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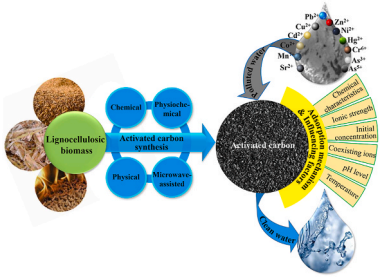
HIGHLIGHTS

- AC characteristics depend on cross-linking and cell morphology of biomass.
- AC production involves biomass carbonization, followed by its activation.
- Microwave-assisted chemical activation produces AC with larger surface area.
- Adsorption of heavy metals by AC occurs via five different mechanisms.
- Cr, Pb, Cu, Zn, Cd, Hg, As are heavy metals adsorbed mainly by biomass-based AC.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of a cheap and effective adsorption approach based on biomass-activated carbon (AC) to remediate heavy metal contamination is clearly desirable for developing countries that are economically disadvantaged yet have abundant biomass. Therefore, this review provides an update of recent works utilizing biomass waste-AC to adsorb commonly-encountered adsorbates like Cr, Pb, Cu, Cd, Hg, and As. Various biomass wastes were employed in synthesizing AC via two-steps processing; oxygen-free carbonization followed by activation. In recent works related to the activation step, the microwave technique is growing in popularity compared to the more conventional physical/chemical activation method because the microwave technique can ensure a more uniform energy distribution in the solid adsorbent, resulting in enhanced surface area. Nonetheless, chemical

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activation is still generally preferred for its ease of operation, lower cost, and shorter preparation time. Several mechanisms related to heavy metal adsorption on biomass wastes-AC were also discussed in detail, such as (i) - physical adsorption/deposition of metals, (ii) - ion-exchange between protonated oxygen-containing functional groups (–OH, –COOH) and divalent metal cations (M^{2+}), (iii) - electrostatic interaction between oppositely-charged ions, (iv) - surface complexation between functional groups (−OH, O^{2-}, −CO–NH-, and –COOH) and heavy metal ions/complexes, and (v) - precipitation/co-precipitation technique. Additionally, key parameters affecting the adsorption performance were scrutinized. In general, this review offers a comprehensive insight into the production of AC from lignocellulosic biomass and its application in treating heavy metals-polluted water, showing that biomass-originated AC could bring great benefits to the environment, economy, and sustainability.

1. Introduction

Water is essential for the existence of all living organisms including plants, animals, and especially humans (Samiee et al., 2019). The modern world is on the brink of serious and irreversible consequences from major environmental disasters caused by worsening pollution, overpopulation, and climate change (Masindi and Muedi, 2018) (Chau et al., 2021) (Hoang et al., 2021a). Consequently, the health and safety of local communities in developing countries are impacted (Zhuang et al., 2019) (Zeng et al., 2019). Industrial activities and manufacturing process are found to discharge heavy metals (Pb, Cu, Cr, Cd, Hg, Zn, Ni, and As), pesticides, dyes, toxic chemicals, and other components containing N, P, and C into the environment (Hoang and Chau, 2018) (Isik et al., 2022), they could cause the contamination of fresh water bodies and underground aquifers (Fu et al., 2021) (Yu et al., 2021). Among the above-mentioned toxic substances, heavy metals can accumulate inside living organisms (Ubando et al., 2021), which can cause severe damages to organs, impair proper bodily functions, and pose high risks of serious terminal illnesses to humans (Tian et al., 2019). Recent news of public health emergencies related to heavy metal poisoning has come out of China, the US, and Europe among which these cases of water supply contaminated with heavy metals were reported in varying levels of severity (Zuo et al., 2018) (Guan et al., 2018) (H. D. Huang et al., 2019). The imminent danger posed by heavy metal pollution is considered one of the greatest risks in maintaining safe and reliable sources of fresh drinking water worldwide (Kumar et al., 2019). Therefore, the requirement for effective treatments of water contaminated with heavy metals has been elevated in its urgency. Consequently, researchers have come up with various methods to treat water, including but not limited to filtration, reverse osmosis, solvent or liquid-to-liquid extraction, ion exchange, chemical precipitation, coagulation, and adsorption (Vardhan et al., 2019) (Hanfi et al., 2020). Nevertheless, the high costs associated with some of these methods coupled with their poor contaminant removal efficiencies are the major disadvantages (Tamjidi and Ameri, 2020). Due to this reason, special consideration should be paid to adsorption as one of the better-preferred methods due to their relative ease of application, cost-effectiveness, the good removal efficiency of pollutants at low concentration, and commonly accessible adsorbent materials (Phan et al., 2017) (Joseph et al., 2019) (Irannajad and Kamran Haghighi, 2021). Seeking an affordable and efficient treatment method is therefore very critical aiming to bring high efficiency in heavy metal removal from polluted water.

Assessing these different methods based on the following properties, including removal capacity, energy efficiency, operational sensitivity, and generation of secondary pollution, it can be concluded that adsorption offers one of the better options (Burakov et al., 2018). There are two main categories of adsorption, including physisorption and chemisorption (Sahmoune, 2019) (Yabalak et al., 2022). Physisorption involves attraction between the adsorbent and the adsorbate by physical forces. The physisorption process is best carried out in low-temperature and high-pressure environments (Ugwu and Agunwamba, 2020). Alternatively, the existing chemical bonding between the adsorbent and the adsorbate facilitates chemisorption. It has been reported that chemisorption is also characterized as an irreversible and slow process (Dong et al., 2016). During this process, the chemical bonding is responsible for the formation of a single layer of adsorbate on the surface of the adsorbent material (Belete, 2017). As part of the process, a variety of affordable materials, carbon-based or modified materials can be used as the primary adsorbents (Duan et al., 2020). These adsorbents can represent several different materials sourced based on their functional characteristics and geographical distribution (Zhou et al., 2015) (Hoang et al., 2018) (Hoang et al., 2021b). Furthermore, several positive features including simple operation, low level of toxicity, and potential use of renewable material as adsorbent have supported the case of adsorption and its wider application potential as an industry-preferred method in heavy metal removal in water treatment (Liu et al., 2020) (Asere et al., 2019).

The production of lignocellulosic biomass-derived activated carbon (AC) presents two major advantages in terms of pollution management strategy. Firstly, it can prevent the potential release and conversion of biomass-based carbon sources into other potent greenhouse gases. Secondly, AC is a non-toxic and environmental-friendly resource with many potential industrial applications. Besides, AC is considered a very safe material that poses no significant threat to the ecosystem and the surrounding environment as it can be recycled from carbon-neutral materials such as lignocellulosic biomass. By taking the advantage of the lignocellulosic biomass waste produced from agricultural activities, the production of carbon-based materials from these various sources can help to eliminate potential pollution resulting from the decomposition process (Freitas et al., 2019) (Vasantharaj et al., 2017). Due to its affordable and accessible nature, the utilization of common byproducts from lignocellulosic biomass processing activities has become an attractive source of raw feedstock for the production of AC (Tuomikoski et al., 2019).

A considerable amount of research effort has been spent on coming up with cost-effective techniques and identifying potential precursors used in the synthesis of AC. Even though there have been multiple studies done on the treatment of heavy metal contaminated wastewater, none of these previous works has focused on the potential associated with practicality and utilization of plant biomass-derived AC for heavy metals removal from polluted wastewater originated from industrial production, livestock, and human daily activities. More importantly, the use of lignocellulosic biomass-derived AC could treat a large quality of wastewater, around hundreds of m^3 of wastewater per day for the industrial scale (Kumar et al., 2021) (Jaria et al., 2022). Therefore, this current review aims to address the knowledge gap on this topic. For these reasons, this paper also contributes to the literature on the use of AC adsorbents in the treatment of heavy metal contaminants by providing an overview of the current state of research, as well as the process characterization (e.g., adsorption mechanism, efficiency, influencing factors). The review also provides a summary of common AC adsorbent modification methods to improve the adsorption capacity for heavy metal ions. The outcomes from the current work not only support the ongoing research effort but also lend new perspectives to future studies.

2. Heavy metal toxicity

Studies have shown the potentially irreversible consequences to aquatic ecosystems from heavy metal contamination when their concentrations are over a limited value that impacts a wide range of life-sustaining natural, physiochemical and biological processes (Guo et al., 2018). The effects of heavy metals on the surrounding environment can be grouped into two categories: including the effects of heavy metals on the surrounding environment and vice versa (Mandich, 2018) (Torres-Cruz et al., 2018). In particular, diversity of species, population density, and make-up, local community structure are aspects of the aquatic ecosystems subjected to the effects of heavy metal contaminants. Furthermore, the characteristics and severity of such impacts vary, depending on the initial concentration of various heavy metal species found in the water sources, sludges, and discharges (Hoang et al., 2022b). Therefore, it is important to anticipate the potential behaviors of the natural ecosystems as the result of the indirect response to the underlying physicochemical processes of the various heavy metals found within the effluents (Defarge et al., 2018) (Z. T. Zhao et al., 2018). On the other hand, the second group of effects is characterized by present conditions of the receiving system, which in turn affects the properties, and potency of the heavy metals. Several variables such as artificial and natural substances, characteristics of industrial discharges, suspended particulate matters, and percentage of chelating agents in the solution, collectively exert a considerable amount of influence on the nature of the heavy metals upon entering the ecosystem (Chen et al., 2022a). The aquatic ecosystem can be characterized mainly by two factors (Gurung et al., 2018), namely (i) variations in the concentration of colloidal crystals, suspended particulate matters, synthetic and natural ligands, and (ii) variation in redox potential, degree of mixing, and population distribution of aquatic organisms. This could be due to the potential changes in the physical state of the aquatic ecosystem caused by the introduction of heavy metal contaminants. However, there is a general decrease in species diversity and distribution of aquatic plant organisms when they face the disruption in ecosystem balance and biological processes (Karlsson et al., 2010) (Das et al., 2019). This strong evidence have provided different perspectives in constructing a comprehensive understanding of the environmental hazard posed by heavy metal water contamination (Street, 2012) (Martínez-Cortijo and Ruiz-Canales, 2018).

For the natural aquatic ecosystem, heavy metal pollution could devastate the ecological balance as well as the diversity of aquatic organisms (Baby et al., 2010). Among aquatic ecosystem species, fishes are believed to be the inhabitants affected directly by the detrimental effects of these heavy metal-derived pollutants (Javed and Usmani, 2015) (Pandey and Madhuri, 2014). Indeed, fish growth could be inhibited as they are exposed to heavy metals-laden polluted water, in which the growth inhibition could be shown as the most distinct symptoms on fish larvae. As a result, the length and mass of fish bodies could be remarkably reduced (Khayatzadeh and Abbasi, 2010) because heavy metals are found to accumulate with the highest concentration in the kidney and liver (Azmat et al., 2016), leading to a decrease in their ability to compete for food and habitat. Moreover, heavy metal-polluted sediments are indicated to threaten creatures such as worms, crustaceans, and insects in the benthic environment, even they could kill the benthic organisms, resulting in a significant reduction of the food availability for larger animals (Bere et al., 2016) (Akindele et al., 2020). Besides, when larger animals feed on heavy metal-contaminated organisms, these heavy metals enter their bodies, causing the bioaccumulation and biomagnification process that threatens their lives (Ali and Khan, 2019) (Yam et al., 2020).

Heavy metals contaminated soil can cause immediate and long-term effects on crop growth and development (Edelstein and Ben-Hur, 2018). Elevated exposure to Cu can cause an imbalance in the production of reactive oxygen species that eventually lead to oxidative stress experienced by plants (Sağlam et al., 2016) (Filetti et al., 2018). In another instance, several studies have pointed out the varying effects of Cd and Zn on plant growth, primary metabolism, and the degree of resistance to oxidative stress by various species due to their differences in phytotoxicity (Břendová et al., 2016) (De Oliveira and Tibbett, 2018). An increased level of Pb and Ni in the soil can lead to deformity of plant tissue (Kushwaha et al., 2018). In their study (Méndez et al., 2014), provided evidence of compromised cell membrane functions as a result of the imbalance in nutrient exchange. Furthermore, normal plant photosynthesis is heavily compromised by an excess amount of Cr absorbed by plants. It is disruptive towards photosynthesis-related processes, such as fixation of carbon dioxide, enzyme activation, photophosphorylation, and photosynthetic electron transport. Evidence of plant phytotoxicity caused by exposure can be observed from the wilting, decay, and rotting of leaves (i.e., putrefaction), stunted growth, and limited stem growth caused by stained root issue (Kumar et al., 2015) (Praveen et al., 2017) (Kumari et al., 2018). The impact of Mn on plant species can be observed from the yellowing of leaves, also known as chlorosis, beginning with older leaves and then moving on to affect new leaves (Santos et al., 2017). In addition, an increased amount of Fe can lead to the excessive generation of free radicals, which negatively affect the structural integrity of plant cells (such as wall membrane, protein, and DNA). Generally, the impact of heavy metal poisoning in plants will be evident among the cells that are the most receptive to heavy metal exposure (i.e., cells that are responsible for nutrient uptake from the soil) (Rizvi and Khan, 2018). Plant exposure to heavy metals can disrupt the normal functions related to ionic homeostasis and enzymatic activity which is the most evident by changes in plant physiology. These effects can first materialize locally in single organs (e.g., plant roots and their ability to absorb nutrients in the soil) and progressively affect overall plant functions (e.g., sprouting, growth and maturity, photosynthesis, water balancing, nutrient digestion, and propagation). Literatures report on the significant negative impacts caused by heavy metals toxicity in plants, such as chlorosis, aging of cells (i.e., senescence), leaf rolling and withering, poor biomass production, shrinking, stunted growth and development, reduced seed generation, and an ultimate plant death and decay (Adrees et al., 2015) (Shahid et al., 2017) (Shi et al., 2018).

High toxicity, which is inherent in various heavy metals, can impair normal functions of the central nervous system, alter blood composition, and cause severe damage to essential organs (including the lungs, liver, and kidneys) (Ma et al., 2016) (Praveena and Omar, 2017). Health problems related to heavy metal poisoning are cancer, mental retardation, kidney failure, compromised immune system, endocrine imbalance, and neurological disorders (Jafari et al., 2018) (Tepanosyan et al., 2018). There are three main pathways through which heavy metals can enter the human body, viz. oral ingestion, inhalation, and skin contact (Asaduzzaman et al., 2017) (El-Kady and Abdel-Wahhab, 2018). The properties of heavy metals play a significant role in the exposure mechanism. For example, water-soluble copper is generally ingested orally through accidental consumption of contaminated water. Similarly, mercury often enters and accumulates inside the human body through the consumption of fish and various types of seafood. These marine organisms are found to have a high amount of an organic form of mercury (i.e., methyl mercury) bio-accumulated inside their tissues (Camacho et al., 2015) (Saleh et al., 2018). The introduction and persistence of heavy metals throughout the food chain is an imminent threat to the overall welfare of humans and animal species (Sang et al., 2018) (Sharma et al., 2018). Even at low concentrations, heavy metal is highly toxic and one of the top environmental and public health hazards (Nasyitah Sobihah et al., 2018). Serious concerns have been raised from the discovery of food and beverages contaminated with heavy metals. Given their urgency, the environmental and health risks posed by heavy metal pollution have provided the need for continued research into treatment technology and process targeting the heavy metal ion removal from the effluents and water supply. Along this line, it is essential to identify appropriate strategies for not only preventing the release of

heavy metals into the environment, but also removing these substances from existing contaminated sources.

3. Activated carbon synthesis from biomass

3.1. Characteristics of biomass for AC synthesis

Based on different thermal and chemical processes, agricultural residues can be converted into several high-value bio-products, such as biofuel, bio-oil, biogas, and bio-solid (Martí Rosselló et al., 2016) (Nguyen et al., 2021). Besides, biomass waste also has the potential to act as an energy storage device (Aziz et al., 2017). Considering the composition of such wastes, it is critical to include those with diverse chemical makeups. A summary of the proximate compositions of different lignocellulosic biomass from a chemical analysis is available in the literature (Sinha et al., 2020) (Feng et al., 2020) (Hoang et al., 2021d). Structurally, lignocellulosic biomass consists of three main constituents: hemicellulose, cellulose, and lignin (Hoang et al., 2021c). Depending on the nature of the conversion methods (i.e., thermo-chemical or biochemical), these components can be found in varying concentrations which can affect the characteristics of the final AC products. There are several advantages in terms of producing bio-based products from agricultural residues such as availability, affordability, renewability, and environmental-friendly (Rashidi and Yusup, 2017) (Yetri et al., 2020) (Hoang et al., 2022a). Nevertheless, there are also some major drawbacks in terms of biomass-based AC. Particularly, Abbas et al. (Ahmed et al., 2020) have demonstrated that leaves are not a good source for AC because of their poor carbon content, high volume to weight ratio, and high ash content. Within a chemical activation process, researchers have shown a better performance of amorphous lignin degradation by activating agents than that of biomass cellulose. Hence, having a good understanding of the material properties is essential to ensure its optimal application.

Between 10% and 30% of lignocellulosic biomass is made up of lignin. Certain biomass materials such as coir can contain up to 45% of lignin. Lignin is a naturally occurring polymer that is water-insoluble (Chen et al., 2022b). Lignin also exhibits a high degree of polarization due to the presence of both aldehydic and carbonyl groups. Initially, the carbonization and activation process is initiated by the removal of volatiles from cellulose and hemicellulose (Sharma et al., 2017). Common AC conversion processes from lignocellulosic biomass are known for their special features (Anyaoha et al., 2018) and affordability which can be based on either acids, bases, or salts (Shamsuddin et al., 2016). To assess the aptness of certain biomass for AC production, one should consider the cross-linking feature of the lignocellulosic constituents and cell morphology (Kongsomart et al., 2015). The energy required for the conversion process also depends on the characteristics of the raw inputs. Furthermore, the inherent structural properties of the biomass resource, as well as the physiognomy and chemical function of the individual constituents, can exert a considerable influence on the reaction sensitivity and its potential role within the AC conversion process (Wazir et al., 2020). Among the three main components in lignocellulosic biomass, there is a high degree of similarity between cellulose and hemicellulose; except that hemicellulose possesses fewer numbers of saccharide units than cellulose (Danish and Ahmad, 2018). In terms of its structure, cellulose is constructed of a straight-chain insoluble polysaccharide that consists primarily of glucose monomers linked together by beta-1, 4 glycosidic bonds (Hoang et al., 2021e). On the other hand, hemicellulose is a heteropolymer containing several cross-linked soluble glucose monomers that are integral to the AC conversion process. Examples of these sugars include glucose, mannose, galacturonic acid, xylose, arabinose, O-methyl-glucuronic acid, and galactose. Within the conversion process, the thermal scission of hemicellulose is initiated at temperatures beyond 200 °C followed by the decomposition of cellulose at 250–400 °C, effectively releasing CO and CO_2 from the glucopyranose rings (Danish and Ahmad, 2018). In contrast to the above-mentioned polysaccharide polymers, lignin is naturally hydrophobic which gives its ability to propel water. Fig. 1 describes the molecular relationship exhibited between ether and β-1,4-Glycosidic bonds (Kan et al., 2016). Hence, it is necessary to break these bonds using either thermal or chemical reactions to produce reactive AC.

3.2. AC preparation

There are two primary stages included in the production of AC: (1)-pyrolysis or carbonization of the biomass precursor and (2)-activation process. After the initial carbonization, the intermediate products exhibit higher structural stability and enhanced porosity (Osman et al., 2016). It is then followed by an activation step, which can be either a physical or a chemical-based process. Activation is responsible for the enlargement of those well-developed pores. To perform carbonization on the biomass feedstock, one can utilize the pyrolysis/gasification method carried out in a high-temperature inert environment that results in biochar (Odetoye et al., 2019). This is an important step since the volatile matters can be effectively thermally broken down and eliminated from the carbon content (Radenahmad et al., 2020). For pyrolysis, important processing parameters are temperature, heating rate, nitrogen flow rate, and residence time. The resulting biochar, an intermediary product, has a poor adsorption capability, which was enhanced by the subsequent activation process. As a result, some key textural properties of AC such as micropore volume (V_{mic}), total pore volume (V_t), and Brunauer-Emmett-Teller surface area (S_{BET}) are significantly increased (X. Yang et al., 2019). Fig. 2a depicts the main production stages, in which the pore formation of empty fruit bunch under three different temperature processes are denoted with A, B, and C corresponding to 350 °C, 500 °C, and 600 °C, respectively (Claoston et al., 2014). Overall, physicochemical activation has demonstrated its role as an alternative option (Xiao et al., 2012). Moreover, higher temperature processes are shown to improve pore structure. Details discussion on raw biomass pre-treatment and processing methods are provided in a report by Pathak et al. (2015).

At the initial carbonization stage, the removal of volatile matters in the carbon content leaves the lignocellulosic biomass accessible to the activating agents that are responsible for developing the microporous carbon structure. Subsequently, these pores undergo a size enlargement by thermally destroying the barriers between these pores. As a result, the micro-pores are replaced with intermediate-size and macro-pores. Due to the variation in the nature of different activation methods, it can be taken up before or after the carbonization of biomass. Unkawa et al. (Ukanwa et al., 2019) have shown that the activation stage is useful in the removal of tar-like substances found in the obtained biochar and enhances the material porosity and surface areas available for AC. Similarly, Yahya et al. (2015) found similar benefits to the activation process beginning with the removal of tars blocking the pores and enhancing the subsequent interaction with the activating agent. Overall, the process starts with thermal decomposition of the carbon content and is then subjected to oxidation via an activating agent. Particularly, activation temperature and reaction time are the two most critical variables in the formation of the porous structure. Previous studies have demonstrated a positive correlation between these two factors and pore volume. However, increases in these parameters negatively affect AC yield. At the initial stage of carbonization, it is critical to closely monitor and control the pyrolysis temperature, as extremely high temperatures can result in the formation of undesirable by-products (González-García, 2018). Fig. 2b illustrates the primary activation that takes place during AC production from the lignocellulosic biomass.

3.2.1. Physical activation

Physical activation is usually completed in two phases, (i) pyrolysis of the precursor materials, which is then followed by (ii) steam or CO_2-assisted activation phase (Ugwu and Agunwamba, 2020) (El-Naggar et al., 2019). Through this process, the elimination of volatile

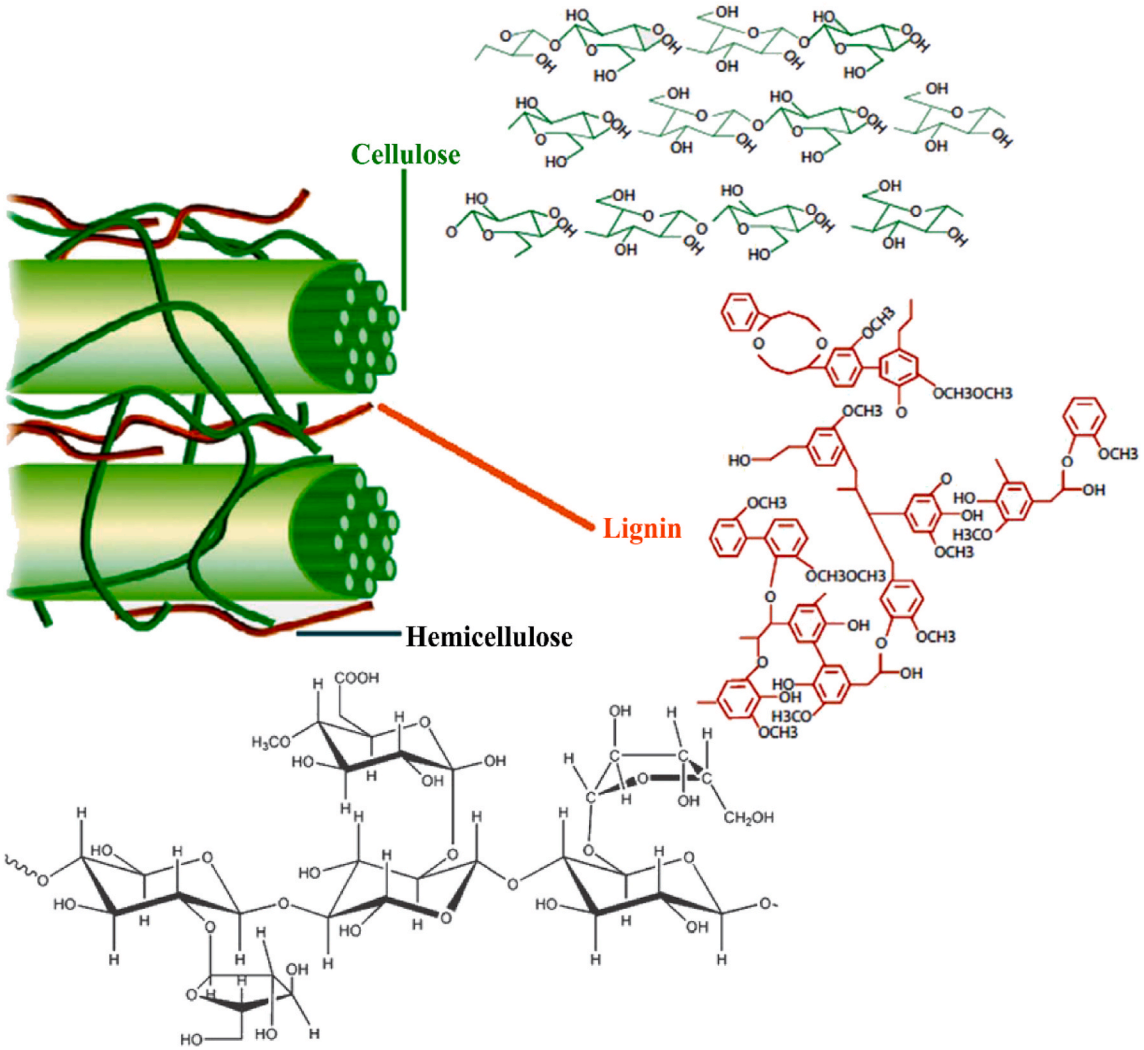


Fig. 1. Structure of components in lignocellulosic biomass molecular (Bamdad et al., 2018) (With permission of Elsevier LN 5153960124051).

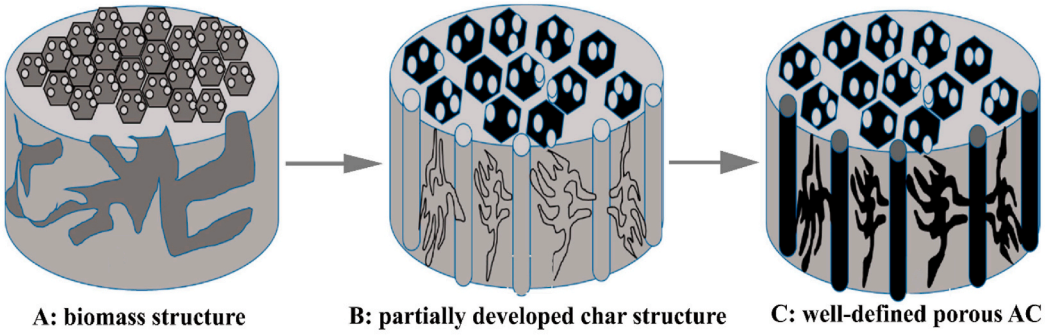
particulates found in the carbon content of the burnt biomass leads to an increase in the porosity and pore volume size as the result of the gasification process (González-García, 2018). Close monitoring and temperature control are highly warranted as it is a significant factor affecting the performance and outcomes of the AC conversion process. Chowdury (Chowdhury, 2013) has observed the initial reactions taking place on the internal surface of the carbonaceous material at lower temperatures. As the temperature begins to rise, the reactions are made up mainly of those interactions occurring externally to the carbon particles. Unfortunately, the low yield of AC presents a major shortcoming for the physical activation process, which prevented it from being widely adopted. Several studies on the physical activation methods are summarized in Table 1.

3.2.2. *Chemical activation*

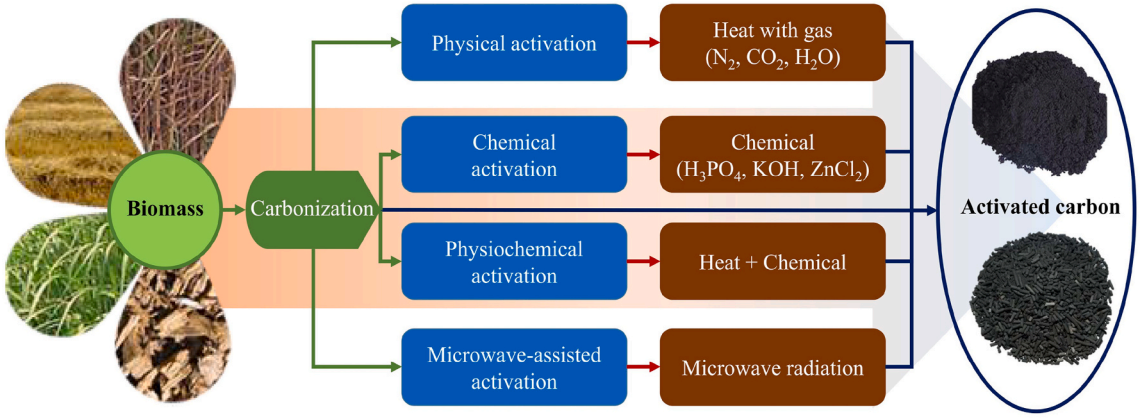
For this particular form of activation, the substances undergo both the activation and carbonization process. Particularly, specified amounts of activating agents are introduced into the precursor materials to absorb any unwanted water content. Some examples of commonly used activating agents are potassium carbonate, zinc chloride, potassium hydroxide, calcium carbonate, sodium hydroxide, and phosphoric acid (Yahya et al., 2018). In contrast to the physical activation method, the process involved in chemical activation is often conducted under lower temperature conditions. Moreover, the chemical activation process also yields relatively larger amounts of active carbon than its counterpart (X. Yang et al., 2019) (Gao et al., 2020). However, an additional washing step is needed to remove any remaining chemicals left on the AC before it can be used. Results from past studies on the chemical activation of different types of plant biomass are listed in Table 2.

3.2.3. *Physiochemical activation*

As pointed out by Chowdhury, there have been several previous studies examining the two types of the activation process, namely physical and chemical (Chowdhury, 2013). Depending on the selected method, the AC produced from these processes includes either high porosity or low surface area (Rashidi and Yusup, 2017) (Danish and Ahmad, 2018). Hence, it is necessary to integrate both physical and chemical activation to achieve both of the above-desired qualities. Based on their research results, Afdhol et al. (2017) believed that improved surface properties can be obtained from the activation of carbon when combining both physical and chemical processes. Indeed, a large surface area is an important quality that can determine the environmental performance of the produced AC (Sulaiman et al., 2018). To facilitate the integrated physical and chemical activation process, biomass pyrolysis is performed and then is followed up by an activation phase via both physical and chemical activating agents. In their study, Nasrullah et al. (2018) recorded both granular and mesoporous ACs with a high surface area. The integrated process enables the opening of the material's pores which contributes positively toward improving the



(a)



(b)

Fig. 2. (a) - Diagram for illustrating the effects of temperature on the process pore development of AC (Ukanwa et al., 2019) (With permission of MDPI policy for open access article); (b) - Main methods for activating process (Reza et al., 2020) (With permission of Taylor & Francis policy for open access article).

Table 1
Physical activation for AC synthesis from biomass waste.

Biomass waste	Conditions for the activation process			Textural properties			Yield, %	Reference
	Activator	T_a, °C	t_a, min	V_t, cm^3/g	S_{BET}, m^2/g	V_{mic}, cm^3/g		
Date pits	CO_2	900	–	0.229	490	0.165	–	El-Naas et al., (2010)
Baobad woods		800	–	–	875	0.4	–	Tchikuala et al., (2017)
Phoenix dactylifera seeds		900	60	–	723.72	0.268	7.25	Ogungbenro et al., (2017)
Pine sawdust pellets		800	60	0.15	275	0.14	–	Jeguirim et al., (2018)
Date pits	Steam	800	60	0.321	702	–	17	Awwad et al., (2013)
Pistachio nut shells		850	20	–	2596	–	10	Niksiar and Nasernejad, (2017)
Camellia oleifera		820	–	1.17	1076	–	–	Min et al., (2017)
Bulgarian peach stones		850	60	0.61	1258	0.45	–	Tsoncheva et al., (2018)
Rice husk		850	105	1.09	1180	–	–	Deiana et al., (2008)
Bamboo waste scraps		900	–	–	1099	0.431	–	Dong et al., (2019)
Dinde stones	CO_2/Steam	850	–	–	1029	0.49	32	Largitte et al., (2016)
Acai seeds	Ar/CO_2	800	180	0.217	496	–	–	Kecira et al., (2018)
Coconut shell	N_2/Steam	900	120	1.26	1926	0.931	9	Ao et al., (2018)

adsorption capacity of the porous adsorbent product (Köseoğlu and Akmil-Başar, 2015). For references to past studies employing the physical/chemical activation process on plant biomass, an overview is provided in Table 3.

3.2.4. *Microwave-assisted activation*

The physical and chemical activation process can be performed in a wide range of devices, such as multiple hearth furnaces, rotary kilns, and fluidized bed boilers (Salvador and Jiménez, 1996). Heating via microwave irradiation has gained special attention among researchers due to its ability to transfer heat at the molecular level. This facilitates more uniform and fast thermal conductivity from the heating source (Xin-hui et al., 2012). The microwave heating method can be combined with physical and/or chemical activation to generate ACs with better performance using either a single-stage (Thue et al., 2016) or a two-stage activation process (Abbas and Ahmed, 2016). In the former process, the carbonization and activation step occurs concurrently in one reactor (e.g. tube reactors, auger reactors). The use of single-stage microwave activation can be referenced from recent studies recording pilot-scale demonstrations upon performing biomass pyrolysis and producing ACs

Table 2
Chemical activation for AC synthesis from biomass waste.

Biomass waste	Conditions for the activation process			Textural properties			Yield, %	Reference
	Activator	T_A, °C	t_a, min	V_t, cm^3/g	S_{BET}, m^2/g	V_{mic}, cm^3/g		
Argan nut shell	NaOH	700	60	0.9	798	–	–	Zbair et al., (2018)
Popcorn		650	120	2.12	3291	–	–	Yu et al., (2019)
Walnut shell	KOH	800	–	1.15	2305	–	–	Jeguirim et al., (2018)
Spent mushroom compost		500	45	–	–	1.12	20	Min et al., (2017)
Distillers grain		700–900	60–120	0.784	1430	0.093	–	Wang et al., (2018)
Tomato paste waste		500	–	0.154	283	–	–	Ozbay and Yargic, (2016)
Baobab woods		400	–	–	915	–	–	Tchikuala et al., (2017)
Walnut shell		700	–	0.766	1239.92	–	–	(K. Li et al., 2018)
Acacia Nilotica sawdust	H_3PO_4	900	60	–	1701	–	–	Gupta and Lataye, (2017)
Bamboo		600	60	0.625	133	50.485	–	Ahmed, (2016a)
Orange peel based		700	60	1.237	2210	1.185		Wei et al., (2019)
Coconut shell		800	120	1.495	2648	0.883	–	(Z. W. Zhang et al., 2020)
Chestnut shell	$ZnCl_2$	700	60	–	173.21	–	–	Altintig et al., (2018)
Dry okra waste		500	60	0.778	1044	–	–	Menya et al., (2018)
Walnut shell		700	–	0.011	5.95	0.005	–	(K. Li et al., 2018)
Sunflower seed husks		500	45	0.35	1511	–	–	Tsoncheva et al., (2018)
Cotton woven	$FeCl_3$	700	120	0.641	942	0.327		Xu et al., (2020)
Mangosteen shell	K_2CO_3	900	120	0.56	1123	0.450	20.7	Ahmed, (2016a)
Paper mill sludge		800	150	1.0	1583	–	3.4	Jaria et al., (2019)

Table 3
Physical/chemical activation for AC synthesis from biomass waste.

Biomass waste	Conditions for the activation process			Textural properties			Yield, %	Reference
	Activator	T_A, °C	t_a, h	V_t, cm^3/g	S_{BET}, m^2/g	V_{mic}, cm^3/g		
Coconut shell	Steam/$ZnCl_2$	900	0.5	1.307	2114	1.142	–	Azevedo et al., (2007)
Sago palm bark	N_2/$ZnCl_2$	700	1	0.649	1633.94	0.335	65	Erabee et al., (2017)
Date pits				0.48	1367.04	0.319	58	
Date pits	Steam/HNO_3	–	3	0.750	950	–	–	Hazourli et al., (2009)
	Steam/H_3PO_4	–	3	0.850	1100	–	–	
	CO_2/KOH	850	2	0.424	763	–	20	Hameed et al., (2009)
Rice husk	CO_2/KOH	800	2	1.126	1836	0.805	23	Shen and Fu, (2018)
Date pits	N_2/H_3PO_4	650	2	1.167	316.9	–	–	Krishnamoorthy et al., (2019)
Tea industry waste	N_2/$ZnCl_2$	700	4	0.806	1141	0.676	35.8	Gundogdu et al., (2013)
Borassus aethiopum shells	CO_2/NaOH	713	2.82	0.48	795.21	–	–	Garba et al., (2014)

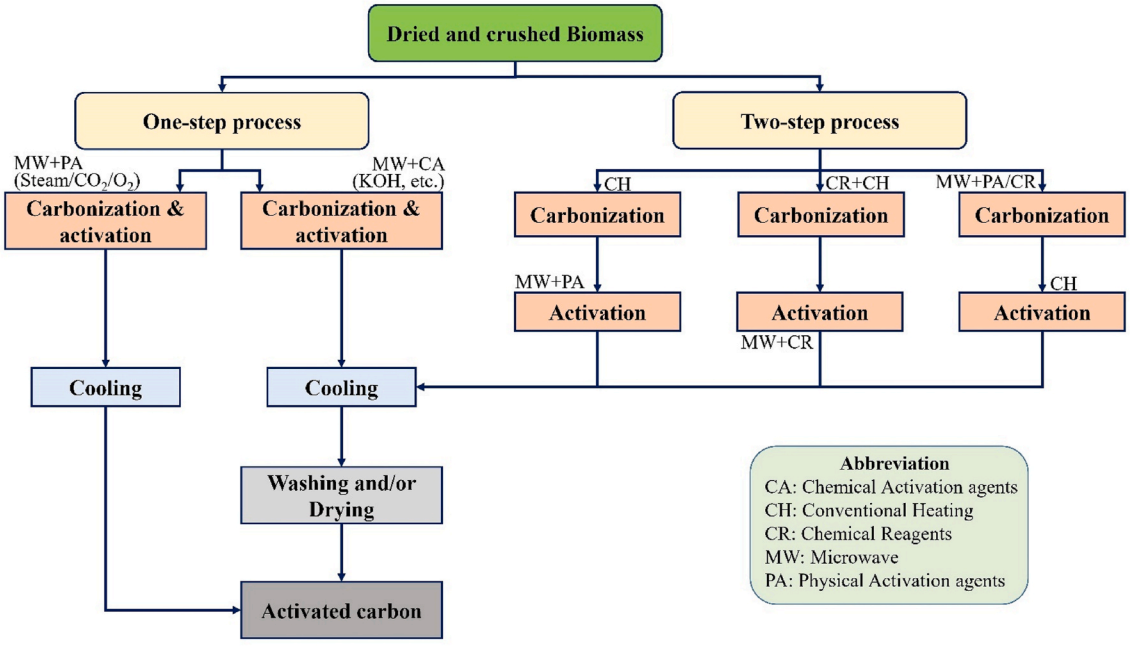


Fig. 3. AC production diagram from biomass waste under microwave irradiation (Ao et al., 2018) ((With permission of Elsevier LN 5153960826305).

(Li et al., 2016) (Zhang et al., 2017) (Lin et al., 2012). Furthermore, the single-stage activation process may be able to encompass drying given the moisture content existing in the biomass feedstock. Under this scenario, one would add the drying time to the carbonization and activation duration to arrive at the total process treatment time. One of the several major advantages of the single-stage microwave activation is the smaller footprint required by the whole operation due to its more compacted structure compared to the traditional two-stage activation method. In the latter process, the primary procedure only allows for either activation or carbonization to be carried out under microwave irradiation (Li et al., 2008). In certain scenarios, microwave irradiation can be utilized as the primary heating source for both carbonization and activation (Kazmierczak-Razna et al., 2015). Based on the characteristics of the used biomass feedstock, the drying step can be separated or included as part of the carbonization phase. Several noteworthy studies have introduced an innovative approach to incorporating microwave heating before performing the biomass pyrolysis and have resulted in improved textural properties of produced AC such as micropore volume (V_{mic}), total pore volume (V_t), and Brunauer-Emmett-Teller surface area (S_{BET}) (Fig. 3) (Ao et al., 2018). Several factors directly influence the final characteristics of the AC products, including the types and sources of biomass feedstock, pyrolysis temperature, power level exerted by the microwave irradiation, reaction time, and type of additives used in the process (Georgin et al., 2016) (Zhao et al., 2008). Given the fact that these controllable variables are highly reliable, microwave heating is preferred for its capability and versatility. Hence, it is considered an optimal method to be integrated with the AC synthesis process given the optimally set parameters to ensure enhanced pore structure and surface property in the AC outputs (Lua et al., 2004) (Angın et al., 2013).

Microwave irradiation can be applied as the heating source during the carbonization and/or activation stages in the AC production process. The power produced from microwave radiation that is required for the activation of the AC precursors can be influenced by the heating rate and the sample's final temperature, which in turn are dictated by its total mass. It has been shown to positively improve the surface area and porosity of the resulting carbon-based material. There have been numerous studies that attempted at examining the observable difference in the properties of ACs, namely surface area, and pore structure, from conventional and alternative activation methods in which the latter employs the use of microwave heating (Foo and Hameed, 2012a) (Foo and Hameed, 2012b) (Hoseinzadeh Hesas et al., 2013). It was found that MW heating is capable of more rapid heat transfer. Nevertheless, there are certain materials that due to their inherent properties, are not a good conduit for microwave heating, resulting in limitations of the potential to reach the anticipated reaction temperature. In these instances, additives can be introduced into the sample to enhance its property making it more receptive to microwave irradiation. Indeed, in one experiment, the observed power and activation time of a single-stage, microwave-assisted, K_2CO_3 catalyzed activation of cotton stalks were seen to positively correlate with the final AC yield until reaching the optimal level. Upon reaching this point, AC yield declined despite the continued increase in either power or reaction time (Deng et al., 2009). A similar trend can also be seen in the case of the two-stage microwave activation process using the almond shell as the biomass feedstock and $ZnCl_2$ as the chemical activator, respectively (TEĞİN et al., 2020). Overall, when applying a higher level of microwave radiation energy to the biomass sample, the greater availability of active sites and increased porosity are observed among the resulting ACs. However, when the amount of power exceeds a certain threshold, it could damage the structural characteristics of the sample due to the partial burning (Foo and Hameed, 2012c) (Foo and Hameed, 2012b) (Foo and Hameed, 2012d). In general, the textural properties of ACs produced by the microwave-assisted activation method is presented in Table 4.

4. Adsorption mechanism and influencing factors

As a carbon-based material, AC possesses several excellent qualities, including high porosity and thermal stability, large specific surface area, high adsorption capacity, excellent mechanical strength, and controllable morphology (Liu et al., 2015) (Özsin et al., 2019). To address water treatment requirements sufficiently, advances in research and development have contributed to the progress made in the introduction of a wide range of carbon-based materials and their derivatives. Available modification processes have been developed to enhance the effectiveness of the adsorbent in attracting and removing heavy metal ions, like magnetization, oxidization, grafting of functional groups, and construction of composite inorganic materials (X. Yang et al., 2019). However, the adsorption mechanism and influencing factors on the adsorption capacity of AC should be clearly and thoroughly analyzed to have potential insights into AC-based adsorbents and their application in removing heavy metals from contaminated water sources.

4.1. Adsorption mechanisms

The main mechanisms in the adsorption of heavy metals by carbonaceous materials can be grouped into five different categories, as shown in Fig. 4.

Physical adsorption is a process whereby the heavy metal ions are

Table 4
Characteristics of AC synthesis from biomass waste through microwave activation.

Biomass waste sources	Microwave parameter	Textural properties			Yield, %	References
		Average pore size, nm	S_{BET}, m^2/g	Vt, cm^3/g		
Peanut shells	Power is700W; Activation time is 20 min	3.54	395.8	0.210	–	Georgin et al., (2016)
Sawdust pellets	Irradiation time is 60 min	2.0	387	0.24	24.7	Kazmierczak-Razna et al., (2015)
	Two-step microwave activation	2.0	426	0.27	25	
	One-step microwave with irradiation time is 60 min	2.56	367	0.23	–	
Orange peels	Microwave activation with irradiation time is 6 min	2.227	1104.45	0.615	–	Foo and Hameed, (2012a)
Wood sawdust	Power is 600W; Activation time is 6 min	2.3	1496	0.864	80	Foo and Hameed, (2012c)
Rice husk	Two-step microwave activation with power is 600W and irradiation time is 7 min	3.414	752	0.64	–	Foo and Hameed, (2011)
Lotus stalks	One-step microwave activation with power is 700 W and irradiation time is 15 min	3.74	1432	1.337	40.1	Huang et al., (2011)
Industrial waste lignin	One-step microwave activation with irradiation time is 4 min	2.08	1164	0.64	60.73	Maldhure and Ekhe, (2011)
Tobacco stems	Power is 700W; Activation time is 30 min	0.6	2557	1.647	16.7	Li et al., 2018
Cotton stalk	Power is 680W; Activation time is 10 min	2.08	729.33	0.38	11	Deng et al., (2010)

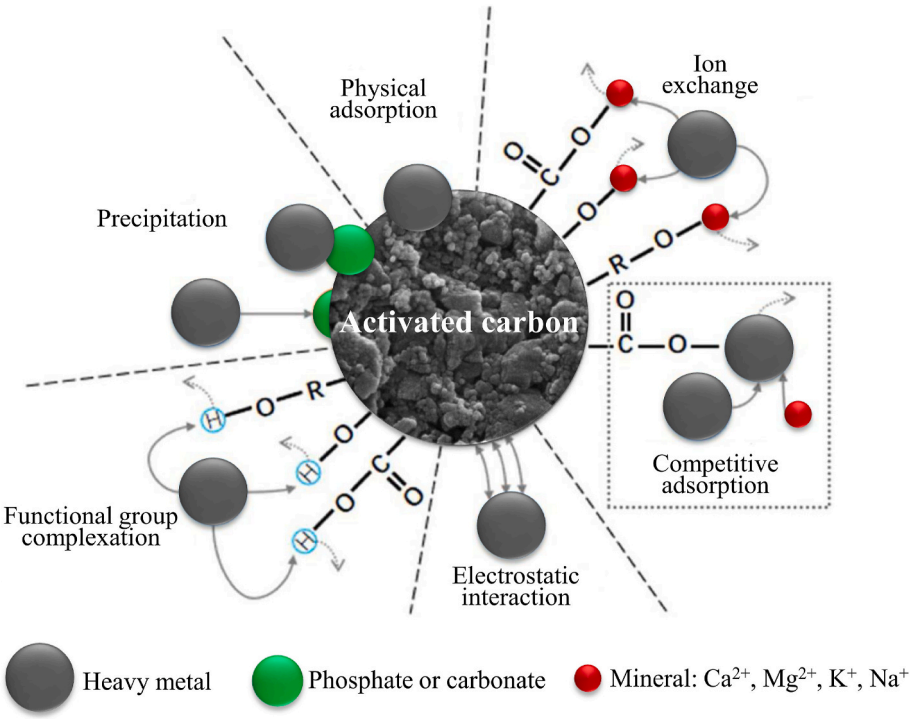


Fig. 4. Main adsorption mechanisms of carbon-based absorbents for heavy metal ions (Duan et al., 2020) (With permission of Elsevier LN 5153960963767).

spread out and deposited into the pore of the adsorbent material through physical means, which do not rely on the binding force of chemical bonds. The physical adsorption mechanism is driven primarily by the pore size distribution and the adsorbent material's surface area. Particularly, the increased presence of mesopores and large surface area can accelerate the dispersion of the pollutants which enhances the overall physical adsorption and related adsorption kinetics (X. Yang et al., 2019).

Ion exchange is a process whereby the exchange of ions is observed between protonated oxygen-containing functional groups (such as –OH, –COOH) and divalent metal cations (M^{2+}) which is dependent on the ion exchange capacity of the cation (X. Yang et al., 2019). According to Lai et al. (2019), the ion exchange accounts primarily for the adsorption mechanism of heavy metals by carbon-based absorbents.

Electrostatic interaction happens when the adsorbent surface having either a negative or positive charge creates the electrostatic attraction force which is responsible for drawing the oppositely charged metal ions toward the adsorbent. According to past research findings on heavy metals removal using AC, electrostatic interaction has been demonstrated as a possible adsorption mechanism (X. Yang et al., 2019). Noteworthy, various carbonaceous materials can possess surfaces with different types of charges. Moreover, the electrostatic interaction is subjected to the effect of pH level and pH_{PZC}. As an example, researchers have observed the electrostatic interaction between different protonated or deprotonated functional groups existing on the surface of the carbonaceous adsorbents and the oppositely charged metal ions (i.e., positively charged NH^{3+} interacting with the following negatively charged metal ions $HCrO^{4-}$, $Cr_2O_7^{2-}$, and CrO_4^{2-}) (H. Wang et al., 2014).

Surface complexation involves the interaction between different functional groups, including –OH, O^{2-}, –CO–NH-, and –COOH, and either heavy metal ions, particularly M^{2+} or complexes (i.e. $Pb(OH)^+$, $Cd(OH)^+$) (Li et al., 2017). Consequently, these interactions enable the development of multi-atom structures as a result of the surface complexation reaction (X. Yang et al., 2019). Several studies have observed the possible complexation reaction between one of the following metal cations, and oxygenated functional groups –OH and –COOH (Supong et al., 2020) (Liang et al., 2018).

Precipitation/coprecipitation: Solid precipitates or coprecipitates can be formed as a result of the reaction between heavy metal ions and other types of ions and/or functional groups existing on the surface of the adsorbent materials. The coprecipitation occurs primarily in aqueous solutions with an increased concentration of heavy metal ions (Liu et al., 2020). Besides, the phenomenon can happen continuously on the surface of the carbonaceous adsorbents (X. Yang et al., 2019), for example, the formation of Cd^{2+} to a certain extent (Zhang et al., 2015). In other instances, the reduction process can also exert a considerable influence on the extraction of heavy metals. Specifically, certain types of high-valence heavy metal ions can be initially reduced to low-valence states before their derivatives are removed from the solutions via means of either complexation or ion exchange mechanism (Li et al., 2017).

4.2. *Factors affecting the adsorption capacity*

Even though industrial effluents account for the primary sources of heavy metal pollution, several studies have shown the equally serious threats posed by the presence of such contaminants in different water sources (Mwanamoki et al., 2015) (Arslan et al., 2022). Due to the varying characteristics and water qualities, the application of adsorbents in removing heavy metals from these various contaminated water sources can differ in terms of their effectiveness and performance (Sridhar et al., 2017). In addition, the presence of acids, compounds containing carboxyl groups, nitrogen, halogen, or high-sensitivity bacteria (such as anammox) in the wastewater could be considered as inhibitors because these compounds with negative charges tend to keep heavy metals (positive charges) in the wastewater environment (Zhang et al., 2022). Hence, to accurately assess the adsorption potential of a particular treatment, it is important to take into account the heavy metal properties and absorbent characteristics under the different physio-chemical conditions present in the specified water source. Among these, some critical factors influencing water quality include pH level, temperature, and ionic strength.

4.2.1. Chemical characteristics of heavy metals

Industrial and agricultural activities are common sources of heavy metal pollution resulting from the unregulated discharges of wastewater into the surrounding environment (Chowdhury et al., 2016). Due to their inherent properties, heavy metals can withstand the natural degradation process and accumulate over time, which poses a serious environmental challenge. Humans and animals are subjected to heavy metals poisoning through the unintentional consumption of food and water contaminated with heavy metals. The accumulation of heavy metals inside the human body can damage internal organs and cause serious illnesses. Although living organisms require small amounts of metallic elements, such as irons of Zn, Cu, and Cr, to ensure proper metabolism, they can seriously endanger human life when exceeding certain safety thresholds (Tchobanoglous et al., 2003).

4.2.2. Ionic strength

The ionic strength of the water source can significantly affect the behavior of the heavy metals and their potential interaction with the adsorbent materials during the treatment process. Higher concentrations of chloride in the water can accelerate the production of neutrally or negatively charged complexes of heavy metal-chloride which are water-soluble and more challenging to remove (Ferraz and Lourençlo, 2000). As reported by Villaescusa et al. (2004), decreases in the adsorption efficiency of Cu^{2+} and Ni^{2+} were observed with increasing ionic strength as a result of the more active formation of heavy metal-chloride complexes. This leads to the lower affinity of the adsorbents toward the metal ions. In a different study, Wang et al. (2017) experimented on trace metals found among river estuaries. The authors found a strong positive correlation between salinity and dissolved metal concentrations, such as copper, cadmium, and zinc. Besides, when subjected to increased electrostatic forces between the heavy metals and adsorbent surfaces, changes in the behavior of the heavy metals and the potential adsorption capacity can be observed as a result of elevated levels of ionic strength in the aqueous solutions. Relying on surface chemistry fundamentals, one can detect the reduction in electric double layer caused by the changes in electrostatic interactions from increasing ionic strength. This phenomenon ultimately results in the overall decline in the adsorption potential of heavy metals by the adsorbents (Anfar et al., 2020). In their investigation, Zhang et al. (Zhang, 2011) examined the influence of ionic strength on heavy metal adsorption efficiency for Cu^{2+}, Pb^{2+}, and Zn^{2+}. The authors confirmed a decline in the removal potential of these heavy metals when subjected to increases in ionic strength. Nevertheless, there are some exceptions to the findings. Yang et al. (2016) reported that the removal of As^{3+} and Ni^{2+} increased up to 25% when the ionic strength of the solution rose from 0.01 to 1.0 M. It was inferred that the inner-sphere surface complexation reaction was primarily responsible for such an unsuspected occurrence. Similarly, Vijayaraghavan et al. (2006) also observed an increase in the removal efficiency from 2% to 5% of Co^{2+} and Cu^{2+} found on crab shell particles under an increased level of ionic strength resulting from the introduction of competing ions, such as Na^{+} and K^{+}.

4.2.3. Initial concentration

The initial concentration of heavy metal can exhibit a positive effect on the removal efficiency of the absorbents given the fact that they have not been fully saturated. Generally, the higher initial concentration also means a higher attraction force drawing the metal ions from the aqueous solution onto the surface of the carbonaceous adsorbent material (Hayati et al., 2017). However, upon exceeding a certain threshold, a higher initial concentration inhibits further adsorption due to the reduced number of available and unoccupied binding sites on the adsorbent surface (Mohan et al., 2017). Elevated levels of initial heavy metal concentration will limit the removal efficiency of the adsorbent in the later phase of the process. Besides, the general model fitness of the selected adsorption isotherm is also subjected to modification in initial heavy metal concentration. The best-performed model in terms of its fitness can change as a result of the rising initial concentration leading to the switch from single to multi-molecular layer adsorption.

4.2.4. Coexisting ions

The presence of co-existing cations and anions with varying ionic strengths can affect the adsorption of heavy metal ions by carbonaceous adsorbent materials in three ways. The difference in the affinity of the binding sites on the adsorbent surface toward the heavy metal ions in binary or multi-system is directly influenced by the competing behaviors of the cations. This, in turn, is characterized by the nature of the charge and hydrated radius (Gan et al., 2015). First, it is evident of the competition exhibited among coexisting heavy metal ions in the same space for the limited number of adsorption sites. Hence, a lower level of adsorption efficiency can be anticipated by the same adsorbent in any system with two or more types of ions (either cations or anions), in contrast to a single heavy metal ion system. Park et al. (2016) reported a lower capacity for heavy metal adsorption in a mixed system containing both Pb^{2+} and Cd^{2+} compared to a system with only either of the aforementioned metals. Second, increased concentrations of Na^{+}, K^{+}, Mg^{2+}, and Ca^{2+} in the aqueous solution also directly compete with the heavy metal ions, resulting in the overall drop in adsorption efficiency (X. J. Wang et al., 2019). In addition, coordination complexes can be formed as the result of the interaction between anions and heavy metal cations, which the resulting precipitates further promote fierce competition for the available binding sites. For example, the precipitation and reduction reactions of Cr^{6+} ion can be promoted by the presence of $SO4^{2-}$, while the Cr^{6+} removal efficiency, as well as the valence transition of Fe, could be reduced by the introduction of HCO^{3-} (Shang et al., 2017). Furthermore, $SO4^{2-}$ negatively affects the adsorption of Cr^{6+} by carbonaceous adsorbent materials due to increased competition and the weaker attraction found in the smaller negative charges of Cl^{-} and NO^{3-} (Xu et al., 2018).

4.2.5. pH level

The pH level, which indicates the degree of H^{+} concentration in the aqueous solution, can significantly affect the ion exchange and electrostatic interaction as part of the overall adsorption process. pH_{PZC} values, which capture the pH value when the zeta potential of adsorbents equals zero, can vary significantly based on the types of carbonaceous materials (Ahmad et al., 2020). In the case of a pH value below the pH_{PZC}, the higher concentration of H^{+} not only allows for the greater ion exchange with the heavy metal ions (X. Yang et al., 2019) but also promotes the protonation of the functional groups that exist on the adsorbent surface (e.g. $–NH_2$, –OH) leading to a more positive charge surface (Ma et al., 2019) (Ma et al., 2018). Consequently, the adsorption of anions (e.g. $HCrO_4-$) improves, and an opposite effect on heavy metal cations is observed due to the electrostatic repulsion (H. Wang et al., 2014). On the other hand, higher pH values above pH_{PZC} facilitate the return of the negative charges to the functional groups (Ma et al., 2019) which have shown a reverse effect on cations and anions compared to the case of lower pH values. Overall, pH_{PZC} should be either more acidic or alkaline depending on the removal of targeted cations or anions in the aqueous solutions, respectively (Ahmad et al., 2020). Furthermore, heavy metal ions can interact with H^{+} (Marbán, 2016) (Li et al., 2017) resulting in different ionic forms that can demonstrate a varying level of affinity to surface functional groups (Shang et al., 2017), this influences the overall adsorption efficiency.

Based on previous studies examining solutions with higher pH values, carboxyl groups have been shown to affect the adsorption of heavy metal ions onto the surface of biomass-derived carbonaceous adsorbents (Takaya et al., 2019) (D.-P. Yang et al., 2019) (Li et al., 2020). The availability of carboxylic acid on the surface of AC facilitates an improved acidic dissociation and formation of chelating agents in forming complexes from the interaction of the heavy metal ions and surface functional groups.

4.2.6. Temperature

Temperature is an important factor that needs to be taken into consideration when assessing the overall adsorption process. At higher temperatures, the lower solution viscosity allows for better dispersion of the adsorbate molecules (i.e., heavy metal ions) all around the surface of the adsorbents leading to greater adsorption capacity. Modification to the solution temperature can potentially alter the adsorption process differently based on whether heat is evolved or absorbed during this process. In an exothermic reaction, elevated temperatures can cause a drop in the adsorption capacity and the opposite is true for an

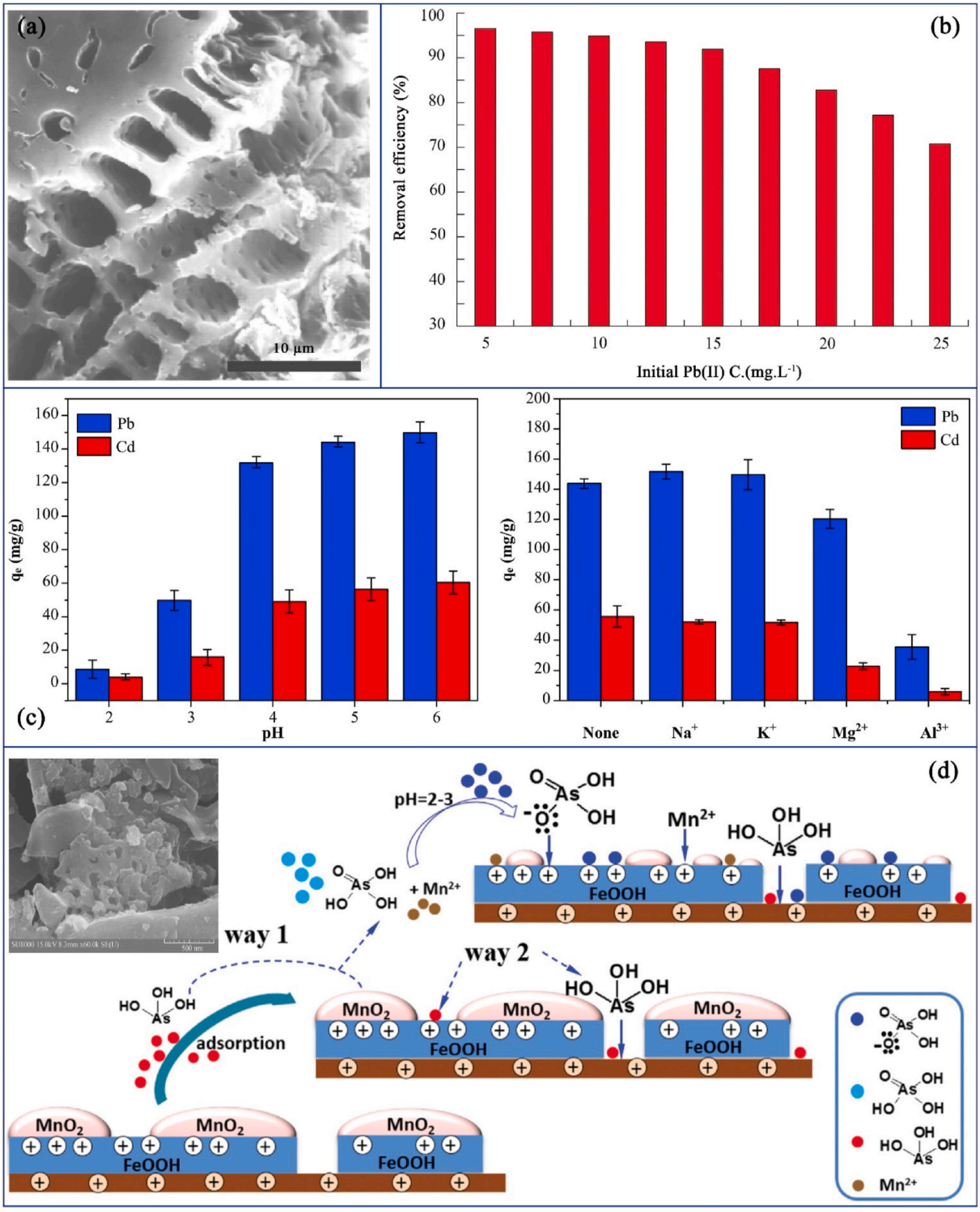


Fig. 5. Characteristics of lignocellulosic biomass-based AC in heavy metal adsorption; (a) – SEM of tropical almond shells-based AC (Largitte et al., 2016) (With permission of Elsevier LN 5153961183433); (b) – The optimal initial ion concentration for adsorption behavior of pistachio wood-derived activated carbon for Pb^{2+} (Sajjadi et al., 2019) (With permission of Elsevier LN 5153961454482); (c) – Effects of pH and coexisting ions on adsorption capacity of $MnFe_2O_4$-supported AC for Pb^{2+} and Cd^{2+} ions (Zhang et al., 2021) (With permission of Elsevier LN 5153970068115); (d) - SEM and adsorption mechanism of FeOOH/MnO_2- modified straw-based AC for As^{3+} (Xiong et al., 2017) (With permission of Elsevier LN 5153970187559).

endothermic reaction. This can cause the higher instability of metal ions from the binding sites on the adsorbent surface. Hence, a continued increase in the solution temperature results in a smaller number of metal ions that can be stably attached to AC. Furthermore, a weaker attraction in the electrostatic interaction between the adsorbent and ions has been observed under high-temperature conditions in an exothermic adsorption process (Dubey et al., 2016). In addition, it is expected that the more active ionic mobility leads to a higher frequency of interaction between the metal ions and the binding sites on the adsorbent surface (Nassar, 2010).

5. Heavy metal adsorption behavior of AC

Due to its inherent toxicity and bio-magnification, heavy metals and metalloids are known pollutants that can contaminate water sources and accumulate throughout the entire food chain. Heavy metal poisoning can impair the normal functions of the central nervous system, cause damage to internal organs and lead to serious long-term illnesses (Burakov et al., 2018) (Hoang and Pham, 2018). Recent studies have demonstrated the cost-effectiveness of AC application in the treatment of heavy-metal contaminated water (Burakov et al., 2018). Due to its relatively small size and possession of electric charge, the interaction of heavy metal ions and the surface of the AC can facilitate the adsorption process via electrostatic attraction (X. Yang et al., 2019). Particularly, Yusuff (2019) has highlighted the special focus on AC application in the removal of several of the following heavy metals, including Cd^{2+}, Pb^{2+}, Cu^{2+}, $Ni^{2+,}$ and Cr^{6+}, given the high levels of toxicity and the value-added benefits from the recovered ions of these heavy metals.

Lead (Pb) has a wide range of industrial and commercial applications, particularly in the manufacturing of pipes, plating of hydraulic accumulators, and additives in fuels and paints (Afroze et al., 2020). The use of lead piping can increase the risk of lead exposure in drinking water as there has been a reported incidence of lead concentration measured up to 2 mg/l found in drinking water supplied by lead service pipes. Thus, it is critical to effectively eliminate the presence of such a highly toxic contaminant from the water supply. In a report, the AC produced from tamarin wood with $ZnCl_2$ as the activating agent has demonstrated a maximum surface area of 1322 m^2/g, increasing the adsorption capacity of Pb^{2+} (González-García, 2018). On the other hand, activation carbon synthesized from tropical almond shells using a combination of CO_2 and steam-assisted activation has attained one of the highest adsorption capacities of 112 mg/g at pH = 6 (Largitte et al., 2016). This could be as-prepared AC possessed high surface areas (≈1000 m^2/g) and high micropore volumes (≈0.40 cm^3/g) (Fig. 5a) (Largitte et al., 2016). Also, approximately 100% and 99.8% removal efficiency have been indicated in the application of AC produced from watermelon peel and oil palm shell, respectively (Min et al., 2017). In a recent study, Sajjadi et al. (2019) have used two consecutive chemical activation processes with NH_4NO_3 and NaOH to prepare activated carbon from pistachio wood. After that, they have evaluated the effects of pH, initial ion concentration, and contact time on the adsorption capacity of Pb^{2+} ion. As a result, they found that as-fabricated pistachio wood-based AC could have a relatively high adsorption capacity, around 190.2 mg/g when initial ion concentration was 5 mg/l, pH was 6–6.5, and contact time was 25 min (Fig. 5b) (Sajjadi et al., 2019). One study has reported the use of rubber wood-based AC in the efficient removal of Pb^{2+} ions and Pb^{2+}-citric acid complex from the aqueous solution (Sreejalekshmi et al., 2009). The underlying adsorption mechanism was tested against different solution pH values and duration. The highest adsorption efficiency was obtained for a pH of 5 for both types of pollutants. The researchers also confirmed the important role of several parameters, including the solution pH level, pH_{ZPC} of the adsorbent, and metal species concentration, on the overall adsorption process (Sreejalekshmi et al., 2009).

As a highly toxic heavy metal, Cadmium (Cd) is another serious water contaminant (Wan Ibrahim et al., 2019). Only permitted at very low concentrations of 5–10 ppm in water, cadmium found at levels above this threshold can pose risks harming aquatic ecosystems and different species existing in these environments (Wang et al., 2010). The release of Cd can originate from the improper disposal of electric batteries, Cd plating equipment, and Cd-rich fertilizers, as well as the discharges from their industrial productions (Burakov et al., 2018). In a study by Min et al. (2017), the author utilized oil palm shell-derived AC in the Cd-contaminated water and obtained a high adsorption efficiency of 99.5%. In another instance, Ahmed (2016b) utilized AC produced from date pits via a chemical activation process. The result showed the adsorption capacity for the above application within the range of 118.1–127.0 mg/g for pH of around 6 and temperature between 25 °C and 30 °C.

Recent attempts at synthesizing different types of ACs have shown positive results in terms of the satisfactory level of adsorption capacity. In their study, Asuquo et al. (2017) have found the adsorption capacity of a market-grade granular AC in removing Cd^{2+} and Pb^{2+} was 17.23 and 16.84 mg/g, respectively. Besides, there are many other types of biowaste-derived ACs with higher adsorption capacity. One of them, in particular, was the AC made from radical press cake as by-products of oil refining activities, which demonstrates the highest adsorption capacity in treating Cd^{2+} and Pb^{2+}. Given the fact that multiple heavy metal contaminants are often found in industrial effluents, it is critical to assess the adsorption capacity and potential effectiveness in multi-metal ion systems. For example, Fatehi et al. (2017) revealed a 27% drop in the adsorption capacity of the AC for Cr^{6+} upon the introduction of Pb^{2+}. The increased competition between similar positively charge Cr and Pb ions for the limited number of available binding sites on the adsorbent surface. Furthermore, the large-size hydrated ions generated from Cr ions were also observed to have a challenging time being adsorbed onto ACs resulting in a lower adsorption efficiency compared to Pb ions in a bi-metallic aqueous solution. In a separate study, He et al. (2017) examined the potential inter-species interaction on the potential removal performance of AC toward Pb, Cd, and tetracycline (TC) using AC produced from vermin compost without activation. In comparison to single-metal solutions, the adsorption of TC is observed to occur under different interaction mechanisms. On the other hand, higher adsorption of Pb is detected with the simultaneous decrease in adsorption of Cd, which is caused by the production of Pb-carbonate in these multi-metallic aqueous solutions. In a recent study, Zhang et al. (2021) have synthesized a novel AC from rape straw with the support of $MnFe_2O_4$ aiming to treat Pb^{2+} and Cd^{2+}-polluted water. They have assessed the effects of pH and coexisting ions on the removal capacity of Pb^{2+} and Cd^{2+}. They found that the largest adsorption capacity of Pb^{2+} and Cd^{2+} was 253.2 mg/g and 73.3 mg/g, respectively (Fig. 5c-right). It could be seen that, at lower pH of 2.6, the surface of $MnFe_2O_4$-supported AC was negatively charged, increasing the adsorption capacity because of the increase in electrostatic attraction. In the case of the presence of other ions, the combination of high-valent ions with the functional groups of $MnFe_2O_4$-supported AC resulted in occupying the active adsorption sites, reducing the adsorption capacity for Pb^{2+} and Cd^{2+} (Fig. 5c-left) (Zhang et al., 2021).

In general, the adsorption efficiency of the carbonaceous adsorbent in removing the various metal ions was noted, it was found to depend significantly on pH level. For a solution with pH value of 2, the reported low adsorption rates of Pb^{2+} and Cd^{2+} ions could be due to the increased competition among several positively charged, fast-moving, low molecular weight ions (Na^+, H^+, Ca^{2+}, Mg^{2+}), and the heavy metal ions for the available negatively charged binding sites on the AC surface. The highly acidic adsorbate-included solution possesses a high concentration of positively charged hydrogen ions. These free-moving H^+ ions were attracted to the negatively charged binding sites and precluded the similarly charged metal ions from being attached to the surface of the AC adsorbent. An increase of solution pH from 2 to 5 resulted in an enhancement of adsorption efficiency up to 90–95%. Further increase in the solution pH value (pH ≥ 8.0) has been shown to facilitate additional

adsorption of heavy metal ions beyond physical adsorption but also using precipitation and formation of metallic salts from the interaction between the metal and OH^- ions. Therefore, the optimal pH value above 5 has been indicated as more optimal for the removal of Cd^{2+} and Pb^{2+} ions. However, the adsorption of As^{3+} has exhibited different behavior compared to that observed from the removal of Cd^{2+} and Pb^{2+}. Particularly, the effective adsorption of As^{3+} achieved by oak wood-derived AC was performed under a pH $\leq$ 2.0 aqueous solution (Malik, 2004). The study also confirmed the insignificant removal effect of other types of pine and oak-based AC in the treatment of As^{3+} contaminated solution. The study confirmed that a pH of 3.5 was the optimal level for the highest adsorption efficiency of wood-based AC toward the removal of As^{3+} (Malik, 2004). However, Budinova et al. (2009) have indicated that the optimal pH value for the highest adsorption efficiency for As^{3+} using bean pods waste-based AC was 7, while Hashim et al. indicated that the optimal pH for adsorbing As^{5+} was 2 (Hashim et al., 2019). In another study, Xiong et al. (2017) have modified the surface of straw-originated AC by using FeOOH/MnO_2 aiming to increase the surface area. As a result, modified AC was found to possess a large surface of 1360.99 m^2/g (Fig. 5d). Moreover, the conversion of As^{3+} into As^{5+} through the presence of MnO_2 on the pore structure of straw-derived AC could be considered as the main adsorption mechanism of As on the surface of FeOOH/MnO_2-supported AC (Fig. 5d). Indeed, around 90% of As^{3+} was oxidized to As^{5+} in the adsorption process and they were trapped on the surface of the adsorbent through the electrostatic interaction resulting in the high adsorption capacity of 75.82 mg/g for As^{3+} at pH = 3 (Xiong et al., 2017).

The adsorption process of Cr^{6+} from the water-based solution by the carbonaceous adsorbent was observed to follow the pseudo-second-order kinetic model (Villabona-Ortíz et al., 2020). In a study of Doke et al. (Doke and Khan, 2017), the authors also examined the adsorption mechanism and capacity in the removal of Cr^{6+} by using wood apple shell-based AC, in which they have used H_2SO_4 to activate wood apple shell to obtain AC with a large surface area of 1898 m^2/g. Resultantly, the adsorption capacity for Cr^{6+} was 151.51 mg/g at pH = 1.8, as well as the removal efficiency of Cr^{6+} was larger than 95%. In addition, they found that pseudo-second-order chemisorption was the adsorption mechanism of Cr^{6+} onto as-prepared AC, followed by film-diffusion mechanism and intra-particle pore-diffusion mechanism. In a different study, Álvarez et al. (2007) formulated the AC adsorbent from an acidic and basic medium to be used in treating and removing Cr^{6+} from both industrial effluents and lab-tested wastewater. Within the synthesis process, Scandinavian pinewood was used as the main biomass feedstock for the initial carbonization, which was conducted at temperatures between 450 °C and 650 °C. The introduction of several acidic ($AlCl_3$, HCl, H_3PO_4, and H_2SO_4) and basic (NaOH) agents were responsible for the subsequent activation process. The assessment of the resulting ACs revealed that the use of H_3PO_4 as the activating agent had led to a high surface area and adsorption efficiency observed in the AC. Furthermore, the particular variety also demonstrated the ability to achieve a satisfactory level of Cr^{6+} removal in a relatively short amount of time before reaching equilibrium. Alternatively, NaOH was the least effective (i.e., low adsorption, long equilibrium time) among the tested agents. NaOH-activated active carbon demonstrated an underwhelming 19% adsorption efficiency in the treatment of Cr^{6+} as opposed to 95% efficiency achieved by H_3PO_4 after three repeated adsorption cycles. In their study, Enniya et al. (2018) attempted to measure the potential adsorption efficiency of apple peels-originated AC for the extraction of Cr^{6+} ions. The authors observed a strong influence the equilibrium pH had on the adsorption efficiency. As a result, they found that the highest adsorption capacity was 36.01 mg/g with pH = 2. In another case study, Sathish et al. (2015) applied ACs produced from mangrove leaves in removing Cr^{6+} from the polluted water. A strong correlation between the overall adsorption capacity of the AC was observed between the following parameters, such as solution pH, adsorbent concentration, adsorbate concentration, and size of the metal ion. Through examining Acacia mangium wood-based AC, Danish et al. (2012) confirmed the effectiveness of the carbonaceous adsorbent in removing Cr^{6+} was directly influenced by the pH value of the aqueous solution. A pH of 2 was indicated as the optimal level for maximum Cr^{6+} removal. Particularly, the authors confirmed that the multi-layer adsorption model (Freundlich isotherm) was sufficient to describe the nature of the adsorption process of Cr^{6+} by the Acacia mangium wood-based AC. Furthermore, rubber wood-derived AC was used in another experiment for Cr^{6+} batch removal (Li et al., 2019). In this example, the adsorption efficiency was driven mainly by the solution pH level, and especially at the low pH of around 2. More interestingly, Ramirez et al. (2020) have found that the formation of complexation, electrostatic interactions, and the reduction reaction of Cr^{6+} to Cr^{3+} were the main mechanisms of adsorbing Cr^{6+} into AC. Multiple studies examining the potential adsorption capacity for a wide range of lignocellulosic biomass in the removal treatment of Zn, Cu, and Hg are available in the literature. The use of corncobs-based AC to adsorb Ni from water has been studied by Banu (2006). The author recorded the adsorption efficiency of 72% and 82% for Zn and Ni, respectively. In another study, Kanawade et al. (Kanawade and Gaikwad, 2011) obtained high adsorption efficiency up to 98% and 91% when using cork powder-based AC in treating synthetic and actual industrial discharges. An innovative application of waste by-products from tea processing was introduced by Thakur et al. (Thakur and Parmar, 2013) in their study on Zn removal from water. A 90% adsorption efficiency was confirmed by the authors in the above study provided the following optimal conditions are maintained, including a metal concentration of 20 mg/l, 2 h of contact duration, pH value of 5, and adsorbent dosage of 0.5 g/l. For various metalloids, Krishnani (KRISHNANI et al., 2008) observed the following highest adsorption capacities of rice husk-based AC in the removal treatment of Zn (0.124 mg/g), Cd (0.149 mg/g), Co (0.162 mg/g), Cu (0.172 mg/g), Ni (0.094 mg/g), Cr (1.0 mg/g), Pb (0.28 mg/g), Hg (0.18 mg/g), and Mn (0.151 mg/g). The authors pointed out that the application of Langmuir isotherm is the best in describing the equilibrium data for the above adsorption process. In their study, Khan et al. (Nasiruddin Khan and Farooq Wahab, 2007) utilized sulphuric acid-treated corncobs as the primary adsorbent for the removal of Cu^{2+}. The authors obtained an adsorption efficiency of 31.45 mg/l given the pH level was maintained at 4.5 and the Langmuir isotherm model was applied. Utilizing wood sawdust in their study, Kalavathy et al. (Kalavathy and Miranda, 2010) applied different modification treatments to the biomass-derived AC including the injection of the content with NaOH and H_3PO_4. Compared with unmodified raw rubber wood sawdust, the modified adsorbent demonstrated an improvement in the adsorption efficiency, particularly from 53% to 68%. In their study, the synthesis of AC from poplar wood sawdust was further subjected to sulphuric acid treatment (Acar and Eren, 2006). The highest Cu^{2+} adsorption efficiency was achieved for the modified and raw poplar wood sawdust under the optimal pH level of 5.0 and 4.0 in which the removal rate was 92.38% and 47.05%, respectively. A correlation between the adsorption data and the zeta potential of the adsorbent surface was performed. As a result, it could be observed that a general positive correlation existed between the zeta potential and the adsorption efficiency. Higher zeta potential means higher adsorption efficiency and vice versa. For a pH level of 5.0, the reported zeta potential was −74.5 mV for the modified AC compared to −48.4 mV for the raw untreated poplar wood sawdust (Acar and Eren, 2006). For Cu^{2+} adsorption efficiency, Sciban et al. (SCIBAN et al., 2006) performed a synthesis of an adsorbent material via a chemically activated process using fir sawdust and poplar wood sawdust with the help of Na_2CO_3 and NaOH as the main activating agents. The NaOH-treated fir sawdust resulted in higher adsorption capacity (12.70 mg g/l) compared to the treated poplar sawdust (6.92 mg g/l). The use of soybean hulls and sugarcane bagasse for AC preparation was explored by Patil et al. (2012) in the removal of Zn and Cu from solutions. The authors confirmed the relative effectiveness of using acid-treated soybean hulls and sugarcane bagasse in removing Zn and Cu ions from the

aqueous solutions. Examining the research conducted by Aguayo--Villarreal et al. (2017), one can learn more about the significant role of chemical activation on the adsorption behavior and properties of carbonaceous adsorbent materials. The study also revealed the effect of competition among the different metal ions in a binary system. The properties of the ACs (i.e., BET specific surface area, pore size, and elemental makeup) depend on the chemical reagent used in the synthesis process. Among the above-mentioned reagents, KCl and NaCl showed better adsorption capacity than the untreated AC samples. It could be explained by the enhancement of surface area and increased availability of oxygenated functional groups found on the AC surface. Among the tested heavy metal species, the study also confirmed the ranking based on the AC's affinity toward these metal ions in a decreasing order of Cu > Zn > Ni > Cd. Particularly, the study also revealed the role of the ion exchange mechanism in the adsorption process that could be observed based on the release of calcium from ACs during the adsorption process of Cu and Zn (Aguayo-Villarreal et al., 2017).

Concerning the removal of Hg^{2+} from aqueous solutions, studies have explored the potential application of eucalyptus wood-based ACs and their sulphuric acid-treated alternatives subjected to varying pH and temperature conditions (Silva et al., 2010). Among the different pH values of 3.0, 7.0, and 10.0, the chemically modified AC yielded a higher adsorption efficiency of Hg^{2+} at pH 3.0. On the other hand, the temperature did not have any significant effect on the adsorption behavior of the H_2SO_4-modified AC. Particularly, the difference in the net charge of the modified AC adsorbent and the Hg^{2+} ions were adjudged to be mainly responsible for the observed reactions. In the case of chemically modified AC, because the pH_{ZPC} was 6.0, the formation of a net positive charge on the adsorbent surface was expected when subjected to the solution pH of 3.0 (Silva et al., 2010). Under this condition, the primary Hg^{2+} form was $(HgCl_2)$ $(HgCl_3)^-$. Hence, the attraction between the negatively charged mercury ions and the positively charged adsorbent surface of acid-treated AC produced from Eucalyptus wood was driven mainly by the electrostatic force. The overall adsorption efficiency was measured at close to 95% (Silva et al., 2010). As reported by Sajjadi et al. (2018), AC produced from pistachio wood with NH_4NO_3 as the chemical activating agent has demonstrated a high surface area of 1448 m^2/g and yielded a high adsorption capacity of 201.095 mg/g at pH = 6 after 30 min of adsorption (Fig. 6a). In a separate study, B. Vulgaris

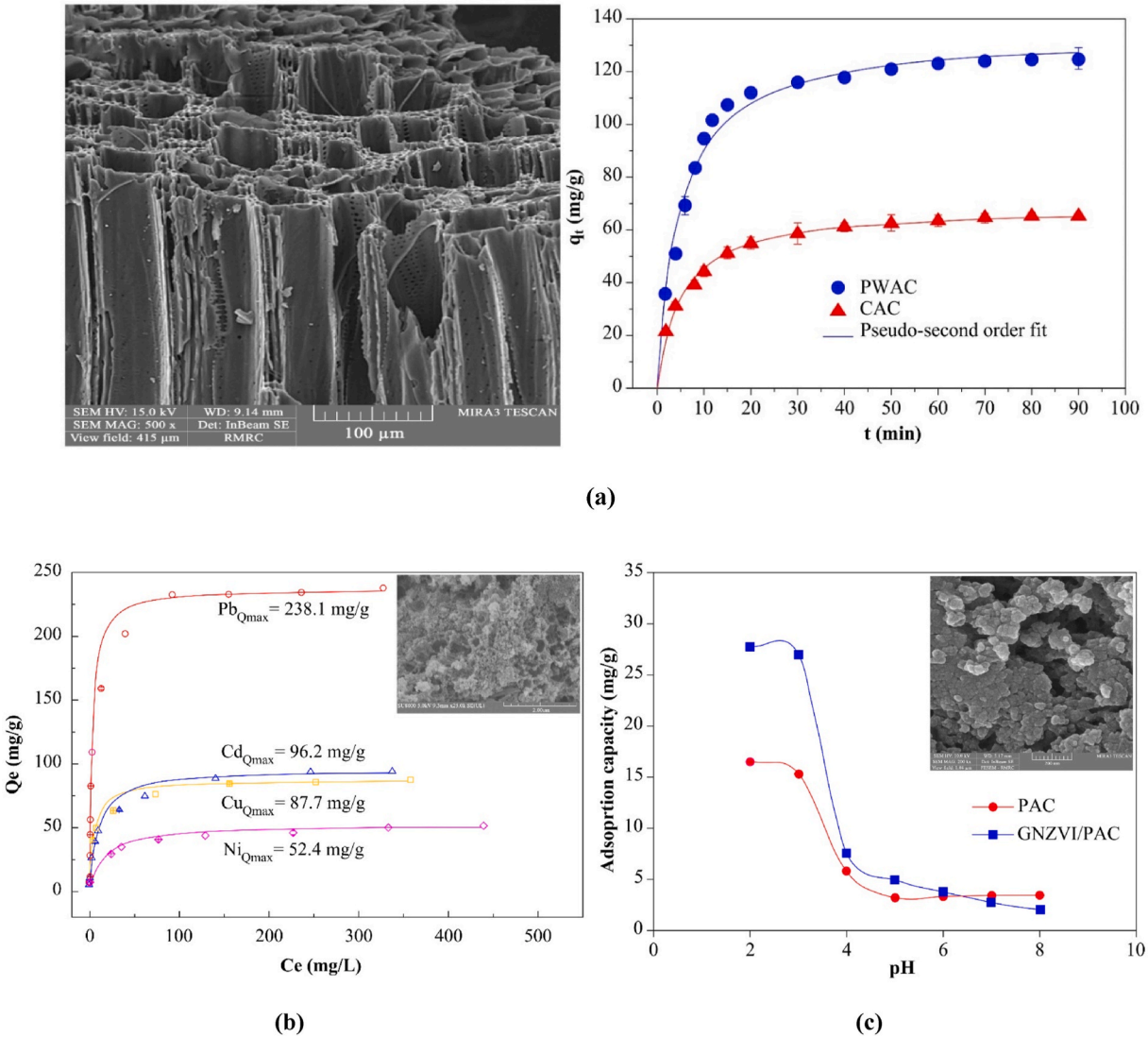


Fig. 6. (a) – SEM and adsorption capacity for Hg^{2+} versus the adsorption time of pistachio wood wastes-originated AC (Sajjadi et al., 2018) (With permission of Elsevier LN 5153970451392); (b) – SEM of modified AC and adsorption capacity for Ni^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} of thiol-functionalized AC (J. Li et al., 2018) (With permission of Elsevier LN 5153970560968); (c) – SEM and adsorption capacity for Cr^{2+} of zero-valent iron nanoparticles-supported AC (Khosravi et al., 2018) (With permission of Elsevier LN 5153970710192).

striata-derived AC has shown a high adsorption capacity of 248.05 mg/g for Hg given a lower solution pH of 3 (González-García, 2018). More importantly, Ambrosy et al. (2020) have found the significant contribution of dissociation energy to the activation energy of Hg adsorption, in which the reaction could take place on the surface of AC after the dissociation process to create the products. It could be assumed that covalent bonds with Hg atom could be formed, in which a bond could be produced with carbon on the surface.

The fact shows that the factors driving the competing behavior of two or more ions depend on the chemistry of the AC surface and the types of metal ions present in the binary system. Nonetheless, a significant challenge remains in identifying the appropriate and suitable AC to be used in a binary or multi-metallic system given that no reliable theories have been proposed to sufficiently capturing the competing relationship among the various metal ions in the same system (Sigdel et al., 2017). Hence, it is necessary to leverage the effectiveness of modified AC derived from plant-based biomass residues in tackling the persistence issue surrounding the presence of heavy metal contaminants in various water sources. Indeed, one can potentially alter the adsorption efficiency of a carbon-based adsorbent material by performing necessary modifications to its inherent properties (Wang et al., 2020). For example, modified AC can be obtained by attaching various functional groups onto its surfaces, such as amino, sulfur, and other functional groups (Liu et al., 2015), or compounding the AC with other inorganic materials. Among the available techniques that can be implemented to promote the formation of functional group species, amino-based, and sulfur-based functionalization (such as S═O or C–S) are commonly utilized and known to effectively attach functional groups containing either nitrogen or sulfur onto the surface of the AC, respectively. Some other functionalization methods also allow for the modification or introduction of various functional groups onto the surface of the carbonaceous adsorbent materials (X. Yang et al., 2019). Faheem et al. (2018) relied on a chemical impregnation method to attach the amino group onto the surface of a corncob-based adsorbent. Results obtained from the above experiment indicated the highest adsorption capacity of 97.6% in the treatment of Hg^{2+}. Besides, the mechanisms supporting the interaction between functional groups (such as $–NH_2$, NH– , – OH, –COOH) and Hg^{2+} ion were recorded as electrostatic attraction, surface complexation, and ion exchange, respectively. Saleh et al. (2017) also detected possible Hg^{2+} interaction with C═O and $–NH_2$ within the adsorption process carried out using polyethyleneimine-functionalized AC. In their study, Li et al. (J. Li et al., 2018) reported on the adsorption performance of thiol-functionalized AC in the removal of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Ni^{2+}. The synthesis process began with a coal-mixed sewage sludge preparation that was then followed by HNO_3 oxidation. Next, the as-oxidized AC was combined with N-dimethylformamide before it could be heated up together with $NaHSO_4{\cdot}H_2O$ and mercaptoacetic acid for a specified amount of time. Lastly, the AC was subjected to $Na_2S{\cdot}9H_2O$ and 95% ethanol solution before being washed with deionized water and dried to produce SH-AC. It was reported that the surface of the modified SH-AC was much more porous than unmodified AC and raw materials. Compared to the unmodified AC, the modified SH-AC demonstrated a superior adsorption capacity for Ni^{2+}, Cu^{2+}, Cd^{2+}, and Pb^{2+} (Fig. 6b) (J. Li et al., 2018). The authors indicated that complex adsorption made up the primary mechanism in addition to the Cu^{2+} reduction reactions. Achieved results have demonstrated that functionalized modification performed by grafting various functional groups onto the surface of the adsorbent has yielded significant improvement in terms of adsorption efficiency for certain ions and other processes involved in the adsorption process (Faheem et al., 2018).

Comparing the results obtained from the experiments performed between powdered AC (PAC), and zero-valent iron nanoparticles (nZVI)/AC to other AC precursors, Khosravi et al. (2018) observed that the highest adsorption efficiency for Cr^{2+} (53.48 mg/g) was achieved by nZVI/AC. This result was superior to that (18.18 mg/g) obtained by PAC although PAC has a larger specific surface area (Fig. 6c). Moreover, other adsorbents also failed to attain an adsorption capacity above 50 mg/g in the treatment of Cr-contaminated water-based solutions. The authors inferred that the increased loading of zero-valent Fe particles led to the modification of functional groups and attraction between the metal ions and the adsorbent surface. Hence, the role of nanoparticles can be ascertained to positively influence the extraction of chromium from aqueous solutions (Khosravi et al., 2018). Similarly, a different study by Sahu et al. (2017) has demonstrated better performance in the application of Fe_3O_4/CSAC than CSAC alone for the removal treatment of As^{5+}/As^{3+} in water. Noteworthy, the use of either nano single oxides or bimetallic oxides, containing MnO_2, MgO, and FeO_x, is effective in obtaining carbonaceous composites (Li et al., 2017). Compared to unmodified AC, the modified alternative demonstrated as much as three times the adsorption capacity of Cd^{2+} and Cu^{2+}, which were measured at 101.0 mg/g and 64.9 mg/g in this experiment, respectively. Low adsorption capacities for Cr (<30 mg/g) were obtained from the application of physically AC produced from Fe-supported walnut shells (Derdour et al., 2018) and Ceiba pentandra hulls AC (González-García, 2018). On the other hand, much higher adsorption capacities of 120.5 mg/g for chemically-activated date pits-based carbon (Ahmed, 2016b), and 85.47 mg/g for chestnut oak shells-based AC (Niazi et al., 2018) were reported. Hence, it can be suggested that chemical activation is the preferred mechanism in the adsorption of Cr. As demonstrated by Min et al. (2017), only chemically-activated watermelon peel AC shown to yield high adsorption capacity against iron and copper, i.e., 91% and 99% respectively. The complexation reactions that took place between the divalent metal ions, namely Cd^{2+} and Cu^{2+} with either –COOH, Fe-MnO_x, or –OH provided the primary mechanism. Besides, the cation-π bounding also contributed positively toward the overall adsorption process. Using a carbon base in providing structural support for inorganic substances has been considered an effective method in pre-application modifications (Shang et al., 2017). Nevertheless, it would be nearly impossible to avoid the counter-productive agglomeration of zero-valent metals and other forms of non-magnetic metal compounds (C. Wang et al., 2014) which presented an opportunity for continued studies on the subject. Table 5 summarizes the adsorption efficiency of several active carbons derived from different types of lignocellulosic biomass.

6. Challenges and perspective

Among currently available treatment methods, ACs stand out for their superior adsorption capability and great overall cost-effectiveness in removing major contaminants in water. Several potential applications of ACs have been tested and proven in laboratory studies. Nevertheless, there continues to be a pressing demand for further research on the potential industry-scale production and commercial applications of AC. One of the potential drawbacks in using ACs as adsorbents is when the contaminants are not susceptible to the carbon atoms' attractive force, including elements like sodium, nitrate, fluoride as well as viral and bacterial pathogens. Future research could look into potential enhancement or modification processes to increase the effectiveness of AC toward these exceptional pollutants. Once reaching the capacity, the contaminated ACs has outlasted their service life and should be replaced or reactivated. Moreover, the regeneration of AC should be further investigated to reduce the secondary pollution and costs of production and operation. Hence, the potential for long-term applications of AC should be thoroughly assessed to ascertain its effectiveness as a wastewater treatment strategy.

Production cost is an important factor that is necessary to include as part of the overall assessment of AC. Among the potential raw biomass sources, wood biomass presents an opportunity to be considered for AC production, which prompts the need for an additional cost evaluation study. Generally, AC with a large surface area and high density of mesopores is much more desirable as an adsorbent as long as it has a reasonable manufacturing cost. In terms of industry-scale production,

Table 5
The adsorption capacity of lignocellulosic biomass waste-derived AC for various heavy metal ions.

Biomass sources	Heavy metal types	pH	Temperature, °C	Adsorption time, min	Adsorption capacity Q_m, mg/g	Reference
Ceiba pentandra hulls	Cr	6	–	–	25.5	(González-García, 2018)
Date pits		1	25	180	120.5	Ahmed, (2016b)
Camellia oleifera		2	20	–	165	Min et al., (2017)
Walnut shell		2	–	–	29.67	Derdour et al., (2018)
Chestnut oak shells		2	20	–	85.47	Niazi et al., (2018)
Peach stones		5.6	30	360	13.4	Khemmari and Benrachedi, (2020)
Peganum harmala seed		2	–	–	53.48	Khosravi et al., (2018)
Sugarcane bagasse		6.7	46	60	11.3621	Karri et al., (2020)
Elm tree		7	80	60	113.63	Kharrazi et al., (2020)
Bermuda grass		2	25	–	403.23	Tu et al., (2020)
Bamboo		9	27	1440	38	(D. H. Huang et al., 2019)
Phoenix tree leaves		2	30	–	55	Liang et al., (2019)
Wheat straw		5.6	25	1440	112.5	Zhang et al., (2019)
Coconut shell		5.6	25	–	125.22	Wu et al., (2020)
Rice straw		3.5	25	–	117.1	Qian et al. (2019a)
Rice straw		3.5	25	1440	111.9	Qian et al. (2019b)
Elm tree	Pb	7	80	60	232.56	Kharrazi et al., (2020)
Date pits		6	30	30	101.35	Krishnamoorthy et al., (2019)
Potato peels		6	25	–	171	Kyzas et al., (2019)
Eichhornia crassipes plants		6	30	30	117.99	Lin et al., (2020)
Cornstalk		4.5	25	300	99.95	(S. J. Fan et al., 2020)
Corn Stalk		5	25	120	99.82	Du et al., (2020)
Corn Stalk		6	25	150	49.7	Liu et al., (2019)
Rice straw		5	25	1440	61.5	(J. S. Fan et al., 2020)
Eichhornia crassipes plants	Cu	6	30	30	26.24	Lin et al., (2020)
Date pits		–	18	10	0.003	Ahmed, (2016b)
Papaya seed		6	–	–	212	Min et al., (2017)
Grape bagasse		5	45	180	43.47	Prabu et al., (2016)
Prawn shell		5	20	–	280	Guo et al., (2019)
Banana Peel		6	25	120	75.9	Oladipo et al., (2019)
Rice Husk		6	25	60	265	Cuong et al., (2019)
Cow bone		–	25	–	287.58	Xiao et al., (2020)
Undaria pinnatifida roots		5.8	25	720	99.01	Jung et al., (2019)
Grapefruit peel		6	30	–	80.6	(W. Z. Zhang et al., 2020)
Date pits	Al	4	22	24	5.831	Ahmed, (2016b)
E. camaldulensis dehn	Zn	5	–	–	57.85	(González-García, 2018)
Tamarind wood		10	–	–	43.85	
Tropical Almond shells		5	30	–	114.8	Largitte et al., (2016)
Guava seeds		5	40	–	92.9	
Dinde stones		5	30	–	53.1	
Coconut shell		5	30	–	3.02	Landin-Sandoval et al., (2020)
Corn Stalks		7	25	240	109.7	Song et al., (2020)
Corn Straw	Cd	6	25	360	48.3	Khan et al., (2020)
Corn straw		6	25	1440	175.44	Tao et al., (2019)
Prawn shell		5	20	–	256	Guo et al., (2019)
Palmae shells		8	25	35	9.87	Egirani et al., (2020)
Date pits		6	25	24	127.0	Ahmed, (2016b)
Aguaje		5	–	–	26.33	Derdour et al., (2018)
Oil Palm Bagasse		6	28	120	17.4	Herrera-Barros et al., (2020)
Pine Tree Residue		6	25	120	85.8	Park et al., (2019)
Rice Husk		7	25	120	102.04	Bai et al., (2020)
Rice husk		8	25	180	81.02	Chen et al., (2019)
Pennisetum sp. straw		5	25	200	95.23	Yin et al., (2020)
P. aureus hull	Hg	7	–	–	23.66	Derdour et al., (2018)
B. vulgaris striata		3	–	–	248.05	
Pistachio wood wastes		6	–	–	201.095	Sajjadi et al., (2018)
Hide waste	Ni	–	–	–	35.17	Kong et al., (2018)
Coconut shell		5	30	–	3.97	Landin-Sandoval et al., (2020)
Z. spina-christi seeds	Mn	4	25	180	172.413	Omri and Benzina, (2012)
Rice straw	Ag	6	25	40	986.5	(J. X. Wang et al., 2019)
Pomelo peel		–	23	1440	137.4	(T. Z. Zhao et al., 2018)
Douglas fir	As	7	25	60	5.49	Navarathna et al., (2019)
Corn Stem		6	25	360	14.9	Lin et al., (2019)
Switchgrass		–	21.5	2880	26.12	Bakshi et al., (2018)
Corn Stalk		4	25	60	1458.5	Yang et al., (2020)

the selection of appropriate woody types of biomass is critical to ensuring the general cost-effectiveness of the synthesis process. Furthermore, additional studies should aim at examining the reusability of AC and the potential strategy to recycle such used materials to improve its economic potential. Nevertheless, there are only a few investigations conducted on this topic.

Among the available literature, studies of AC have thus far focused on a single activation method (i.e., chemical, physical, or integrated physical/chemical). Hence, the lack of comparative studies on the different activation methods included in the production of AC should be sufficiently addressed. Furthermore, most current and past investigations on AC have focused on the adsorption capacity of a single type of heavy metal. Given that there is a wide range of heavy metal pollutants existing in a potentially contaminated water source, future

studies should also pay attention to the behavior of AC in a multi-metal-containing system given that there might be cross-species interaction among the different metal ions. Additionally, experiments have only been conducted using AC as the sole adsorbent in the treatment of heavy-metal contaminated water. The potential application of more than one type of adsorbent presents another avenue of research. Besides, available optimization studies on the conversion process of AC have only focused on one parameter at a time, which can be troublesome and time-consuming due to the high number of reiterations. These current technical challenges can be potentially resolved with the help of response surface methodology that its application can deliver the multi-variable optimal conditions when subjecting the AC to various heavy metal ions in the aqueous solution.

Up until recently, the bulk of the research on heavy metal removal has only prioritized batch adsorption. Experts have reasons to believe that the rising potential of AC as a highly effective adsorbent will prompt future research on column study and industrial bed type adsorption. The current conditions are prime for the deployment of industrial-scale production and application of ACs produced from various biomass wastes. Last, but not the least, most types of AC research in water pollution treatment have not expanded their scope beyond heavy metals to include other non-conventional pollutants such as non-metallic organic contaminants and/or pesticides. The aforementioned suggestions provide areas of potential research on the current topic that would potentially yield valuable results in contributing toward the current progress in the development of AC. Future studies can consider including a pilot-scale study on the treatment process of industrial wastewater using the specified AC. Although there are still major shortcomings and obstacles remaining in the research, development, and application of AC, future progress is highly warranted given the recent breakthrough in the field. Besides, special attention should be spent on examining the use of biomass waste-based AC as a cost-effective absorbent over other more expensive options in water pollution treatment. Furthermore, utilizing biomass waste as the primary source of feedstock for AC production is considered as a part of the larger waste reduction scheme. Besides, it is necessary to develop a variety of modified AC-based adsorbents with highly effective in removing heavy metal species from aqueous solutions.

7. Conclusions

From the environmental perspective, biomass wastes provide a widely available, and eco-friendly source of feedstock for the production of AC. In terms of affordability, the production of AC from biomass waste presents a cost advantage and potential replacement over other more expensive coal-based AC. This reason provides the incentive to carry out the present work focusing on the potential application of biomass waste-derived AC as adsorbents used in the treatment of heavy metal contaminated water. The synthesis of AC from different types of biomass waste can take several forms, in which chemical activation is generally preferred for shorter preparation time and lower activated temperature. In addition, costs for each method of AC preparation should be further analyzed to have comprehensive assessments of the applicability of each method to synthesize AC from biomass waste. However, to continuously enhance the potential performance and adsorption capacity of AC in removing heavy metals from contaminated sources of water, there should be an improved strategy for identifying the optimal synthesis parameters, such as choice of precursors, carbonization process, and optimal activation conditions.

Overall, this review article has provided important highlights on the present synthesis method of AC derived from biomass waste, adsorption mechanism and capacity for the removal of heavy metals, controllable process parameters, as well as remaining obstacles in the current application of ACs. For AC-based adsorbents, some main mechanisms for removing heavy metals such as surface complexation, ion exchange, and electrostatic interaction were detailed in this paper. Furthermore, pH was concluded to play a vital role in the heavy metal adsorption process. More importantly, the adsorption mechanism and efficiency of AC for each type of heavy metal were thoroughly analyzed. The study also provided new perspectives for future research on this topic. By sufficiently addressing the previously mentioned challenges and shortcomings, there is potential to realize industry-scale production and application of AC in large wastewater treatment operations.

Credit author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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