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Applicability of bio-adsorbents synthesized from maize/corn plant residues for heavy metals removal from aquatic environments: an insight review

Jonas Bayuo[1,2]*, Mwemezi J. Rwiza[1], Kelvin Mark Mtei[1]

1School of Materials, Energy, Water, and Environmental Sciences, The Nelson Mandela African Institution of Science and Technology, Arusha, Tanzania
2Department of Science Education, School of Science, Mathematics, and Technology Education, C. K. Tedam University of Technology and Applied Sciences, Navrongo, Upper East Region, Ghana

*Corresponding author E-mail: bayuoj@nm-aist.ac.tz/jbayuo@cktutas.edu.gh

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Abstract
The underutilization of agricultural waste products in recent years has resulted in environmental issues owing to improper disposal. As a result, heavy metals removal from aqueous systems utilizing sorbent materials produced from agricultural wastes has received a lot of attention. The current study provides an insightful review of the use of bio-adsorbents synthesized from maize/corn residues to decontaminate various toxicants from wastewater. Although bio-adsorbents made from maize/corn residues have shown to be efficient in the sequestration of heavy metals from wastewater, no study has looked at hybrid bio-adsorbents made from various parts of the maize/corn plant. Moreover, all studies practically investigate the sorption processes using the one-factor design technique, which exceedingly consumes time and is expensive for a significant number of biosorption/adsorption factors. Besides, the majority of the studies used bio-adsorbents produced from maize/corn biomass to remove heavy metals from single sorption systems. Furthermore, very few studies have focussed on heavy metals desorption from the exhausted maize/corn bio-adsorbents following the adsorption process to recycle the spent bio-adsorbents for future usage, which would be more cost-effective. Based on the gaps revealed in this review, it is recommended that further investigations on the usefulness of bio-adsorbents derived from maize/corn biomass in cleansing different water toxicants should be carried out.

Keywords
Adsorption, Bio-adsorbent, Environment, Heavy metal, Maize, Wastewater, Remediation

Introduction

Heavy metals as eminent environmental pollutants are generally present in agricultural, mining, and industrial wastewater. Among the most pressing environmental pollution issues to be eradicated in recent times is the decontamination of poisonous heavy metals from water and wastewater. Due to heavy metals toxicity, persistence, and bioaccumulation in the food chain, the unauthorized discharge of these ions into the aquatic environment results in various health-related problems (Bayuo *et al.,* 2020). Nowadays, due to overpopulation, water resources are depleting due to recalcitrant metal ions, therefore, there is a need to re-evaluate the patterns of waste disposal to save water reservoirs (Iqbal & Khera, 2015).
The most common heavy metals triggering substantial health threats to all living species based on their persistence in the ecosystem include arsenic(III, V), cadmium(II), chromium(III, VI), lead(II), mercury(II),

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Nickel(II), and Zinc(II). As recalcitrant pollutants, they are non-biodegradable and cause a lot of health disorders in human beings for example anemia, brain damage, anorexia, malaise, infertility, liver and kidney diseases (Baylan & Meriçboyu, 2016).

Considering the lethal effects of heavy metals, some purification techniques are required to decrease their concentration in water to allowable levels. As stated by the World Health Organization (WHO), each heavy metal has its permissible concentration level in wastewater and drinking water. However, adherence to strict standards is estimated to be more expensive, and hence, the purification efficiency of toxic wastes around the world is one of the biggest worries especially when purifying water polluted with heavy metal ions (Acar & Malkoc, 2004).

The search for new, simple, low-cost, and innovative treatment technologies has focused attention on adsorption/biosorption using agricultural waste materials since the traditional treatment methods have some serious inadequacies. For example, if there is a small amount of the contaminant in the solution, they are ineffective, required large reagents and energy consumption, and creation of secondary pollutants (Cochrane *et al.,* 2006; Dadzie, 2012). Many natural and waste products from agriculture are comprised of lignocellulosic materials with different functional groups on their surfaces, which are capable of binding metal ions in aqueous media (Safatian *et al.,* 2019; Adane *et al.,* 2020).

Maize/corn is used as a raw material in many businesses, including food, pharmaceuticals, cosmetics, and paper products (Sharma *et al.,* 2019; Bayuo *et al.,* 2023). Nevertheless, after the grains of the maize/corn have been harvested, the residues including the leaves, tassels, roots, husks, cobs, silks, and stalks, are hardly useful. Thus, the biomass of maize and corn is frequently dumped into landfills, though the bulk is burned outdoors, which potentially endangers the quality of the atmosphere and the environment. However, it has been found that the residues of the maize/corn plants have been utilized proficiently and economically in the removal of many contaminants from water and wastewater. Hence, this study presents an insightful review of the decontamination of various heavy metals from water and wastewater using maize/corn residues.

Properties and toxicity of heavy metals

Heavy metals are distinguishable from many other harmful contaminants by their inability to degrade. As a result, higher heavy metal concentrations in the aqueous environment can lead to phytotoxicity, bioconcentration, and biomagnification by living species (Ayyappan e*t al.,* 2005). In addition, heavy metals have the potential to harm the human body's physiological and neurological systems (Wong *et al.*, 2003). They pile up in plants, soils, and aquatic ecosystems (Suciu *et al.,* 2008; Obodai, 2011; Wuana & Okieimen, 2011). Heavy metals can linger in organic and inorganic suspended particles for a long period before being available to biological organisms (Friedlova, 2010; Adelekan & Abegunde, 2011). They do not deteriorate over time and are biomagnified if they are excreted at a faster rate than they are taken in. As a result, heavy metals may pose a health threat to humans and wildlife and they do have comparatively high densities than other trace elements (Obodai, 2011; Lenntech, 2012). Heavy metals, in addition to having high densities, are found at the base of the periodic table and are harmful due to their prolonged biological half-lives (Rajaganapathy *et al.*, 2011). They can also be present as ionic species, which interact strongly with the soil matrix. Ever-increasing industrial and agricultural activities are the main culprits behind all environmental contamination hitches and damage resulting from the buildup of pollutants including toxic heavy metals for instance arsenic, chromium, copper, cadmium, mercury, nickel, lead, and zinc (Pino *et al.*, 2006). The pollution of surface and groundwater water, as well as soils, sediments, and air with perilous heavy metals, cause health problems to living organisms and environmental damage (Ansari & Malik, 2007). Heavy metals are known to be dangerous pollutants and their presence in wastewater due to many industrial developments has led environmentalists and researchers to be much more concerned attributable to their harmfulness (Kang *et al.*, 2007). The ingestion of excessive heavy metal ions through the food chain leads to many health risks (Adepoju-Bello & Alabi, 2005). Their destructiveness is associated with the creation of complexes with proteins where amine (NH_2), carboxylic (COOH), and thiol (SH) groups are mainly involved (Valentine Uwamariya, 2013). Through, the binding of heavy metal ions to these complexes, some significant protein structures, and enzymes are denatured.

Environmental pollution with heavy metals

In recent years, there is a growing public awareness about environmental protection, which can be seen both globally and locally. Global worries have suddenly

EQA 56 (2023): 15-35

DOI: 10.6092/issn.2281-4485/16951

increased over pollution due to heavy metals discharged from various sources into the environment (Emenike *et al.,* 2016). These heavy metals continue to remain in the ecosystem because they are non-degradable nor destroyable. The availability of heavy metals in the biosphere is attributable to numerous environmental parameters, notably among them are natural phenomena and several anthropogenic activities (Samaniego & Tanchuling, 2019).

Understanding the speciation of heavy metal ions in the environment is valuable in investigating the level at which these metal ions are present and their capability of permeating into water sources (Ghaemi *et al.*, 2015). The emission of harmful substances for example heavy metals is detrimental to human health, other living organisms, and the natural environment at large. Hence, when environmental pollution due to heavy metals become evident, remediation is problematic and chronic toxicity is likely and maybe obvious after several years of bioaccumulation (Abood *et al.*, 2015). Heavy metals and other contaminants released into the milieu can be transported via water, air as well as living creatures including man, animals, and plants through the food chain (Gadzała-Kopciuch *et al.*, 2004). A considerable amount of pollution load and in most cases, wastewaters are generated by small-scale industries and are directly released into the environment without any appropriate treatment. The effluents of these industries often contain substantial amounts of polluting and toxic heavy metals and their occurrence in the environment leads to a rapidly growing number of environmental issues such as the deterioration of the ecosystem due to its persistent accumulation (Dar *et al.,* 2013).

In geochemical cycling, the mobilization of heavy metals in the ecosystem by the activities of humans has become a very serious environmental problem (Addo *et al.*, 2012). This can be observed in industrial vicinities where mobile and stationary sources discharge huge amounts of toxic chemicals into water sources. Naturally, all heavy metals are at trace levels in the ecosystem and some are required as micro-elements by living species (Onder *et al.*, 2007). In the environmental assessment of the noxiousness of heavy metals, their distribution between soil and vegetation is a significant subject under study (Abulude & Adebusoye, 2006). The existence of excessive heavy metals inhibits plant development and growth, photosynthesis and enzymatic activities, bioaccumulation of other micro-elements, and also damages the root systems (Addo *et al.*, 2012). Certainly, the environment is not only a habitat for living organisms but also a route of many contaminants especially heavy metals to surface and groundwater as well as the atmosphere (Ato *et al.*, 2010).

Technologies for heavy metals removal from the aquatic environment

The main conventional and non-conventional methods used in heavy metals decontamination from water and wastewater as shown in Figure 1 include the following electrodialysis, reverse osmosis, ion exchange, chemical precipitation, adsorption, and biosorption (Zenebe, 2014; Mohd *et al.*, 2021; Bayuo *et al.*, 2023). However, the technique preferred in heavy metals removal is dependent on several factors namely technique efficiency, environmental influence, and cost of operation. In this review, some of the conventional and non-conventional treatment technologies for the sequestration of heavy metals from water systems are discussed.

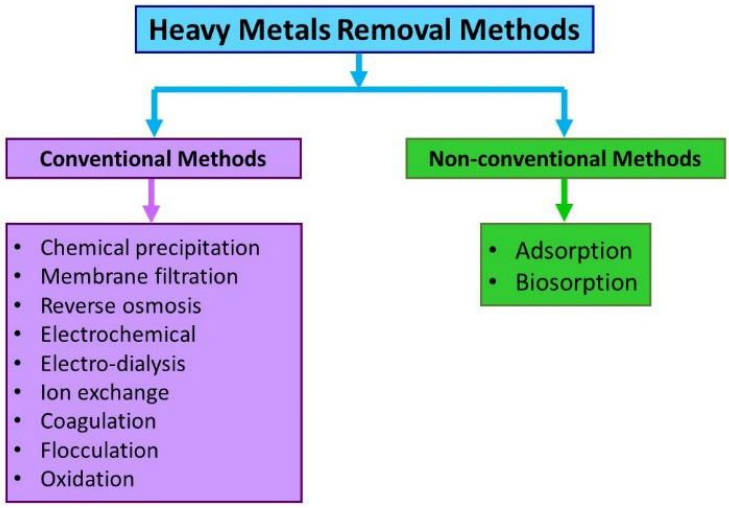

Figure 1. *Different conventional and non-conventional methods for heavy metals removal from aquatic environments*

DOI: 10.6092/issn.2281-4485/16951

Electro-dialysis method. This approach removes ionic species from aqueous solutions when ion-exchange membranes are used together with electrical potential differences (Charles & Ed, 2017). In between the anode and the cathode are a succession of cation and anion exchange membranes (Xu, 2005). The anions travel to the anode, while cations migrate to the cathode. These ions pass through the membrane and are captured by the electrodes with opposite charges (Choi, 2016). The cost and low efficacy of this approach for removing trace concentrations of contaminants from aqueous systems are its drawbacks (Bhatnagar & Minocha, 2006; Zhang *et al.*, 2012).

Ion exchange. An ion exchanger is a solid that can exchange cations or anions from the environment (Baysal *et al.*, 2013). Ion exchange is the process of replacing an ion that has been removed from a liquid phase with another ionic species. The ion exchange process continues until the resin exchange capacity of the resin is depleted. Other chemicals must be used to regenerate the exhausted resin, replacing the ions acquired during the ion exchange process, restoring the resin to its original composition, and allowing it to be reused in the next cycle (Xu and Dong, 2008).

Generally, water is often routed through an ion-exchange polymer, which is a water-insoluble material capable of exchanging a portion of its ions in an aqueous solution for other ions with identical charges (Kumar & Jain, 2013). For the exchange to take place, the electrical charge of the toxic substance and the ions inside the polymer have to be similar (Alguacil, 2003; Mbugua *et al.,* 2014). According to Kumar & Jain (2013), ion-exchange properties can be found in a variety of natural organic materials, or they can be added to them through chemical modification. By employing nitric acid as an oxidant or introducing the sulphonic acid group with strong sulphuric acid, ion exchangers are produced from natural materials such as wood, fibers, peat, and coal. Although the resins are quite pricey, ion exchange may effectively and selectively remove heavy metal ions (Kim *et al.,* 2006). Ion exchange has several drawbacks when it comes to removing heavy metals, including poor wettability, small surface area, poor selectivity, sluggish adsorption rates, and regeneration concerns (Sonune & Ghate, 2004). The efficacy of the ion-exchange process may be impaired by the presence of suspended particles. In practice, however, ion exchange is unable to meet the treatment goal, and pre-filtration is required to remove suspended materials that could clog the resin bed mechanically (Xu & Dong, 2008). Furthermore, the ion-exchange method of water treatment is environmentally favorable. It does, however, have drawbacks, including fouling by suspended solids in water and low efficacy in removing trace levels of contaminants (Bhatnagar and Minocha, 2006; Zhang *et al.*, 2012).

Chemical precipitation. This approach entails converting dissolved elements into insoluble solids, then removing them using sedimentation or filtration (Harrison, 2005). The most popular method for detoxifying dissolved metal ions from contaminated water sources is chemical precipitation. Metal ions are converted to suspended particles using precipitating chemicals such as calcium hydroxide, ferric chloride, sodium hydroxide, or ferrous sulphate. By settling and/or filtration, the particles that have been formed are removed from the solution (Li *et al.*, 2019). The precipitation process is straightforward and cost-effective. However, because the method is not adaptable, it is not a feasible choice for some end-users (Onyango *et al.,* 2004). Furthermore, the fundamental weakness of these procedures is that they produce sludge with harmful substances, which must be disposed of in a landfill and this is the European Union's last priority when it comes to waste management policies (Cavaco *et al.,* 2007). Moreover, the generated sludge needs a license to be disposed of (Dash *et al.*, 2009). An additional problem with the precipitation treatment approach is that the concentration of the metal ions in the treated wastewater cannot be decreased below the precipitate's solubility (Kim *et al.*, 2006). It also changes the pH of water, necessitating pH correction (Ayoob *et al.*, 2008). As a result, alternative approaches like adsorption should be used to safeguard the environment.

Reverse osmosis. In this technique, water molecules are forced through a semi-permeable membrane at increased pressure (Malik *et al.*, 2010). This pressure should be sufficient to counteract osmotic pressure. The pressure needed is determined by the pollutant concentration in the water supplied and to be treated (Rani *et al.,* 2014). The water molecules are allowed to pass through the membrane, however, other pollutants and salts are prohibited and are dumped into the concentrate stream. The reverse osmosis membrane rejects toxins based on sizes and charges (Yoon & Lueptow, 2005). The impurities in the feed water could include ions, particles, colloids, or microorganisms (Wimalawansa, 2013). This process is extremely efficient, produces no waste, and does not necessitate pH balancing or regeneration. However, it comes at a high capital and operating expense, poses a disposal challenge

DOI: 10.6092/issn.2281-4485/16951

for wastewater containing heavy metal ions, and results in the loss of 20-40% of the water (Feenstra *et al.*, 2007). More specifically, membrane treatment of industrial wastewater is confined to a few applications where the membrane's characteristics and environmental resistance are appropriate for the application (Mulopo, 2015).

Membrane separation techniques. Pressure, concentration, electrodialysis, electrically driven membrane processes, and temperature-driven membrane processes are all examples of water treatment processes. Reverse osmosis, ultrafiltration, and nanofiltration, as well as high-pressure and low-pressure filtration, are among the processes used. Contaminants including heavy metals, color, and dissolved solids can be removed from wastewater via membrane filtering. This technique's ability to produce solid- free effluents is a particularly appealing characteristic (Wang *et al.,* 2005).Membrane separation methods also have many advantages, including a small system, low chemical consumption, and easy operation and maintenance. The membrane separation technology has the disadvantage of inadequate removal of small molecular weight molecules and consumes a lot of energy, notwithstanding the benefits (Gambolas *et al.,* 2004). Membrane fouling, which can develop from the clogging of inorganic and organic elements in the membrane pores, is another constraint of membrane processes. Membrane fouling reduces the rate of treated water production and shortens the membrane life, lowering the economic efficiency of membrane operations (Laslo & Hodur, 2007).

Coagulation and flocculation technologies Coagulation refers to the process of destabilizing colloids by removing the forces that hold them apart. Cationic coagulants decrease colloids' negative charge (zeta potential) by supplying positive electric charges. Particles collide, as a result, forming huge particles (flocs). Coagulation is always used in conjunction with flocculation to remove particles that sedimentation or filtration alone cannot remove (Mohd *et al.,* 2021). Colloids are small particles with a size of less than one meter. They are accountable for the color and water turbidity due to their poor settling qualities. Clays, metal oxides, proteins, and microorganisms, as well as some organic molecules, are among them. The fact that they all have a negative charge keeps them from aggregating and settling in still water and so this, combined with the colloidal particles' interactions with the water, prevents them from aggregating and settling. Colloids and trivalent ions such as Al^{3+} and Fe^{3+}, which are present in aluminum and ferric salts can be used as chemical coagulants to aggregate the particles (Amuda & Alade, 2006). These technologies, coagulation, and flocculation are utilized in municipal wastewater purification plants to handle both industrial and treated sewage effluent. The most widespread application, however, is found in the field of potable water purification (Bratby, 2016). Amuda and Alade (2006) employed the coagulation/flocculation procedure to treat abattoir effluent and discovered that coagulation is costly when chemicals and sludge disposal are factored in. As a result, it is vital to develop and employ low-cost alternatives for wastewater treatment (Mohana *et al.,* 2009).

Oxidation treatment processes. For water and wastewater treatment, ozone is a potent oxidant. Ozone interacts with a greater amount of organic molecules once it has been dissolved in water in one of two ways: either directly as molecular ozone or indirectly as secondary oxidants for instance free radical species, particularly radicals of hydroxyl. The radicals of both hydroxyl and ozone are powerful oxidants, which oxidize a wide range of substances (Bes-Pia *et al.*, 2003). Ozonation may be utilized to help with the coagulation-flocculation process by removing inorganic species (Laslo & Hodur, 2007). Dyes, pesticides, and phenolics have all been treated with ozone, which simply changes the chromophore groups in the effluent without destroying the dark-colored polymeric com pounds (Pena et al., 2003). According to Satyawali & Balakrishnan (2008), chemical decolorization using ozone and chlorine results in transient color reduction due to chromophore group change, hence they are not preferred methods. If not managed, ozone treatment can produce undesired by-products like formaldehyde and bromate, which can be hazardous to one's health. Furthermore, ozone is ineffective in the removal of dissolved salts and minerals (Johnson, 2005).

Electrochemical method. The electrochemical procedure for wastewater treatment was developed by mixing sewage and saltwater in a ratio of 3:1 and electrolyzing it to purify the sewage produced onboard ships. The electrochemical method was widely used to treat industrial wastewater such as tannery effluent, distillery effluent, cattle effluent, olive mills, and textiles effluents (Vijayaraghavan *et al.*, 2008). Electrolytic procedures are costly, and they necessitate specialized equipment and upkeep. As a result, the creation of an alternate treatment approach is critical (Dash *et al.*, 2009).

EQA 56 (2023): 15-35

DOI: 10.6092/issn.2281-4485/16951

Treatment techniques including solvent extraction, complexation, electrodeposition, foam flotation, and cementation can also remove heavy metals, but they have drawbacks such as slow kinetics and insufficient selectivity (Wang & Zhu, 2007). However, among these, adsorption technology has emerged as the first line of defense, particularly for contaminants that are resistant to other methods of removal (Sharma *et al.*, 2019; Mohd *et al.*, 2021).

Adsorption technique. The adsorption method is the most reliable and appropriate in several purifications, separations, waste treatment processes, and chemical compound recovery, especially in industrial systems. Adsorption is widely replacing almost all the other purifications and separations methods attributable to its high efficiency in removing most pollutants from aqueous media (Noroozi & Sorial, 2013). The other methods have been recognized to be expensive and required high consumption of time, chemicals, and energy, as well as the creation of secondary pollutants (Bayuo *et al.,* 2019). Adsorption is the mass transfer of the contaminant (adsorbate) to be removed from the liquid or gas phases onto a solid (adsorbent) interface where it gets accumulated due to physical and/or chemical interactions as represented in Figure 2. Hence, adsorption may occur as a result of neither physical nor chemical interactions and it can also involve both interactions. While in physical adsorption the adsorbate molecules form a multilayer on the adsorbent surface, chemical adsorption leads to the formation of a monolayer by the adsorbate molecules as displayed in Figure 2.

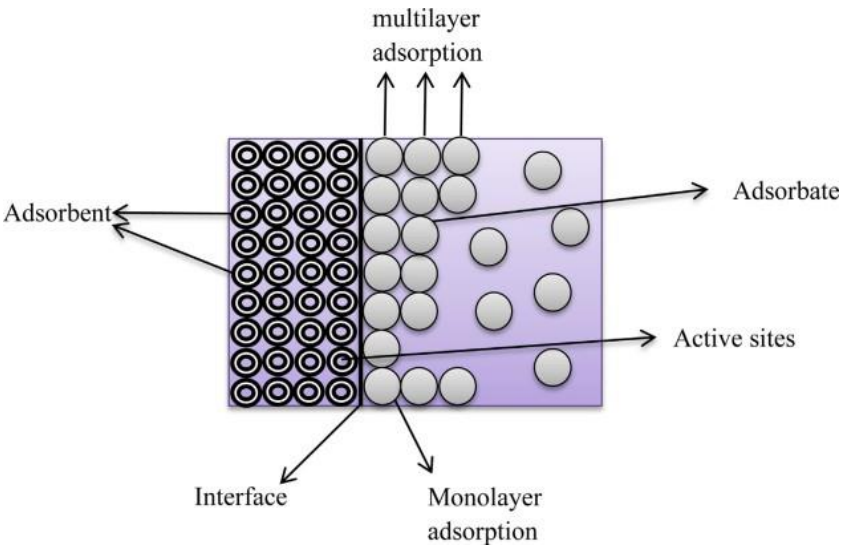

Figure 2. *A schematic diagram showing the adsorption of adsorbate molecules on the surface of the adsorbent (this figure is reproduced from Soliman &Moustafa (2020) with permission from Elsevier, copyright 2020)*

In adsorption, the high price of commercial adsorbents is recognized as the main hindrance to industrial applications. For instance, considering the economic factors and industrial applications, it is not advisable to employ commercial adsorbents in water and wastewater purification. As a result, the emphasis on heavy metals adsorption is directed toward using natural materials in addition to certain waste products resulting from agricultural and industrial operations, which are abundantly present. According to Dinesh & Pittman (2007) generally, these materials have little economic value, are inexpensive, and are available everywhere in large quantities. Therefore, adsorption using naturally and locally available materials as bio-adsorbents is highly recommended and the main relevance of this technique against conventional water and wastewater treatment techniques are cost-effectiveness, high efficacy, fewer chemicals consumption, and, bio-adsorbent recycling and metal ions retrieval capabilities (Vilar *et al.*, 2007). For instance, studies have shown the effective use of plant biomasses including jack fruit peel and orange peels, papaya seeds, rice husks, and spent tea in decontaminating heavy metals (Deshmukh *et al.*, 2009; Grassi *et al.*, 2012; Rahdar *et al.*, 2019).

Adsorption of heavy metals from aquatic environments by various adsorbents is usually influenced by several independent variables as a function of two dependent variables, which include removal efficiency (%) and uptake capacity (mg/g). Some of these independent influencing variables include contact time, pH of the

EQA 56 (2023): 15-35

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solution, adsorbent particle size, adsorbent dose, initial metal ion concentration, and temperature. Figure 3 is the schematic diagram showing the adsorption-desorption process of heavy metals using non-conventional adsorbents derived from natural, agricultural, and industrial waste materials.

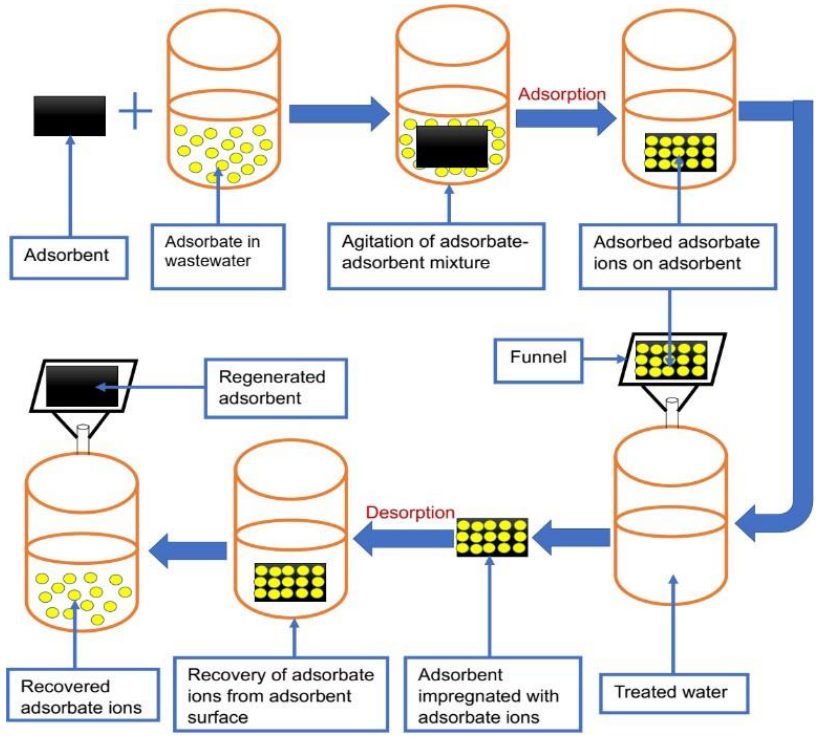

Figure 3. *Schematic diagram showing the adsorption-desorption of heavy metals using non-conventional adsorbent*

Materials and Methods

To identify the articles focusing on heavy metals removal from aquatic environments using bio-adsorbents derived from maize/corn plant biomass, databases including SpringerLink, ScienceDirect, PubMed, Research Gate, and Google scholar were searched. The literature search was performed using the English Language and the eligible articles that were published between 2010-2020 were downloaded if they were open access or contacted the corresponding authors to access the full text. The following key search words: 'heavy metal removal', 'heavy metal adsorption', 'heavy metal biosorption', 'heavy metal decontamination', 'heavy metal elimination', 'aqueous solution', 'wastewater', 'aquatic environment', 'aqueous media', 'maize/ corn husk', 'cob', 'tassel', 'silk', 'stalk', 'root', 'leaf ', 'adsorbent', 'biosorbent', 'bio-adsorbent', 'biochar', and 'activated carbon-derived from maize/corn residues' were used to carry out a comprehensive search of the literature to identify studies on the main theme of this review. These search terms were used in the "Advance Search" field of all the databases, therefore the articles which contained these terms in their abstract, title, or text were filtered out. The articles from each database were collated and screened to make sure the selected articles meet the inclusion criteria by studying and extracting relevant information. Following scrutinizing the selected articles from all the databases, some other articles were excluded and others were included in the dataset for this review for meeting the inclusion criteria as follows:

1. Original research articles and full-text availability.
2. All articles published in English Language and online between 2010-2020 were included.
3. All articles reporting appropriate procedures for the preparation of the bio-adsorbent from maize/ corn plant biomass were added.
4. All articles on heavy metals removal by adsorption or biosorption in batch or column mode using maize/corn plant biomass were also included.
5. All articles on the removal of various heavy metals from aquatic media (synthetic or real wastewater) using maize/corn plant biomass were included.

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Results and discussion

The chosen databases were searched from 2010-2020 to identify potential and relevant articles on the adsorptive removal of different heavy metals from aqueous media using various sorbent materials derived from maize/ corn plant biomass. Each chosen database was searched autonomously and then the downloaded articles were collated. At first, 215 articles were identified as eligible and suitable for this review after de-duplication and screening of the titles and abstracts of these selected articles. However, after applying the selection criteria, 35 articles were retained and used in this review, while a large proportion of the studies that were not laboratory-based (original research) were excluded using the exclusion criteria below:

1. All articles that were published in English Language and were not between 2010-2020 were excluded.
2. All articles with irrelevant abstracts or with no full text available through any source were removed.
3. All articles on dyes or other pollutants removal using bio-adsorbents from maize/corn plant biomass were not considered.
4. All articles reporting on heavy metals removal from soil or other media either than aquatic environments using bio-adsorbents from maize/corn plant biomass were excluded.
5. All published review articles, book chapters, conference proceedings, and preprints were omitted.

Figure 4 shows the percentage of articles that were included and excluded in the review. The 35 articles representing 16.28% that were included for the final review have been comprehensively discussed in the next section and Table 1, respectively, in which all the eligible articles, atomic absorption spectrometer, mercury analyzer, ultra violet atomic absorption spectrometer, and inductively coupled plasma mass spectrometer were used to measure heavy metals levels in the aqueous solutions. All studies report appropriate preparation of bio-adsorbents from the maize/corn plant residues. Batch adsorption or biosorption experiments were conducted in almost all studies for the heavy metals' elimination from their aqueous solutions, synthetic wastewater, and real or industrial wastewater using various sorbent materials synthesized from maize/corn plant residues.

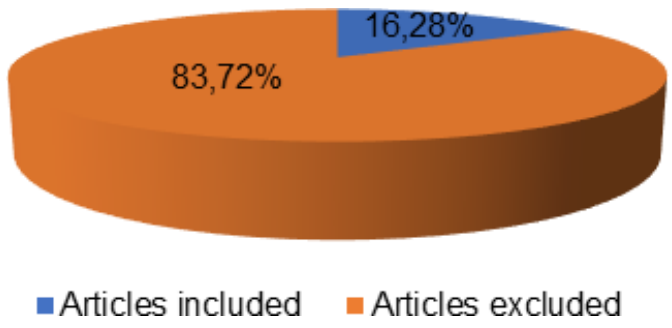

Figure 4. *A pie chart showing the number of articles that met the inclusion and exclusion criteria*

Heavy metals removal using bio-adsorbents derived from maize/corn residues

Several studies have reported on maize/corn plants and their various parts have been examined in removing different heavy metals from water and wastewater through adsorption/biosorption as discussed in this section.

Chen *et al.* (2020) studied Cr(III) and Cr(VI) adsorption characteristics of wheat straw (WS) and maize straw (CS) in solution. Batch experiments were conducted to determine how the uptake capacity of the bio-adsorbent is affected by agitation time, solution pH, temperature, and initial metal ion concentration. According to the study, the WS and CS adsorption isotherms for Cr(VI) and Cr(III) satisfied the Langmuir equation, and the adsorption kinetics was found to follow the pseudo-second-order model. The maximum Langmuir adsorption capacities of WS and CS for Cr(VI) and Cr(III) were reported to be 125.60 and 68.90 mg/g and 87.40% and 62.30 mg/g, respectively. The bio-adsorbents derived from the straws were found to be efficient and the adsorbed Cr(VI) and Cr(III) ions could be totally desorbed from both bio-adsorbents surfaces indicating great recyclability and reusability.

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Table 1. *Shows the adsorptive removal of various heavy metals using bio-adsorbents derived from maize/corn plant residues.*

Adsorbent	Heavy metal(s)	Optimum adsorption parameters	Best-fitted adsorption model(s)	Adsorption capacity (mg/g)	Reference
Maize tassel-magnetite nanohybrid	Cd(II)	pH=3.50 Contact time=240.00 min, Bio-adsorbent dosage=0.53 g Initial concentration=44.60 mg/L Temperature=20 °C	Langmuir and Pseudo-second order	52.05	(Guyo *et al.*, 2015)
Un modified corn straw	Pb(II)	pH=6.00 Contact time=3.00 h Bio-adsorbent dosage=0.20 g Temperature=25.00 °C	Langmuir and Pseudo-second order	15.03	(Jia & Li, 2015)
Modified corn shafts	Mn(II)	pH=3.00 Contact time=80.00 min Bio-adsorbent dosage=1.00 g Initial concentration=300.00 mg/L Temperature=80.00 °C	Langmuir and Pseudo-first order	5.20	(Ofudje *et al.*, 2015)
Activated Maize cob	Pb(II)	Contact time=120.00 min Initial concentration=44.47 mg/L Activation temperature= 500.00 °C Phosphoric acid volume=90.00 mL	Langmuir and Pseudo-first order	24.95	(Okafor *et al.*, 2015)
Unmodified maize husk and oxalic acid-treated maize husk	Mn(II) and Pb(II)	pH=4.00 [Mn(II)] pH=2.00 [Pb(II)] Contact time=30.00 min Bio-adsorbent dosage=0.80 g Initial concentration=100.00 mg/L Temperature=25.00 °C	Langmuir and Pseudo-second order	Unmodified maize husk Mn(II)=8.52 Pb(II)=7.38 Oxalic acid-treated maize husk Mn(II)=9.00 Pb(II)=9.33	(Adeogun *et al.,* 2013)
Maize leaves	Cd(II)	pH=6.00 Contact time=40.00 min Bio-adsorbent dosage=0.50 g Initial concentration=15.00 mg/L Temperature=30.00 °C	Langmuir	0.44	(Nadeem, 2013)
Activated corn cob	Cr(VI)	pH=2.00 Contact time=300.00 min Bio-adsorbent dosage=0.10 g Initial concentration=125.00 mg/L Particle size=120.00 µm Temperature=27.00 °C	Langmuir, Freundlich, and Pseudo-second order	57.37	(Nethaji *et al.*, 2013)
Corn cob	Cr(VI)	pH=4.00 Contact time=120.00 min Bio-adsorbent dosage=10.00 g/L Initial concentration=4.00 mg/L Temperature=80.00 °C	Langmuir and Freundlich	> 90.00%	(Sallau *et al.,* 2012)

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Maize cob	Pb(II) and Ni(II)	pH=8.00 Contact time=90.00 min Bio-adsorbent dosage=0.20 g Initial concentration=20.00 mg/L Particle size=355.00 µm Temperature=30.00 °C	Langmuir and Pseudo-second order	Pb(II)=3.150 Ni(II)=4.70	(Nale *et al.,* 2012)
Modified corn stalk	Cd(II)	pH=3.00 Bio-adsorbent dosage=0.50 g Initial concentration=100.00 mg/L Temperature=20.00 °C	Langmuir	21.37	(Liuchun Zheng *et al.*, 2012)
Corn straw biochar	Zn(II) and Cu(II)	pH=5.00 Contact time=120.00 min Bio-adsorbent dosage=l.00 g/L Initial concentration=10.00 mg/L Temperature=37.00 °C	Langmuir and Pseudo-second order	Cu(II)=12.52 Zn(II)=11.00	(Chen *et al.,* 2011)
Modified corn stalk	Cd(II)	pH=7.00 Contact time=350.00 min Bio-adsorbent dosage=0.50 g/L Initial concentration=100.00 mg/L Temperature=20.00 °C	Langmuir and Pseudo-second order	12.73	(Zheng *et al.,* 2010)

Also, Liu *et al.* (2020) investigated the synthesis, characterization, and applicability of activated carbon obtained from corn cob for Hg(II) depollution from aqueous media using KOH activation. The equilibrium isotherms were verified using the Langmuir and Freundlich adsorption models. According to their findings, when 0.02 g/L of adsorbent was employed and the starting Hg(II) concentration was 60.00 µg/L, the Hg(II) adsorption rate reaches 97.20% after 120.00 min. The Langmuir model accurately simulated the isothermal data, implying monolayer adsorption. The maximum Langmuir monolayer sorption capacity attained by the bio-adsorbent was 2.39 mg/g. Also, the kinetic data showed a good fit to the pseudo-second-order model, suggesting chemisorption is the main mechanism of adsorption. The study demonstrated that the corn cob was effective in removing Hg(II) from the aqueous solution with a specific surface area of 1054.20 m^2/g.

Similarly, KOH-derived activated carbon was obtained from corn stalks and applied as a bio-adsorbent for the elimination of Cr(VI) ions from wastewater using batch adsorption experiments (Zhao *et al.,* 2020). The bio-adsorbent showed high adsorption performance for Cr(VI) and its maximum uptake capacity when treated with 4.0% KOH solution was found to be 89.50 mg/g at a pH of 4.50 and bio-adsorbent dosage of 2.50 g/L. The isothermal and kinetic data of Cr(VI) well correlated to the Freundlich and pseudo-second-order models, respectively.

In batch studies, the removal of Pb(II) ions by corn husk and cob were studied, and several influencing adsorption factors such as time, pH, mixing speed, and temperature were investigated to find the best conditions in the adsorption process (Mahdi & Jaafar, 2020). According to the adsorption experiments, the capacity of the corn cob to adsorb Pb(II) from industrial wastewater samples was more than the capacity of the corn husk adsorption. Under the optimum settings of 20.00 min, 100.00 rpm, pH 5.50, and 55.00°C , the percentage removal and uptake capacity of the corn cob was found to be 79.05% and 2.70 mg/g, respectively whereas the corn husk's removal efficiency and uptake capacity was 55.38% and 0.71 mg/g, correspondingly. The study revealed the ability to use these corn waste products as efficient bio-adsorbents for the adsorptive removal of Pb(II) ions from aqueous systems.

A study was conducted to determine the likelihood of Ni(II), Cr(VI), and Mn(II) removal utilizing low-cost adsorbents such as raw and carbonized rice, millet, and corn husks (Batagarawa & Ajibola, 2019). Batch studies were performed to see how the different variables including medium pH, contact time, adsorbent dose, and agitation rate affected the results. The results demonstrate that the three adsorbents utilized in the study (rice husk, millet husk, and corn husk) are promising for removing Ni(II), Cr(VI), and Mn(II) ions from the aqueous solution. At a constant period of 20.00 min, agitation rate of 200.00 rpm, an adsorbent dose of 0.20 g/L, and metal ion concentration of 0.60 mg/L, the maximum adsorption of all three heavy metals occurred. The study demonstrated that all

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the husks were efficient in removing Ni(II), Cr(VI), and Mn(II) from their aqueous solutions and these bio-adsorbents could be employed as inexpensive and highly effective to remove other heavy metal ions from industrial effluents.

Duru *et al.* (2019) evaluated the variations in Cu(II) adsorption in single and binary Cu(II)-Zn(II) aqueous solutions, as well as predicted the mechanism of Cu(II) adsorption onto maize husk lignocellulose in the two solution systems. It was found that Cu(II) removal from the two solution systems fitted the Freundlich isotherm model, indicating that the adsorption mechanism was chemisorption, with stronger linkages in the binary solution system. The adsorption kinetics of Cu(II) in the single and binary solutions were better explained by the pseudo-second-order kinetic model. The study showed that employing maize husk as a bio-adsorbent for Cu(II) adsorption is effective.

Similarly, the potential of chemical pretreatment of maize husk for Cu(II) adsorption in an aqueous solution was investigated and compared (Duru, Duru, *et al.*, 2019). Tartaric acid, methanoic acid, and phenol were used to pretreat maize husk biomass. The methanoic acid pretreatment resulted in a large and noticeable increase in the removal efficiency and adsorptive capacity of the husk. The removal rate of Cu(II) ions was 92.00% with methanoic acid-treated maize husk and 74.00% with phenol-treated maize husk. For all of the biomass types investigated, the Cu(II) kinetic data was well represented by the pseudo-second-order model. The equilibrium uptake capacity of Cu(II) ions by the raw maize husk was found to be 11.52 mg/g, and after pretreatment with methanoic acid, the adsorption capacity reached a maximum of 35.71 mg/g. Therefore, the methanoic acid pretreated maize husk was found to be more efficient for treating Cu(II) ion-polluted water.

Li *et al.* (2019) used bio-adsorbents produced from corn stalks, wheat stalks, chitosan, and starch to investigate Cd(II) and Pb(II) sequestering from simulated wastewater. The removal efficiency of Cd(II) and Pb(II) was highest with corn stalk than the other three bio-adsorbents. The findings of the kinetic studies revealed that the process was attributable to physical-chemical adsorption and the pseudo-second-order model adequately explained the adsorption mechanism. The optimal conditions for Cd(II) and Pb(II) adsorption using the corn stalk adsorbent were found as 2.00 h of contact time, temperature range of 20.00–25.00°C, and pH ranging from 6.00–8.00. The results of the study revealed that these plant residues were promising in the decontamination of Cd(II) and Pb(II) from aqueous media.

Lin *et al.* (2019) used corn husk leaves that had been chemically treated with bismuthiol I to remove trace Hg(II) from wastewater. The results showed that the adsorbent has a high degree of selectivity for trace Hg(II) in wastewater. Under pH 1.00-7.00, Hg(II) can be adsorbed, with a removal efficiency of 98.50%. The adsorption isothermal data correlated well with the Hill model, and the adsorbent's saturated adsorption capacity for Hg(II) was 707.00 mg/g. Also, the kinetic data were well described by the pseudo-second-order kinetic model. The Hg(II) concentration dropped from 10.00 ppm to around 30.00 ppb after adsorption, satisfying the Hg(II)-containing wastewater discharge limits. The regeneration and reusability of the bio-adsorbent showed that, even after three regeneration cycles, the Hg(II) removal efficiency was still over 99.00%. This implied that the bio-adsorbent had a high capacity for removing Hg(II) from wastewater from a sustainable standpoint.

Again, Lin *et al.* (2019) produced a new tri-thiocyanic acid-modified maize bract and studied its Hg(II) removal characteristics. In mixed ion solutions, the adsorbent demonstrated excellent selectivity for Hg(II). Adsorption kinetics tests revealed that Hg(II) was quickly removed from the adsorbent, with a removal efficiency of 99.07% under 5.00 min. Furthermore, the removal efficiency of Hg(II) was greater than 98.00% under all the tested pH conditions, and the equilibrium and experimental results were effectively fitted by the Hill and pseudo-second-order models, respectively. Similarly, the removal rate of Hg(II) was observed to be above 99.00% after three adsorption-desorption cycles. Therefore, due to its high affinity, uptake capacity, and stability, the tri-thiocyanuric acid-modified maize bract was proficient in the removal of Hg(II) from ppm to ppb.

The chromium cations [Cr(III) and Cr(VI)] decontamination capabilities by maize cob immobilized biomass were investigated (Manzoor *et al.*, 2019). The process factors including pH, contact time, dose, and Cr ions initial concentrations were optimized after immobilizing the corn cob biomass in calcium alginate beads. Under the optimum conditions, the Cr(III) and Cr(VI) ions were substantially adsorbed on the maize cob immobilized biomass with removal and adsorption rates of 64.52% and 277.57mg/g; and 55.98% and 208.60 mg/g, respectively. The experimental data of both Cr ions best agreed with the Langmuir and the

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pseudo-second-order models. The maximum Langmuir monolayer sorption capacities were found to be 250.00 and 166.67 mg/g for Cr(III) and Cr(VI), respectively. The study discovered that the immobilization method was feasible in producing the bio-adsorbent and was successful in removing Cr species from industrial wastewater.

Hexadecyl trimethyl ammonium bromide and sulphuric acid were used in modifying corn leaves by Zhang *et al.* (2019) and Cr(VI) was decontaminated from wastewater using the modified leaves. Adsorption factors were explored using batch experiments and the removal of the Cr(VI) with the modified corn leaves was found to be affected by pH, adsorbent dose, and temperature. According to the findings, the hexadecyl trimethyl ammonium-bromide and sulfuric acid-modified leaves of the corn perform as potential bio-adsorbent for the sequestration of Cr(VI) ions from the wastewater. Similarly, by altering corn husk and sawdust by employing MgO and $MgCl_2$, Xu *et al.* (2019) were able to produce biochar. The study pointed out that biochar generated from maize husk boosts its sorption capacity for cationic pollutants.

For the confiscation of As(V) from wastewater at various pH levels, biochar was obtained by impregnating corn straw with iron (Fan *et al.,* 2018). The best pH range for removing As(V) was discovered to be between 2.00 and 8.00. The sorption kinetic data was best described by the pseudo-second-order model indicating that the mechanism of As(V) removal was due to chemisorption. Meanwhile, the adsorption process is closely correlated to the Langmuir isotherm, with an optimal uptake capacity of 14.77 mg/g. The findings indicated that using biochar made from iron-impregnated corn straw as a purification approach for arsenic-contaminated water or soil can be effective.

Herrera-Barros *et al.* (2018) used corn cob residual biomass to make a biosorbent for Cd(II) and Ni(II) decontamination that was chemically modified using alumina nanoparticles. Since the pH has been shown to have a substantial effect on the removal efficiency rate, a pH of 6.00 was chosen as an optimum operating value for further experiments. The removal rates for Cd(II) and Ni(II) were 91.00 and 86.00%, respectively, using chemically modified biomass, which was greater than those derived from the raw biomass, showing that modification by the alumina nanoparticles improved the adsorption process.

A batch process was used to produce a corn cob silica-nano bio-composite and its efficiency was tested for removing hexavalent chromium [Cr(VI)] from wastewater (Kumari *et al.*, 2018). The results revealed that the removal efficiency of Cr(VI) showed significant dependence on the pH of the solution as well as temperature. The adsorption kinetic data of Cr(VI) indicated that the pseudo-second-order equation explained the experimental data well. The selective adsorption ability of the synthesized corn cob silica-nano bio-composite towards Cr(VI) was found to be effective. It was observed that only 0.10 g of the bio-adsorbent has shown to be efficient in the removal of the Cr(VI) ions with a maximum uptake capacity of 11.10 mg/g.

Lin *et al.* (2018) developed a new sorbent by combining functionalized corn bract with hypophosphorous acid and used it to selectively depollute Hg(II) ions from an aqueous media. The results revealed that the corn bract had high selectivity for Hg(II) in the existence of competing ions for instance Cu(II), Co(II), Cd(II), Ni(II), and Zn(II). The Langmuir and pseudo-second-order models showed great fitness to the isothermal and kinetic data, respectively. The results suggested that monolayer adsorption and chemisorption were the rate-determining steps, respectively. From the Langmuir isotherm model, the adsorbent's predicted optimum uptake capacity of Hg(II) was 1293.71 mg/g, which was close to the experimental data.

Rwiza *et al.* (2018) explored the use of corn and rice husks as bio-adsorbents to remove Pb(II) from aqueous solutions. The husks were used in the unmodified form, pyrolyzed form, and chemically modified form. Four isotherm models including Langmuir, Freundlich, Dubinin-Radushkevich (D-R), and Temkin were employed to explain Pb(II) sorption mechanisms. The study showed that all three produced bio-adsorbents could remove more than 90.00% of the Pb(II) from the aqueous solution. However, the biochar of $ZnCl_2$-treated corn husk was found to have the highest uptake capacity in all instances. The sorption equilibrium data of Pb(II) for all the bio-adsorbents fitted well to both Freundlich and D-R models with correlation coefficients (R^2) values close to one.

Activated carbon made from waste corn cobs was tested by removing Pb(II), Cu(II), and Cd(II) from minerals processing effluent (Buah, 2016). The heavy metals adsorption by the activated carbon produced was rapid for the first 15.00 min of contact time and was dependent on the activated carbon' surface areas as well as on their pore volumes. The removal efficiencies of Pb(II), Cu(II), and Cd(II) ions from the effluent

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were found to be 99.90%, 99.80%, and 99.70%, respectively, indicating that the activated carbon can drastically reduce heavy metal concentrations to levels below WHO criteria for safe drinking water.

The batch mode was used to examine the sorption characteristics of biochar derived from corn stalks for the depollution of Cd(II) ions from an aqueous environment (Ma *et al.,* 2016). The findings revealed that the solution pH had an impact on the adsorption system. The amount of Cd(II) adsorbed on the biochar reduced as the particle size, dosage, and ionic strength rose, but it augmented as the initial pH and temperature increased. The biochar, with a maximum capacity of 33.94 mg/g, efficiently removed Cd(II) from the aqueous solutions. The pseudo-second-order model accurately described the adsorption process with a coefficient of determination greater than 0.986. Among the isotherm models tested, the Langmuir was the best-fitted model for the equilibrium adsorption data. More so, the thermodynamic investigations revealed that the Cd(II) adsorption on the biochar was found to be a spontaneous and exothermic process.

Corn silk was tested for adsorption of Pb(II) ions without any modifications, and the influence of corn silk dose, solution pH, initial metal concentration, and contact time on the adsorption process was examined utilizing a batch adsorption approach (Petrović *et al.*, 2016). The findings of the study depicted that the operating factors for example adsorbent dose, pH, initial Pb(II) concentration, and contact time had a significant influence on Pb(II) uptake capacity by the adsorbent. The experimental data were best fitted to both Langmuir and Freundlich isotherm models, with the Freundlich model providing the best data fit. Furthermore, the pseudo-second-order model aligned well with the kinetic data of Pb(II). At higher temperatures, the obtained thermodynamic characteristics suggested a spontaneous, endothermic, and energetically favorable adsorption process.

The reduction of Cu(II) ions in aqueous media onto a bio-adsorbent derived from a mixture of corn stalk and tomato wastes through nitric acid oxidization was performed by Vafakhah *et al.* (2016). From the sorption investigations, Cu(II) ions depollution was pH-dependent, with the highest uptake of Cu(II) occurring at 4.54 mg/g using a pH of 6.00. It was observed that the uptake capacity of the treated corn stalk augmented from 20.80-25.00 mg/g utilizing the modified tomato waste as an effective biosorbent. The experimental results were well represented by the pseudo-second-order kinetic model suggesting chemisorption being the rate-controlling step.

A novel adsorbent produced by modified corn silk with dilute nitric acid was applied to remove Cu(II), Co(II), and Ni(II) from wastewater using batch mode (Yu *et al.*, 2016). At a pH of 6.00, the optimum uptake of Cu(II), Co(II), and Ni(II) was found as 96.15 mg/g, 90.09 mg/g, and 76.92 mg/g at 25.00 °C, respectively. The equilibrium data were analyzed by two adsorption isotherms with Langmuir being the well-fitted model and the maximum uptake capacities of Cu(II), Co(II), and Ni(II) on the bio-adsorbent were 96.15 mg/g, 90.09 mg/g, and 76.92 mg/g at 25.00°C, respectively. The kinetic data were found to best fit the pseudo-second-order and intra-particle diffusion models while the thermodynamic parameters were determined, revealing that these heavy metals' adsorption on the adsorbent is spontaneous and endothermic.

Norozi & Haghdoost (2016) investigated the adsorption capability of corn cob for removing Mn(II) from an aqueous solution. The relationship between adsorption studies and thermodynamic variables was explored to predict the mechanism of the sorption process. The removal of Mn(II) by the corn cob was endothermic in nature, as evidenced by a positive value of the change in enthalpy, indicating an increase in temperature during the process. Similarly, Petrović *et al.* (2017) experimented to determine the potential of raw corn silk as a biosorbent. According to the study's findings, corn silk is a possible biosorbent for Cu(II) and Zn(II) elimination from water, and the thermodynamic studies revealed the spontaneous and endothermic nature of the system. More so, Bandela *et al.* (2016) examined copper(II) ion biosorption using affordable and efficient biosorbents derived from agricultural waste materials. The study showed that the biosorbents obtained from corn, sugarcane, wheat, and bajra agro-wastes were proficient in removing Cu(II) from wastewater, with bajra being the most efficient in removing Cu(II) by up to 98.00%.

Conclusion and future perspective

It is found from this insightful review that the bio-adsorbents prepared from the maize/corn residues proved to be promising in the sequestration of heavy metals from wastewater and thus can find use in water purification. However, some gaps have been identified that need to be addressed adequately.

Almost all the studies dealt with the adsorption/

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biosorption of heavy metals using only one part of the maize/corn plant. No study considered a bio-adsorbent derived from all the parts of the maize/corn plant. Widespread studies are essential to explore the possibilities of a hybrid bio-adsorbent derived from all diverse parts of an agricultural by-product that can effectively enhance adsorption/biosorption capacities and maximize waste reduction.

More so, all the studies investigated adsorption/ biosorption processes using a one-factor design, which consumes time extremely and is highly costly for a large number of adsorption/biosorption factors. Besides, the one-factor-at-a-time approach ignores interactive effects between factors and, as a result, fails to show the full impact of the factors on the sorption process.

Furthermore, almost all the studies applied the bio-adsorbents derived from the maize/corn residues for the sequestration of heavy metals from a single adsorption/ biosorption system. However, real contaminated water comprises a mixture of several cations, anions, and compounds instead of a single ion. Hence, conclusions made from these studies may not certainly be valid when employing adsorption/biosorption to the binary and multi-solutes system for instance the one with a mixture of several metal ions.

Besides, there are very few studies on the desorption of heavy metal ions from the exhausted maize/corn bio-adsorbents after the adsorption/biosorption process to regenerate or recycle the used bio-adsorbents for future use, which is more economical.

Based on the limitations identified in this insightful review, it is recommended that the potentialities shown by the adsorption/biosorption of heavy metals by the different parts of the maize/corn plant biomass warrant further investigations and their applicability in water toxicants removal.

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