, is low when $pH < pH_{PZC}$ and increases when $pH > pH_{PZC}$, which suggests a significant presence of electrostatic forces in the adsorption process (Leyva-Ramos et al., 2005; Singha and Das, 2013). The influence of electrostatic forces can also be seen with variations in ionic strength.

Adsorption has also been attributed to interactions between heavy metals and various functional groups on the surface of biomass. The functional groups that are often identified as adsorption sites for heavy metals include carboxylate ($-COO^-$), amide ($-NH_2$), phosphate (PO_4^{3-}), thiols ($-SH$), and hydroxide ($-OH$) (Onyancha et al., 2008; Qi and Aldrich, 2008). The ability of these functional groups to serve as adsorption sites for heavy metals is significantly impacted by the pH of the solution. The dissociation constant (pK_a) of many functional groups, including carboxylic and phenol groups, range from 3.5 to 5.5, which means that the majority of these groups will be deprotonated in this pH range and that an increased number of negatively-charged sites will be available for adsorption (Torab-Mostaedi et al., 2013). Fig. 5 demonstrates this mechanism by showing the interactions between $-OH$ groups and Mn(II).

The operation of this mechanism during the removal of heavy metals has been demonstrated by increasing the overall adsorption by modifying various adsorbents. Shukla and Pai (2005) modified the adsorbents used in their study using reactive dye to expose the metal ions to $-OH$ groups to enhance removal (Shukla and Pai, 2005). As shown in Fig. 6, the $-OH$ groups on the modified dye-loaded adsorbent are positioned to allow for better chelation and subsequent heavy metal removal.

5. Conclusions

In the developing world, increased water scarcity and pollution contribute to a significant lack of access to clean drinking water. While various forms of water pollution exist, heavy metal contamination in drinking water sources is a growing concern. Moreover, developing countries do not have access to common

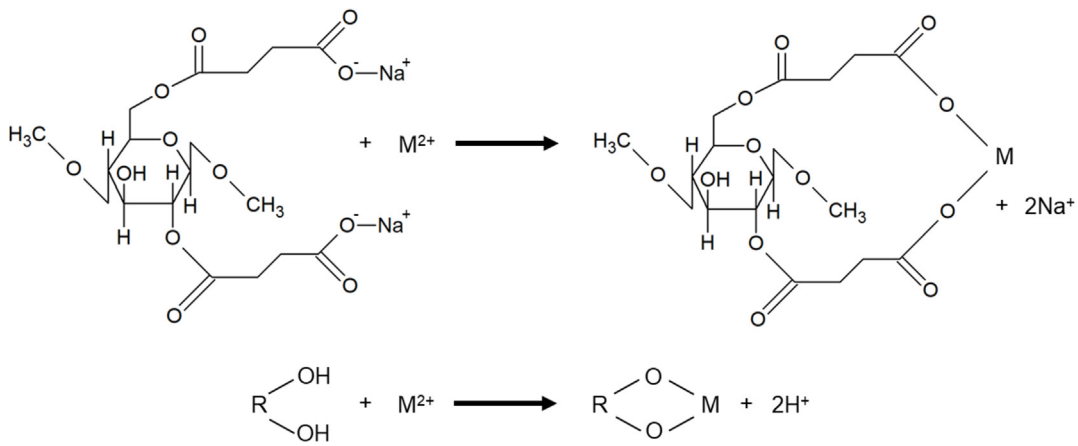

Fig. 4. Ion exchange with release of Na^+ and H^+ ions (Dai et al., 2018).

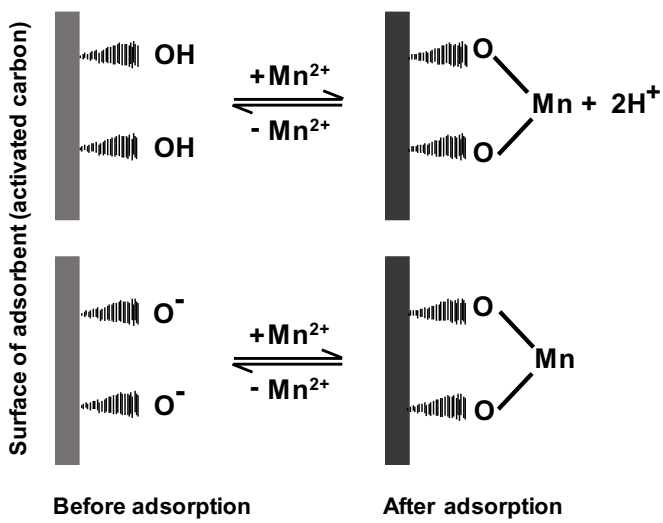

Fig. 5. Adsorption of Mn(II) by –OH functional group (Sulyman et al., 2017).

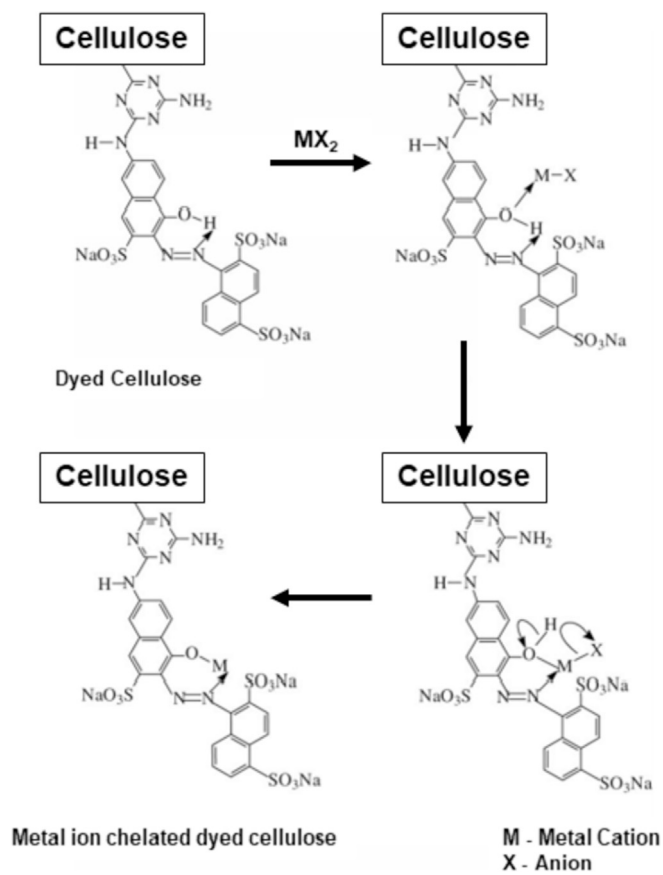

Fig. 6. Heavy metal removal mechanism using dyed adsorbent (Shukla and Pai, 2005).

water treatment methods that would remove heavy metals. As a result, a significant amount of research has been conducted to investigate the use of low-cost adsorbents to remove heavy metals from water sources. The low-cost adsorbents that have been investigated include different types of agricultural waste, soil and mineral deposits, aquatic and terrestrial biomass, and various abundant materials. Researchers have reported that these materials can effectively remove heavy metals. When evaluating each category outlined in this review paper, agricultural waste and byproducts appear to be the most effective at removing heavy metals, while natural soil and mineral deposits appeared to be the least effective. Though chemical modifications to the adsorbents increased the overall adsorption capacities of the materials tested, these methods are not typically available to communities in the developing world.

However, the effectiveness of these materials at removing heavy metals depends heavily on the water quality conditions, such as pH, ionic strength, and temperature, along with the characteristics of the material (*e.g.*, specific surface area, surface chemistry, *etc.*). These conditions can affect the speciation and stability of the heavy metals, along with the adsorptive characteristics of the adsorbent. Furthermore, in terms of the manner in which heavy metals are removed, ion exchange is the most cited mechanism, along with the influence of electrostatic forces. The efficiencies of these mechanisms are heavily influenced by water quality conditions.

Overall, these low-cost adsorbents are viable, cost-effective materials that can be used to remove heavy metals from water. In the developing world, these materials are readily available in large quantities, and limited technology and expertise would be required to integrate these materials into a water treatment process. Future research in this area should continue throughout the developing world to identify additional low-cost materials that are effective at removing heavy metals. Special attention should be given to the

waste materials and other residual byproducts that are abundant in these countries, along with countries with significant industrial activities, which most often contribute to increases in heavy metal contamination. The implementation of these types of materials in water treatment processes in these locations is potentially environmentally-sustainable as it will reduce the disposal of waste while simultaneously improving the quality of the local water sources. Furthermore, future research should evaluate the capabilities of these materials with true, local water sources, such as industrial effluent, river and lake sources, and domestic wastewater, using bench-scale testing. Future research in this area should also determine the full impact of varying water conditions on heavy metal removal and assess the true viability of the proposed low-cost materials in developing countries through pilot-scale studies.

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