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Review

Competitive Adsorption of Metal Ions by Lignocellulosic Materials: A Review of Applications, Mechanisms and Influencing Factors

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Abstract: The rapid expansion of industrial and agricultural activities in recent years has significantly contributed to water pollution leading to a decline in water quality and the need for effective treatment and reuse strategies. Metal contamination in water bodies poses severe environmental and health risks, making the development of cost-effective and sustainable remediation methods essential. Among the various treatment approaches, biosorption using biological adsorbents has emerged as a promising alternative due to its low cost and high efficiency. However, while the adsorption mechanisms of single metals are well understood, the competitive interactions between multiple metal ions during the sorption process remain less explored. In this review, we analyze the competitive biosorption of metals in multi-metallic wastewater systems. Key factors influencing metal removal, such as pH, contact time, biosorbent dosage, and initial metal concentration, are discussed, along with the intrinsic properties of biosorbents and metal ions that affect sorption efficiency. Additionally, we highlight recent studies on agroforestry byproducts as effective biosorbents for metal removal, showcasing their potential for sustainable water treatment. Heavy metals pose significant risks even at low concentrations, necessitating robust regulations and advanced treatment technologies; biomass byproducts, as cost-effective biosorbents, can be optimized through pre-treatment, activation, pH and temperature control, and particle size reduction, while effectively managing competitive multi-metal adsorption remains crucial for industrial effluent treatment.

Keywords: wastewater treatment; multi-metallic adsorption process; mechanisms of sorption; main influence factors; lignocellulosic byproducts; biosorbents

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Academic Editor: Marija M. Vukčević

Received: 21 February 2025
Revised: 11 March 2025
Accepted: 14 March 2025
Published: 16 March 2025

Citation: Macena, M.; Pereira, H.; Cruz-Lopes, L.; Grosche, L.; Esteves, B. Competitive Adsorption of Metal Ions by Lignocellulosic Materials: A Review of Applications, Mechanisms and Influencing Factors. *Separations* **2025**, *12*, 70. https://doi.org/10.3390/separations12030070

1. Introduction

Water is a valuable resource that is under pressure in Europe, with only 40% of surface water bodies in good ecological status and 35% in good chemical status [1].

The expansion of industrial and agricultural activities in recent years has contributed to an increase in environmental pollution and is also associated with public health issues, due to the large amount of heavy metals released in the nature by these sectors [2,3]. Some of the pollutants usually found in natural environments are iron (Fe), copper (Cu), zinc (Zn), cadmium (Cd), chromium (Cr), nickel (Ni), lead (Pb), tin (Sn), arsenic (As), and mercury (Hg) that are generated by agricultural, metallurgical, batteries and microelectronics sectors, among other sources [3]. Long exposure to or the ingestion of toxic metals can cause gastric pain, nausea, vomiting, diarrhea, hemorrhage and even cancer [4]. Prevention of these negative effects requires not only the control of metals discharged by the industries but also the removal of their excessive concentration from polluted environments [5].

Water treatment and reuse can become a solution for the scarcity and poor quality of water resources [6]. The most used technologies to remove toxic metals from wastewater include membrane filtration, ion exchange, coagulation/flocculation, chemical precipitation, and carbon adsorption, which are expensive methods [7–10].

Recently, adsorption with biological adsorbents, also named biosorption, has gained attention presenting some advantages such as low cost, ease of operation, and the possibility of reuse and recovery of adsorbent and adsorbate, offering an effective alternative method for treating water and wastewater contaminated with metal ions [11–13]. It is a process based on the use of biomass for the uptake of metal ions or other pollutants through physicochemical reactions or other mechanisms, such as ion exchange, complexation, inorganic microprecipitation, chelation, and hydrolysis [14,15].

Traditional commercial sorbents have high costs, e.g., the widely used activated carbon. Therefore, efforts are underway to reduce sorbent cost by investigating the potential of biomass wastes and byproducts as sustainable biosorbent materials [16]. Promising results have been obtained, allowing for the development of a circular economy strategy where byproducts can be used to treat wastewater [17].

In general, the existing studies explore sorption systems composed of a single metal ion, although this does not represent the real condition of wastewaters or water bodies contaminated with metals. Each metal has an inhibitory effect on the others which plays a significant role in the biosorption process. The effect that individual metals may have on their own removal and on the removal of other metals in the aqueous multi-component system was found to be analytically significant [14]. The competitive interaction between metal ions in sorption as well as the preference of a biosorbent for the adsorbate are determined mainly by their physicochemical properties, such as ionic radius, atomic weight, electronegativity and valence state [18].

This review explores trends of a competitive biosorption method of metals from wastewaters based on published studies about complex systems. It aims to synthesize the mechanisms that can occur in multi-metal adsorption, focusing on aspects of the competitive effect between ions. Also, this review presents some results found on agroforestry byproduct materials that have been successfully evaluated as biosorbents to remove metal ions from water.

2. The Risks of Toxic Metals

Toxic metals such as Cd, Pb, Zn, Ni, Cu, Hg and Cr are very polluting due to their non-biodegradability and perpetuation throughout the food chain [1,5,19,20]. In particular, Cd, Cu, Pb, and Zn are considered carcinogenic and are commonly related to immune system problems [21]. Further effects of toxic metals in humans are mutations, teratogenicity, and congenital disorders, and they can also affect brain development in children [5].

Lead can be described as the oldest known toxic metal. Contact can happen through drinking water, or due to various industrial processes, and even at low concentrations, exposure to this metal can affect multiple clinical functions, such as brain damage and anemia [22,23].

Cadmium, zinc and chromium have high mobility and are harmful even at low levels. These elements are usually found in the effluents of fertilizer and textile industries, electroplating, leather tanning, and pigment manufacturers. Cadmium toxicity can be characterized by anemia, renal and lung deficiency, bone lesions and hypertension. Zinc intoxication can cause loss of appetite, nausea, irritability and muscle stiffness. Chromium can exist under six oxidation states, but the trivalent Cr(III) and hexavalent Cr(VI) are those most found in water and wastewater. Cr is classified as a carcinogenic, mutagenic and teratogenic agent and can cause nausea, diarrhea, dermatitis, kidney and liver damage, and respiratory problems [23,24].

Copper and nickel are among the most found elements in effluents from industrial operations or mining drainage. Cu is linked to cardiovascular and neurological disease, reproductive damage, atherosclerosis, and diabetes [22,23]. Ni is associated with dermatitis, gastrointestinal and respiratory complications, and lung and kidney diseases [25].

The main source of mercury contamination in the environmental is industrial activity [26]. Hg is associated with neurological and renal disturbances, is corrosive to skin and eyes, and can be related to headache, abdominal pain, diarrhea, gum inflammation, loosening of teeth, and loss of appetite [23,27].

Some EU legislations, such as the Water Framework Directive (WFD) or the Industrial Emissions Directive (IED), aim to protect and regulate Europe's water bodies from this kind of industrial emissions preventing environmental pollution and its negative effects on human health [1]. The IED fixed the emission limit of Hg at 0.05 mg/Nm^3, and of Sb, As, Pb, Cr, Co, Cu, Mn and Ni at 0.5 mg/Nm^3.

In conclusion, heavy metals pose severe health and environmental risks, even at low concentrations. Effective regulations, such as the EU's Water Framework and Industrial Emissions Directives, help mitigate pollution, but stricter measures and improved treatment technologies are needed to reduce their impact.

3. Methods for Industrial Wastewater Treatment

Several techniques for removing metals from industrial effluents have been studied. Some of the most commonly used treatments are chemical precipitation, ion exchange, reverse osmosis, membrane separation, flocculation, electrocoagulation, ultrafiltration, and adsorption with activated carbon [28]. Their main advantages and disadvantages are presented in Table 1. Several disadvantages are associated with a reduced efficiency under low concentrations of metals, high use of electrical energy or chemical reagents, generation of sludge or other toxic byproducts that require additional treatments [19,29,30].

Table 1. Positive and negative points of the most used wastewater treatment methods.

Treatment Methods	Positive Points	Negative Points
Membrane filtration	Efficient method with minimal space required [31].	Membrane development with improved thermal stability and performance is still a challenge [31]; large amount of sludge, and very expensive because of the membrane cost [27,28].
Ion exchange	Effective to remove metal ions, high regeneration rates, and can be metal-selective [27,28].	High labor and operational costs, and not suitable for low concentration of metals [27,28].
Coagulation/ flocculation	Low-cost and easy to operate [27,28].	Important amount of sludge, high utilization of chemicals [27,28].
Electrochemical treatment	Easy to operate, high efficiency, and requires simple equipment [31].	High energy costs [31] and maintenance of electrodes [28].
Adsorption	Simple, profitable, easy to operate and environmental-friendly, effective in reducing the concentration of metal ions to very low levels [32].	Extensive use sometimes restricted because of the activated carbons' cost [33]; regeneration requires the use of chemicals [28].
Biosorption	Minimal amount of sludge generation, short time of operation, and possibility of metal recovery [34]; biosorbents are cheaper, available locally and in large quantities, and more sustainable than commercial activated carbons [30,35].	Sometimes, activation is required to enhance the sorption capability of the biosorbent which adds costs. Desorption process requires chemicals [28].

To choose the best treatment method for an effluent, it is necessary to take into account a series of factors, such as the type and concentration of the metals present, the coexistence of other components, the desired metal removal rate, the current environmental standards regarding the discharge of treated wastewater, operating costs, and the amount of sludge or waste generated and its subsequent treatment or disposal [36].

4. Biomass Byproducts with Potential to Be Used as Biosorbents

Biomass waste or byproducts are promising materials for wastewater treatment. The application of these materials aims to achieve the dual objective of solid waste management and wastewater treatment [37]. Usually, these materials are seen as useless and often their potential is ignored. However, research is moving towards developing a closed-loop approach to the valorization of residual materials [32]. The transformation and use of biomass byproducts generated by industrial activities, agricultural exploration and forestry into biosorbents helps in the efficient and productive management of these wastes. It also generates value for these products, previously considered commercially worthless [28].

Agricultural activities and agro-industries generate a large diversity of lignocellulosic byproducts such as straws, husks, leaves, roots, shells, fruit peels and stones, pulps, bagasse, and corn cobs that have been studied as biosorbents [38]. The residues originating from forestry exploitation and industrial wood processing include decayed or non-commercial trees, branches, needles and leaves, stumps and roots, barks, trimmings, wood shavings and sawdust [39]. Many of these residues are frequently deposited in dumps or incinerated, which impacts the environment due to the emission of greenhouse gases.

However, these byproducts can be valued and, among other ways, applied as biosorbents [30]. Biomaterials from plant origin are considered as good biosorbents due to their static binding capacity that occurs through sorption on the cell surface, with intracellular and extracellular accumulation [28]. Therefore, agro-industrial and forestry exploitation activities could be an extensive and consistent source of natural materials with potential to remove metals from contaminated environments. Materials such as tangerine peels [32], olive stones [15], rice husks and sawdust [36], pinecones [9], cork and pine barks [3], tree bark [40], walnut and chestnut shells, pine wood and burnt pine wood [25], banana, orange and potato peel beads [41], *Michelia figo sawdust* [42], *Abies bornmulleriana cones* [43], and *Jatropha curcas leaves* [44] have been successfully tested as biosorbents to uptake toxic metals.

The lignocellulosic wastes are mostly formed by cellulose, hemicelluloses and lignin [38]. Lignin is a key component for the sorption of metals, given the abundance in electron-donor active sites due to its polyhydroxy and polyphenol functional groups, and offers an exceptional frame for the binding of cationic heavy metals [38,45]. The involvement of hemicelluloses and cellulose in the biosorption of Ni and Zn has also been reported [46].

Biosorbents prepared from biomass have abundant functional groups, such as hydroxyl and carboxyl groups [32] that are negatively or partially negatively charged, thereby contributing to cation exchange [24].

Biosorbent materials can be used without any treatment, or they can receive chemical or physical pre-activation to increase the specific surface area or the selectivity of the active sites. Biosorbents are often washed with acids, bases or inorganic salts as a chemical pre-activation. An important difference in basic treatment is the increase in negative charge, which results in greater selectivity for metal cations. Physical pre-treatment of biosorbents can be carried out by mechanical disruption, boiling, heating, autoclaving, freeze-drying or vacuum [28].

To be considered a good biosorbent, the material should possess high surface area, selectivity, sorption capacity and compatibility with the contaminant and the process [25].

Also, the desorption capacity and the biosorbent recovery are of great importance, since it is preferable to use biosorbents capable of undergoing several adsorption–desorption cycles, significantly reducing the operational cost of the process [28].

Overall, biomass byproducts are effective biosorbents for heavy metal removal, turning waste into a valuable resource. Their performance can be enhanced through pre-treatments, and reusability is key to cost-effective wastewater treatment.

5. The Main Factors That Affect the Adsorption Process in Multi-Metal Systems

The removal of a mixture of toxic metals is considered cost-effective. However, in a multivariate experiment, many parameters can limit the removal rate of metal ions, such as the temperature and pH of the medium, the initial metal concentration, the organic and inorganic functional groups present in the sorbent surface, the ion strength and chemical modification [7,11]. High removal efficiencies can be achieved by controlling these parameters [32]. There is a tendency to increase the removal efficiency when increasing pH and biosorbent dosage, simultaneously with a decrease in the initial metal concentration [42].

Understanding the mechanisms that occur in biosorption is very important to understand how the metal binds to the surface of the biosorbent and, consequently, may increase the efficiency of biosorbent materials. In addition, it helps in choosing the most appropriate method for biosorbent regeneration. Generally, the biosorption process is affected by the active sites of the biosorbent and its availability and affinity for the metal [28].

5.1. Adsorption Method and Contact Time

In fixed-bed adsorption, the adsorption of metal ions on the biosorbent surface depends strongly on the effluent flow rate. A slow flow rate offers a longer residence time for mass transfer, allowing metal ions to access more active sites on the adsorbent, and, consequently, a better retention rate while increasing the flow rate reduces the resistance to mass transfer, culminating in a rapid saturation of the active sites [19].

On the other hand, batch experiments are easier to perform and can provide good insight into the biosorbent properties, mechanisms and kinetics of the process. Also, a relation between contact time and the percentage of removal was found [36]. Tests between 5 min and 24 h of contact showed that the percentage of removal increased with contact time before stabilizing and reaching a plateau around 60 min, for single- and multi-metal adsorption [47]. The higher initial rates of sorption were related to the greater availability of active sites on the adsorbent surface, which stabilized with the decrease in unoccupied active sites. Also, the repulsion between the retained and free metals present in solution could explain the stabilization process.

However, batch adsorption is not very common at the industrial scale due to an inability to treat large volumes of effluents. Therefore, the fixed-bed column method is more popular for industrial applications [28].

Overall, while batch experiments offer valuable insights into biosorption kinetics and mechanisms, fixed-bed adsorption—with its optimized flow rates and capacity to handle large effluent volumes—remains the preferred method for industrial applications.

5.2. pH

Metal ions tend to form complexes with inorganic compounds, and the type of complex formed will depend mainly on the pH value [48]. Variations in pH alter the characteristics and availability of metal ions in solution, as well as the chemical state of the functional groups responsible for sorption, since they influence the electrostatic interactions with the solution [25,32].

The optimum pH for the biosorption process depends on the zero-point charge (pHzpc) value of the biosorbent and the target metal ions. The pHzpc represents the pH value at which the surface charge of the biosorbent is equal to zero. For pH < pHzpc, the surface of the biosorbent develops a positive charge and thus repels positively charged metal ions. In opposition, for pH > pHzpc, the surface of the biosorbent acquires a negative charge and thus attracts the positively charged metal ions [28].

Ionic exchange is one of the main factors involved in biosorption of metals, where the most abundant ions, such as H^+ and Ca^{2+}, are displaced by the metal ions [49]. Usually, a high pH value may benefit the adsorption process by the formation of hydroxylated cations, although high pH can also cause a specificity for alkaline metals due to the tendency of metal ions to hydrolyze [48].

Increasing pH from 3 to 5 increased the sorption rate of Cr, Cu, Mn, Co, Ni, Cd, Pb and Zn, which can be explained by the high concentration of H^+ ions at lower pH that occupy most of the active sites in the biosorbent surface [32]. At pH above 4, the functional groups are negatively charged and thus attract positively charged metal ions. While at pH above 5, the formation of hydroxides and phenolic polymerization may occur, which also reduces the sorption rate [32].

A pH range of 4–6 was reported as ideal for most metal ions' adsorption due to the amounts of OH^- ions present in the solution [34,50]. In a study using crab shell to adsorb Zn and Ni ions, both monometallic and bimetallic systems were strongly dependent on pH, with the optimum biosorption occurring at a pH of 6.0 [18]. The same pattern was observed using *Lemna gibba* [46] and *Sargassum ilicifolium* [51], which were used to remove Zn, Ni, and Cu, with optimal pH values of 6.0, 5.0, and 5.0, respectively. Similarly, bush mango and flamboyant biomasses were used to adsorb Cd, Pb, and Ni and achieved best rates at pH 5.0 [52].

With *Jatropha curcas* leaf biomass, the removal was more efficient at pH 6.0 for Cu, at pH 5.0 for Zn, and at pH 2.0 for Cr ions [44]. A similar behavior was observed with the maximum adsorption at pH 2.0 for Cr, 5.0 for Ni and Cd and 6.0 for Zn and Cu ions [36]. At low pH, the sorption increase of Cr^{6+} might be linked to the improved protonation of biosorbent surface which enhances electrostatic attractions. On the other hand, the reduced adsorption observed for other metals is due to electrostatic repulsions between the positively charged biosorbent and the metal ions [36].

In conclusion, pH plays a crucial role in metal biosorption, influencing ion availability and biosorbent surface charge. Optimal adsorption generally occurs at pH 4–6, though specific metals exhibit varying preferences. Understanding these interactions helps optimize biosorption efficiency.

5.3. Temperature

Temperature is directly related to the kinetic energy of the metal ions in solution [36,48]. As temperature increases, the kinetic energy also increases, accelerating the diffusion of adsorbate molecules from the solution to the adsorbent [12]. Diffusion is an endothermic process, and an increase in temperature results in the enlargement of pore size, causing the micropores to widen and deepen, thus creating more surface area for adsorption [12]. Additionally, higher temperatures enhance the diffusion rate of sorbate, promoting its transport within the porous adsorbent.

Temperature variations also influence the equilibrium adsorption capacity due to the increase in active sites, which are generated by the cleavage of internal bonds. For instance, temperature was identified as the key factor influencing the biosorption of Cr(III), Cu(II), and Zn(II) by wine-processing waste sludge (WPWS) in a ternary system [53]. The effect of temperature on biosorption depends on whether the process is endothermic or exothermic.

For endothermic adsorption, increasing the temperature enhances the sorption rate, while for exothermic adsorption, it decreases [34]. The biosorption process has been considered endothermic in many studies, with room temperature being optimal for the process [36,48]. A temperature of 30 °C is reported to be sufficient for the complete removal of lead and nickel [34].

However, very high temperatures can lead to physical damage reducing its adsorption capacity [36,48]. If the temperature is too high, the active biomolecules may degrade, resulting in altered active sites in terms of their structure and pore size in the biosorbent [28].

Overall, temperature plays a key role in biosorption, enhancing diffusion and adsorption at moderate levels. However, excessive heat can degrade biosorbent structure, reducing its effectiveness.

5.4. Initial Concentration of Metal Ions

A change in initial concentration affects the rate of saturation of active sites, as well as the breakthrough time and the length of the adsorption zone in the case of fixed-bed adsorption. A higher influent metal concentration results in faster breakthrough and saturation that may be due to the greater concentration gradient or lower resistance to mass transfer at a higher metal concentration [19].

At low adsorbate concentrations, there is a greater relative number of active sites available on the adsorbent surface for a smaller number of adsorbate ions. As the initial concentration increases for the same adsorbent dose, the relative number of active sites is reduced, which causes a decrease in the percentage of removal of metal ions in solution [48].

In contrary, another study observed that as the initial concentration increased from 10 to 100 ppm, the amount of metal ion uptake from the solution also increased, obtaining higher removal rates at 60 ppm [12]. Thus, it concluded that increasing the competition for the available binding sites enhances removal to a certain level, decreasing afterwards, which might be explained by the increase in electrostatic interactions instead of covalent bonds.

The effect of varying the initial concentration of Cr, Ni, Cu, Cd and Zn from 100 to 500 mg/L was studied using rice husk and saw dust [36]. The percentage of removal decreased with increasing concentration of metal ions. The biosorbents showed higher sorption at the beginning of the process, due to the number of unoccupied sites on their surface, while later, the remaining sites impeded the sorption by repulsive interactions between the solute molecules and bulk phase. Similarly, a study on biosorption of Pb/Cu and Pb/Cd in fixed-bed column using algae *Gelidium* and granulated agar extraction algal waste showed that although lead ions have a higher affinity than copper ions for biosorption on *Gelidium* algae, copper uptake was observed to be higher than lead due to its greater initial concentration [54].

In the case of fixed-bed adsorption, a study showed that the breakthrough times were shorter using a metal concentration of 10 mg/L compared to a concentration of 30 mg/L [19].

Ultimately, initial adsorbate concentration is a key factor in adsorption, as higher concentrations accelerate breakthrough and reduce active site availability, while optimal levels enhance removal efficiency through balanced competitive interactions.

5.5. Biosorbent Dosage

Generally, adsorption increases with increasing biosorbent dosage, since the number of active sites also increases [12,48]. However, in case of very high dosage, the particles tend to agglomerate and the active sites may overlap, which results in a decrease in removal efficiency [28].

A decrease in removal efficiency with adsorbent dosages higher than 300 mg was reported, which may result from aggregation phenomena, causing a decrease in the active surface of the biosorbent. Furthermore, when the batch method is used, a large mass of biosorbent may hinder the agitation of the mixture, penalizing retention rates [32]. Another study suggests that increasing the adsorbent dosage from 300 to 500 mg also increased the removal efficiency [34], which may be a consequence of the direct increase in the number of active sites available for adsorption of metals. However, above 500 mg, the adsorption rate tends to decrease, due to the overlap of active sites.

A study tested biosorbent amounts ranging from 0.5 to 4.5 g of biosorbent and found higher removal rates with 2–2.5 g with an almost linear relationship between biosorbent dose and ion removal [12]. The adsorbent dosage of *Jatropha curcas* leaf was evaluated from 0.1 to 2.0 g, showing that the maximum removal was achieved at 0.5 g, although no significant difference was observed between 0.75, 1.0, and 2.0 g [44].

A total of 6 concentrations between 0.14 and 4 g/L of flax fibers were tested to remove Pb, Cd, Zn, Cu, Ni, and Hg ions. It was observed that the metal uptake increased as the flax fiber mass increased, until reaching a plateau around 0.5 g/L for single-metal systems and 2 g/L for multi-metal systems. Moreover, for single- and multi-metal systems, the orders of selectivity were found to be $\mathrm{Pb} \approx \mathrm{Cd} \approx \mathrm{Zn} > \mathrm{Cu} \approx \mathrm{Ni} > \mathrm{Hg}$ and $\mathrm{Pb} > \mathrm{Cd} > \mathrm{Cu} > \mathrm{Zn} \approx \mathrm{Ni} > \mathrm{Hg}$, respectively [47].

In conclusion, initial adsorbate concentration impacts adsorption by affecting saturation rate, breakthrough time, and removal efficiency. Higher concentrations can speed up breakthrough but reduce the availability of active sites, while moderate increases may enhance removal due to stronger competition for binding sites. Optimizing the biosorbent dosage is key for effective metal ion removal.

5.6. Biosorbent Characteristics: Porosity and Surface Area

Biomass characteristics of morphology and surface composition are crucial to determinate the adsorption process. The adsorption capacity is intrinsically linked to specific surface area, pore volume, and pore size distribution of the adsorbent [55].

Generally, smaller particle sizes have a larger specific surface area available for adsorption, and greater removal is achieved with adsorbents with smaller particle sizes [56,57]. In large particles, the diffusional resistance to mass transport is greater, and the internal surface of the particle may not be used for adsorption [9,58].

The pore size distribution and total porosity dictates the proportion of porous space accessible to adsorbates [59]. Pore sizes are classified by diameters: macropores (> 500 Å), mesopores (20–500 Å), secondary micropores (8–20 Å) and primary micropores (< 8 Å) [60]. A higher surface area can provide a larger pore volume [56].

The competitive adsorption of atrazine and methylene blue showed that when the adsorbent contains only a narrow range of primary micropores (pore width < 8 Å), the simultaneous adsorption process and dye preloading significantly affect atrazine adsorption. However, increasing the micropore volume and expanding the pore size distribution into the secondary micropore range (8 Å < pore width < 20 Å) reduces competition for adsorption sites [61]. The mechanism of competition was controlled by pore size distribution, when the pores are large enough to bind more than one adsorbate, direct site competition becomes the main competition mechanism [60].

Different particle sizes (< 75 µm, 75–150 µm, 150–300 µm and > 300 µm) of a mixture of tea waste, maple leaves, and mandarin peels were tested in the adsorption of Cd, Cu, Pb, and Zn ions, and the results showed that the adsorption capacity increased by decreasing the particle size [62].

In conclusion, the characteristics of biomass, including particle size, surface area, and pore distribution, play a key role in determining adsorption efficiency. Smaller particle sizes provide a larger surface area and reduce diffusional resistance, improving adsorption. Pore size distribution also affects the competition for binding sites, with broader pores reducing competitive adsorption. Optimizing these factors enhances the overall adsorption capacity of biomass materials.

5.7. Effects of Activation Processes

The distinctive adsorption properties are primarily governed by functional groups, which can be enhanced by activation processes. Two kinds of processes can be considered: physical and chemical activations.

The most common physical activation is comprised by a two-step process: first, the carbonization or pyrolysis, in an inert atmosphere, followed by activation in oxidizing gases such as steam, carbon dioxide, nitrogen–carbon dioxide mixtures, or air occurring at progressively increasing temperatures within the range of 800–1100 °C [63]. The second step is important because only a low adsorption capacity is achieved in the first step, since part of the products re-polymerize and condense on the surface of the particle, filling or blocking the pores [64].

The final product is influenced by the characteristics of the raw material, particularly particle size, and by key process conditions such as temperature, reaction time, heating rate, and the type of reactor used [65]. Carbon structures comprise key functional groups, including carboxyl, carbonyl, phenol, lactone, and quinone, which play a crucial role in contaminant adsorption. Additionally, oxygen, hydrogen, sulfur, and nitrogen are present either as functional groups or as chemical atoms within the activated carbon structure [63]. The temperature also plays a pivotal role, affecting the yield, morphology, and purity of the resulting materials [66]. The activation temperature influences the BET surface area, the micropore surface area, micropore volume, and total pore volume [55].

Biochar prepared from *Ligustrum vulgare* presented less surface porosity when produced at lower temperatures (400 and 550 °C) than at 700 °C, but the intensity of the O–H and C=C functional groups decreased or disappeared when the pyrolysis temperature changed from 400 to 700 °C [10]. The use of lower heating rates and moderate temperatures, in the order of 750 °C results in adsorbents with a high surface area [67].

Physical treatments of distillery sludge biomass derived from sugarcane, such as boiling and autoclaving, removed mineral components and created additional sorption sites on the biomass surface. Heating further decomposes organic matter, enhancing the biomass's metal sorption capacity by increasing the availability of sorption sites [57].

In chemical activation, the adsorbent material is impregnated with chemical agents such as KOH, H_3PO_4 or $ZnCl_2$, and may be subsequently subjected to a carbonization process at about 550 °C [64]. The hydroxide agents can be added by two main methods: impregnation and physical mixing. In the first, the activating agent, in liquid solution, is mixed into the solid material, which is then filtered and dried. In the second, the activating agent is mixed with the adsorbent in solid form (lentils, powder, etc.) [63]. The modification with chemical agents can change the types and the quantity of functional groups on the adsorbent surface, consequently changing its adsorption capacity [68].

The sorption of Cd, Cu, Pb and Zn by a biosorbent made of a mixture of tea waste, maple leaves, and mandarin peel increased after modification by NaOH. It was also observed that ester groups decreased and carboxylate groups increased after NaOH modification. The activation with $CaCl_2$ and formaldehyde enhanced Pb removal, while the adsorption rate of Cd, Cu and Zn decreased with formaldehyde-treated biosorbent. Furthermore, the HCl, HNO_3 and H_2SO_4 treatment led to a reduction in the metal binding [62].

The treatment of olive tree pruning biomass with NaOH increased the specific area from 0.63 to 3.53 $m^2\ g^{-1}$, the total pore volume from 1.54×10^{-3} to $5.85 \times 10^{-3}\ cm^3\ g^{-1}$, and the pore size from 97.44 to 66.38 Å, enhancing the adsorption capacity of Pb from 13.376 mg/g to 15.518 mg/g [69].

In conclusion, the adsorption properties of biomass are largely influenced by functional groups, which can be enhanced through physical and chemical activation processes. Physical activation, typically involving carbonization followed by activation at high temperatures, increases surface area and pore volume, improving adsorption capacity. Chemical activation with agents like NaOH or KOH alters functional groups on the adsorbent surface, further enhancing its ability to adsorb contaminants. Both activation methods play a critical role in optimizing biomass materials for efficient metal ion removal.

5.8. Competitive Adsorption of Metal Ions in Multi-Metal Systems

5.8.1. Affinity and Selectivity

The adsorption mechanisms in single-metal and multi-metal systems differ significantly due to competition for binding sites, which alters selectivity. Biosorbents can attract and bind heavy metals through complex processes such as ion exchange, precipitation or surface adsorption, and metal transformation [70]. The biosorbent–metal affinity can be justified by the degree of complexation exhibited by the metal ions with the sorbent binding groups that have a –COOH group. Similarly, the higher affinity of cabbage biosorbent towards Pb and Cd was related to its functional groups [71]. According to this type of interaction, studies suggest that the degree of complexation follows the classification: Al ≈ Pb > Cu > Cd > Co ≈ Mn ≈ Ni ≈ Zn. Thus, in equimolar multi-metal solutions, the excess metals will be those whose interaction with the adsorbent material is weaker. A process of substitution by the metal of coordination positions for which the adsorbent has a greater affinity occurs [22].

Similar selectivity was found for the sorption of metal ions in a quaternary system onto biosorbents made from mango (*Mangifera indica*) and guava (*Psidium guiag*) barks [72]. Maximum sorption capacities of mango and guava biosorbent followed the order Pb > Cd > Cu > Hg, but guava had slightly higher adsorption capacities. A different result was found using sesame-straw-derived biochar as biosorbent for multi-metal adsorption isotherms [73], which reached a selectivity sequence of Pb > Cu > Cr > Zn > Cd.

The competition between metals enhances their mobility in soils [74]. The metals that have lower compatibility with the sorbent surface migrate and occupy the available sites and subsequently are replaced by the ions with more affinity. It was also observed that the Cd and Zn lose out in the competition to Pb and Cu ions for the surface sites of the sediment particles.

Studies on bimetallic adsorption have identified two distinct behavioral tendencies: metals such as Cd, Ni, and Zn exhibit significant reductions in adsorption when another metal is present, whereas Cu and Pb show only minor changes in sorption efficiency in the presence of another ion [2,75]. The inhibitory effect of competitive ions is concentration-dependent; increasing the heavy metal concentration in solution generally leads to greater interference [14]. When metal ions compete for the same adsorption sites, those with higher affinity tend to displace weaker competitors, following a preferential sorption hierarchy [17,24].

Selective adsorption behavior has been observed in multi-metal systems, with studies reporting preferential sorption sequences such as Pb > Cu > Cd > Zn > Ni, while others identified Ni as having a higher affinity over Pb [34]. The factors influencing this selectivity include molecular mass, ionic charge, electrostatic interactions, and metal–sorbent binding affinities [34]. In addition, the electrostatic binding of metals on biomasses may be associated with their hydration state, with ions with lowest hydration radius being more promptly adsorbed [52]. The covalent index and softness index also significantly influence adsorption preferences. The covalent index quantifies the relative importance of covalent bonding versus ionic interactions in metal adsorption, while the softness index reflects a metal ion's ability to accept electrons when interacting with active sites, affecting its competitive adsorption behavior [76]. Pb, for example, has a smaller hydrated radius, allowing it to penetrate adsorption sites more effectively [52]. It also has a greater affinity for functional groups in organic matter and higher electronegativity compared to Cd or Zn, enhancing its binding strength. Also, higher adsorption rates of copper may be associated with its paramagnetic nature and high electronegativity [75].

To summarize, the adsorption mechanisms in single-metal and multi-metal systems differ due to competition for binding sites, which affects selectivity. In multi-metal systems, metals with weaker interactions are displaced by those with higher affinity for the biosorbent. This selectivity follows a predictable hierarchy, influenced by factors like ionic charge, electrostatic interactions, and hydration state. The competitive nature of adsorption in multi-metal systems highlights the complex behavior of metal ions based on their chemical properties and affinities.

5.8.2. Competition Between Metal Ions

Industrial effluents contain various metal ions that interact with each other during adsorptive treatments, influencing removal efficiencies. The presence of multiple metal ions in solutions can result in antagonistic or synergistic effects, altering the sorption behavior of individual metals. An antagonistic effect occurs when the presence of one metal reduces the adsorption of another, whereas a synergistic effect enhances the sorption capacity [36]. These effects persist even under optimal adsorption parameters and are crucial for understanding the efficiency of biosorbents in real-world applications.

The interaction between different ions was assessed by evaluating the ratio of the adsorption capacity of an ion in a multi-element system (Qmix) to its adsorption capacity in a single-element system (Qmono). A Qmix/Qmono ratio greater than 1 indicates a synergistic effect, where adsorption is enhanced due to the presence of other ions. A ratio equal to 1 suggests no significant interaction between ions, while a ratio lower than 1 signifies a antagonist effect, where adsorption is inhibited [77,78].

Most of the studies carried out consider binary [17,18,24,46,79–81], ternary [10,12,42,44,51], or quaternary [7–9,15,72,82] systems. Some studies also analyzed systems with five [2,14,36,43], seven [41,83,84], eight [32] and ten [85] toxic metals. Studies have demonstrated that the combined action of Zn and Ni can be antagonistic, leading to reduced adsorption efficiency [18]. The same pattern was observed in the adsorption of Cd and Ni, with a reduction from 7.5 to 75.0% for Cd and from 8.5 to 97.4% for Ni sorption rates in a binary system [86]. Studies comparing single, binary, and ternary systems have revealed that ternary metal solutions often exhibit significantly lower adsorption capacities than binary or single-metal solutions [36,42].

Milled olive stones were tested as a biosorbent for Cd, Cu, Pb, and Cr, and a reduction in the percentage of metal removal in the presence of competing ions was observed. The highest reduction in sorption capacity in the multi-metal experiments was seen for Pb, indicating that Pb had the most significant inhibitory effect in competitive systems [15].

In competitive adsorption, the presence of Cu and Cd had minimal influence on Pb removal, while Pb ions in solution strongly suppressed the adsorption of other metals [42]. In multi-component experiments, Pb consistently dominated adsorption, regardless of metal concentration. Other ions were suppressed until Pb concentrations decreased to sufficiently low levels, allowing the remaining metals to bind [87]. Some studies suggest that in the presence of multiple metal ions, the system maintains a consistent selectivity order, but with varying degrees of sorption efficiency [44]. In addition, the competitiveness offered by Pb may be strongly associated with electrostatic interactions [52].

In conclusion, industrial effluents containing multiple metal ions can exhibit antagonistic or synergistic effects during adsorptive treatments, influencing the removal efficiency of individual metals. These interactions, assessed by the Qmix/Qmono ratio, determine whether adsorption is enhanced or inhibited in the presence of other ions. Understanding these interactions is crucial for optimizing biosorbents in real-world applications where multiple contaminants are present.

5.8.3. Precipitation and Co-Adsorption

In addition to direct adsorption, precipitation and co-adsorption influence competitive adsorption. Pb removal in some studies suggests that complexation, precipitation, and cation exchange play a significant role in adsorption [79]. A study using sesame-straw-derived biochar for Pb, Cu, Cd, Cr, and Zn adsorption confirmed Pb’s dominance, showing significantly higher distribution coefficient values in L/kg: Pb (108,728) >> Cd (65,846) >> Cr (36,500) >> Cu (9534) > Zn (5333) [73]. Additionally, studies using biochar rich in Ca, Mg, K, and Na have demonstrated that these elements are critical in metal ion adsorption. Mg and Ca promote cation exchange, enhancing Pb and Cd removal, while Na and K facilitate complexation with carboxyl and hydroxyl groups, influencing Pb adsorption. Furthermore, S and Cl in biochar contribute to Hg adsorption through sulfur binding [79].

5.8.4. Displacement Effects

Displacement effects play an essential role in multi-metal adsorption. The inhibitory effect of competitive ions is often concentration-dependent, with increasing heavy metal concentrations generally leading to greater interference [14]. Competitive adsorption studies have demonstrated that certain metals exert stronger inhibitory effects on others. For instance, the presence of Zn and Cd had little effect on Cr adsorption, whereas Cr significantly reduced the adsorption of Zn and Cd [24]. Similarly, Ni adsorption was negatively impacted by the presence of Zn and Cd [17,18]. When multiple metals coexist, stronger binding ions can displace weaker ones. In ternary systems, Pb has been observed to outcompete Cu and Cd, occupying the majority of binding sites [87]. In biosorption using *Michelia Figo* wood sawdust, Cu and Cd showed significantly different removal rates between single-metal and ternary systems, while Pb remained unaffected. The stronger Pb adsorption was attributed to its larger ionic radius, which enables stronger complexation with binding sites [42].

Ultimately, displacement effects in multi-metal adsorption demonstrate that, as concentrations increase, stronger binding ions like Pb can outcompete weaker ones, underscoring the importance of these competitive interactions in optimizing biosorption processes.

5.9. Implications for Industrial Wastewater Treatment

Understanding competitive adsorption is critical for designing efficient biosorbent materials and treatment systems for industrial effluents. The main factors that should be optimized for improved heavy metal removal are pH adjustment, adsorbent selection, pre-treatment strategies, and sequential adsorption techniques. For example, adjusting pH can enhance selectivity for target metals since lower pH values increase competition between metals. Biosorbent selection should prioritize materials with high Pb affinity, such as biochars with sulfur-rich functional groups, when Pb removal is a priority. Additionally, modifying biosorbents (e.g., chemical activation, functionalization) can improve selectivity and increase adsorption efficiency. Sequential adsorption techniques may allow for selective removal, preventing high-affinity metals from monopolizing binding sites.

Competitive adsorption in multi-metal systems is a complex process influenced by metal affinity, electrostatic interactions, covalent bonding, ionic size, and solution conditions. Future research should focus on optimizing biosorbent modifications and multi-stage adsorption strategies to improve real-world wastewater treatment performance.

Table 2 presents the maximum adsorption capacity (mg/g) found for various biosorbents in competitive systems with different metal ions. The highest removal rate (mg/g) for Pb, Cd, and Cu was achieved by the mixture of tea waste, corncob and sawdust. Almond shell demonstrated the biggest removal rate for Cr(IV). Pinecone was the best biosorbent to remove Ni ions, and lemon peel to remove Co. Comparison between biosorbents was not possible for the removal of Zn, Mn and Cr(III) ions because only one study was available for each one.

Table 2. Maximum adsorption capacities (mg/g) of different biosorbents in competitive medium.

Biosorbent Materials	Pb(II)	Cd(II)	Cu(II)	Zn(II)	Cr(IV)	Ni(II)	Mn(II)	Cr(III)	Co(II)	Reference
Tea waste, corncob and sawdust	94.00	41.48	39.48	27.23						[7]
Olive stones	0.58	0.30	0.56		2.35					[15]
Abies bornmulleriana cone	11.40	4.37	6.33			2.36			2.13	[43]
Pinecone	23.80		10.34		1.51	13.41				[9]
Lemon peel	8.17	7.34	7.17			5.73	5.17	7.56	5.63	[83]
Almond shell			2.39		21.92					[80]
Moringa stenopetala seeds	16.13	23.26	10.20							[12]

In summary, optimizing factors like pH, adsorbent selection, and biosorbent modifications is key to improving heavy metal removal in competitive adsorption systems. Sequential adsorption can also enhance selectivity. Future research should focus on refining biosorbent strategies to improve real-world wastewater treatment.

6. Conclusions

This review highlighted a growing concern regarding the remediation of environmental contamination by toxic metals accompanied by a growing search for more sustainable water and wastewater treatment methods, such as adsorption with materials of biological origin. While several treatment methods are available, the economic component is highly relevant, as it is a determining factor in the choice of the treatment method. The application of biomass wastes or byproducts in the process is therefore an added value, as it reduces operating costs.

While the number of research studies on biosorbents has increased, and some relevant advances have been made to understand the mechanisms that occur in competitive adsorption, the range of metals studied is still restricted, and there are many gaps to fill. Understanding the interaction between metal ions and the relation between metal and biosorbent is essential to obtain good results when applying this method in real-world conditions. Therefore, it is important to continue exploring new materials with sorbent potential in complex adsorption systems, comprising various types of metals, mimicking real-world conditions for applying biosorption treatment.

The literature on multi-metal adsorption is not very extensive, but efforts have been made to understand the mechanisms of biosorption in competitive media, as this would be a greener alternative method for the treatment of water or wastewater containing toxic metals. Thus, it is expected that this line of research will continue to be highlighted, especially the search and improvement of biosorbents and their application on a real scale in wastewater treatment plants.

Author Contributions: Conceptualization, M.M., H.P., L.C.-L., L.G. and B.E.; methodology, M.M.; investigation, M.M.; writing—original draft preparation, M.M.; writing—review and editing, H.P., L.C.-L., L.G. and B.E.; supervision, H.P., L.C.-L., L.G. and B.E.; funding acquisition, M.M, H.P. and L.C.-L. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by National Funds through the FCT—Foundation for Science and Technology, I.P., by the doctoral scholarship with reference 2023.03677.BDANA, by CERNAS-IPV Research Centre under the project UIDB/00681 and by Forest Research Centre (CEF), within the projects UIDB/00239 and UIDP/00239/2020.

Data Availability Statement: Data is contained within the article.

Acknowledgments: This work was supported by FCT—Foundation for Science and Technology, I.P. Furthermore, we would like to thank the CERNAS Centre and the Polytechnic Institute of Viseu for their support.

Conflicts of Interest: The authors declare no conflicts of interest.

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