Removal of heavy metals from wastewater using agricultural byproducts

Hayder A. Alalwan, Mohammed A. Kadhom and Alaa H. Alminshid

ABSTRACT

The use of agricultural waste to remove heavy metals from wastewater has attracted much attention due to its economic advantages and high removal efficiency which is attributed to different functional groups. The sorption mechanism of biomass can consist of several steps including chemisorption, complexation, adsorption on surface, diffusion through pores, and ion exchange. Heavy metals were removed in different rates depending on the adsorbent and metal itself. For instance, coconut waste showed adsorption capacities of 263 and 285 mg/g in removing lead and cadmium ions, respectively. Also, black oak bark has adsorbed mercury in an adsorption capacity of 400 mg/g, while wheat brans adsorption capacity for chromium was 310 mg/g. The adsorption capacity is commonly calculated by Lagergren's first-order equation, the Redlich Peterson model, and the Brunauer–Emmett–Teller (BET) model. However, Langmuir and Freundlich models were intensively used to calculate the adsorbed amount by a unit weight of solid sorbents. This review article aims to present the recently available information on utilizing the biomass materials for heavy metals removal. Here, we highlight the increasing use of these materials due to their low cost, regeneration ability, high adsorption efficiency, and small chemical or biological sludge with a possibility of metal recovery.

Key words | adsorption, agricultural wastes, heavy metals, wastewater

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INTRODUCTION

Pollutants, such as heavy metals, are serious threats to the environment. They get introduced to aquatic streams due to industrial activities, i.e. mining, refining ores, fertilizer industries, tanneries, batteries, paper industries, and pesticides (Hao & Liu 2016; Alalwan *et al.* 2018a). Water pollution affects human health and ecosystems, as well as aquatic plants and animals. Heavy metals of chromium (Cr), iron (Fe), selenium (Se), vanadium (V), copper (Cu), cobalt (Co), nickel (Ni), cadmium (Cd), mercury (Hg), arsenic (As), lead (Pb), and zinc (Zn) represent the major toxic hazardous materials to humans and other forms of life. The uptake of heavy metals from wastewater is important not just to eliminate their toxic impact, but also to recover precious materials. Figure 1 shows the classification of heavy metals. Conventional methods for removing these pollutants from wastewater include chemical precipitation, ion exchangers, chemical oxidation/reduction, reverse osmosis, electro dialysis, and ultrafiltration (Abbas *et al.* 2016). However, these techniques have some limitations such as low efficiency, sensitive operating conditions, and the production of secondary sludge, which increases the cost (Neoh *et al.* 2016). The removal of heavy metals by adsorption using activated carbon is a powerful technology to treat domestic and industrial wastewater due to its easy operating requirements and low cost (Jabbari *et al.* 2016; Abbas & Alalwan 2019). However, the main limitation of this technique is the high cost of activated carbon (Liu *et al.* 2017a). Table 1 summarizes the most common techniques to remove metal ions from wastewater.

The adsorption of heavy metals by low cost biomass of seaweeds, molds, yeasts, and agricultural waste materials has attracted much attention since the 1990s (Sud *et al.* 2008; Abourriche *et al.* 2018). Agriculture wastes or biosorption materials have several advantages over conventional treatment methods, such as their low cost, regeneration ability, high

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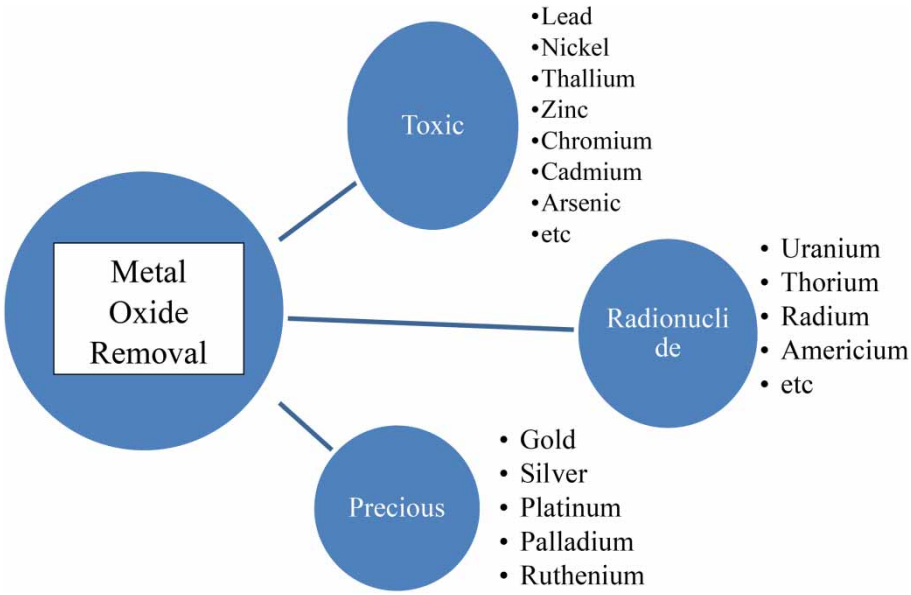

Figure 1 | Outline of heavy metal removal classifications.

Table 1 | Most common techniques of metal ion's removal from wastewaters (Taka *et al.* 2017; Acharya *et al.* 2018)

Methods	Advantages	Disadvantages
Chemical precipitation	➢ Simple ➢ Inexpensive ➢ Apply for wide kind of metals	➢ Sludge forms in a large amount and its disposal is a serious problem
Chemical coagulation	➢ Sludge settling ➢ Dewatering	➢ High cost ➢ High consumption of chemicals
Ion-exchange	➢ High regeneration of materials ➢ Metal selective ➢ Fast kinetics	➢ High cost ➢ Less number of metal ions removed
Electrochemical method	➢ Metal selective ➢ No consumption of chemicals ➢ Pure metals can be achieved	➢ High capital and running costs due to membrane fouling and high energy consumption
Adsorption using activated carbon	➢ Most metals can be removed ➢ High efficiency (>99%)	➢ Cost of activated carbon ➢ No regeneration ➢ Performance depends upon adsorbent
Using natural zeolite	➢ Most metals can be removed ➢ Relatively less costly materials	➢ Low efficiency
Membrane process and ultrafiltration	➢ Less solid waste produced ➢ Less chemical consumption ➢ High efficiency (>95% for single metal) ➢ Small space requirement ➢ Low pressure requirement	➢ High initial and running cost ➢ Low flow rates ➢ Removal (%) decreases with the presence of other metals ➢ Complex process

adsorption efficiency, lesser chemical or biological sludge, and the possibility of metals recovery (Burakov *et al.* 2018; Alalwan *et al.* 2019). Agricultural materials in general, especially cellulosic materials, show a high potential biosorption capacity due to their structures that include hemicellulose, lignin, extractives, lipids, proteins, simple sugars, water hydrocarbons, and starch (Noor *et al.* 2017). The high adsorption efficiency of agricultural waste biomass is attributed to acetamido, alcoholic, carbonyl, phenolic, amido, amino, and sulfhydryl groups functional groups (Renu *et al.* 2017). The sorption mechanism of biomass can consist of several steps including chemisorption, complexation, adsorption on surface, diffusion through pores, and ion exchange. Investigating the agricultural waste has included materials such as rice husk, black gram and wheat brans and husks, peels of lemon, lime, orange, apple, and banana, bark of trees, groundnut, coconut shells, hazelnut and walnut shells, cotton seed hulls, waste tea and Cassia fistula leaves, maize corn cob, jatropa deoiled cakes, sugarcane bagasse, soybean hulls, grapes and cotton stalks, water hyacinth, sugar beet pulp, sunflower stalks, coffee beans, and arjun nuts (De Gisi *et al.* 2016).

These agricultural waste materials have shown promising removal efficiency for different pollutants in general, and for heavy metals in particular, from wastewater either in their natural form or after some physical or chemical modifications (De Gisi *et al.* 2016). In addition, biomasses such as *Vicia faba* (*V. faba*) and *Allium cepa* (*A. cepa*) are used to monitor environmental changes, especially the cytogenetic and mutagenic agents (Iqbal 2016; Iqbal *et al.* 2019; Iwuoha & Akinseye 2019). Vibrio fischeri bioluminescence inhibition bioassay (VFBIA) is also used for toxicity monitoring due to its important advantages such as the shorter test duration, high sensitivity, cost-effectiveness and ease of operation. In addition, VFBIA is equally applicable to all types of matrices (organic and inorganic compounds, metals, etc.) for toxicity monitoring (Abbas *et al.* 2018).

This review article provides new insights about the utilization of agricultural waste materials as biosorbents for the removal of heavy metals from aqueous streams. Based on the Scopus database, it is noteworthy that the number of research articles is increasing remarkably each year, which indicates the importance of this subject. This article reviews and summarizes 147 papers, more than 54% of which were published within the last three years

REMOVAL OF HEAVY METALS

Water pollution associated with heavy metal resulting from industrial and urban activities is a serious global issue due to its high toxicity, low biodegradability, and accumulation in the food chain (Afroze & Sen 2018). The commonly released toxic heavy metals are zinc, thallium, copper, nickel, mercury, cadmium, lead, and chromium (Tóth *et al.* 2016). Figure 2 summarizes the maximum permissible limit of heavy metals according to the World Health Organization (WHO), and the potential health effects of heavy metals in higher percentages (Rangabhashiyam *et al.* 2019).

The main sources of these metals are refineries, coal-fired power plants, and municipal wastewater for Hg (Streets *et al.* 2017); mining operations, tanneries, and electronics for Cu (Tóth *et al.* 2016); batteries, metal plating, phosphate fertilizers, pigments, and stabilizers for Cd (Suksabye *et al.* 2016); fertilizer, petrochemicals, electroplating, tanneries, metal processing, and mining for manganese (Mn) (Ojedokun & Bello 2016); effluents from metal plating and smelters, paint industry, plastics, mining, textiles, preservative-producing industries, and use of fertilizers for Pb (Ince *et al.* 2017); brass and bronze manufacturing, steel production, electroplating, pharmaceuticals, galvanizing, paints, pigments, insecticides, and cosmetics for highly concentrated Zn (Tóth *et al.* 2016). The removal of these metals by agriculture waste absorbance is carried out either with direct application, or by using additional treatment methods such as thermal or chemical treatments to enhance their adsorption capacity.

Mercury removal

Mercury in its simplest form or mercury compounds are toxic for humans and harmful to the environment (Carolin *et al.* 2017). When mercury is released from fossil fuels, mineral deposits or ores, it accumulates in bottom sediments, water sources and surface soils (Liu *et al.* 2016). Mercury is not degradable and it is highly mobile. Methylmercury is the most toxic mercury compound and its ability to accumulate is very high. Short-term exposure to mercury compounds negatively impacts the nervous system, while long-term exposure is harmful to the reproductive and immune systems as well as kidneys. The accepted levels of Hg in the urine and blood of humans is approximately 4 and 8 g/L, respectively

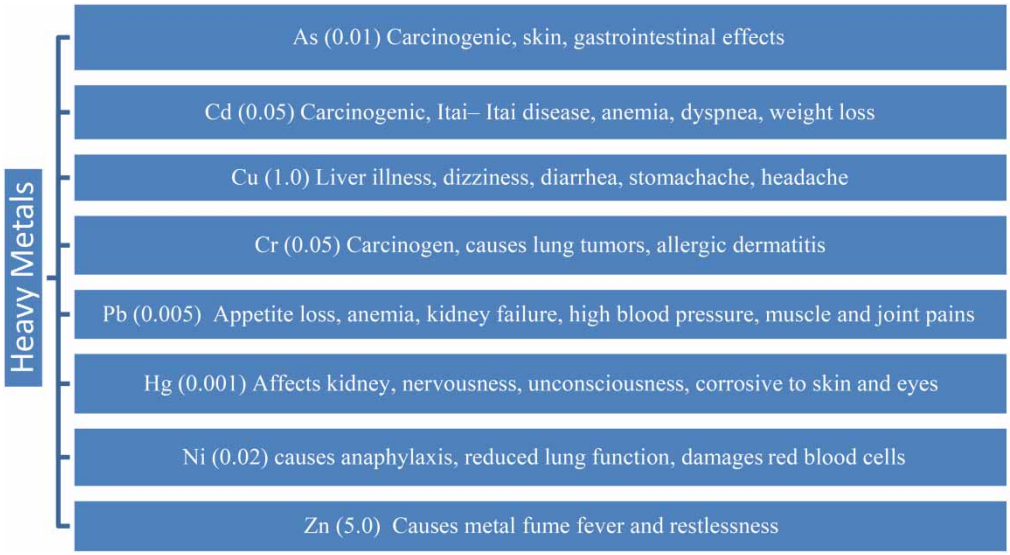

Figure 2 | Outline of the maximum permissible limit of heavy metals according to the World Health Organization, and the potential health effects of heavy metals existence in higher percentages.

(Abbas *et al.* 2016; Bjørklund *et al.* 2017; Genchi *et al.* 2017). Several agriculture waste materials such as rice husk and straw, Douglas fir bark, black oak bark, redwood bark, sawdust, dry redwood leaves, and dyed and undyed bamboo pulp have been evaluated for Hg adsorption (Kumar 2006; Jamshaid *et al.* 2017). Black oak bark showed the highest adsorption capacity for Hg achieving 400 mg/g, while it showed lower adsorption capacity for other heavy metals such as Cd, where only 25 mg/g was achieved (Kumar 2006).

Copper removal

Copper compounds are involved in several industrial and agricultural activities and, thus, can be released into the environment and reach water sources (Poole 2017). Copper has been identified as the second most dangerous toxic metal after mercury; it causes damage to the livers, kidney, and respiratory system (Abbas *et al.* 2016). Several agriculture waste materials such as the shells of watermelons, wheat, ocra, hazelnuts, cashew nuts, and palm oil fruit, the peels of pomegranates and oranges, coconut and rice husks, tobacco, sawdust, cassava waste, loquat leaves, garden grass, poplar forest litter, azolla, barley straw, palm fruit fiber, kenaf fiber, peanut hull pellets, capsicum annum seeds, and uncaria gambir have been evaluated for Cu adsorption (Aksu & İşoğlu 2005; Bilal *et al.* 2013; Ben-Ali *et al.* 2017). The maximum adsorption capacity of copper varies depending on the adsorbing materials. Peanut hulls and uncaria gambir showed the lowest adsorbing capacity at only 9 mg/g, while garden grass showed the highest adsorption rate at 58.34 mg/g (Johnson *et al.* 2002; Tong *et al.* 2011; Hossain *et al.* 2012; Ben-Ali *et al.* 2017). However, activation carbon prepared from biomass such as molasses showed very high adsorbing capacity, 525.32 mg/g, due to its high surface area (Legrouri *et al.* 2017; Fazal-ur-Rehman 2018).

Chromium removal

Several industrial activities such as tanning, dyes manufacturing for plastic, paints, wood preservation and pigments, and textiles manufacturing release chromium to the environment (Kazakis *et al.* 2018). Chromium is a toxic heavy metal which exists in several oxidation states, but chromium (VI) and chromium (III) are the largest threats to the environment (Yu *et al.* 2000). Numerous investigations have been conducted into the utilization of waste agricultural materials to remove chromium metal and ions from wastewater (Carolin *et al.* 2017; Malik *et al.* 2017). Several agricultural wastes such as hazelnut and peanut shells, banana, lemon and orange peels, maize cobs, soybean and rice hulls, and jack fruit were investigated for chromium removal and excellent removal efficiency was reported (Bansal *et al.*

2009; Nasseh *et al.* 2017; Panda *et al.* 2017; Wen *et al.* 2017). Furthermore, different plant parts such as coconut fiber pith and shell fiber, plant bark (Acacia arabica, Eucalyptus), pine needles, Moringa aptera Gaertn, cactus and neem leaves have also been reported as promising adsorbent materials for chromium removal, showing efficiency higher than 90% at optimum pH (Carolin *et al.* 2017). Rice brans have been found to be less effective as adsorbent materials for chromium because the reported efficiency did not exceed 50% (Farajzadeh & Monji 2004; Oliveira *et al.* 2005; Sud *et al.* 2008). Wheat brans have shown the highest adsorption capacity for Cr (VI) at 310.58 mg/g.

Lead removal

Plastics, finishing tools, cathode ray tubes, ceramics, solders, pieces of lead flashing and other minor by-products of steel and cable reclamation are the main sources of lead discharges into the environment (Adiana *et al.* 2017; Rosca *et al.* 2018). Its removal has attracted much attention due to the wide harmful biological effects of high Pb concentration and exposure time (Kennish 2017), as well as its strong adherence to particles in the environment such as oil, sediments and sewage sludge (Shaheen *et al.* 2017). Several agricultural byproducts such as rice and black gram husk, groundnut (*Arachis hypogaea*), peanut and walnut shells, lemon grass (*Cymbopogon citratus*), olive stone and grape stalk wastes, orange peel, coir pith waste of coconut and chitosan have been tested for Pb adsorption and the results have shown an adsorption capacity in the range of between 8.3 mg/g for chitosan and 263.0 mg/g for coir pith waste of coconut (Babarinde & Onyiaocha 2016; Hassan 2016; Nadeem *et al.* 2016).

Cadmium removal

Cadmium metal and ions are very serious pollutants due to their high solubility in water, which makes them mobile in soil with a tendency to bioaccumulate (Qi *et al.* 2018). Long duration exposure to Cd may lead to lung cancer and kidney and bone damage (Liu *et al.* 2017b). Increasing Cd concentration can occur naturally due to volcanic eruptions or from anthropogenic sources such as fertilizer application, power plants, sewage irrigation, solid waste, mining, smelting, and fuel combustion (Dou *et al.* 2017; Khan *et al.* 2017). Rice and wheat bran have shown the best efficiency in adsorbing Cd, as well as rice and black gram husks. In addition, tree bark, peas and orange peels, fig leaves, and jack fruits have been reported as promising adsorbents at acidic pH ranges. Furthermore, the adsorption efficiency of Cd by activated carbon from agriculture waste has been reported to be between 50 and 98% (Sud *et al.* 2008). Coconut waste has shown the highest adsorption capacity for Cd (II) at 285.70 mg/g compared with other material such as olive branches, Musa paradisiacal peels, and potato peels which showed only 38.17, 10.0, and 125 mg/g, respectively (Ogundipe & Babarinde 2017; Chidi & Kelvin 2018; Ibisi & Asoluka 2018; Alkherraz *et al.* 2020).

Removal of other metals

The removal of other metals such as zinc, cobalt, nickel, thallium (Tl), and iron are also of great interest due to their existence in various industrial effluents and their high toxicity. Zinc has effective impacts on several biochemical processes of living tissues, where high concentrations cause several health issues such as skin irritations, stomach nausea, cramps, vomiting, and anemia (Abbas *et al.* 2016). The main sources of zinc include agricultural activities, wood pulp production, brass plating, ground and newsprint paper production, groundwater intrusion, zinc and brass metal works, and steel works with galvanizing lines, or from a combination of these sources with different waste concentrations ranging between 1 and 48,000 mg/L (Abbas *et al.* 2016).

Co-compounds widely exist in nature and are involved in industrial activities such as the metallurgical industry, electroplating, mining, and manufacturing of oxygen carriers, paints, catalyst, pigments, electronic, and nuclear power plants (Bonner & Bridges 2016; Alalwan *et al.* 2017, 2018b; Egorova & Ananikov 2017; Zadnipryany *et al.* 2017). The acceptable levels of Co in irrigation water and livestock wastewater are 0.05 and 1.0 mg/L, respectively. Long-term exposure to Co causes serious health issues to the hematological, respiratory, endocrine, and nervous systems (Leyssens *et al.* 2017). Nickel metal and ions have no odor or taste; batteries, power plants and trash incinerators are the main sources of Ni in the environment (Zambelli *et al.* 2016). Cassia fistula biomass, waste tea leaves, and the sawdust of maple, oak and black locust trees have shown promising efficiency for nickel

removal. *Acacia leucocephala* bark have shown the highest adsorption capacity at 294.10 mg/g.

The toxicity of thallium compounds have been found to be higher than many other materials, including lead, cadmium, and mercury (Campanella *et al.* 2016). Thallium compounds are involved in several applications such as alloys, dyes, rodenticides, glass, pigments, mining, and electronic industries (Adio *et al.* 2018). Memon *et al.* (2008b) used sawdust to adsorb Tl (I) and they reported that modifying sawdust with sodium hydroxide (NaOH) increased the adsorption capacity from 2.71 to 13.18 mg/g. Their results indicate that the sorption process is pH dependent, and optimal sorption was observed at pH values between 6 and 9. Alalwan *et al.* (2018a) used rice husk to adsorb Tl (III); their results showed that adsorption is a function of temperature, pH, flow rate, initial concentration, and adsorbent amount. The maximum adsorption capacity was 42.85 mg/g at optimal conditions. Fibrous waste tea and sugar beet pulp have also been reported as promising adsorbent materials (Eroğlu *et al.* 2009; Zolgharnein *et al.* 2011).

The presence of arsenic in water sources is a result of both natural and human activities (Sarkar & Paul 2016). More than 5 l g/L of As compounds are present in 21% of ground water and 10% of surface water, as reported by the National Arsenic Occurrence Survey (Abbas *et al.* 2016). Several agricultural wastes such as hazelnut, pecan nut, water chestnut, and coconut shells, jackfruit and fruit peels, and rice husk have been used for As removal from water and the efficiency varied between 71 and 96% (Shakoor *et al.* 2016). Several agriculture wastes such as defatted rice bran, waste tea leaves, dry pine needles, sawdust of oak and black locust hard wood, bamboo pulp, hazelnut shell, orange peel, maize cob, peanut hull, kenaf core, kenaf bast, sugarcane bagasse, cotton, and coconut coir are investigated to remove heavy metals (Malladi *et al.* 2018; Naseer *et al.* 2019). Table 2 shows different agricultural waste materials that have shown promising adsorption capacities for different heavy metal compounds.

ABSORPTION MODELS

The rate at which adsorption takes place has attracted much attention due to its high importance in the adsorption process. The impact of several parameters on the adsorption rate has been investigated to determine the best operating conditions. Specifically, residence time, solution pH, temperature, and concentration have been recognized as parameters that affect the adsorption rate (Alalwan *et al.* 2018a). Several kinetic models have been investigated to describe the dynamic process of adsorption systems, namely, Thomas, Yoon-Nelson, Bed Depth Service Time (BDST), Clark models, Adams-Bohart, and Wolborska (Alalwan *et al.* 2020).

Based on either solution concentration or the capacity of the adsorbent, many kinetic models have been developed to predict the reaction order, as well as the rate-controlling steps of adsorption systems, such as metal transport and physicochemical interactions (Rangabhashiyam *et al.* 2019). These kinetic models provide important information on the dynamics of the biosorption process, reaction pathways, and associated mechanisms. The most common models based on solution concentration are the first- and second-order reversible and irreversible models, in addition to pseudo first- and second-orders (Ho 2006; Harmsen 2017; Nagy *et al.* 2017). On the other hand, the most commonly adopted models based on the adsorption capacity are Lagergren's first-order equation, the Redlich Peterson model, and the BET model (Sud *et al.* 2008).

Among several isotherm models including Temkin, Jovanovic, and Halsey, both Langmuir and Freundlich are intensively used to describe the relationship between the amount adsorbed by a unit weight of solid sorbent, and the amount of non-adsorbed solute at equilibrium. These models have been reported to be suitable for describing adsorption of heavy metal molecules by different sorbent materials. The isotherm models provide vital information about the interactive behavior between biosorbent and metal at constant temperature and equilibrium solute concentration. These models play significant roles in analyzing the biosorption mechanism and optimizing the biosorbent use through the estimation of the biosorbent amount required to uptake a determined concentration of metal from the aqueous solution. In addition, isotherm models can precisely predict the distribution of biosorption sites and heavy metal ions biosorbed on the biomass surface.

Table 2 | Biosorption capacities of various biomass of plant origin for removal of toxic metal ions from wastewater

Toxic metal ions	Biomass source	Biomass	Adsorption capacity (mg/g)	Reference
Cd (II)	Rice husk	Natural rice husk	73.96	Akhtar *et al.* (2010)
Cd (II)	Wheat waste	Wheat bran	15.82–22.78	Nouri *et al.* (2007); Nouri & Hamdaoui (2007)
Cd (II)	Wheat waste	Wheat straw	11.60–39.22	Tan & Xiao (2009); Farooq *et al.* (2011)
Cd (II)	Coconut waste	Puresorbe	285.70	Pino *et al.* (2006)
Cd (II)	Coconut waste	Coir pith	93.40	Kadirvelu & Namasivayam (2003)
Cd (II)	Coconut	Copra meal	4.99	Ho & Ofomaja (2006)
Cd (II)	Peel	Orange peel	47.60	Sha *et al.* (2009)
Cd (II)	Peel	Mango peel	68.92	Iqbal *et al.* (2009b)
Cd (II)	Peel	Banana peel	5.71–35.52	Memon *et al.* (2008a); Anwar *et al.* (2010)
Cd (II)	Peel	Pomelo peel	21.83	Saikaew *et al.* (2009)
Cd (II)	Seeds	Raw date pit	35.90	Kahraman *et al.* (2008)
Cd (II)	Coffee waste	Raw coffee powder	15.65	Azouaou *et al.* (2010)
Cd (II)	Tea	Tea waste	11.29	Cay *et al.* (2004)
Cd (II)	Bark	*Pinus roxburghii* bark	3.01	Padmini & Sridhar (2007)
Cr (VI)	Wheat	Wheat bran	310.58	Cankara *et al.* (2016)
Cr (VI)	Wheat	Wheat straw	21.34	Wang *et al.* (2010)
Cr (VI)	Peel	Banana peel	131.56	Memon *et al.* (2009)
Cr (VI)	Fruit	Bael fruit	17.27	Anandkumar & Mandal (2009)
Cr (VI)	Husk	Groundnut husk	7.00	Dubey & Gopal (2007)
Cr (VI)	Shell	Almond shell	3.40	Pehlivan & Altun (2008)
Cr (VI)	Shell	Hazelnut shell	8.28	Pehlivan & Altun (2008)
Cr (VI)	Shell	Walnut shell	8.01	Pehlivan & Altun (2008)
Cr (VI)	Bark	*Pinus roxburghii* bark	4.15	Sarin & Pant (2006)
Cu (II)	Wheat	Wheat bran	6.85–17.42	Aydın *et al.* (2008); Wang *et al.* (2009)
Cu (II)	Peel	Orange peel	50.94	Sha *et al.* (2009)
Cu (II)	Peel	Mango peel	46.09	Iqbal *et al.* (2009a)
Cu (II)	Hull	Peanut hull	9.00–21.25	Johnson *et al.* (2002); Zhu *et al.* (2009)
Cu (II)	Hull	Peanut hull pellet	12.00	Johnson *et al.* (2002)
Cu (II)	Seed	*Cicerarientinum*	18.00	Mohammad *et al.* (2010)
Cu (II)	Shell	Chestnut shell	12.56	Yao *et al.* (2010)
Cu (II)	Bark	*Casuarina equisetifolia* bark	16.58	Mohan & Sumitha (2008)
Cu (II)	Bark	*Rhizophoraapiculata* tannin	8.78	Oo *et al.* (2009)
Cu (II)	Bark	*Pinus roxburghii* bark	3.81	Pehlivan & Altun (2008)
Cu (II)	Tea	Tea waste	8.64–48.00	Cay *et al.* (2004); Amarasinghe & Williams (2007)
Co (II)	Coconut	Coir pith	12.82	Parab *et al.* (2006)
Co (II)	Peel	Lemon peel	22.00	Bhatnagar *et al.* (2010)
Pb (II)	Wheat	Wheat bran	87.00	Bulut & Baysal (2006)
Pb (II)	Coconut	Coir pith waste	263.00	Kadirvelu & Namasivayam (2000)
Pb (II)	Tea	Spent black tea	129.90	Zuorro & Lavecchia (2010)

(*continued*)

Table 2 | continued

Toxic metal ions	Biomass source	Biomass	Adsorption capacity (mg/g)	Reference
Pb (II)	Tea	Spent green tea	90.10	Zuorro & Lavecchia (2010)
Pb (II)	Tea	Tea waste	65.00	Amarasinghe & Williams (2007)
Pb (II)	Peel	Mango peel	99.05	Iqbal *et al.* (2009b)
Pb (II)	Peel	Banana peel	2.18	Anwar *et al.* (2010)
Pb (II)	Bark	*Moringa oleifera* bark	34.60	Reddy *et al.* (2010)
Pb (II)	Bark	*Rhizophoraapiculata* tannin	31.32	Oo *et al.* (2009)
Pb (II)	Shell	Shell carbon	30.00	Sekhar (2008)
Pb (II)	Shell	Hazelnut shell	28.18	Pehlivan *et al.* (2009)
Pb (II)	Seed	*Cicerarientinum*	20.00	Mohammad *et al.* (2010)
Pb (II)	Shell	Almond shell	8.08	Pehlivan *et al.* (2009)
Ni (II)	Bark	*Pinus roxburghii* bark	3.53	Sarin & Pant (2006)
Ni (II)	Bark	*Acacia leucocephala* bark	294.10	Subbaiah *et al.* (2009)
Ni (II)	Peel	Orange peel	158.00	Ajmal *et al.* (2000)
Ni (II)	Peel	Pomegranate peel	52.00	Bhatnagar & Minocha (2010)
Ni (II)	Peel	Mango peel	39.75	Iqbal *et al.* (2009a)
Ni (II)	Seed	Guava seed	18.05	Ramana *et al.* (2010)
Ni (II)	Coconut	Coir pith	15.95	Parab *et al.* (2006)
Ni (II)	Tea	Tea waste	73.00	Ahluwalia & Goyal (2005)
Zn (II)	Seed	*Cicerarientinum*	20.00	Mohammad *et al.* (2010)
Zn (II)	Wheat	Wheat bran	16.40	Dupont *et al.* (2005)
Zn (II)	Tea	Tea waste	8.90	Wasewar *et al.* (2009)
Zn (II)	Peel	Mango peel	28.21	Iqbal *et al.* (2009a)

EVALUATION OF CURRENT ADSORPTION MATERIALS AND OUR INSIGHTS

Several materials (namely, activated carbon, biomaterials, rubber waste, nanoparticles, etc.) have been evaluated as promising adsorbents for the removal of heavy metals from wastewater (Burakov *et al.* 2018; Nag *et al.* 2018; Sadegh *et al.* 2018; Sy *et al.* 2018; Fato *et al.* 2019). However, there are several drawbacks related to each of the above-mentioned materials, especially in terms of cost effectiveness and efficiency. Although much work has been carried out in developing novel adsorbents for wastewater treatment, agriculture byproducts show promising performances in terms of cost effectiveness and adsorption capacity. The main drawback of the synthetic materials is their low adsorption efficiency as well as their higher manufacturing cost compared to agriculture byproducts (Gupta *et al.* 2015). Several researchers have been working on adsorbent modification such as activated carbon loaded with nanoparticles for more effective and efficient removal of pollutants (Kataria & Garg 2018). However, these modified materials are very expensive because they must be regenerated to achieve acceptable cost levels for the adsorption process. The regeneration step brings some challenges such as decreasing the adsorption capacity due to different reasons such as the damage caused by the desorption media. Using agriculture byproducts can overcome this limitation because no regeneration is required due to the abundance of those byproducts.

The biowaste cost is much less expensive than other removal materials. For instance, the black liquor waste price is $1/1,000 kg, while lignin and activated carbon prices are $60/1,000 kg and $100/1,000 kg, respectively (Bailey *et al.* 1999). Also, in addition to the enormous amount of its waste (100+ million tons/year), the maximum

price of rice husk is no more than $0.025/kg (Rafatullah *et al.* 2010). It is worth mentioning that the clay price is $0.04–0.12/kg (Crini 2006). Although the adsorption capacity of the biowaste could be less than conventional and developed materials, the total efficacy is higher due to their low cost. In some cases, the biowaste performs better than other adsorbents in terms of heavy metals removal. In addition, biochar, ash, etc., could be synthesized from biowaste via modification treatments, such as pyrolysis, to increase the materials' removal efficiency. Here, the biowaste, specifically agricultural waste, has many advantages that place it as one of the important adsorbents.

In addition to its low price and abundance, biowaste can be multi-employed, as it can be regenerated. Yang *et al.* (2019) used the pulp of pomelo peel to adsorb uranyl ions, where it was chemically modified; the unmodified and modified peel adsorption amount reached up to 32.28 and 42.73 mg/g. NaOH solution was used to wash the adsorbate from the adsorbent. After five desorption cycles, the adsorption efficiency decreased by only 6%. Similarly, Mallampati *et al.* (2015) used avocado and hamimelon peels to adsorb lead and nickel ions. Hamimelon adsorption rates for lead and nickel were 7.89 and 9.45 mg/g, respectively; while they were 9.82 and 4.93 mg/g, respectively, when avocado was used. The adsorption/desorption test was conducted five times to investigate biowaste reliability. The performance was maintained at almost the same value after five cycles. Ultimately, Chen *et al.* (2018) employed litchi, pomegranate, orange, and banana peels to remove cadmium ions. The peel efficiency followed the order of litchi > orange > pomegranate > banana. With regard to the reuse of peel, the adsorption-desorption test was run ten times to study the adsorption stability after adsorbent regeneration. After 10 cycles, the adsorption capacity reduced by 6.5% for litchi peel, 7.6% for orange peel, 8.4% for pomegranate peel, and 11% for banana peel. It can be noted that higher adsorption capacity peel had higher removal efficiency stability, following the same order above. Here, from the aforementioned examples, it can be deduced that the agriculture waste is reliable and stable in terms of regeneration and reuse.

The major features of agriculture byproducts in wastewater treatment are the high versatility for a wide range of operational conditions, high selectivity for metals rather than metal salts, low influence by alkaline earth and common light metals, high tolerance to organics, independence of concentration, and good regeneration. Surface modifications help to enhance their binding properties, which improves their performances but increases the overall cost of the process. The expenses would be closer to the price of other adsorbent materials and methods such as activated carbon or ion-exchange resins. In addition, the modification step should be carefully evaluated because of the incorporation of new functional groups as a result of chemical modification, which can decrease sorption due to steric, conformational, or other effects. Although the modification process has been reported as an active method to increase the adsorption capacity of the raw waste materials, it cuts the cost efficiency of the treatment process and has a negative impact on the environment (Shafiq *et al.* 2018). Both modified and non-modified agriculture wastes have demonstrated their potential when tested with real industrial effluents, but the application of such materials at an industrial scale has not yet been tested. Indeed, employing raw or even modified agriculture wastes for wastewater treatment on an industrial scale has some problems related to cost effectiveness, stability issues, availability, and extremely large-scale requirement (Shafiq *et al.* 2018). However, the utilization of agriculture wastes instead of sand as a filtration media for the secondary and tertiary treatments of industrial wastewater has shown promising results due to their low-density, higher filtration rate, lower head loss, longer filtration time, and less backwash water usage (Shafiq *et al.* 2018).

SUMMARY

Heavy metal biosorption using inexpensive and efficient biosorbents from agricultural waste materials has been reported as a promising replacement for existing conventional systems. This review summarizes the most recent and important information reported in the literature of this field. From the listed results, it can be concluded that coconut waste showed high adsorption results for cadmium and lead ions. Also, wheat and banana peels have efficiently removed chromium ion, while *Acacia leucocephala* bark and orange peel were effective in nickel ion removal. Likewise, spent black tea was used in lead removal. Although the agriculture waste materials have

several advantages over currently used carbon and organic resins for heavy metal removal, they have not yet been significantly commercialized. The main reason could probably be the lack of knowledge about the engineering of such materials. The collaboration of multidisciplinary scientists such as engineers, chemists, biologists, material scientists, microbiologists, agriculture scientists, and computer programmers could help to speed up the adoption of these materials in industry. Future research should focus on filling some of the knowledge gaps, such as adsorption at the biosorbent–water interface, pre-treatment methods that enhance the adsorption capacity without limiting the cost effectiveness, and the eco-friendly advantages of these materials.

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