



The application of agricultural wastes for heavy metals adsorption: A meta-analysis of recent studies

Muhammad Imran-Shaukat^{*}, Rafeah Wahi, Zainab Ngaini

Faculty of Resource Science and Technology, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia

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ABSTRACT

Numerous studies have been carried out to investigate the suitability of various agricultural wastes as biosorbent for heavy metals removal. Previous published reviews on heavy metal removal by agricultural waste-based biosorbent were limited to narrative and systematic reviews, with no statistical analysis to compare outcomes across different biosorbents sources. In this work, meta-analysis technique was applied to identify gaps in contemporary biosorbents research. A meta-analysis was undertaken using several packages of R programme on publications over the last five years to evaluate the capability of eleven different types/components agricultural wastes for the adsorption of eight heavy metal. Based on the findings, agricultural wastes have the potential to be employed for heavy metal adsorption from aqueous media in general. However, the disparities in the findings suggest that when utilising different types of raw biomass as adsorbents, modifying the biomasses into carbon-enriched forms would be a preferable option.

1. Introduction

Heavy metals can be found in water, the atmosphere and sediments through a variety of natural and anthropogenic causes such as inadequate water treatment, urbanisation, industrialisation and the intensification of agricultural output (Rhaman et al., 2020). Heavy metal concentrations in the environment have been reported to be elevated in the wastewater generated by numerous industries like mining, textiles, fertiliser production, pharmaceuticals (Mustapha et al., 2019), pesticide production, smelting (Liu et al., 2019), electroplating (Surendran and Baral, 2018), leather tanning, wood preservation, metal cleaning, processing, alloy preparation (Sinha et al., 2015), photography, mining, battery storage operations (Mohammed and Ibrahim, 2016), stainless-steel welding, construction, structure demolition, lead piping and fittings (Shilawati Ehishan and Sapawe, 2018), electronic-circuit production, steel and nonferrous processes and chemical industries (Gupta et al., 2015).

Heavy metals bioaccumulate rapidly in living tissues through the food chain (Bendjeffal et al., 2018; Zhang et al., 2018). Human exposure to excessive Cadmium can cause nausea, diarrhoea, yellowing of the teeth, lung defects and hypertension (Ali et al., 2020), Itai-itai disease and bone-softening (Gupta et al., 2015). Excessive human ingestion of chromium results in kidney damage, capillary damage, gastrointestinal

issues and irritation of the central nervous system (Ali et al., 2020; Bayuo et al., 2019). Prolonged subjection to Ni can result in cancer and lung fibrosis, together with dermatitis (eczema) after it comes into contact with the skin (Fawzy et al., 2016). Copper ingestion can cause mucosal inflammation, renal injury, gastrointestinal issues, depression and kidney damage (Banerjee et al., 2019; Kebede et al., 2018). Long-term contact with high concentrations of manganese may lead to damage to the central nervous system, including Parkinson's disease (Kul et al., 2016). Long term exposure to Lead, even in limited quantities, can cause severe health conditions such as cancer, semi-permanent brain stroke, and renal and lung ailments (Alhogbi, 2017). Central nervous system and peripheral nervous system manifestations, elevated blood pressure and haemolytic anaemia are typical signs of Pb (II) poisoning (Ali et al., 2020). Higher concentrations of zinc can cause stunted growth to living organisms, reductions in immunisation, increased risk of tumour formation (Liu et al., 2019), fever and gastrointestinal disturbances (Ferreira et al., 2019).

A large array of technology is used in the physicochemical and biological treatment techniques used in industry for heavy metal extraction from water and wastewater. These include filtration, ion-exchange, reverse osmosis (Abdolali et al., 2015), chemical and electrochemical precipitation, membrane filtration (Semerjian, 2018), ultra-filtration, solvent extraction (Basu et al., 2017a) electrolysis and coagulation

^{*} Corresponding author.

E-mail address: imranchemi@gmail.com (M. Imran-Shaukat).

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(Kebede et al., 2018). According to extensive studies, adsorption is top-notch to other treatment techniques in terms of removing contaminants at very low concentrations, broader applicability in the removal of diverse types of pollutants, environmental friendliness and resistance to fouling from toxic pollutants (Gupta et al., 2015). It is also easy to adapt, highly effective, cost-saving for removal of heavy metal removal from aqueous medium (Zhang et al., 2018).

A wide variety of materials have been examined as potential adsorbents for removing heavy metals from aqueous media (Paduraru et al., 2015). Some effective adsorbents that have been used for this purpose include activated carbon/charcoal/alumina, numerous resins, polymers, graphene and carbon nanotubes (Takdastan et al., 2019). The use of these expensive adsorbents has been limited because the cost of their regeneration is often excessive (Ngabura et al., 2018; Saha et al., 2017). Alternative approaches that can be used in the adsorption of metal ions using inexpensive organic material have increasingly been identified since the 1990s (Khokhar et al., 2015; Paduraru et al., 2015). Examples of these materials include agricultural wastes, pulverised industrial wastes, chitosan derivatives, chitin, fungi, bacteria and algae (Bonilla-Petriciolet et al., 2017).

Many economical agricultural waste-based biosorbents have been reported for the removal of heavy metals. These require minimal pre-treatment such as washing, drying, grinding, or minor acid or alkali treatment, which avoids the need for any severe form of physical or chemical treatment (Lee and Choi, 2018). Many materials have been used as agricultural waste-based biosorbents, including milled olive stone biomass (Amar et al., 2020), Alhaji maurorum seeds (Ebrahimi et al., 2015), *Moringa stenopetala* seeds (Kebede et al., 2018), lemon peel (Nahar et al., 2018), durian peel (Ngabura et al., 2018), banana peel, tangerine peel, kiwi peel (Al-Qahtani, 2016), raw pomegranate peel (Ben-Ali et al., 2017), *Albizia lebbek* pods (Mustapha et al., 2019), *Adansonia digitata* roots (Ekere et al., 2016), *Moringa stenopetala* bark (Kebede et al., 2018), watermelon shells (Gupta and Gogate, 2016), coconut coir (Asim et al., 2020), Groundnut husk (Gupta and Sen, 2017), Marula seed husk (Moyo et al., 2015), Apricot stone shells (Šoštarić, 2018), the pith core of rape straw (Liu et al., 2019), *Tradescantia pallida* plants (Sinha et al., 2015), *Phragmites australis* plants (Kahrizi et al., 2016), *Artocarpus odoratissimus* leaves (Zaidi et al., 2018), *Boehmeria lysteri* leaves (Bose et al., 2016), and *Colocasia esculenta* leaves (Nakkeeran et al., 2016). The aforementioned studies discussed the adsorption capacity and removal efficiency of these materials and related these qualities to adsorption isotherms and kinetic studies. Various factors affecting adsorption have also been discussed, such as the initial pH of the solution, temperature, contact time, initial metal concentration, adsorbent dosage and rotation speed (Ebrahimi et al., 2015).

Because of its high porosity, excellent adsorption capacity, and superior surface reactivity, activated carbon has been widely employed as an adsorbent commercially (Liao et al., 2019). In addition to traditional sources, agricultural by-products such as almond, hazelnut, and coconut shells, as well as olive, apricot, and peach fruit seeds, have been utilized to make activated carbon (Ani et al., 2020). Biochars, which are derived from a variety of agricultural wastes, have sparked the interest of many researchers as an eco-friendly material that has proven to be effective in a variety of disciplines (Park et al., 2019). The addition of non-carbon moieties to the surface of porous materials enhances the efficiency of activated carbon in wastewater treatment. (Kharrazi et al., 2020). Soy hull was treated with sodium nitrate solution (Blanes et al., 2016), teff husk was alkali treated followed by carbonization at 550 °C (Adane et al., 2020), and calabash peel was treated with nitric acid and formaldehyde (Ahmed et al., 2018). Zinc chloride-impregnated *Senna siamea* seedpods were activated by thermal treatment at 550 °C (Ajmani et al., 2019). Dead palm leaves were impregnated with Ferric Chloride in an alkaline medium, then before treatment at 600 °C to develop nanocomposite (Allothman et al., 2020). Poplar sawdust was used to develop activated carbon by impregnating it in potassium hydroxide and zinc chloride separately under different condition and then pyrolyzing at

300–600 °C (Nayak et al., 2017), jackfruit peel was impregnated in concentrated sulphuric acid, rinsed with distilled water, soaked in sodium carbonate solution, pyrolyzed at 400–600 °C, and microwave pyrolysis at 200 W for 10 min. to prepare a biochar (Nayak et al., 2021).

Apart from the reported limitations of unprocessed adsorbents and demonstrated improvement through modification, extensive studies have recently been conducted to determine the applicability of various agricultural wastes, such as shells, leaves, roots of plants without any complex physical or chemical modification. The necessity to summarise the outcomes of various investigations develops as more studies are undertaken on a certain subject (Van Assen et al., 2015). Several review articles summarising the use of agricultural wastes to remove heavy metals from water and wastewater have been published, but no statistical analysis of agricultural wastes as biosorbents without complex modifications has yet been reported.

Systematic reviews and meta-analyses collect and evaluate data from multiple studies conducted on comparable research subjects to draw the conclusions, and both of these methods have become increasingly popular in recent years in a variety of sectors (Ahn and Kang, 2018). Being comprehensive and time taking work, this procedure takes at least a year on average (Julian Higgins, 2021). The current work includes a meta-analysis of recent research on the applicability of agricultural wastes as adsorbents without modifications, as well as an outline of the factors that determine their adsorption capabilities and a synopsis of adsorption mechanism. Because extensive reviews were carried out before presenting it for publication, this work took around a year and a half, which is a bit longer than the average time for such analytical work. In this article, the term “biosorbent” refers to agricultural waste biomass.

2. Materials and methods

2.1. Selected literature and inclusion criteria

The meta-analysis was conducted based on guidelines developed by (McInnes et al., 2018; Moher et al., 2015). The flow of data extraction and analysis is carried out on the selected set of studies as summarized in “Appendix A”. The literature search was conducted using the Elsevier, Taylor & Francis, PubMed, and Springer databases using the search words “heavy metals removal”, “agricultural waste”, “plant waste”, “adsorption”, “biosorption”, “biosorbent”, “sorption”; publication dates spanned the period 1st January 2015 to 1st June 2020. Out of 11,427 articles retrieved, all the article titles were reviewed, and any irrelevant and duplicated articles were deleted, leaving 480 articles shortlisted for further review. In the next step, the abstracts of all these articles were examined and analysed against the inclusion protocol. Articles were selected for further analysis only if they contained adequate information relevant to research methods, that is, if they were not review papers. After this, the methods and results mentioned in the remaining articles were analysed for their reporting of non-agricultural waste-based biosorbent or biosorbent prepared through severe physical or chemical treatments (for example, activation, biochar, or hydro char formation).

The remaining articles were reviewed thoroughly, and articles were shortlisted only if they contained information on the type and part of biomass used, percentage of heavy metal removed, initial metal concentration, biosorbent dosage, temperature, pH and contact time. As the literature indicates, different types of agricultural waste biomass have been used raw and with several types of physical and chemical modifications. However, in the present work, the only studies considered were those in which the biomass underwent washing, drying, grinding, or minor acid/base treatment (up to 1 N NaOH/1 N HCl), while studies implementing severe treatments and modifications were excluded. Overall, 75 articles qualified according to these criteria and were subjected to the meta-analysis.

2.2. Statistical analyses

The meta-analysis was conducted using different packages of the “R” programme (Schwarzer et al., 2015). Each selected research article was considered independently, in compliance with the principles of integrated research. Data was recorded for the adsorption percentage, type of agricultural waste biomass, adsorbent dosage, initial metal concentrations, pH values, temperature and contact time. Transformation studies were conducted to compare the capability of various forms of biomass to adsorb heavy metal ions, based on the data recorded in each paper.

Effect Size (ES) is the reaction ratio, i.e., the difference between two groups, and no units enable the analysis of results from different independent studies (Yu et al., 2018). The calculation formula of ES (Hedges et al., 1999) is shown in Eq. (1). The present study focused on the differences in the heavy metal adsorption capacity of various forms of agricultural waste biomass. In addition, factors like heavy metal concentration, biomass dosage, pH and temperature were examined in terms of how they affect the adsorption efficiency.

$$ES = \ln\left(\frac{X_e}{X_c}\right) = \ln X_e - \ln X_c \quad (1)$$

where X_e denotes the concentration of heavy metal ions adsorbed by agricultural waste biomass (i.e., the initial concentration of heavy metal ions in the solution minus the surplus concentration of heavy metals in the water after adsorption by the agricultural waste biomass). The concentration of heavy metal in ambient water is denoted by X_c (Lin et al., 2020). This compact parameter was initially suggested by Hedges et al. (1999) and has been reported in several studies. The greater the ES value, the greater potential the agricultural waste biomass has to extract heavy metal ions from water and, subsequently, the greater the adsorption efficiency (Shim and Kim, 2019).

The R software packages “Meta” and “ggplot2” were used to calculate the ES mean and with a 95% confidence interval (CI). The Random Effect Model of Meta-Analysis was followed in this study (Bell et al., 2019). The heterogeneity of studies identified within the group was quantified by estimating the between-study variance “tau²” (T^2), while heterogeneity between the different groups of studies was quantified by the Q value. Heterogeneity larger than a critical value indicates consequential dissimilarities between groups ($p < 0.05$). If CI 95% was present, it was transformed and shown as a percentage change from ES (Schwarzer et al., 2015). The results are listed below in Table 1.

3. Results and discussion

3.1. Sorbate characterization

On the whole, 184 data points are outlined in Table 1. By segregating these with respect to sorbates, there were forty-six data points for Cd(II), seven for Co(II), twenty-eight for Cr(VI), thirty-five for Cu(II), five for Mn(II), nine for Ni(II), thirty-one for Pb(II) and twenty-three for Zn(II). Agricultural wastes expressed varying removal capabilities for different heavy metals, as shown in Fig. 1. The range of Effect Size (ES) of the heavy metals under discussion was observed to be between -0.685 and -0.004 . In ascending order, the sequence was Mn(II) > Pb(II) > Cd(II) > Cu(II) > Cr(VI) > Co(II) > Zn(II) > Ni(II). The standard error of the effect size for Mn(II), Pb(II), Cd(II), Cu(II), Cr(VI) and Zn(II) gradually increased from 0.008 to 0.07, while it was 0.319 and 0.341 for Ni(II) and Co(II) respectively. The data reliability increased with reductions in standard error (Lin et al., 2020). Agricultural waste biomass has been shown to have a relatively higher adsorption capacity for Mn(II), Pb(II), Cd(II), Cu(II) and Cr(VI). Meanwhile, a moderate adsorption capacity was identified for Co(II), Zn(II) and Ni(II).

According to Ronda et al. (2014), the higher affinity of the functional groups of biosorbent to one metal ion is connected to the ionic

characteristics of the relevant metal, which are determined by such parameters as the ionic radius (r), the electronegativity (X_m) or covalent index $CI = X^2_m (r + 0.85)$. Metals with a higher covalent index have a greater sorption capability compared to other metals. The findings illustrated in Fig. 1 are comparable to those previously published. Lead has a covalent index of 11.1, whereas copper and cadmium have covalent indexes of 5.56 and 5.14, respectively (Amar et al., 2020).

3.2. Agricultural waste biomass

Various forms of agricultural waste biomass have demonstrated certain heavy metal adsorption capabilities. As described in Table 1, a total of 171 datasets were distributed across eleven biomass groups. Six data points were found for bark, 26 for husk, 36 for leaves, 15 for Peels, 28 for whole plants and three for roots. Meanwhile, six data points were identified for sawdust, 21 for seeds, 17 for shells, two for spent tea coffee and 11 for straw/stems; these adsorbents were investigated for their capacity to remove heavy metal ions from an aqueous medium.

The effect size of agricultural waste biomass varied from -0.101 to -0.444 , as shown in Fig. 2. In ascending order, the sequence of ES was found to be Spent tea/coffee > Seeds > Roots > Leaves > Straw/Stems > Bark > Sawdust > Husk > Whole plants > Peels > Shells. The standard error of the effect size for Roots, Shells, Spent Tea/Coffee, Bark, Sawdust, Whole Plants, Peels, Leaves, Husk, Straw/Stems and Seeds gradually increased from -0.143 to -0.038 , respectively. The standard error of the effect size for Roots, Shells, Spent Tea/Coffee, Bark, Sawdust, Whole Plants, Peels, Leaves, Husk, Straw/Stems and Seeds gradually increased from -0.143 to -0.038 , respectively.

A comparison of the effect sizes of all the categories of agricultural waste biomass has been expressed in Fig. 2. Among all agricultural wastes, shells exhibited the lowest heavy metal adsorption efficiency, possibly due to their morphological characteristics and chemical composition. The BET surface areas of the shell biomass-based adsorbents were $1.83 \text{ m}^2/\text{g}$ for peanut shells, $11.27 \text{ m}^2/\text{g}$ for almond shells (Banerjee et al., 2019) and $32.96 \text{ m}^2/\text{g}$ for groundnut shells (Bayuo et al., 2019), figures that are much lower in comparison to $89.74 \text{ m}^2/\text{g}$ for activated carbon (Bayuo et al., 2019). As previously reported, the percentage of hemicellulose, lignin and cellulose in apricot stone shells decreased and the cellulose percentage increased slightly when treated with 1 M NaOH, which indicated the potential for extensive physical or chemical treatments to increase the efficiency of adsorbents whose materials are based on shells (Šostarić, 2018).

In the meta-analysis of adsorption studies, for the different metals under consideration, within-group heterogeneity T^2 for each group of biomass is illustrated in Table 2. In this case, heterogeneity T^2 is mentioned as undetermined because only one study was found for the respective biomass group. In most cases, Tau^2 values showed as insignificant for within-group heterogeneity except for Chromium adsorption by seeds biomass, Nickel adsorption by leaves biomass and Zinc adsorption by husk and shells biomass. One interpretation is that the findings reported in studies of the metal adsorption by these forms of biomass are not uniform; meanwhile, for most biomass groups, the results of the studies resemble each other. On the other hand, between different biomass groups, the heterogeneity of studies investigating the adsorption of each heavy metal was determined based on the Q values. For between-group heterogeneity, the p -value for all the studies was much lower than the limit of $p = 0.05$, which indicates that in the heavy metals' adsorption by different forms of agricultural waste biomass, the findings are dissimilar to each other. The Q value was found to vary between 16.53 and 509.81 for different levels of heavy metals adsorption by different groups of agricultural waste biomass. The sequence of Q values shows significant variations can be identified in the findings of studies utilising different biomasses. The Q value is lowest for Manganese adsorption and highest for Cobalt, with the sequence being Mn(II) < Cr(VI) < Zn(II) < Cd(II) < Ni(II) < Cu(II) < Pb(II) < Co(II).

As seen in Table 2, different types and components of agricultural

Table 1
Sorbent biomass sources and their calculated effect sizes for the sorbate heavy metal.

Sorbent source	Effect size (ln R)								Reference
	Cd (II)	Co (II)	Cr (VI)	Cu (II)	Mn (II)	Ni (II)	Pb (II)	Zn (II)	
Biomass									
Bark									
<i>Eucalyptus sheathiana</i> bark								−0.913	(Afroze et al., 2016)
<i>Eucalyptus sheathiana</i> bark (0.1 M NaOH)								−0.366	(Afroze et al., 2016)
<i>Moringa stenopetala</i> bark	−0.009			−0.004			−0.003		(Kebede et al., 2018)
<i>Sapindus saponaria</i> bark				−0.051					(Suresh et al., 2016)
Husk									
Coconut husk				−0.121		−0.212	−0.323	−0.392	(Malik et al., 2017)
Coffee husk							−0.02		(Alhogbi, 2017)
Green walnut husk	−0.04								(Dalali and Haggghi, 2016)
Groundnut husk				−0.223					(Gupta and Sen, 2017)
Groundnut husk (0.1 M NaOH followed by 0.1 M citric acid)				−0.105					(Gupta and Sen, 2017)
Lentil husk	−0.211								(Basu et al., 2017a)
<i>Marula</i> seed husk				−0.128			−0.024		(Moyo et al., 2015)
<i>Moringa oleifera</i> seed husk	−0.136			−0.107					(Garcia-Fayos et al., 2016)
Peanut hull				−0.182					(Ali et al., 2016)
Peanut husk	−0.478	−1.204		−0.799		−0.942	−0.01	−0.968	(Abdelfattah et al., 2016)
Rice husk							−0.22		(Masoumi et al., 2016)
Rice husk				−0.013	−0.001			−0.001	(Nahar et al., 2018)
Soy hull			−0.223						(Blanes et al., 2016)
Leaves									
<i>Aloe barbadensis</i> Miller leaves						−0.284			(Gupta et al., 2019)
<i>Artocarpus odoratissimus</i> leaves							−0.223		(Zaidi et al., 2018)
<i>Bambusa arundinacea</i> leaves (initial metal conc. = 500 ppm)	−0.396					−1.187	−0.377		(Pap et al., 2016)
<i>Bambusa arundinacea</i> leaves (initial metal conc. = 5 ppm)	−0.099					−0.821	−0.057		(Pap et al., 2016)
<i>Boehmeria listeri</i> leaves	−0.033								(Bose et al., 2016)
<i>Colocasia esculenta</i> leaves			−0.023						(Nakkeeran et al., 2016)
<i>Desmostachya bipinnata</i> leaves	−0.11								(Pandey et al., 2015)
<i>Gliricidia sepium</i> leaves			−0.001						(Suganya et al., 2019)
<i>Hevea brasiliensis</i> leaves			−0.013						(Nag et al., 2016)
Jackfruit leaves	−0.044								(Nag et al., 2016)
Mango leaves	−0.044								(Nag et al., 2016)
<i>Melia azedarach</i> L. leaves (0.1 M NaOH)							−0.026		(Khokhar et al., 2015)
<i>Melia azedarach</i> L. leaves (0.1 M HCl)							−0.018		(Khokhar et al., 2015)
Oil palm frond			−0.168				−0.063		(Shilawati Eshisan and Sapawe, 2018)
<i>Olea europaea</i> L. leaves (M50 ppm)	−0.205								(Fawzy et al., 2016)
<i>Olea europaea</i> L. leaves (M100 ppm)	−0.052								(Fawzy et al., 2016)
Persimmon leaves	−0.389			−0.47			−0.078		(Wang et al., 2018)
Rubber leaves	−0.051								(Nag et al., 2019)
Tangerine leaves	−0.021	−0.054	−0.117	−0.03	−0.078	−0.067	−0.073	−0.033	(Abdić et al., 2018)
Peels									
Banana peel	−0.821							−1.139	(Al-Qahtani, 2016)
Banana peel				−0.431					(Mohammed and Ibrahim, 2016)
Cucumber peel							−0.041		(Basu et al., 2017b)
Durian peel								−0.149	(Ngabura et al., 2018)
Kiwi peel	−0.248							−0.562	(Al-Qahtani, 2016)
Lemon peel				−0.117					(Meseldzija et al., 2019)
Lemon peel				−0.248					(Mohammed and Ibrahim, 2016)
Lemon peel				−0.001	−0.001			−0.001	(Nahar et al., 2018)
<i>Mangifera indica</i> -immobilized peel							−0.799		(Nadeem et al., 2016)
Mosambi peel			−0.004						(Mondal et al., 2019)
Raw pomegranate peel				−0.106					(Ben-Ali et al., 2017)
Tangerine peel	−0.315							−0.654	(Al-Qahtani, 2016)
Plants									
<i>Caryota urens</i> inflorescence (initial metal conc. = 500 ppm)			−0.985						(Rangabhashiyam and Selvaraju, 2015)
<i>Caryota urens</i> inflorescence (initial metal conc. = 100 ppm)			−0.076						(Rangabhashiyam and Selvaraju, 2015)
<i>Datura stramonium</i>			−0.402						(Kumar et al., 2020)
<i>Diplotaxis harra</i>	−0.238	−0.693							(Tounsadi et al., 2015)
<i>Equisetum</i>	−0.186	−0.198							(Al-Senani and Al-Fawzan, 2018)
<i>Glebionis coronaria</i> L.	−0.168	−0.526							(Tounsadi et al., 2015)
<i>Mentha piperita</i> waste	−0.097	−0.322	−0.238				−0.07		(Ali et al., 2020)
Oak waste	−0.099								(Takdastan et al., 2019)
<i>Phragmites australis</i> plant	−0.099								(Kahrizi et al., 2016)
<i>Phragmites australis</i> plant	−0.154								(Farasati et al., 2016)
<i>Quercus ithaburensis</i> acorn					−0.001				(Kul et al., 2016)

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Table 1 (continued)

Sorbent source	Effect size (ln R)								Reference
	Cd (II)	Co (II)	Cr (VI)	Cu (II)	Mn (II)	Ni (II)	Pb (II)	Zn (II)	
<i>Phytolacca americana</i> L.							−0.198		(Wang et al., 2018)
Rapeseed waste (2 g/L) 72 ppm								−0.942	(Paduraru et al., 2015)
Rapeseed waste (2 g/L) 119 ppm								−0.562	(Paduraru et al., 2015)
Rapeseed waste (30 g/L) 72 ppm								−0.117	(Paduraru et al., 2015)
Rapeseed waste (30 g/L) 119 ppm								−0.02	(Paduraru et al., 2015)
<i>Sorghastrum nutans</i> L.			−0.281						(Surendran and Baral, 2018)
<i>Stipa tenacissima</i> L. (Alfa)			−0.041						(Samir et al., 2019)
<i>Teucrium</i>	−0.03	−0.02							(Al-Senani and Al-Fawzan, 2018)
<i>Tradescantia pallida</i>						−0.062			(Sinha et al., 2015)
<i>Typha domingensis</i>	−0.247					−1.171			(Fawzy et al., 2016)
Roots									
<i>Adansonia digitata</i> roots	−0.001			−0.412			−0.105		(Ekere et al., 2016)
Sawdust									
<i>Acacia nilotica</i> sawdust			−1.022						(Khalid et al., 2018)
<i>Acacia nilotica</i> sawdust (1 M HCl)			−0.635						(Khalid et al., 2018)
Pine sawdust				−0.073					(Semerjian, 2018)
Sawdust				−0.001	−0.072			−0.002	(Nahar et al., 2018)
Seeds, seed pods, milled seeds									
<i>Adenantha pavonina</i> seeds							−0.02		(Sen et al., 2018)
<i>Albizia lebbeck</i> pods	−0.288			−0.236			−0.223	−0.198	(Mustapha et al., 2019)
<i>Alhaji maurorum</i> seeds	−0.157								(Ebrahimi et al., 2015)
<i>Crataegus oxyacantha</i> stones	−0.357								(Ebrahimi et al., 2015)
Globe artichoke	−0.073			−0.073			−0.073		(Fernández-López et al., 2019)
Milled olive stone biomass	−0.256		−0.777	−0.217			−0.057		(Amar et al., 2020)
Moringa pods			−0.091	−0.102		−0.378			(Matouq et al., 2015)
<i>Moringa stenopetala</i> seeds	−0.004			−0.006			−0.003		(Kebede et al., 2018)
<i>Punica granatum</i> seeds	−0.163								(Ebrahimi et al., 2016)
Shells									
Almond shells				−0.01					(Banerjee et al., 2019)
<i>Andean Sacha inchi</i> shells				−0.613			−0.185		(Kumar et al., 2016)
Apricot stone shells			−0.223	−0.211		−1.109	−0.139	−1.966	(Šoštarčić, 2018)
Coconut coir				−0.42					(Asim et al., 2020)
Groundnut shells			−0.203						(Bayuo et al., 2019)
Peanut shells				−0.03					(Banerjee et al., 2019)
<i>Picea smithiana</i> cones			−0.001						(Mittal et al., 2016)
Shells of rape straw								−1.772	(Liu et al., 2019)
Walnut shells							−0.001		(Lu and Guo, 2019)
Watermelon shells				−0.105					(Mohammed and Ibrahim, 2016)
Watermelon shells				−0.157					(Gupta and Gogate, 2016)
White bean shells								−0.462	(Ferreira et al., 2019)
Straw/stems									
Agave bagasse			−0.03						(Marín-Allende et al., 2017)
Corn cob				−0.55			−0.723	−0.595	(Cerrahoglu Kaçakgil and Bingöl, 2019)
Date palm empty fruit bunch			−0.544						(Rambabu et al., 2020)
Jute stick			−0.22						(Rhaman et al., 2020)
Maize cane			−0.105						(Marín-Allende et al., 2017)
<i>Mentha piperita</i> plant residue after oil extraction			−0.355						(Rawat and Singh, 2019)
Pineapple bran	−0.785								(Zhuang et al., 2020)
Pith core of rape straw								−0.001	(Liu et al., 2019)
Rice bran									(Basu et al., 2017a)
Seedpods of rape straw								−0.248	(Liu et al., 2019)
Sesame leaves and stems	−0.073								(Cheraghi et al., 2015)
<i>Solidago canadensis</i> stem biomass	−0.051								(Zhang et al., 2018)
Taro stems							−0.001		(Saha et al., 2017)
Sugarcane straw	−0.054								(Farasati et al., 2016)
Wheat bran	−0.416								(Basu et al., 2017a)
Wheat straw							−0.128		(Azizi Haghighat and Ameri, 2016)
Spent tea/coffee									
Mixed waste tea			−0.050						(Cherdchoo et al., 2019)
Ground coffee waste			−0.160						(Cherdchoo et al., 2019)

waste behave differently when applied as biosorbents. Diverse agricultural wastes differs in the surface active groups and functional groups, so the metal binding of each of them may vary (Abdolali et al., 2015). Different agricultural wastes contain hemicellulose, lipid, protein, simple sugars, starch, fat and tannin in varying proportions (Dai, 2019; Lee and Choi, 2018), and these components contain different levels of carboxyl, carbonyl, hydroxyl, thiol, phosphate, aldehyde, ketones,

aromatic, methyl, methylene, methoxy, alkanes, amines, amides, sulfones, polysaccharide, esters, carbonate, ethers, phenolic, phenyl and amino functional groups, which have a strong affinity for metal ions and can adsorb them. Therefore, in the presence of these functional groups, the adsorption process involves ion exchange and complexation (Rambabu et al., 2020; Zhuang et al., 2020). Such functional groups can interact with heavy metal ions in different ways (Meseldzija et al., 2019;

Table 2
Heterogeneity of studies with respect to agricultural waste biomass groups.

Heavy metal	Group	Differences based on Random Effect Model				
		Within-group		Between-group		
		K	Tau ²	d.f.	Q	p-Value
Cd	Bark	1	N.D.	7	84.98	0.0001
	Husk	6	0.0375			
	Leaves	12	0.0108			
	Peels	3	0.0871			
	Whole plants	9	0.0043			
	Roots	1	N.D.			
	Seeds	7	0.0109			
	Straw	1	N.D.			
Co	Husk	1	N.D.	2	509.81	0.0001
	Leaves	1	N.D.			
	Whole plants	4	0.0466			
Cr	Leaves	5	0.0013	7	45.8	<0.0001
	Peels	1	N.D.			
	Whole plants	7	0.0625			
	Sawdust	2	0.0724			
	Seeds	2	0.2333			
	Shells	3	0.0217			
	Spent tea/coffee	2	0.0051			
	Straw	5	0.0344			
Cu	Bark	2	0.0009	8	236.88	<0.0001
	Husk	8	0.0305			
	Leaves	3	0.0932			
	Peels	4	0.0311			
	Roots	1	N.D.			
	Sawdust	2	0.0022			
	Seeds	5	0.0091			
	Shells	7	0.0226			
Mn	Straw	1	N.D.	4	16.53	0.0024
	Husk	1	N.D.			
	Leaves	1	N.D.			
	Peels	1	N.D.			
	Whole plants	1	N.D.			
Ni	Sawdust	1	N.D.	4	232.45	<0.0001
	Husk	2	0.0215			
	Leaves	4	0.2809			
	Whole plants	1	N.D.			
	Seeds	1	N.D.			
Pb	Shells	1	N.D.	8	286.8	<0.0001
	Bark	1	N.D.			
	Husk	5	0.0049			
	Leaves	9	0.0054			
	Peels	1	N.D.			
	Whole plants	2	0.0071			
	Roots	1	N.D.			
	Seeds	5	0.0023			
Zn	Shells	3	0.0122	8	57.87	<0.0001
	Straw	2	0.0076			
	Bark	2	0.1477			
	Husk	3	0.2632			
	Leaves	1	N.D.			
	Peels	5	0.2154			
	Whole plants	4	0.1367			
	Sawdust	1	N.D.			
	Seeds etc.	1	N.D.	8	57.87	<0.0001
	Shells	3	0.5388			
	Straw	2	0.0297			

Note: N.D. = not determined because of insufficient studies for the respective biomass.

Ngabura et al., 2018). On the other hand, it has been reported that significant quantities of H^+ , K^+ , Na^+ , Ca^{2+} , Mg^{2+} ions are primarily released from biomass during the adsorption of heavy metal, indicating the involvement of an anionic exchange mechanism (Ali and Alrafai, 2016; Khalid et al., 2018).

Different types of agricultural waste biomass possess varying adsorption capabilities, as illustrated in Fig. 2 and Table 2, these results can be related to previous findings. Different biosorbents based on untreated or slightly treated agricultural waste biomass have been reported to demonstrate a high degree of metal adsorption because of their cellulosic constituents such as lignin, hemicellulose, lipids, extractives, simple sugars, proteins, water hydrocarbons and starch, all of which have a number of functional groups that participate in heavy metals complexation (Khokhar et al., 2015). The rate of adsorption is also affected by chemical interactions (Dalali and Haggghi, 2016). The adsorption of certain metals was generally more effective due to differences in the employed biosorbent affinity for various ions, which was influenced by different factors, for example, the electronegativity of different ions; their covalent index or hydrated radius; and the potential competition for adsorption sites between tested metal ions (Abdić et al., 2018).

3.3. Agricultural wastes' adsorption mechanism

Previous studies have reported that adsorption on a porous adsorbent involves multiple stages, including the transport of sorbate from the solution, film diffusion and intra-particle diffusion into pores in the solid phase, as well as adsorption on the active sites (Ben-Ali et al., 2017). Various adsorption mechanisms have been documented in the literature, including cation or anion exchange, complexation, chemisorption, surface adsorption, adsorption with reduction, and adsorption-complexation (Surendran and Baral, 2018). A weak Van der Waal's force of attraction can result in physical adsorption but chemisorption can be caused by a rather strong chemical bonding between metal ions and the surface functional groups of biosorbent (Suganya et al., 2019). Views vary as to how complexation emerges between adsorbent and metal ions (Surendran and Baral, 2018). The presence of functional groups on the surface of biomaterials, however, does not guarantee that chemisorption is the only mechanism of heavy metal ion elimination, since the biosorption process may be influenced by a variety of factors, including the number of active sites, their accessibility, their chemical condition and their preference for the targeted metal (Šoštarić, 2018). In this work, 118 studies were analysed for the reported adsorption mechanisms as described in Table 3.

It can be summarized that out of 8 different reported mechanisms, chemisorption was identified by 66 studies for all the heavy metal ions covered in this analysis, 4 reported physisorption followed by 19, 11, 8, 6, 2 and 2 studies reported combination of physisorption and chemisorption; ion exchange; complexation; intraparticle diffusion; intraparticle diffusion along with chemisorption; and ion exchange in

Table 3
Assortment of mechanisms adopted by agricultural waste for heavy metals adsorption.

Metal	A	B	C	D	E	F	G	H
Cd(II)	15	3	5	2	4	3	–	–
Co(II)	5	–	–	–	–	–	–	–
Cr(VI)	10	–	6	2	–	2	–	–
Cu(II)	13	–	1	3	–	–	–	1
Mn(II)	4	–	1	–	–	–	–	–
Ni(II)	5	–	–	–	–	–	–	–
Pb(II)	10	1	1	3	1	1	–	1
Zn(II)	4	–	5	1	3	–	2	–

A = chemisorption; B = physisorption; C = physisorption + chemisorption; D = ion exchange; E = complexation; F = intraparticle diffusion; G = intraparticle diffusion + chemisorption; H = ion exchange + complexation.

combination to complexation respectively. These findings are consistent with previously reported, leading to conclusion that the adsorption of heavy metal ions by agricultural wastes-based biosorbents involves several physicochemical mechanisms including absorption, ion exchange, complexation and precipitation (Fawzy et al., 2016; Zaidi et al., 2018), Physisorption (Kebede et al., 2018; Matouq et al., 2015), chemisorption, adsorption–complexation (Pandey et al., 2015), intra-particle pore diffusion (Sen et al., 2018), coordination, chelation and micro-precipitation may occur simultaneously, and any of these mechanisms can dominate too (Saha et al., 2017).

3.4. Effect of adsorbent dosage

The collected studies were segregated into three levels of agricultural waste biomass dosage (High > 10 g/L, Medium $2 \text{ g/L} < x \leq 10 \text{ g/L}$ and Low $\leq 2 \text{ g/L}$) for the adsorption of heavy metals. As outlined in Table 1, this study included a total of 170 data points encompassing eight heavy metal ions: Cd(II), Co(II), Cr(VI), Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II). From these, 72 data points fitted at the low level, 69 at the medium and 29 at the high level in terms of the adsorbent dosage. Out of the 40 data points for Cd(II), 17 were low, 17 were medium and six were at a high level of adsorbent dosage. Out of a total of six data points for Co(II), two each were found to be at the low, medium, and high levels. For the adsorption of Cr(VI), out of 27 data points, the low and medium levels were found to have 13 data points each, while only one was found at a high level of dosage. Cu(II) adsorption data points were 32 in total, comprising 13 each at the low and medium levels and six at a high level of adsorbent dosage. Only five data points were found for Mn(II), out of which one was at the low level, one at medium and three belonged to a high level. For Ni(II) adsorption, five and four data points were at the low and medium levels, respectively, while no study was found at the high level. An analysis of 29 data points for Pb(II) adsorption resulted in ten at the low level, 14 at the medium and five at the high level of adsorbent dosage. Out of a total of 22 data points for Zn(II) adsorption, 11 were at the low, five at the medium and six at the high levels of adsorbent dosage.

The adsorption efficiency of high-level dosages of agricultural waste biomass was greater than those of low and medium dosage levels, as demonstrated in Fig. 3. This is consistent with previous studies which found that when the biomass dosage was high, there was a considerably increase in heavy metal adsorption (Fernández-López et al., 2019). Similar patterns were found in the current study, with Cr (VI), Cu(II), Zn (II) and Pb (II) achieving the highest adsorption efficiency, with agricultural waste biomass dosages greater than 10 g/L and with ES values of -0.004 , -0.015 , -0.016 and -0.051 , respectively. Co(II) and Ni(II) exhibited the highest adsorption with a low level of biomass dosage ($\leq 2 \text{ g/L}$) and with ES of -0.185 and -0.532 , respectively. Mn(II) and Cd(II) demonstrated the highest adsorption with a medium level of biomass dosage ($2 \text{ g/L} < x \leq 10 \text{ g/L}$) and with ES of -0.0001 and -0.134 , respectively.

The increased removal efficiency at higher adsorbent dosages is due to an increase in the surface area caused by a rise in the adsorbent mass which increases the number of active exchangeable binding sites on the adsorbent and as a result, adsorption increases (Afroze and Sen, 2018). However, because overlapping adsorption sites reduces overall surface area, and adsorption capacity has been shown to decrease as sorbent dosage with increases (Fernández-López et al., 2019). Although counterintuitive, the decrease in adsorption capacity with a rising adsorbent dosage may be explained by the large number of unsaturated adsorption sites. As a result, the decrease per unit mass was observed, as was the overlap of adsorption sites and the overcrowding of the adsorbent particles, as previously demonstrated in heavy metal ion adsorption (Fletcher et al., 2020).

As expressed in Table 4, the variation in studies was significant within the low and medium levels of sorbent dosage for nickel and zinc adsorption, but only for the medium level in Co adsorption. For the

adsorption of chromium, copper and zinc, heterogeneity at three levels of sorbent dosage was found to be significant. Based on these findings, it can be concluded that the studies under consideration demonstrate dissimilarities in terms of the levels of sorbent dosages and for the heavy metals discussed.

3.5. Effect of initial metal concentration

The effect of the initial concentration on the adsorption efficiency of agricultural waste biomass was determined by segregating the studies into three levels (low: ≤ 10 ; medium: $10 < x \leq 100$; high: > 100). The heavy metal ions covered in this study were Cd(II), Co(II), Cr(VI), Cu(II), Mn(II), Ni(II), Pb(II) and Zn(II). As shown in Table 1, this study included 171 data points, from which Cd(II) provided 40 data points, Co(II) had six, Cr(VI) had 27, Cu(II) had 33, Mn(II) had five, Ni(II) had nine, Pb(II) had 30 and Zn(II) had 22. Out of 171 studies, 69 were found to be at the low level, 86 at the medium level and 16 data points at the high level in terms of the initial metal concentration in the aqueous medium.

At the low level of initial metal concentration, the effect size of adsorption (calculated using Eq. (1)) was found to result in the sequence $\text{Pb(II)} > \text{Mn(II)} > \text{Cd(II)} > \text{Co(II)} > \text{Cr(VI)} > \text{Cu(II)} > \text{Zn(II)} > \text{Ni(II)}$. The standard error of the effect size at the low level of initial metal concentration increased gradually from 0.023 to 0.694, with the lowest being for lead and the highest for nickel. At the medium level of initial metal concentration, the effect size was found to be in the order of $\text{Mn(II)} > \text{Pb(II)} > \text{Cu(II)} > \text{Cr(VI)} > \text{Ni(II)} > \text{Zn(II)} > \text{Co(II)} > \text{Cd(II)}$. The standard error of the effect size at the low level of initial metal concentration increased gradually from 0.002 to 0.437, with the lowest being for Mn(II) and the highest for Co(II). At the high level of initial metal concentration, the effect size was found to result in the sequence $\text{Ni(II)} > \text{Cu(II)} > \text{Pb(II)} > \text{Cr(VI)} > \text{Zn(II)} > \text{Cd(II)}$. The standard error of the effect size at the low level of initial metal concentration increased gradually from 0.059 to 0.362, with the lowest being for Cu(II) and the highest for Zn(II).

As Table 4 shows, variations across the studies were found at all three levels of initial metal concentration for nickel adsorption. Meanwhile, dissimilarities were found at the high level of initial metal concentration for lead adsorption and at the low level of initial metal concentration for Zn adsorption. For the adsorption of cadmium, copper, manganese and lead, variations across the three levels of initial metal concentration were found to be significant. Based on these findings, it can be concluded that the studies under consideration demonstrate dissimilarities in terms of the mentioned levels of initial metal concentration and for these heavy metals.

3.6. Effect of temperature

The consequences of temperature on the adsorption efficiency of agricultural waste biomass were determined by segregating the studies into three levels, High: $45^\circ\text{C} < x \leq 60^\circ\text{C}$, Medium: $30^\circ\text{C} < x \leq 45^\circ\text{C}$ and Low: $20^\circ\text{C} \leq x \leq 30^\circ\text{C}$. Out of the total of 168 studies analysed for the effect of temperature, 156 were found to be at the low level of temperature, four studies at the medium level and 16 studies at the high temperature level, in respect of the aqueous medium during adsorption. Meanwhile, this study included eight different heavy metals, of which Cd(II) provided 38 data points, Co(II) had six, Cr(VI) had 27, Cu(II) had 33, Mn(II) had five, Ni(II) had nine, Pb(II) had 29 and Zn(II) had 21, as shown in Fig. 4.

The adsorption effect size was found to result in the order of $\text{Mn(II)} > \text{Pb(II)} > \text{Cu(II)} > \text{Cr(VI)} > \text{Co(II)} > \text{Zn(II)} > \text{Ni(II)} > \text{Cd(II)}$ at the low temperature level and $\text{Pb(II)} > \text{Cd(II)} > \text{Zn(II)}$ at the medium level. Meanwhile, for the high level of temperature, the order was $\text{Cd(II)} > \text{Pb(II)} > \text{Cr(VI)} > \text{Cu(II)}$. The standard error of the effect size at the low temperature level was in the range of 0.008 to 0.6341; at the medium level it was 0.028 to 0.195; and at the high temperature level it was 0.078 to 0.333, as illustrated in Fig. 4.

Table 4

Heterogeneity in this meta-analysis with respect to different levels of sorbent dosage, initial metal concentration, solution pH, Temperature and contact time.

Parameter	Heavy metal	Group	Heterogeneity based on Random Effect Model				
			Within-group		Between-group		
			k	Tau ²	d.f.	Q	p-Value
Sorbent dosage	Cd	Low	17	0.0233	2	4.17	0.1243
		Medium	17	0.0046			
		High	6	0.0119			
	Co	Low	2	0.0344	2	3.85	0.1456
		Medium	2	0.2275			
		High	2	0.1204			
	Cr	Low	13	0.0384	2	58.46	0.0001
		Medium	13	0.0174			
		High	1	N.D.			
	Cu	Low	13	0.017	2	49.77	0.0001
		Medium	13	0.0189			
		High	6	0.0002			
	Mn	Low	1	N.D.	2	9.05	0.0108
		Medium	1	N.D.			
		High	3	<0.0001			
	Ni	Low	5	0.2149	1	1.33	0.2482
		Medium	4	0.179			
		High	N.D.	N.D.			
	Pb	Low	10	0.0075	2	8.89	0.0118
		Medium	14	0.0067			
		High	5	0.0009			
	Zn	Low	11	0.1573	2	24.48	0.0001
		Medium	5	0.1454			
		High	6	0.0002			
Initial concentration	Cd	Low	17	0.0113	2	21	0.001
		Medium	22	0.0095			
		High	1	N.A.			
	Co	Low	2	0.0344	1	3.27	0.0706
		Medium	4	0.1968			
		High	0	0			
	Cr	Low	7	0.0209	2	0.18	0.9128
		Medium	16	0.0246			
		High	4	0.0659			
	Cu	Low	17	0.0134	2	14.97	0.0006
		Medium	14	0.0031			
		High	2	0.0007			
	Mn	Low	2	0	1	16.44	0.0001
		Medium	3	0			
		High	0	N.D.			
	Ni	Low	3	0.3751	2	0.01	0.9973
		Medium	4	0.1876			
		High	2	0.4736			
	Pb	Low	13	0.0011	2	8.79	0.0123
		Medium	12	0.0041			
		High	4	0.365			
	Zn	Low	8	0.3382	2	1.23	0.5403
		Medium	11	0.0166			
		High	3	0.1007			
Solution pH	Cd	Low	28	0.0085	2	2.22	0.329
		Medium	9	0.006			
		High	3	0.0116			
	Co	Low	4	0.282	2		
		Medium	1	N.D.			
		High	1	N.D.			

(continued on next page)

Table 4 (continued)

Parameter	Heavy metal	Group	Heterogeneity based on Random Effect Model				
			Within-group		Between-group		
			k	Tau ²	d.f.	Q	p-Value
Temperature	Cr	Low	25	0.0095	2	28.41	<0.0001
		Medium	0	N.D.			
		High	1	N.D.			
	Cu	Low	22	0.0126	1	0.74	0.391
		Medium	2	0.2524			
		High	4	0.0162			
	Mn	Low	2	0.0027	2	1.01	0.625
		Medium	X	X			
		High	X	X			
	Ni	Low	7	0.2936	0	0	N.D.
		Medium	1	N.D.			
		High	X	X			
	Pb	Low	23	0.0018	1	5.73	0.0167
		Medium	3	0.0028			
		High	1	N.D.			
	Zn	Low	17	0.0018	2	10.62	0.005
		Medium	2	0.0057			
		High	X	X			
	Cd	Low	36	0.0131	1	0.03	0.8701
		Medium	1	N.D.			
		High	1	N.D.			
	Co	Low	6	0.1796	2	92.3	<0.0001
		Medium	x	x			
		High	x	x			
	Cr	Low	23	0.0111	0	0	N.D.
		Medium	2	0.0191			
		High	2	0.0563			
	Cu	Low	30	0.0029	2	2.16	0.3389
		Medium	x	x			
		High	3	0.0331			
	Mn	Low	5	<0.0001	1	17.84	<0.0001
		Medium	x	x			
		High	x	x			
	Ni	Low	9	0.2367	0	0	N.D.
		Medium	x	x			
		High	x	x			
	Pb	Low	26	0.0019	0	0	N.D.
		Medium	1	N.D.			
		High	2	0.002			
Contact time	Zn	Low	21	0.27	2	23.32	<0.0001
		Medium	X	X			
		High	X	X			
	Cd	Short	37	0.0088	0	0	N.D.
		Medium	3	0.0016			
		Long	x	x			
	Co	Short	6	0.1796	1	9.99	0.0016
		Medium	x	x			
		Long	x	x			
	Cr	Short	18	0.0065	0	0	N.D.
		Medium	5	0.1108			
		Long	2	0.0022			
	Cu	Short	25	0.0219	2	14.41	0.0007
		Medium	2	<0.0001			
		Long	5	0.0002			

(continued on next page)

Table 4 (continued)

Parameter	Heavy metal	Group	Heterogeneity based on Random Effect Model				
			Within-group		Between-group		
			k	Tau ²	d.f.	Q	p-Value
Mn		Short	2	0.0027	1	56.13	<0.0001
		Medium	x	x			
		Long	3	<0.0001			
Ni		Short	8	0.2248	0	0	0.4337
		Medium	x	x			
		Long	x	x			
Pb		Short	26	0.0011	1	207.77	<0.0001
		Medium	1	N.D.			
		Long	X	X			
Zn		Short	17	0.1546	1	32	<0.0001
		Medium	x	x			
		Long	4	<0.0001			

N.D. = not determined because of insufficient studies for the respective biomass, x = no studies were found for the mentioned level.

As shown in Table 4, variations across studies for low levels of temperature in Co, Ni and Zn adsorption were found to be significant, based on the Tau² value. For the adsorption of cadmium, copper and lead, between-groups dissimilarities at the three levels of temperature were found to be significant, based on the Q value. Therefore, it can be concluded that the studies under consideration demonstrate dissimilarities in the mentioned levels of temperature and for these heavy metals when types of agricultural waste biomass were applied as adsorbents.

Temperature has been found to exert a distinct influence on the biosorption mechanism (Ekere et al., 2016). The removal of metal ions changed slightly with rises in the temperature, while a gradual increase in the removal rate occurred, as reported in some studies. This is because as the adsorption temperature increased, the thermal motion of the metal ions intensified, which not only boosted the metal ions diffusion rate but also enabled greater levels of activation energy in the reaction between the adsorbent and metal ions, resulting in enhanced adsorption (Zhuang et al., 2020). Temperature is a valuable indicator of the exothermic or endothermic nature of the adsorption process (Mondal et al., 2019). The removal rate of metal ions gradually increased by raising the temperature to a certain level, and then the removal rate again decreased, suggesting that the removal of metal ions was an endothermic process (Ekere et al., 2016; Safinejad et al., 2017). This result is typical of a chemical reaction or bonding in the adsorption phase. The increase in the removal percentage when the temperature rose may be attributed to the enhanced mobility and diffusion of ionic species (Bayuo et al., 2019).

On the other hand, in some studies, the effect of temperature on the equilibrium of the adsorption process and metal ion removal was investigated across the temperature points of 20 °C, 35 °C, 45 °C and 60 °C. The results indicated that the removal percentage increased with rises in temperature, but the adsorption processes were not strictly dependent on temperature. As the temperature increased, the removal of metal ion rose to a level and then stabilised or the removal percentage decreased; overall, therefore, the removal of metal ions increased slightly at high temperatures compared to ambient temperature. In such cases, the adsorption was not endothermic but had a physical nature (Kul et al., 2016).

3.7. Effect of pH value

The influence of the solution pH on the adsorption efficiency of agricultural waste biomass was determined using three levels (low: <6.5; mid: 6.5–7.5; high: >7.5). Out of 156 studies, 40 data points were

provided by Cd(II), Co(II) had six, Cr(VI) had 26, Cu(II) had 28, Mn(II) had two, Ni(II) had eight, Pb(II) had 27 and Zn(II) had 19. Most studies (128) examined the low pH level, 18 the medium level and 10 studies were the high level of solution pH. In studying the adsorption, the effect sizes were found to result in the sequences Mn(II) > Pb(II) > Zn(II) > Cd(II) > Cu(II) > Cr(VI) > Co(II) > Ni(II) for the effect of low level of solution pH; Pb(II) > Zn(II) > Cd(II) > Ni(II) > Cu(II) > Co(II) for the effect of medium pH level; and Cd(II) > Co(II) > Cr(VI) > Pb(II) > Cu(II) for the effect of high pH level on adsorption. The standard error of the effect size at the low pH level was in the range –0.458 to 0.403; at the medium level, the range was 0.054 to 0.698; and at the high pH level, the range was 0.076 to 0.131, as shown in Fig. 5.

As illustrated in Table 4, variations across the studies for low levels of solution pH in terms of Co and Ni adsorption were found to be significant. Meanwhile, for the medium level in terms of Cu adsorption, dissimilarities were found to be significant, based on the Tau² values. For the adsorption of cobalt, nickel and lead, variations across the studies for the three levels of solution pH were found to be significant based on the Q values. Therefore, it can be concluded that studies under consideration demonstrate dissimilarities in the mentioned levels of solution pH and for the heavy metals when types of agricultural waste biomass were applied as adsorbents.

In general, metal adsorption increases in line with pH in a specific pH range, before decreasing as the pH rises. The surface functional groups on the cell walls of biomass, as well as the metal chemistry of the solution, can be attributed to the sensitivity of metal adsorption to pH. The pH value influences the system's equilibrium (Abas et al., 2013). The removal of heavy metals is believed to be achieved mainly through ion exchange and hydrogen bonding. Several parameters, including the chemical components and complexing properties; the heavy metals characteristics and adsorption behaviour; and the impact of pH on speciation in aqueous media confirm this theory (Rafatullah et al., 2009).

The effect size of Cd(II) was –0.133, –0.143 and –0.188, which was found to decrease according to the sequence of high, medium, and low pH levels. In previous studies, (Foo et al., 2012) reported that the removal of Cd(II) improved when pH level rose from 1.0 to 6.0 pH, with optimum removal occurring at pH 6.0 and then decreasing at higher pH values. (El-Sayed et al., 2011) found similar results while utilising *Ananas comosus* peels, *Parkia speciosa* pods and *Psidium guajava* peels as adsorbents. The maximum Cd(II) removal occurred at pH 7 and a decrease was observed beyond this pH. The effect size of Cu(II) was –0.196, –0.252, and –0.428, which was found to decrease according to the sequence of low, high and medium pH levels. The effect size of Ni(II)

was -0.284 and -0.786 and was found to be in this sequence at medium and low pH level while no studies were found at the high level. Similar results had been reported. The removal of Cu(II) and Ni(II) ions increased as pH rose, reaching maximum adsorption at pH 6. A mild reduction in the adsorption of Cu(II) and Ni(II) ions appeared at higher pH values (Rafatullah et al., 2009).

The effect size of Mn(II) was -0.035 and found for the low pH level while no studies were found for the medium and high levels. This does not differ extensively from earlier reported results. The optimum removal of Mn(II) occurred at pH 7.0 (El-Sayed et al., 2011). The effect size of Pb (II) was -0.065 , -0.097 and -0.223 , which decreased in the sequence of medium-low-high, pH levels. They found that constant adsorption of Pb(II) occurred between pH 4.5 and 5.5, after which it increased again, possibly due to the onset of precipitation. The removal of Pb(II) ions increased as pH rose, reaching maximum adsorption at pH 6, while a mild reduction in Pb(II) ions adsorption appeared at higher pH (Rafatullah et al., 2009). The effect size of Zn(II) was -0.101 and -0.111 , which was found to decrease in the sequence of low to medium pH levels, while no studies were found for the high level. These findings are consistent with those of El-Sayed et al. (2011), who found that the metal uptake of Zn(II) increased when pH rose from 1.0 to 5.0, then fell as pH increased further.

3.8. Effect of contact time

The impact of contact time on the adsorption efficiency of agricultural waste biomass was determined using three levels (long: >12 h; medium: $3-12$ h; short: <3 h). From the total of 164 data points, 40 were for Cd(II), six for Co(II), 25 for Cr(VI), 32 for Cu(II), five for Mn(II), eight for Ni(II), 27 for Pb(II) and 21 data points were for Zn(II). In the analysis of the effect of contact time on adsorption, most studies (139) were found to be at the short level of contact time, 11 at the medium level of contact time and 14 studies were found at the long level of contact time. As illustrated in Fig. 6, the effect size of all eight heavy metals were found to be in the sequence of Mn(II) $>$ Pb(II) $>$ Zn(II) $>$ Cd(II) $>$ Cr(VI) $>$ Cu(II) $>$ Co(II) $>$ Zn(II) $>$ Ni(II) at the short level contact time; the sequence was Cu(II) $>$ Cd(II) $>$ Cr(VI) $>$ Pb(II) at the medium level contact time; for the long level contact time, the sequence was Mn(II) $>$ Zn(II) $>$ Cu(II) $>$ Cr(VI). The standard error of the effect size at the low level of contact time was in the range of 0.016 to 0.341, at the medium level it was 0.017 to 0.293 and at the long level of contact time it was 0.011 to 0.097.

As expressed in Table 4, the differences in studies referring to the short level of contact time for the adsorption of Co, Ni and Zn were found to be significant, while Cr adsorption was denoted at the medium level. On the other hand, heterogeneity in the three levels of contact time was found to be significant for the adsorption of cadmium, chromium, copper, lead and zinc, based on the Q values. Thus, it can be concluded that the studies under consideration demonstrate dissimilarities in the mentioned levels of contact time and for these heavy metals when types of agricultural waste biomass were applied as adsorbents.

The effect sizes of Co (II) -0.499 and -0.632 of Ni (II) were found to be in the short period of contact time only, which was similar to findings reported by Hegazi (2013). The contact time necessary for the maximum adsorption of Ni (II) was found to be 2 h. No studies were found for these heavy metals in the long and medium periods of contact time. The ES for Cu (II) adsorption was -0.014 , -0.016 and -0.248 , respectively for long, medium, and short periods of contact time which is consistent with the previous findings that the capacity biosorbents to remove copper(II) rises in proportion to contact time (Bandara et al., 2020). Previously, it has been reported that the difference in contact time in respect of adsorption efficiency did not depend on only the metal type but also the type of biomass (Abas et al., 2013). Furthermore, it has been reported that biosorption occurs in two stages, according to kinetic analysis. The first phase consists of fast surface adsorption lasting 15 min, followed by slow intracellular adsorption lasting until the end time (Zafar et al.,

2013).

4. Future work and recommendations

Analysis of the studies within the scope of this paper confirms previous findings, in that adsorbents prepared from agricultural waste biomass offer major benefits over the costly commercially-activated carbons that are currently available for water emission management (Bhatnagar et al., 2015). Additionally, the release of soluble organic compounds into the water during the adsorption process is a significant drawback of biosorbents based on agricultural waste biomass, as this restricts their usage in large-scale applications; further study is required in this regard. To prevent secondary contamination and overcome the other deficiencies reported in different sections of this study, the biosorbent may also be modified using environmentally friendly chemicals. Despite the various current disadvantages and obstacles, substantial and important advancements can be anticipated in this sector in the future. Commercially available activated carbons (ACs) have been derived from various carbonaceous bulk materials and their physical and chemical properties have been reported to vary between the precursor materials and the activation process. Recently, however, the use of natural agricultural by-products or waste dead biomasses as substitute precursor materials for the acquisition of ACs has gained traction. Due to the availability of micro- and mesopores, Bronsted acid/base properties surface of present functional groups, and relatively large specific surface areas, the application of activated carbon (AC) in advanced wastewater or industrial wastewater treatment has received greater attention in recent studies (Tiwari et al., 2015).

Another option could be ultrasound treatment for the modification of agricultural waste biomass to increase mass transfer rates utilising the cavitation phenomenon. This could induce the formation of several micro-cracks on the solid surface, increasing the surface area between the solid-liquid in separation activities such as extraction and adsorption or desorption. Using the phosphoric acid-microwave process and low-temperature phosphoric acid activation from Bagasse waste, highly mesoporous biochars with various mesopore size distributions were successfully prepared. The effect of HNO₃ treatment on the adsorption capability of mesoporous biochars of different mesoporous size distributions was studied (Li et al., 2016).

Several studies have reported the efficient removal of heavy metals using activated carbons, biochars and other modified adsorbents based on agricultural waste biomass. Further studies could, however, be conducted to assess the efficiency of agricultural waste-based activated carbons using real effluents before they are used on a wider scale. The durability of activated carbons and their regeneration after many cycles of usage must be further investigated (Enaime et al., 2020; Bdaiwi Ahmed et al., 2019). It is apparent that after conversion into biochars, the use activated carbon and the chemical alteration of low-cost plant waste adsorbent, the adsorption ability of the adsorbent would increase due to the higher number of binding sites after the alteration and development of the new functional groups required to absorb metal ions (Bhatnagar et al., 2015; Komkiene and Baltreinaite, 2016).

Various techniques can also be utilized on agricultural wastes which have been reported to prepare biosorbents from activated municipal sludge, including solvent supported aerobic digestion (Xia et al., 2017), chemical and physical extraction of biopolymer (Zhou et al., 2017; Zhou et al., 2016) and ultrasound treatment followed by centrifugation (Zhou et al., 2016).

5. Conclusion

The adsorption efficiency of biosorbents obtained from various types/fractions of agricultural waste varied depending on the type of agricultural waste employed and other adsorption factors. Furthermore, because unprocessed biosorbents include a variety of functional groups, numerous adsorption mechanisms may be active at the same time,

resulting in secondary contamination, implying that unprocessed bio-sorbents are unsuitable for industrial applications. As a result, rather of depending just on basic drying and grinding, diverse physical and chemical modifications might potentially increase the utilization of agricultural waste biomass.

CRedit authorship contribution statement

Muhammad Imran-Shaukat: Data collection, systematic review, statistical analysis, original drafting and revision writing

Rafeah Wah: Conceptualization, writing, reviewing, and editing

Zainab Ngaini: Writing, reviewing, and editing

Declaration of competing interest

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

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Appendix A. Supplementary data

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