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Towards a Circular Economy: Analysis of the Use of Biowaste as Biosorbent for the Removal of Heavy Metals

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Abstract: Industrial human activity has led to the release of substantial amounts of heavy metals into the environment. Contamination of water with heavy metals such as lead, cadmium, copper, zinc, chromium, or nickel represents a serious problem. As part of the circular economy, it is appropriate to use biowaste from agriculture, fisheries, and the timber industry as biosorbents. In this literature review, the potential of using these biowaste groups as biosorbents for metal removal is presented. This biowaste is characterized by the presence of carboxyl, hydroxyl, carbonyl, amide, amine, sulfydryl, and other groups on their surface, which form complexes and chelates with metals present in water. Biosorption seems to be a potential alternative to conventional technologies for removing or recovering heavy metals from water or wastewater, which are uneconomical and generate additional waste. The paper demonstrates that harnessing the potential of biowaste to remove metals is beneficial to the environment as they can solve the problem of incineration and realise recycling that meets the circular economy. Although the choice of a suitable biosorbent for the removal of a particular metal involves a lot of research, the high biosorption efficiency, low cost, and renewability justify their use.

Keywords: circular economy; biowaste; biosorbents; sorption; metals

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1. Introduction

In recent years, the circular economy model is a kind of solution to the problems of environmental degradation and economic development because it emphasizes the care for the environment by influencing what we produce, how we work, buy, or live. The circular economy (CE) offers a promising approach to solving environmental problems related to biowaste, with a CE strategy combining the hierarchy of waste management and bioeconomy. The bioeconomy focuses on the conversion of renewable carbon reserves from forest biomass, agricultural biomass, and organic waste into various products and biomaterials. The use of waste in bioprocesses for biosorbent production meets the assumptions of sustainable circular bioeconomy.

The circular economy (CE) concept aims to bring the best possible balance between rapid economic growth and scarcity of raw materials and energy [1]. There are three simple principles of CE: reduce, reuse, and recycle [2–4].

Circular economy (CE) offers the concept of cascade biomass use in systemic economic development. The CE model makes it possible to utilize the potential inherent in bioproducts that, after one life cycle as biowaste, can be reused in the same form or after processing in a new cycle [5]. It is known that waste is a potential resource and therefore it needs to be used effectively. This can be done by managing waste as a biosorbent for water treatment or recovering, for example, metals following the principles of circular economy (Figure 1) [2,5,6]. Today, industrial production focuses on the overall improvement of processes, rarely taking into account sustainability aspects. It is therefore important to show the possibilities of using biowaste and not only treating it in biological disposal processes. Efficient use and treatment of biowaste will be important for the development of the circular economy. Due to its sorption potential, biowaste can be a potential source of biosorbents. Therefore, biowaste can be used as a product to achieve zero waste production.

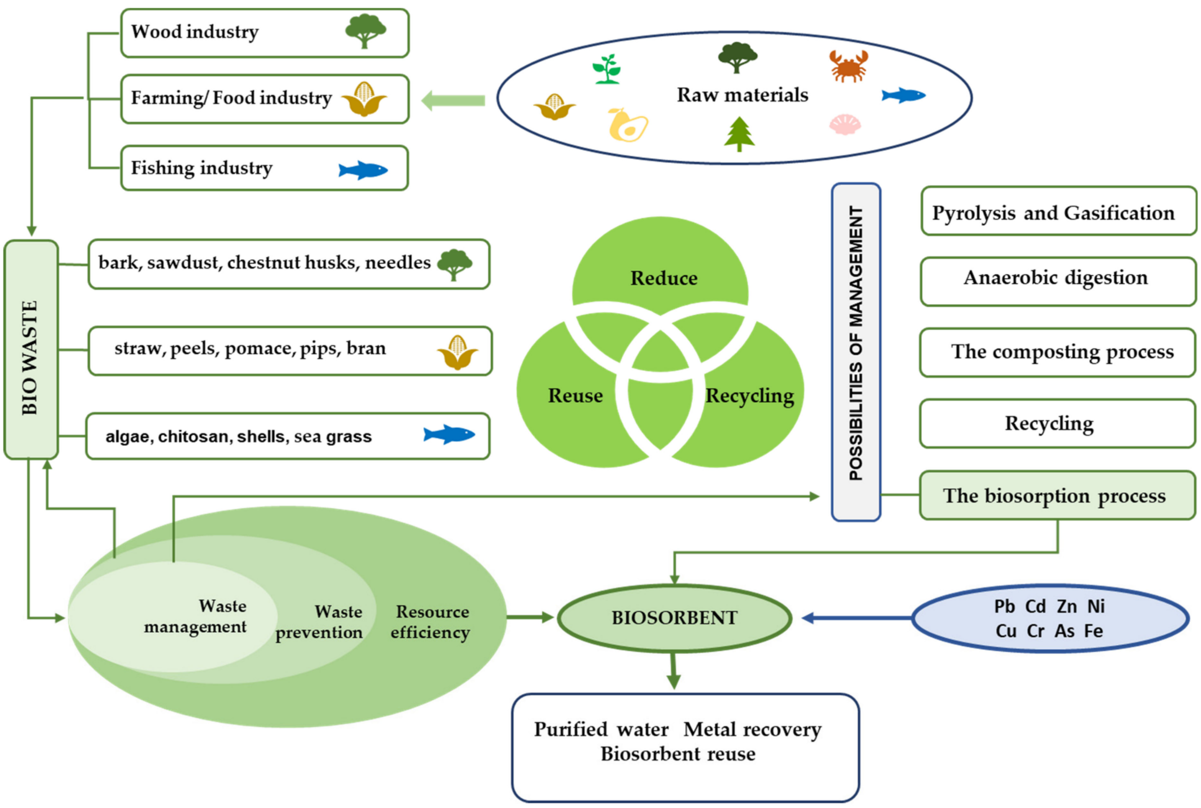

Figure 1. Concept of managing biowaste towards a circular economy, based on materials.

Bioprocesses using waste materials of different types, such as waste from agricultural production [7–9], food industry [10,11], paper, wood processing [12,13], or fisheries [14–16] are of increasing interest due to sustainability initiatives. Biosorbents are produced using biomaterials in their natural form or with improved pollutant removal properties. Their ability to remove various pollutants from water is due not only to the typical characteristics of adsorbents such as specific surface area or porosity but mainly to their high content of polysaccharides (cellulose, hemicellulose, lignin, pectin, chitin), which contain numerous functional groups capable of binding various compounds [17–21]. Biosorption can be an effective and inexpensive process for water and wastewater treatment, especially when cheap and locally available waste biomass from agriculture or other industrial sectors are used as sorbents.

Metal sorption involves several mechanisms that vary qualitatively and quantitatively depending on the type, origin, and biowaste treatment procedure. Among the main mechanisms, electrostatic interaction, ion exchange, physical adsorption, and complex formation between metal cations and ligands contained in the cell wall of the biopolymer structure can be highlighted [22]. The possible mechanisms of biosorption are shown in Figure 2 [23–25]. The capacity of biowaste to bind metals is largely due to the presence of functional groups such as hydroxyl, carboxyl, carbonyl, and ether groups, which can attract and sequester heavy metal ions in aqueous solutions [26]. They are related to surface charge, which affects electrostatic interactions [22]. The ion exchange characteristics of most biological materials, including agroindustrial, wood, and other types of waste have been studied extensively [27–30].

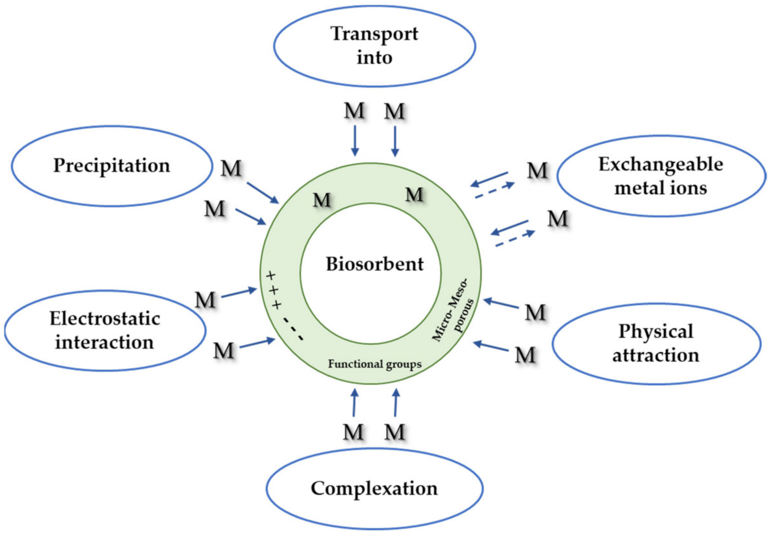

Figure 2. Possible mechanisms of metal biosorption.

Biosorption of metal ions is strongly dependent on pH and is considered an important parameter because pH affects the capability of ionization of heavy metals and the adsorbent surface. It also affects the formation of metal hydroxide, which is poorly soluble in solution [31]. For example, the range of optimum pH for metal removal for lignocellulosic biosorbents such as *sugarcane* bagasse, corn cobs, sawdust, or fruit waste is between pH 4 and 7 [26]. Taking into account the surface area, pore accessibility, and intraparticle diffusion, the size of the biosorbent particle also plays an important role. It is often observed that biosorbents with smaller particle sizes exhibit greater sorption capacity due to their larger specific surface area, which increases the availability of binding sites for adsorbates [32,33].

Metals make up a significant portion of the pollutants contained in wastewater from various industries. Heavy metal ions pose an environmental threat due to their cumulative, toxic, and non-biodegradable characteristics. With a certain concentration threshold, heavy metals are harmful to humans, causing damage to the gastrointestinal, cardiovascular, and renal systems, as well as peripheral and central nervous systems [34]. The toxicity of heavy metals results from their ability to form compounds with cellular components containing sulfur, oxygen, or nitrogen, causing inhibition of enzymes or modification of protein structures and leading to cellular dysfunction in the body **[34]**. Among aquatic pollutants, mercury, cadmium, copper, zinc, nickel, lead, chromium, aluminum, and cobalt are considered a priority for removal due to their toxicity [35]. It is possible to effectively remove metals from wastewater and leachate by sorption to very low concentrations in water, using cheap and readily available biowaste [36,37].

The present review aims to highlight the use of biowaste as biosorbents for metal removal, which fits into the concept of circular economy and promoting an ecological approach to processes. Three groups of biowaste were presented: from agriculture and food production, from forestry and wood industry, and from fisheries. The main compounds present in the biowaste analyzed and responsible for the biosorption of metals on their surface were described. Biowaste was compared in terms of its sorption capacity to remove cadmium, lead, copper, zinc, nickel, chromium, iron and arsenic, among others. In addition, attention was paid to desorption processes in order to reuse the biosorbent. Prospects for biosorbent applications are presented.

2. Biowaste

2.1. Preparation of Biowaste

In recent years, there has been an increased interest in research into the production of alternative sorbents to replace expensive commercial activated carbon. Attention has focused on different biowaste that are able to remove harmful substances from polluted water at low cost. An adsorbent can be considered cheap if it requires little processing, is present in large quantities or is a by-product or waste from another industry.

Biosorption using biowaste can be an efficient and beneficial method of water treatment due to its sorption capacity, but biowaste needs to be properly prepared. Biowaste is first washed to remove adhering dust and soluble contaminants from its surface, then dried at different temperatures depending on the technology [38–40]. Then the biowaste is ground which improves the sorption on its surface. However, the efficiency of sorption on biosorbents often needs to be modified if the natural surface area was too small and inefficient for sorption [41]. Chemical modification methods are commonly used, where the biowaste is: acid (HCl, HNO_3, H_2SO_4, CH_3COOH) or base (NaOH, Na_2CO_3, $Ca(OH)_2$), treatment, cross-linking with glutaraldehyde or epichlorohydrin [42–45]. Studies report that N-functional groups on the biosorbent surface promote the adsorption of heavy metal ions from aqueous solutions through a chelation mechanism [46,47].

Biowaste used for metal removal should be available locally and in large quantities and attention should be paid to its transport, collection, and storage.

2.2. Agricultural Biowaste

Part of the biowaste from agricultural production and food industry is one of the better and widely available sources for the production of sorption materials. This waste is often problematic during disposal or recycling and has little or no economic value. Due to its biochemical composition, biowaste is environmentally friendly, inexpensive, and renewable. The biochemical composition of agrifood waste includes, among others, cellulose, hemicellulose, lignin, lipids, simple sugars, proteins, hydrocarbons, and starch. These compounds contain various functional groups that are capable of binding and removing harmful substances from water and wastewater. Therefore, conversion of this waste into low-cost biosorbents is a good option in terms of the circular economy. This waste can be used directly after recycling, with the preparation of particles of the desired size or after modification using specific methods of pretreatment of the material before use. Many studies have been conducted to test agro-industrial waste as biosorbents for the removal of metals from aqueous solutions. The most commonly studied biosorbents include those made from fruit stones and peels, vegetable waste, nut, and almond shells, coconut pulp, sugar cane bagasse, cereal straw, *rice* hulls, or corn waste [7,48,49].

Studies have shown that adsorption of pollutants on biosorbents made from agricultural and food waste can be effective, although it depends on the process conditions and the dose and particle size of the biosorbent, the number of reactive sites on the biosorbent surface, or the concentration of the substance to be removed [50]. Table 1 shows examples of biosorbents and their ability to adsorb various metals. One of the types of agricultural waste is *rice* hulls produced during *rice* production. About 500 million tons of rice are produced worldwide, of which *rice* hulls account for 10 to 20%. Dry *rice* hulls contain 70 to 85% organic matter, where the main components are cellulose (32.24%), hemicellulose (21.34%), and lignin (21.44%). About 15% is mineral ash, sugars, and silica present in the cell membrane. Due to their chemical constancy, *rice* hulls have high mechanical strength and are insoluble in water, making them one of the best adsorbents for the removal of heavy metals (Cd, Pb, Zn, Cu, Co, Ni, and Au) [51]. The removal efficiency of up to 100% for metals such as iron, manganese, zinc, copper, cadmium, and lead has been reported in small wastewater treatment plants where *rice* hulls were used as biosorbents [52].

Table 1. Biowaste from agricultural production and the food industry used to remove heavy metals from water.

Metals	Biowaste	Sorption Capacity (mg/g)	References
Cd(II)	*Agave* bagasse	13.27	[8]
	Rice straw	13.90	[53]
	Citrus maxima peel	135.2	[54]
	Passion fruit shell	86.75	[54]
	Sugarcane bagasse	23.23	[54]
	Cabbage waste	22.12	[10]
	Agave bagasse (HCl)	12.50	[8]
	Agave bagasse (HNO_3)	13.50	[8]
	Agave bagasse (NaOH)	18.32	[8]
Pb(II)	*Agave* bagasse	35.60	[8]
	Lentil husk	81.43	[55]
	Barley straws	23.20	[56]
	Citrus maxima peel	154.50	[54]
	Passion fruit shell	109.92	[54]
	Sugarcane bagasse	28.27	[4]
	Mango seed *Mangifera indica*	183.00	[57]
	Maize silk	70.80	[58]
	Peach kernels	25.14	[58]
	Sunflower husks	36.90	[59]
	Cabbage waste	61.27	[10]
	Wheat bran	87.00	[60]
	Agave bagasse (HCl)	42.31	[8]
	Agave bagasse (HNO_3)	54.29	[8]
	Agave bagasse (NaOH)	50.12	[8]
Cu(II)	*Citrus maxima* peel	83.7	[54]
	Passion fruit shell	30.09	[54]
	Sugarcane bagasse	16.09	[54]
	Mango peel	46.09	[61]
	Sunflower husks	34.89	[62]
	Beet pulp	31.4	[63]
	Gooseberry waste	24.0	[64]
Zn(II)	*Agave* bagasse	7.84	[8]
	Mango peel	28.21	[61]
	Cabbage waste	12.24	[10]
	Agave bagasse (HCl)	12.40	[8]
	Agave bagasse (HNO_3)	14.43	[8]
	Agave bagasse (NaOH)	20.54	[8]
Ni(II)	*Citrus maxima* peel	70.79	[54]
	Passion fruit shell	20.64	[54]
	Sugarcane bagasse	12.04	[54]
	Mango peels	39.75	[61]
	Calamansi peels	11.00	[65]
Cr(VI)	*Walnut* shells	138.89	[66]
	Bean waste	21.20	[67]
	Bean shells	96.05	[11]
	Waste from tea manufacture	54.65	[68]
	Rice husk	379.63	[69]
	Passion fruit peel amino-riched	675.65	[70]
Cr(III)	*Carrot* residues	45.09	[71]
	Watermelon rinds	172.6	[30]
Fe(III)	*Bean* shells	66.63	[11]
As(V)	*Orange* peels	36.81	[72]

Wheat processing produces a lot of biowaste and by-products such as straw, *wheat* bran, *wheat* hulls, etc., which have been studied for sorption. Bulut and Baysal investigated the adsorption of Pb(II) ions from aqueous solutions on *wheat* bran as a function of initial metal concentration, adsorbent dose, adsorbent particle size, mixing rate, temperature, contact time, and solution pH. Adsorptions were described by the Langmuir isotherm model with maximum sorption capacities of 69.0, 80.7, and 87.0 mg/g at 20, 40, and 60 °C, respectively. Adsorption was studied at pH 1.85–7.01 and initial Pb(II) concentrations ranging from 0 to 1000 mg/L. The lowest Pb(II) removal was observed at pH 2.0, while an increase in Pb(II) adsorption on *wheat* bran was observed for pH ranging from 4 to 7 [60].

The sugar industry produces biowaste where cane pulp remains after sugar juice extraction. The compounds present in it are cellulose, pentosans, and lignin. *Sugarcane* bagasse was tested for the removal of Cd(II), Ni(II), Pb(II), and Cu(II) from aqueous solution, and yielded adsorption capacities of 23, 12, 28, and 16 mg/L, respectively. The biosorbent properties were characterized by scanning electron microscopy (SEM), zeta potential analyzer, Fourier transform infrared spectroscopy (FTIR), elemental analyzer, and cation exchange capacity (CEC) method. The results showed that the biosorbent has many carboxyl (-COOH) and hydroxyl (-OH) groups, which make it possible to form complexes with heavy metals. Furthermore, the negative surface charge of the biosorbent can adsorb metal ions through ion exchange. Adsorption isotherms indicated ion exchange and complexation reactions as mechanisms for adsorption of metal ions on *sugarcane* bagasse [54].

A large amount of fruit waste is generated during agricultural and food production, mainly fruit residues such as peels, seeds, stones, and hulls. Using *watermelon* (Citrullus lanatus) as an example, the fruit has the highest yield (117 million tons/year) of fruits in the world [73], with almost 50% of its weight remaining as waste in the form of rind. *Mango* (*Mangifera indica*) is one of the most valued tropical fruits sold in the world. With its global production of about 40 million tons/year [73], it generates biowaste in the form of seeds (30–45% of the fruit weight) and rind. The potential of waste *mango* rind as an adsorbent material for the removal of Cu(II), Ni(II), and Zn(II) from wastewater of the electroplating industry was investigated by Iqbal et al. [61]. The process was pH-dependent, with maximum adsorption occurring at pH 5–6. The adsorption of metal ions was investigated, and the adsorption equilibrium was established within 60 min with maximum metal ion adsorption of 46.09, 39.75, and 28.21 mg/g for Cu(II), Ni(II), and Zn(II), respectively. The experimental adsorption data of all three metals fitted well to the Langmuir isotherm model with a correlation coefficient of 0.99. The release of light metal cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and H^+ protons from waste *mango* rinds during Cu^{2+}, Ni^{2+} and Zn^{2+} capture and EDX (Energy Dispersive X-ray Spectrometry) analysis of the biowaste before and after the sorption process showed that ion exchange was the main mechanism in the process. Furthermore, FTIR analysis showed that carboxyl and hydroxyl functional groups were mainly involved in metal sorption. The study confirmed that *mango* rinds are effective in adsorbing metal ions from wastewater from the electroplating industry, as they removed all three metal ions to acceptable levels set by environmental agencies.

Several studies have been conducted on modified biowaste, including *agave* pom-ace, which is a byproduct of the alcohol industry [8]. *Agave* pomace was modified with sodium hydroxide and hydrochloric and nitric acids, among others. Carboxyl, hydroxyl, sulfur, and nitrogen groups were identified in the pomace. Sorption of Zn(II), Cd(II), and Pb(II) ions from water at pH 5 was carried out on the prepared biosorbents. Adsorption capacities of 7.84, 13.27, and 35.60 mg/g for zinc, cadmium, and lead, respectively, were obtained on raw *agave* pomace. The best results of metal ion adsorption were obtained for *agave* pomace modified with sodium hydroxide.

2.3. Wood Biowaste

Biowaste from the forestry and wood industries is a potential adsorbent that can be used to remove pollutants from water and wastewater. Table 2 summarizes the potential biowaste from this industry used for heavy metal removal. This waste is available in large quantities and has considerable potential due to its physical and chemical properties and low cost. One type of biowaste is sawdust which contains various organic compounds such as lignin, cellulose, and hemicellulose. With their functional groups, this biowaste can effectively bind harmful compounds. In the studies [12,74,75], sawdust proved to be a promising effective material for removing harmful compounds from aqueous solutions. Albadarin et al. conducted a study of Cd(II) sorption on sawdust. Based on the Langmuir model, they obtained a sorption capacity of 41.21 mg/g. At different initial cadmium concentrations, biosorption exhibited pseudo-second-order kinetics [75].

Table 2. Biowaste from the wood processing industry used to remove heavy metals from water.

Metals	Biowaste	Sorption Capacity (mg/g)	References
Cd(II)	Sawdust	41.21	[12]
	Chestnut shells	34.77	[75]
	Pine cones	4.29	[75]
Pb(II)	*Pine* cones	15.17	[75]
	Chestnut shells	74.35	[75]
	Pine needles	25.86	[75]
Cu(II)	*Willow* bark	0.173	[76]
	Wood chips	2.90	[13]
Zn(II)	*Eucalyptus* bark	128.21	[77]
	Eucalyptus bark (NaOH)	250.0	[77]
	Wood chips	3.0	[13]
Cr(VI)	Bark of *Ziziphus mauritiana*	18.8	[78]
	Neem sawdust	58.82	[79]

Another wood waste used in the metal sorption process is bark [76], showing high efficiency due to its high content of tannins, derivatives of polyphenols, which are active compounds in the sorption process. Afroze et al. studied zinc adsorption from aqueous solutions using *eucalyptus* (*Eucalyptus sheathiana*) bark in its natural and modified (NaOH) state [77]. A strong pH dependence of sorption was observed, the adsorption capacity of Zn^{2+} increased with increasing pH of the solution ranging from 2.5 to 5.1. It was also found that adsorption depended on contact time, initial metal ion concentration, and biosorbent dose. Metal adsorption was analyzed using an intramolecular diffusion kinetic model. The measurements showed that the process occurred at multiple stages and was diffusion-controlled, while the thermodynamic parameters confirmed that the adsorption was spontaneous and exothermic. The maximum monolayer adsorption capacity was obtained at 30 °C and at optimum pH 5.1, which was 128.21 mg/g and 250.0 mg/g for natural and modified bark, respectively. Therefore, both natural and chemically modified *eucalyptus* bark can be effective alternatives to many expensive adsorbents used in the removal of zinc ions from aqueous solutions.

Forest residues such as *pine* cones and needles have also been used as biosorbents [75,80,81]. The sorption potential of cones was represented by cell walls composed of hemicellulose (46.5%), cellulose (18.8%), lignin (37.4%), and other compounds (resin, tannins) that contain polar functional groups, e.g., hydroxyl, carbonyl, carboxyl, and phenyl as active sites for binding contaminants on the biomass surface [82]. The sorption capacity of *pine* cones as biosorbents for the removal of cationic metals Pb(II) and Cd(II) was examined. Better results were obtained for lead, and they were 3.5 times higher than cadmium [75].

Pine needles were investigated for the removal of heavy metal ions using cadmium and lead as examples. Sorption was described by pseudo-second-order equation and Langmuir model. The maximum sorption capacities for Cd(II) and Pb(II) were 6.65 and 25.86 mg/g, respectively [75]. FTIR studies showed that the carboxyl groups located on the biosorbent surface were the most involved in metal biosorption.

Richards et al. examined wood chips as adsorbents for removing copper (Cu^{2+}) and zinc (Zn^{2+}) from aqueous solutions. They obtained a removal rate of 49% for copper ions at an initial metal concentration of 0.157 mM/L and pH 4.9. A slightly higher removal rate was obtained for zinc ions (57%) at an initial metal concentration of 0.015 mM/L and pH 4.1. It was found that the main active sites on wood biomass were deprotonated functional groups such as hydroxyl, carboxyl, and amine groups, capable of capturing metal ions from water [13].

Research on *eucalyptus* bark can be presented as an example of improving the sorption capacity of a biosorbent [77]. The adsorption efficiency of raw *eucalyptus* bark was enhanced by activation with NaOH. The study showed that sorption depends on the metal ion concentration, contact time, biosorbent dose, and the initial solution pH and temperature. After NaOH modification of *eucalyptus* bark, the adsorption capacity was twice higher than on raw *eucalyptus* bark. The authors concluded that crude and modified *eucalyptus* bark can be an effective biosorbent for the removal of Zn^{2+} metal ions from wastewater, and therefore can be an alternative to many expensive adsorbents.

2.4. Biowaste from Fisheries

Seafood processing produces large amounts of by-products that can be used as biosorbents due to the chitin content in shells and exoskeletons of mollusks and crustaceans, and cellulose in algae (Table 3). As a cellulose-like polymer, chitin has many functional groups that increase the binding efficiency of many chemicals and maximize the chemical charge [83].

Table 3. Biowaste from fisheries used to remove heavy metals from water.

Metals	Biowaste	Sorption Capacity (mg/g)	References
Cd(II)	Green algae *Ulva onoi*	61.90	[84]
	Green algae *Ulva lactuca*	127.00	[15]
	Red algae *G. oblongata*	85.50	[85]
	Chitosan	85.47	[86]
	Chitosan (NaOH)	357.14	[86]
Pb(II)	Chitosan	34.98	[14]
	Myriophyllum spicatum	48.50	[58]
	Green algae *Ulva lactuca*	230.00	[15]
	Red algae *P. capillacea*	34.10	[85]
	Red algae *C. mediterranea*	64.30	[85]
Cu(II)	Green algae *Ulva lactuca*	112.00	[15]
	Green algae *Ulothrix zonata*	176.20	[87]
	Brown algae *Turbinaria ornate*	147.06	[87]
	Macroalgae *Fucus vesiculosus*	72.37	[13]
Zn(II)	Crab shells *Portunus sanguinolentus*	123.70	[88]
	Green algae *Ulva fasciata* sp.	13.5	[89]
	Brown algae *Bifurcaria bifurcate*	30.30	[9]
	Brown algae *Fucus spiralis*	34.30	[90]
	Macroalgae *Fucus vesiculosus*	52.40	[13]
Ni(II)	Green algae *Ulva lactuca*	67.00	[15]
Cr(III)	Red algae *Polysiphonia nigrescens*	16.11	[91]
	Palmaria palmata	29.63	[92]
	Red algae *C. mediterranea*	70.30	[85]
	Red algae *G. oblongata*	105.20	[85]
Fe(II)	Chitosan	51.81	[93]
Mn(II)	Crab shells *Portunus sanguinolentus*	69.90	[88]
	Seagrass *Zostera marina*	58.43	[94]
Ce(III)	Crab shells	144.90	[95]
Co(II)	Red algae *P. capillacea*	52.60	[85]

The main chitin derivative is chitosan, which has highly desirable properties such as biodegradability, biocompatibility, membrane-forming ability, bioadhesion, multifunctionality, hydrophilicity, and good adsorption properties. Most of these features may be due to its cationic nature, which is unique among numerous polysaccharides and natural polymers [77]. It has long been of great interest to researchers due to its relatively low cost compared to commercial activated carbon, easy availability, good pollutant binding capacity, selectivity, and biodegradability [96]. Since chitosan exhibits a high capacity of metal chelation of up to six times more compared to chitin due to the exposed numerous amino groups formed during the deacetylation process, it has great potential for commercial applications [86–88,97–99]. Furthermore, it is capable of forming hydrogen bonds and interactions such as ion exchange and electrostatic attraction due to the presence of many free hydroxyl groups in its molecular structure and protonating of NH_2 groups. The high chemical reactivity may also be related to the flexible structure of the biopolymer chain [86].

In their study, Kaveeshwar et al. used porous chitosan as a biosorbent for iron(II) removal from synthetic fracking of wastewater [94]. The post-fracking water contained iron(II) up to 55 mg/L, which represented a major concern. The chitosan used in this study had a specific surface area of 1.05 m^2/g with an average pore diameter of 319 Å. Kinetic studies showed that the adsorption process was controlled by intramolecular diffusion. Good fitting results for Langmuir isotherm were obtained, the adsorption capacity of iron on porous chitosan was 51.81 mg/g. Furthermore, thermodynamic studies showed the spontaneous and endothermic nature of the process where entropy was the driving force.

Crab shell is one of the most widely used natural products used as a biosorbent to treat water contaminated with metals [40,88,93,95]. It consists mainly of chitin (26.65%), calcium carbonate and protein (29.19%), ash (40.60%), and lipids (1.35%). In their study, Aris et al. used crab shells for biosorption of copper(II) and cobalt(II) [100]. Based on the results, they concluded that crab shells are very good materials with high heavy metal removal efficiency. A 94.7% removal of copper (for a starting concentration of Cu 5 mg/L) and 85.1% of cadmium (for a starting concentration of Cd 1 mg/L) were obtained, respectively. The experiments were carried out at constant pH 6 and temperature maintained at 25 °C.

One of the very good biosorbents is algae, due to their high sorption capacity and their abundance [87,101–103]. Algae can be divided into several subgroups according to evolutionary pathways into brown algae (Phaeophyta), red algae (Rhodophyta), and green algae (Chlorophyta) along with mosses, ferns, and several other plants. The main differences between them are in the composition of the cell wall. In the case of brown algae, the components usually include cellulose, alginic acid, polymers of mannuronic and guluronic acids, and sulfated polysaccharides [104]. Alginates and fucoidans (sulfated polysaccharides) are probably the most dominant active groups in brown algae [105]. The cell wall of green algae consists mainly of cellulose and a high content of polysaccharide-linked proteins, forming glycoproteins [106]. Cellulose is also present in the cell wall of red algae, and the adsorption capacity is attributed to the presence of sulfated polysaccharides composed of galactans.

Most studies have been conducted on brown algae mainly for the removal of heavy metals [107–109]. More and more research has been conducted on biosorption using green and red algae [15,85,110]. A study was conducted on four species of the red seaweeds *Corallina mediterranea*, *Galaxaura oblongata*, *Jania rubens*, and *Pterocladia capillacea* for the removal of Co(II), Cd(II), Cr(III), and Pb(II) ions from industrial wastewater under two successive adsorption/desorption cycles [85]. Maximum biosorption of metal ions was achieved at a biosorbent dose of 10 g/L, pH 5, and contact time of 1 h. Among the listed seaweeds, *Galaxaura oblongata* was found to be the most effective in metal removal with an average biosorption of 84%. Studies have shown that algae are potential materials for removing contaminants from aqueous solutions.

Among the studied biomaterials, chitin and its derivative, chitosan, have been used in water purification processes due to their high content of amine and hydroxyl functional groups, which can effectively bind various types of pollutants. Algae, characterized by high sorption capacity towards heavy metals, turned out to be an equally valuable sorption material.

2.5. Desorption of Biosorbent

Desorption and regeneration of used biosorbents is the basis for determining the economic viability of the process of sorption of pollutants from water. Biosorbents loaded with metal ions can be regenerated by desorption. The metal ions retained on the sorbent can be released in aqueous solution so that the sorbent can be reused in subsequent biosorption cycles [111].

There are several methods for desorption of metals from sorbent surfaces, one of which uses inorganic acids such as: HCl, HNO_3, and H_2SO_4, which recover bound metals via proton exchange [9,112]. However, they can damage the surface of the biosorbent to some extent, causing a reduction in its biosorption capacity. In contrast, organic acids CH_3COOH and $C_6H_8O_7$ are usually compatible and environmentally friendly alternative desorbents as they do not damage their surface structure [113]. The second desorption method uses salts such as $CaCl_2$, $Ca(NO_3)_2$, NaCl, and $NaHCO_3$, which provide competing cations for ion exchange with adsorbates. In contrast, anions present in salt solutions: HCO_3^-, CO_3^{2-}, Cl^-, and SO_4^{2-}, can destabilize the biosorbent-metal complex and capture bound metal ions to form complexes with them [114,115]. A complexing agent such as EDTA can also be used for the desorption process, which forms a stable complex with heavy metal ions, being a competitor to the sorbent [116,117]. It is important to use a suitable desorbent, which, on the one hand, will be efficient and on the other hand, will not damage the surface of the biosorbent which will allow its reuse.

2.6. Application of Biosorbents and Perspectives

In recent years, the concept of circular economy and its three principles are considered: reduce, reuse and recycle, taking into account economics, energy, and natural resource conservation, resulting in minimization of industrial waste and its impact on health and the environment. The use of biowaste as biosorbents for heavy metal removal and recovery fulfills the CE concepts. More research is needed for the use of non-conventional sorbents on an industrial scale, however, some examples of practical applications of biosorbents are presented below.

Research was carried out on wastewater from a galvanizing process, which contained metals such as Cu, Ni, Zn, and Fe. The choice of biosorbent was guided by availability; cones of coniferous trees were chosen which had good sorption capacity. The biosorbent was pre-treated mechanically and then chemically modified with sodium hydroxide. A significant reduction in pollutants was achieved. After one day of contact between wastewater and biosorbent, the concentrations of Cu, Ni, Zn, and Fe decreased from 2252, 4056, 4020, and 1853 mg/L to 13, 24, 18, and 28 mg/L, respectively. Based on the research, the cones of coniferous trees' mixture were found to be suitable for treatment with a total of 10,000 L of galvanic process wastewater [116]. In the study of Aimal et al. peels of different fruits such as *orange*, *watermelon*, *mango* etc., were used as biosorbent for metal removal. For the removal of nickel from galvanic wastewater, suitably prepared *orange* peel was used as biosorbent. A column method was used for the sorption process, obtaining a nickel removal rate of 89%. The used biosorbent can be reused after regeneration [118]. Moreover, for the removal of chromium (VI) from tannery wastewater, column tests were carried out using neem sawdust. A maximum adsorption capacity of 58.82 mg/g was obtained during sorption. It was shown that for the treatment of 1.5 L of the studied wastewater, 20 g of biosorbent is enough to achieve 99% of treatment efficiency [119].

Different researchers [113,120] have indicated that it would be useful to determine the effect of varying process conditions in relation to the removal of heavy metals from water and to assess the suitability of the proposed biowaste as a biosorbent on a pilot scale.

Many researches carried out on biowaste from agriculture and food production, from forestry and wood industry, and from fisheries for production of biosorbents, show wide perspectives for their use in the sorption process. The use of such produced biosorbents should be part of the implementation of sustainability initiatives at both local and national levels. The following factors taken into account are local differences in climate, environment, agricultural economy and energy sources, and the biowaste produced is different and produced in different quantities, which is, in perspective, an important condition and a possibility of its use.

3. Conclusions

The use of biowaste from the wood processing industry, agricultural production, and fisheries to remove harmful substances from aqueous solutions has many advantages, such as the unique adsorption capacity for a wide range of pollutants, the possibility of managing a variety of biowaste whose landfilling is a major problem, and the fact that these materials are cheap, readily available, non-toxic, and biodegradable. The use of biowaste fits well with the concept of the circular economy through its positive impact on environmental issues related to industrial wastewater treatment and solid waste recycling.

Examinations of plant- and animal-based sorbents from various biowaste in both natural and pre-treated forms were presented. It can be concluded from the findings that agricultural waste shows high adsorption of lead and chromium ions. In the agricultural biowaste analyzed in the present study, differences in the sorption of the metals studied can be observed. On the other hand, biowaste from the wood processing industry showed higher removal efficiency for zinc and lead. However, it should be noted that the fisheries' waste showed the highest efficiency of removal of various heavy metals. It was shown that the adsorption properties of a given biosorbent were significantly improved after appropriate surface pre-treatment.

The application of biosorbents for water treatment should take into account their efficiency, specific sorption properties, and their environmental impact. Analyses of their commercial applications should also take into account the availability of biowaste data close to the place of use. To this end, it seems helpful to assess the opportunities and constraints of using biowaste as a biosorbent using life cycle analysis (LCA) to assess its environmental impact at all stages of the production chain. It will also enable the comparison of these types of biosorbents with commercial sorbents at the stages of their production, use, and disposal.

Further research into the use of biowaste as biosorbents for metal removal will contribute to the further development of biosorption technologies in line with the principles of circular economy and the sustainability initiatives. However, important issues related to the sorption capacities of biosorbents, desorption and recovery of metals, and regeneration and recycling of biosorbents need to be resolved.

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References

1. Christis, M.; Athanassiadis, A.; Vercalsteren, A. Implementation at a city level of circular economy strategies and climate change mitigation—The case of Brussels. *J. Clean. Prod.* **2019**, *218*, 511–520. [CrossRef]
2. Ahmadi, M. Evaluating the performance of 3Rs waste practices: Case study-region one municipality of Tehran. *Adv. Recycl. Waste Manag.* **2017**, *2*, 2. [CrossRef]
3. Huang, B.; Wang, X.; Kua, H.; Geng, Y.; Bleischwitz, R.; Ren, J. Construction and demolition waste management in China through the 3R principle. *Resour. Conserv. Recycl.* **2018**, *129*, 36–44. [CrossRef]
4. MacArthur, E. Towards the circular economy. *J. Ind. Ecol.* **2013**, *2*, 23–44.
5. Ellen MacArthur Foundation. Towards a Circular Economy: Business Rationale for an Accelerated Transition. 2015. Available online: https://www.ellenmacarthurfoundation.org/assets/downloads/publications/TCE_Ellen-MacArthur-Foundation_26-Nov-2015.pdf (accessed on 7 May 2020).
6. EEA. Circular Economy in Europe—Developing the Knowledge Base. Copenhagen: European Environment Agency. 2016. Available online: http://www.eea.europa.eu/publications/circular-economy-in-europe (accessed on 10 July 2021).
7. Abid, M.; Niazi, N.K.; Bibi, I.; Farooqi, A.; Ok, Y.S.; Kunhikrishnan, A.; Ali, F.; Ali, S.; Igalavithana, A.D.; Arshad, M. Arsenic(V) biosorption by charred *orange* peel in aqueous environments. *Int. J. Phytoremediat.* **2016**, *18*, 442–449. [CrossRef]
8. Velazquez-Jimenez, L.H.; Pavlick, A.; Rangel-Mendez, J.R. Chemical characterization of raw and treated *agave* bagasse and its potential as adsorbent of metal cations from water. *Ind. Crop. Prod.* **2013**, *43*, 200–206. [CrossRef]
9. Huang, D.; Li, B.; Ou, J.; Xue, W.; Li, J.; Li, Z.; Li, T.; Chen, S.; Deng, R.; Guo, X. Megamerger of biosorbents and catalytic technologies for the removal of heavy metals from wastewater: Preparation, final disposal, mechanism and influencing factors. *J. Environ. Manag.* **2020**, *261*, 109879. [CrossRef] [PubMed]
10. Hossain, A. Development of Novel Biosorbents in Removing Heavy Metals from Aqueous Solution. Ph.D. Thesis, University of Technology, Sydney (UTS), Sydney, Australia, 2013.
11. Parate, R.; Talib, I. Study of metal adsorbent prepared from tur dal (*Cajanuscajan*) husk: A value addition to agrowaste. *IOSR J. Environ. Sci. Toxicol. Food Technol.* **2014**, *8*, 43–54. [CrossRef]
12. Albadarin, A.B.; Mangwandi, C.; Walker, G.M.; Allen, S.J.; Ahmad, M.N. Biosorption characteristics of sawdust for the removal of Cd(II) Ions: Mechanism and thermodynamic studies. *Chem. Eng. Trans.* **2011**, *24*, 1297–1302.
13. Richards, S.; Dawson, J.; Stutter, M. The potential use of natural vs commercial biosorbent material to remediate stream waters by removing heavy metal contaminants. *J. Environ. Manag.* **2018**, *231*, 275–281. [CrossRef]
14. Ngah, W.S.W.; Fatinathan, S. Pb(II) biosorption using chitosan and chitosan derivatives beads: Equilibrium, ion exchange and mechanism studies. *J. Environ. Sci.* **2010**, *22*, 338–346. [CrossRef]
15. Zakhama, S.; Dhaouadi, H.; M'Henni, F. Nonlinear modelisation of heavy metal removal from aqueous solution using *Ulva lactuca* algae. *Bioresour. Technol.* **2011**, *102*, 786–796. [CrossRef]
16. De Souza Coracao, A.C.; dos Santos, F.S.; Duarte, J.A.; Lopes-Filho, E.A.; De-Paula, J.C.; Rocha, L.M.; Krepsky, N.; Fiaux, S.B.; Teixeira, V.L. What do we know about the utilization of the *Sargassum* species as biosorbents of trace metals in Brazil? *J. Environ. Chem. Eng.* **2020**, *8*, 103941. [CrossRef]
17. Habets, S.; Wild, P.J.; Huijgen, W.J.J.; Van Eck, E.R.H. The influence of thermochemical treatments on the lignocellulosic structure of *wheat* straw as studied by natural abundance 13C NMR. *Bioresour. Technol.* **2013**, *146*, 585–590. [CrossRef]
18. Wang, Q. Deciphering and Optimizing the Process of Removal and Recovery of Pb(II) and Cd(II) from Wastewater by Biosorbent Derived from Fruit Waste. Ph.D. Thesis, Hong Kong Polytechnic University, Hong Kong, China, 2019.
19. Farinella, N.V.; Matos, G.D.; Arruda, M.A.Z. Grape bagasse as a potential biosorbent of metals in effluent treatments. *Bioresour. Technol.* **2007**, *98*, 1940–1946. [CrossRef] [PubMed]
20. Zhang, L.; Xia, W.; Teng, B.; Liu, X.; Zhang, W. Zirconium cross-linked chitosan composite: Preparation, characterization and application in adsorption of Cr(VI). *Chem. Eng. J.* **2013**, *229*, 1–8. [CrossRef]
21. Kupich, I.; Madeła, M. Sorption as effective and economical method of waterborne pathogens removal. In *Waterborne Pathogens*; Butterworth-Heinemann: Oxford, UK, 2020; pp. 301–319.
22. Tan, X.; Liu, Y.; Zeng, G.; Wang, X.; Hu, X.; Gu, Y.; Yang, Z. Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere* **2015**, *125*, 70–85. [CrossRef] [PubMed]
23. Gaur, N.; Flora, G.; Yadav, M.; Tiwari, A. A review with recent advancements on bioremediation-based abolition of heavy metals. *Environ. Sci. Process. Impacts* **2014**, *16*, 180–193. [CrossRef] [PubMed]
24. Mathew, B.B.; Jaishankar, M.; Biju, V.G.; Beeregowda, K.N. Role of bioadsorbents in reducing toxic metals. *J. Toxicol.* **2016**, *2016*, 436960. [CrossRef] [PubMed]
25. Sud, D.; Mahajan, G.; Kaur, M.P. Agricultural waste material as potential adsorbent for sequestering heavy metal ions from aqueous solutions—A review. *Bioresour. Technol.* **2008**, *99*, 6017–6027. [CrossRef] [PubMed]
26. Abdolali, A. Detoxification of Heavy Metal Ions from Aqueous Solutions Using a Novel Lignocellulosic Multi-Metal Binding Biosorbent. Ph.D. Thesis, University of Technology, Sydney (UTS), Sydney, Australia, 2017.
27. Hackbarth, F.V.; Girardi, F.; Santos, J.C.; Souza, A.A.U.; Boaventura, R.A.R.; Guelli, S.M.A.; Souza, U.; Vilar, V.J.P. Ion-exchange breakthrough curves for single and multi-metal systems using marine macroalgae *Pelvetia canaliculata* as a natural cation exchanger. *Chem. Eng. J.* **2015**, *269*, 359–370. [CrossRef]

28. Liu, C.; Ngo, H.H.; Guo, W. *Watermelon* rind: Agro-waste or superior biosorbent? *Appl. Biochem. Biotechnol.* **2012**, *167*, 1699–1715. [CrossRef]
29. Pozdniakova, T.A.; Mazur, L.P.; Boaventura, R.A.R.; Vilar, V.J.P. Brown macro-algae as natural cation exchangers for the treatment of zinc containing wastewaters generated in the galvanizing process. *J. Clean. Prod.* **2016**, *119*, 38–49. [CrossRef]
30. Reddy, N.A.; Lakshmipathy, R.; Sarada, N.C. Application of *Citrullus lanatus* rind as biosorbent for removal of trivalent chromium from aqueous solution. *Alex. Eng. J.* **2014**, *53*, 969–975. [CrossRef]
31. Kayranli, B. Cadmium removal mechanisms from aqueous solution by using recycled lignocelluloses. *Alex. Eng. J.* **2021**, *61*, 443–457. [CrossRef]
32. Ali, R.M.; Hamad, H.A.; Hussein, M.M.; Malash, G.F. Potential of using green adsorbent of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. *Ecol. Eng.* **2016**, *91*, 317–332. [CrossRef]
33. Liu, C.; Ngo, H.H.; Guo, W.; Tung, K.L. Optimal conditions for preparation of banana peels, *sugarcane* bagasse and *watermelon* rind in removing copper from water. *Bioresour. Technol.* **2012**, *119*, 349–354. [CrossRef] [PubMed]
34. Ibrahim, D.; Froberg, B.; Wolf, A.; Rusyniak, D.E. Heavy metal poisoning: Clinical presentations and pathophysiology. *Clin. Lab. Med.* **2006**, *26*, 67–97. [CrossRef] [PubMed]
35. Farooq, U.; Kozinski, J.A.; Khan, M.A.; Athar, M. Biosorption of heavy metal ions using *wheat* based biosorbents—A review of the recent literature. *Bioresour. Technol.* **2010**, *101*, 5043–5053. [CrossRef] [PubMed]
36. Kamizela, T.; Worwag, M. Processing of Water Treatment Sludge by Bioleaching. *Energies* **2020**, *13*, 6539. [CrossRef]
37. Kamizela, T.; Grobelak, A.; Worwag, M. Use of *Acidithiobacillus thiooxidans* and *Acidithiobacillus ferrooxidans* in the Recovery of Heavy Metals from Landfill Leachates. *Energies* **2021**, *14*, 3336. [CrossRef]
38. Samant, R.A.; Gurav, V.L. A biosorption of heavy metal ions from effluent using waste fish scale. *Asian J. Res. Chem.* **2018**, *11*, 775–777. [CrossRef]
39. Ansari, T.M.; Shaheen, S.; Manzoor, S.; Naz, S.; Hanif, M.A. Litchi chinensis peel biomass as green adsorbent for cadmium (Cd) ions removal from aqueous solutions. *Desalin. Water Treat.* **2020**, *173*, 343–350. [CrossRef]
40. Porpino, K.K.P.; Carvalho Filho, J.R.; Conceição Silva Barreto, M.; Beltrão Cambuim, K.; Toscano, I.A.S.; Azevedo Lima, M. Fe(II) adsorption on *Ucides cordatus* crab shells. *Quim. Nov.* **2011**, *34*, 928–932. [CrossRef]
41. Sweidan, H.; Hamouda, M.; El-Hassan, H.; Maraqa, M. A framework for the investigation of biowaste materials as potential adsorbents for water treatment. In Proceedings of the 4th World Congress on Civil, Structural, and Environmental Engineering, Rome, Italy, 7–9 April 2019; pp. 7–9.
42. Wan Ngah, W.S.; Hanafiah, M.A.K.M. Removal of heavy metal ions from wastewater by chemically modified plant wastes as adsorbents: A review. *Bioresour. Technol.* **2008**, *99*, 3935–3948. [CrossRef] [PubMed]
43. Ghimire, K.N.; Inoue, K.; Ohto, K.; Hayashida, T. Adsorptive separation of metallic pollutants onto waste seaweeds, Porphyra yezoensis and Ulva japonica. *Sep. Sci. Technol.* **2007**, *42*, 2003–2018. [CrossRef]
44. Biswas, B.K.; Inoue, K.; Ghimire, K.N.; Harada, H.; Ohto, K.; Kawakita, H. Removal and recovery of phosphorus from water by means of adsorption onto *orange* waste gel loaded with zirconium. *Bioresour. Technol.* **2008**, *99*, 8685–8690. [CrossRef]
45. Benis, K.Z.; Damuchali, A.M.; McPhedran, K.N.; Soltan, J. Treatment of aqueous arsenic—A review of biosorbent preparation methods. *J. Environ. Manag.* **2020**, *273*, 111126. [CrossRef]
46. Nieto, L.M.; Alami, S.B.D.; Hodaifa, G.; Faur, C.; Rodríguez, S.; Giménez, J.A.; Ochando, J. Adsorption of iron on crude olive stones. *Ind. Crop. Prod.* **2010**, *32*, 467–471. [CrossRef]
47. Demirbas, A. Heavy metal adsorption onto agro-based waste materials: A review. *J. Hazard. Mater.* **2008**, *157*, 220–229. [CrossRef]
48. Nyazi, K.; Yaacoubi, A.; Baçaoui, A.; Bennouna, C.; Dahbi, A.; Rivera-Utrilla, J.; Moreno-Castilla, C. Preparation and characterization of new adsorbent materials from the olive wastes. *J. Phys. IV* **2004**, *123*, 121–124. [CrossRef]
49. Elizalde-González, M.P.; Mattusch, J.; Wennrich, R. Chemically modified *maize* cobs waste with enhanced adsorption properties upon methyl *orange* and arsenic. *Bioresour. Technol.* **2008**, *99*, 5134–5139. [CrossRef]
50. Banu, I.S.I.; Aprodu, I. Potential of *maize* cobs for removal Zn(II) and Ni(II) in aqueous systems. *Rev. Chim. Buchar.* **2008**, *59*, 1375–1377. [CrossRef]
51. Chuah, T.G.; Jumasiah, A.; Azni, I.; Katayon, S.; Thomas Choong, S.Y. *Rice* husk as a potentially low-cost biosorbent for heavy metal and dye removal: An overview. *Desalination* **2005**, *175*, 305–316. [CrossRef]
52. Daifullah, A.A.M.; Girgis, B.S.; Gad, H.M.H. Utilization of agro-residues (*rice* husk) in small waste water treatment plans. *Mater. Lett.* **2003**, *57*, 1723–1731. [CrossRef]
53. Ding, Y.; Jing, D.; Gong, H.; Zhou, L.; Yang, X. Biosorption of aquatic cadmium(II) by unmodified *rice* straw. *Bioresour. Technol.* **2012**, *114*, 20–25. [CrossRef] [PubMed]
54. Chao, H.P.; Chang, C.C. Adsorption of copper(II), cadmium(II), nickel(II) and lead(II) from aqueous solution using biosorbents. *Adsorption* **2012**, *18*, 395–401. [CrossRef]
55. Basu, M.; Guha, A.K.; Ray, L. Biosorptive removal of lead by *lentil* husk. *J. Environ. Chem. Eng.* **2015**, *3*, 1088–1095. [CrossRef]
56. Pehlivan, E.; Altun, T.; Parlayici, S. Utilization of *barley* straws as biosorbents for Cu^{2+} and Pb^{2+} ions. *J. Hazard. Mater.* **2009**, *164*, 982–986. [CrossRef]
57. Nadeem, R.; Manzoor, Q.; Iqbal, M.; Nisar, J. Biosorption of Pb(II) onto immobilized native *Mangifera indica* waste biomass. *J. Ind. Eng. Chem.* **2016**, *35*, 185–194. [CrossRef]

58. Milojković, J.; Stojanović, M.; Mihajlović, M.; Lopičić, Z.; Šoštarić, T.; Petrović, M.; Petrović, J. Pb(II) biosorption by selected waste biomass. *Zast. Mater.* **2016**, *57*, 418–423. [CrossRef]
59. Bozęcka, A.; Sanak-Rydlewska, S. Sorption of Pb^{2+} ions from aqueous solutions on organic wastes (part I). *Arch. Min. Sci.* **2013**, *58*, 1241–1250.
60. Bulut, Z.; Baysal, Y. Removal of Pb(II) from wastewater using *wheat* bran. *J. Environ. Manag.* **2006**, *78*, 107–113. [CrossRef]
61. Iqbal, M.; Saeed, A.; Kalim, I. Characterization of adsorptive capacity and investigation of mechanism of Cu^{2+}, Ni^{2+} and Zn^{2+} adsorption on *mango* peel waste from constituted metal solution and genuine electroplating effluent. *Sep. Sci. Technol.* **2009**, *44*, 3770–3791. [CrossRef]
62. Stanković, S.; Šoštarić, T.; Bugarčić, M.; Janićijević, A.; Pantović-Spajić, K.; Lopičić, Z. Adsorption of Cu(II) ions from synthetic solutions by *sunflower* seed husks. *Acta Period. Technol.* **2019**, *352*, 268–277. [CrossRef]
63. Aksu, Z.; Işoğlu, I.A. Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar *beet* pulp. *Process. Biochem.* **2005**, *40*, 3031–3044. [CrossRef]
64. Rao, R.A.K.; Ikram, S. Sorption studies of Cu(II) on *gooseberry* fruit (*Emblica officinalis*) and its removal from electroplating wastewater. *Desalination* **2011**, *277*, 390–398. [CrossRef]
65. Siangko, C.N.; Escasinas, P.J.; Florida, H.A. Biosorption Optimization and Kinetic Modeling of Ni2+ and Zn2+ Removal from Aqueous Solution Using Calamansi (Citrofortunella microcarpa) and Dalandan (Citrus aurantium) Peels. Conference Paper, DLSU Research·Congress, August 2021. Available online: https://www.dlsu.edu.ph/wp-content/uploads/pdf/conferences/research-congress-proceedings/2021/SEE-10.pdf (accessed on 23 August 2021).
66. Farhan, A.M.; Salem, N.M.; Al-Dujaili, A.H.; Awwad, A.M. Biosorption Studies of Cr(VI) Ions from Electroplating Wastewater by *Walnut* Shell Powder. *Am. J. Environ. Eng.* **2012**, *2*, 188–195. [CrossRef]
67. Anwar, J.; Shafique, U.; Muhammad Salman, W.; Hussain, Z.; Saleem, M.; Shahid, N.; Mahboob, S.; Ghafoor, S.; Akram, M.; Rehman, R.; et al. Removal of chromium from water using pea waste—A green approach. *Green Chem. Lett. Rev.* **2010**, *3*, 239–243. [CrossRef]
68. Malkoc, E.; Nuhoglu, Y. Potential of tea factory waste for chromium(VI) removal from aqueous solutions: Thermodynamic and kinetic studies. *Sep. Purif. Technol.* **2007**, *54*, 291–298. [CrossRef]
69. Khalil, U.; Shakoor, M.B.; Ali, S.; Ahmad, S.R.; Rizwan, M.; Alsahli, A.A.; Alyemeni, M.N. Selective Removal of Hexavalent Chromium from Wastewater by *Rice* Husk: Kinetic, Isotherm and Spectroscopic Investigation. *Water* **2021**, *13*, 263. [CrossRef]
70. Zhao, X.; Zheng, J.; You, S.; Liu, C.; Du, L.; Chen, K.; Liu, Y.; Ma, L. Selective Adsorption of CR (VI) onto Amine-Modified *Passion Fruit* Peel Biosorbent. *Processes* **2021**, *9*, 790. [CrossRef]
71. Nasernejad, B.; Zadeh, T.E.; Pour, B.B.; Bygi, M.E.; Zamani, A. Camparison for biosorption modeling of heavy metals (Cr (III), Cu (II), Zn (II)) adsorption from wastewater by *carrot* residues. *Process. Biochem.* **2005**, *40*, 1319–1322. [CrossRef]
72. Khaskheli, M.I.; Memon, S.Q.; Siyal, A.N.; Khuhawar, M.Y. Use of *orange* peel waste for Arsenic remediation of drinking water. *Waste Biomass Valoriz.* **2011**, *2*, 423–433. [CrossRef]
73. FAOSTAT. *Food and Agricultural Commodities Production*; Food and Agricultural Organization of United Nations, Economic and Social Department, The Statistical Division: New York, NY, USA, 2016. Available online: http://www.fao.org/faostat/en/#home (accessed on 20 January 2021).
74. Hamed Mosavian, M.T.; Khazaei, I.; Aliabadi, M. Use of sawdust of aspen tree for the removal of chromium(VI) from aqueous solution. *Iran. J. Earth Sci.* **2012**, *4*, 25–30.
75. Kim, N.; Park, M.; Park, D. A new efficient forest biowaste as biosorbent for removal of cationic heavy metals. *Bioresour. Technol.* **2015**, *175*, 629–632. [CrossRef] [PubMed]
76. Biegaska, M.; Cierpiszewski, R. Utilization of cellulose and wicker bark of *Salix americana* for copper adsorption from aqueous solutions. *Proc. ECOpole* **2010**, *4*, 313–317.
77. Afroze, S.; Sen, T.K.; Ang, H.M. Adsorption removal of zinc(II) from aqueous phase by raw and base modified *Eucalyptus sheathiana* bark: Kinetics, mechanism and equilibrium study. *Process Saf. Environ. Prot.* **2016**, *102*, 336–352. [CrossRef]
78. Pravalika, K.V.; Janaki Sriram, P.; Meghana, P.K.; Ravindhranath, K. A new effective adsorbent derived from the barks of *Ziziphus mauritiana* plant for the removal of chromate from polluted water. *Rasayan J. Chem.* **2018**, *11*, 1750–1756. [CrossRef]
79. Vinodhini, V.; Das, N. Mechanism of Cr (VI) biosorption by neem sawdust. *Am.-Eurasian J. Sci. Res.* **2009**, *4*, 324–329.
80. Ofomaja, A.E.; Naidoo, E.B. Biosorption of lead(II) onto *pine* cone powder: Studies on biosorption performance and process design to minimize biosorbent mass. *Carbohydr. Polym.* **2010**, *82*, 1031–1042. [CrossRef]
81. Ofomaja, A.E.; Naidoo, E.B.; Modise, S.J. Removal of copper(II) from aqueous solution by *pine* and base modified *pine* cone powder as biosorbent. *J. Hazard. Mater.* **2009**, *168*, 909–917. [CrossRef] [PubMed]
82. Deniz, F. Color removal from aqueous solutions of metal-containing dye using *pine* cone. *Desalin. Water Treat.* **2013**, *51*, 22–24, 4573–4581. [CrossRef]
83. Rinaudo, M. Chitin and chitosan: Properties and applications. *Prog. Polym. Sci.* **2006**, *31*, 603–632. [CrossRef]
84. Suzuki, Y.; Kametani, T.; Maruyama, T. Removal of heavy metals from aqueous solution by nonliving Ulva seaweed as biosorbent. *Water Res.* **2005**, *39*, 1803–1808. [CrossRef]
85. Ibrahim, W.M. Biosorption of heavy metal ions from aqueous solution by red macroalgae. *J. Hazard. Mater.* **2011**, *192*, 1827–1835. [CrossRef]

86. Sankararamakrishnan, N.; Sharma, A.K.; Sanghi, R. Novel chitosan derivative for the removal of cadmium in the presence of cyanide from electroplating wastewater. *J. Hazard. Mater.* **2007**, *148*, 353–359. [CrossRef]
87. Bilal, M.; Shah, J.A.; Ashfaq, T.; Gardazi, S.M.H.; Tahir, A.A.; Pervez, A.; Haroon, H.; Mahmood, Q. Waste biomass adsorbents for copper removal from industrial wastewater-A review. *J. Hazard. Mater.* **2013**, *263*, 322–333. [CrossRef]
88. Vijayaraghavan, K.; Winnie, H.Y.N.; Balasubramanian, R. Biosorption characteristics of crab shell particles for the removal of manganese(II) and zinc(II) from aqueous solutions. *Desalination* **2011**, *266*, 195–200. [CrossRef]
89. Prasanna Kumar, Y.; King, P.; Prasad, V.S.R.K. Adsorption of zinc from aqueous solution using marine green algae—*Ulva fasciata* sp. *Chem. Eng. J.* **2007**, *129*, 161–166. [CrossRef]
90. Freitas, O.M.M.; Martins, R.J.E.; Delerue-Matos, C.M.; Boaventura, R.A.R. Removal of Cd(II), Zn(II) and Pb(II) from aqueous solutions by brown marine macro algae: Kinetic modelling. *J. Hazard. Mater.* **2008**, *153*, 493–501. [CrossRef]
91. Blanes, P.; Cong, C.; Cortadi, A.; Frascaroli, M.; Gattuso, M.; García, S.; González, J.; Harada, M.; Matulewicz, C.; Niwa, Y.; et al. Biosorption of Trivalent Chromium from Aqueous Solution by Red Seaweed *Polysiphonia nigrescens*. *J. Water Resour. Prot.* **2011**, *3*, 832–843. [CrossRef]
92. Murphy, V.; Hughes, H.; McLoughlin, P. Comparative study of chromium biosorption by red, green and brown seaweed biomass. *Chemosphere* **2008**, *70*, 1128–1134. [CrossRef]
93. Kaveeshwar, A.R.; Sanders, M.; Ponnusamy, S.K.; Depan, D.; Subramaniam, R. Chitosan as a biosorbent for adsorption of iron(II) from fracking wastewater. *Polym. Adv. Technol.* **2018**, *29*, 961–969. [CrossRef]
94. Deniz, F.; Tezel Ersanli, E. A renewable biosorbent material for green decontamination of heavy metal pollution from aquatic medium: A case study on manganese removal. *Int. J. Phytoremediat.* **2021**, *23*, 231–237. [CrossRef] [PubMed]
95. Vijayaraghavan, K.; Balasubramanian, R. Single and binary biosorption of cerium and europium onto crab shell particles. *Chem. Eng. J.* **2010**, *163*, 337–343. [CrossRef]
96. Guibal, E. Interactions of metal ions with chitosan-based sorbents: A review. *Sep. Purif. Technol.* **2004**, *38*, 43–74. [CrossRef]
97. Crini, G.; Badot, P.M. Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. *Prog. Polym. Sci.* **2008**, *33*, 399–447. [CrossRef]
98. Bergmann, C.P.; Machado, F.M. *Carbon Nanomaterials as Adsorbents for Environmental and Biological Applications*; Volume Carbon; Springer International Publishing Bergmann: New York, NA, USA, 2015; pp. 1–105.
99. Chen, A.; Shang, C.; Shao, J.; Lin, Y.; Luo, S.; Zhang, J.; Huang, H.; Lei, M.; Zeng, Q. Carbon disulfide-modified magnetic ion-imprinted chitosan-Fe (III): A novel adsorbent for simultaneous removal of tetracycline and cadmium. *Carbohydr. Polym.* **2017**, *155*, 19–27. [CrossRef] [PubMed]
100. Aris, A.Z.; Ismail, F.A.; Ng, H.Y.; Praveena, S.M. An experimental and modelling study of selected heavy metals removal from aqueous solution using *Scylla serrata* as biosorbent. *Pertanika J. Sci. Technol.* **2014**, *22*, 553–566.
101. Michalak, I.; Chojnacka, K.; Witek-Krowiak, A. State of the art for the biosorption process—A review. *Appl. Biochem. Biotechnol.* **2013**, *170*, 1389–1416. [CrossRef] [PubMed]
102. He, J.; Chen, J.P. A comprehensive review on biosorption of heavy metals by algal biomass: Materials, performances, chemistry, and modeling simulation tools. *Bioresour. Technol.* **2014**, *160*, 67–78. [CrossRef]
103. Ruangrit, K.; Pekkoh, J.; Duangjan, K.; Phinyo, K.; Kamopas, W.; Jeerapan, I.; Pathom-aree, W.; Srinuanpan, S. Effectiveness of Using Oleaginous Microalgae as a Green Biosorbent to Remove Copper from Aqueous Media. *EnvironmentAsia* **2021**, *14*, 14–23.
104. Romera, E.; González, F.; Ballester, A.; Blázquez, M.L.; Muñoz, J.A. Comparative study of biosorption of heavy metals using different types of algae. *Bioresour. Technol.* **2007**, *98*, 3344–3353. [CrossRef] [PubMed]
105. Sheng, P.X.; Ting, Y.P.; Chen, J.P.; Hong, L. Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: Characterization of biosorptive capacity and investigation of mechanisms. *J. Colloid Interface Sci.* **2004**, *275*, 131–141. [CrossRef]
106. Romera, E.; González, F.; Ballester, A.; Blázquez, M.L.; Muñoz, J.A. Biosorption with algae: A statistical review. *Crit. Rev. Biotechnol.* **2006**, *26*, 223–235. [CrossRef] [PubMed]
107. Davis, T.A.; Volesky, B.; Mucci, A. A review of the biochemistry of heavy metal biosorption by brown algae. *Water Res.* **2003**, *37*, 4311–4330. [CrossRef]
108. Lodeiro, P.; Cordero, B.; Barriada, J.L.; Herrero, R.; Sastre De Vicente, M.E. Biosorption of cadmium by biomass of brown marine macroalgae. *Bioresour. Technol.* **2005**, *96*, 1796–1803. [CrossRef]
109. Kleinübing, S.J.; Silva, E.A.; Silva, M.G.C.; Guibal, E. Equilibrium of Cu(II) and Ni(II) biosorption by marine alga *Sargassum filipendula* in a dynamic system: Competitiveness and selectivity. *Bioresour. Technol.* **2011**, *102*, 4610–4617. [CrossRef]
110. Deng, L.; Zhang, Y.; Qin, J.; Wang, X.; Zhu, X. Biosorption of Cr(VI) from aqueous solutions by nonliving green algae *Cladophora albida*. *Miner. Eng.* **2009**, *22*, 372–377. [CrossRef]
111. Bădescu, I.S.; Bulgariu, D.; Ahmad, I.; Bulgariu, L. Valorisation possibilities of exhausted biosorbents loaded with metal ions–a review. *J. Environ. Manag.* **2018**, *15*, 288–297. [CrossRef]
112. Abdolali, A.; Ngo, H.H.; Guo, W.; Zhou, J.L.; Du, B.; Wei, Q.; Wang, X.C.; Nguyen, P.D. Characterization of a multi-metal binding biosorbent: Chemical modification and desorption studies. *Bioresour. Technol.* **2015**, *193*, 477–487. [CrossRef] [PubMed]
113. Jing, Y.D.; He, Z.L.; Yang, X.E. Effects of pH, organic acids, and competitive cations on mercury desorption in soils. *Chemosphere* **2007**, *69*, 1662–1669. [CrossRef] [PubMed]
114. Filote, C.; Volf, I.; Santos, S.C.R.; Botelho, C.M.S. Bioadsorptive removal of Pb(II) from aqueous solution by the biorefinery waste of *Fucus spiralis*. *Sci. Total Environ.* **2019**, *648*, 1201–1209. [CrossRef] [PubMed]

115. Stirk, W.A.; Van Staden, J. Desorption of cadmium and the reuse of brown seaweed derived products as biosorbents. *Bot. Mar.* **2002**, *45*, 9–16. [CrossRef]
116. Pertile, E.; Vaclavik, V.; Dvorsky, T.; Heviankova, S. The Removal of Residual Concentration of Hazardous Metals in Wastewater from a Neutralization Station Using Biosorbent—A Case Study Company Gutra, Czech Republic. *Int. J. Environ. Res. Public Health* **2020**, *17*, 7225. [CrossRef] [PubMed]
117. Koduru, J.R.; Chang, Y.Y.; Yang, J.K.; Kim, I.S. Iron oxide impregnated *Morus alba*, L. fruit peel for biosorption of co(II): Biosorption properties and mechanism. *Sci. World J. Vol.* **2013**, *2013*, 917146.
118. Ajmal, M.; Rao, R.A.; Ahmad, R.; Ahmad, J. Adsorption studies on Citrus reticulata (fruit peel of *orange*): Removal and recovery of Ni(II) from electroplating wastewater. *J. Hazard. Mater.* **2000**, *79*, 117–131. [CrossRef]
119. Vinodhini, V.; Das, N.; Vinodhini, V.; Das, N. Relevant approach to assess the performance of sawdust as adsorbent of chromium (VI) ions from aqueous solutions. *Int. J. Environ. Sci. Technol.* **2010**, *7*, 85–92. [CrossRef]
120. Joseph, L.; Jun, B.M.; Flora, J.R.; Park, C.M.; Yoon, Y. Removal of heavy metals from water sources in the developing world using low-cost materials: A review. *Chemosphere* **2019**, *229*, 142–159. [CrossRef] [PubMed]