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Review

Review of Heavy Metal Adsorption Processes by Several Organic Matters from Wastewaters

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Abstract: Heavy metal contamination of natural rivers and wastewaters is a problem for both the environment and human society. The accumulation and adsorption of heavy metals could happen with several organic and inorganic matters, but the most used adsorbents are (biological and chemical) organic compounds. This review article presents the basics of heavy metal adsorption on several organic surfaces. There are many organic matters, which seem to be useful as agents for heavy metal adsorption. All of the cited authors and articles present the adsorption kinetics by the most used isotherm models (such as Langmuir and Freundlich isotherms). By comparing several research results presented by a pre-selected assortment of papers, we would like to give an overview of the microbiological, organic chemical, and other surface adsorption possibilities. We draw conclusions for two new adsorption fields (adsorption with biosorbent and artificial materials). We present an optional possibility to study adsorption kinetics, efficiency and regeneration methods to successfully conclude the heavy metal treatment process, and we make some recommendations about the efficient water usage calculations using the water allowance coefficient (WAC) indicator.

Keywords: heavy metals; adsorption capacity; biosorption; isotherm models; adsorption kinetics; water allowance coefficient (WAC)

1. Introduction

Heavy metals are unique elements in the environment because most of them are biogenic (each of them are necessary for nature and human bodies in small concentrations) but can accumulate in the human body and biological organisms if most of them are in high concentrations. The effects of several factors influence the environmental mobility of heavy metals. Typically, they turn into a form of metal complexes in the environment (the general heavy metal treatment process presented by Figure A1 in Appendix A).

Several chemical and physical technological solutions have been used and developed to remove high concentrations of each potential toxic heavy metal from wastewater, including: precipitation, solvent extraction, ion-exchanger, reverse osmosis, oxidation/reduction, sedimentation, filtration, electrochemical techniques, and cation surfactant, etc. Extensive study of heavy metal removal includes: Jeppu et al., 2012 [1] studied some potential adsorbent for the treatment of heavy metals, and they determined the adsorption isotherm and kinetic model also. Optimization of the conditions for maximum sorption was developed by Jeppu and Clement 2012 [2]; the effect of process parameters such as initial concentration, temperature, adsorbent dose and contact time on the removal of copper, nickel, chromium and zinc from aqueous solution was studied by Xue et al., 2009 [3]. In addition, earlier studies showed that *Moringa oleifera* (MO) seeds' powder is effective in heavy metal remediation of water. However, these traditional methods require further research and development due to their high operational cost, low removal efficiency at low concentration, and toxic sludge generation that requires additional treatment. Results showed that the removal of toxic metals by using MO seeds could be considered an economically and environmentally safe method for wastewater treatment [4]. Therefore, the Word Heath Organization (WHO) and the Environmental Protection Agency (EPA) have regulated the maximum acceptable levels of discharge into the environments [5].

Industrial wastewaters containing copper, zinc and cadmium, which are produced by various industrial technologies (such as mining, and heavy industry i.e., steel and aluminum production). The accumulation of heavy metals in the environment makes it necessary to develop new sewage treatment technologies. In this regard, Ahmed and Ahmaruzzaman 2016 [6] developed a technology-based biosorption and sedimentation method. Asuquo et al., 2017 [7] studied the comparison of different types of biomass-based waste treatment technologies, such as the methods using bacteria, yeast, and artificial sludge, and their efficiency compared to sedimentation/biosorption technologies. During the biosorption process, copper, zinc and nickel ions were successfully accumulated by *A. nodosum*, *S. rimosus* and *F. vesiculosus*. Based on their investigations, they concluded that *A. nodosum*, *S. rimosus*, *F. vesiculosus* and *P. chrysogenum* are the most suitable for the elimination of heavy metals from sewage [7,8].

2. Adsorption Efficiency

The kinetics of the heavy metal adsorption mechanism were described by several scientific studies [9,10]. Most researchers could measure heavy metals and Fe together because the habitat of each element is the same. The occurrence and the fate of heavy metals (Cd, Pb, Cu, Zn and Ni) were investigated in wastewater. Anirudhan et al., 2012 [11] analyzed active sludge technology in the wastewater treatment plant in Thessaloniki, Greece.

The six types of wastewater sludge used and analyzed for their study were taken from different points of the plant, to the inlet and outlet of the primary sedimentation tank, or only from the wastewater from the secondary settling tank. In their investigations, a strong correlation was found between the heavy metal partition coefficient (log K_p) and the suspended solid concentration [12,13]. Hayati et al., 2017 [13] reported in their work that the phase distribution of individual heavy metals during the cleaning process changed very little. Gupta and Suhas 2009 [14] used copper and cadmium ions to activate carbon, compost, cellulose pulp and sewage sludge. Their investigations show that copper was not sealed in sewage sludge, with the other materials being successfully sealed [14]. Tovar-Gómez et al., 2015 [15] demonstrated that osmotic and nanofiltration technological solutions are well-suited for sealing heavy metal content in sewage. For underlying tests, sewage samples that contained copper and cadmium were used among laboratory conditions. Their results showed that osmosis and nanofiltration efficiency were 98% for copper and 99% for cadmium [15]. Due to the efficiency of copper removal, synthetic sewage samples decreased the average copper concentration to 3.5 ± 0.7 ppm [15,16]. Figure 1 shows the comparison of Langmuir and Freundlich isotherms for Cu adsorption.

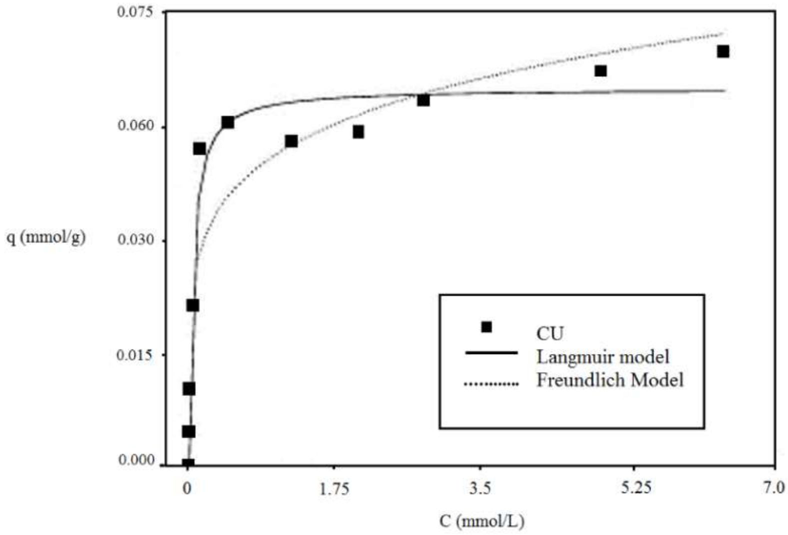

Figure 1. Demonstration of Cu adsorption mechanism by Langmuir and Freundlich isotherms [16].

Guiza 2017 [17] experimented with heavy metal-contaminated rainwater samples using compost and sand. For compost, he found the best physical-chemical properties for copper and zinc ions. The properties of heavy metal removal with average compost type at pH 5 followed the typical Langmuir equation [17–19]. It has been observed that various mixtures of compost, sand and other materials resulted in increasing the heavy metal removal efficiency (Zn 75–96%, Cu 90–93%). In other related studies, the 2012 results of Ranieri and Young [20] on heavy metal sorption were based on the 88–97% efficiency of composting. The relative heavy metal adsorption properties of compost were in the following order: $Pb^{2+} > Cu^{2+} > Zn^{2+}$ [21,22]. The heavy metal adsorption based on the Langmuir isotherm was the same [22–24]. Their research has shown that composts with smaller particles have better adsorption properties. Abbas et al., 2017 [25] reported that it is necessary to extend the use of solid biogas fermentation (composting), produced by biogas from agricultural sources [25–27]. At the same time, this activity carries negative environmental effects of undesirable heavy metals [28,29]. During their investigation, two stages were conducted, using biogas residue and compost respectively. In their work lasting six days, water samples of different origins were tested, as well as samples of solid fermentation and compost which had heavy metal adsorbing properties. They found 70% efficiency for Ni, 40% for Zn and 25% for Cd. Only Cu and Pb had significant values [30,31]. Kolbasov et al., 2017 [32] reported the biosorption potential of heavy metal contaminants using *Phallusia nigra* in two Indian cities. During their investigation, they focused on Cd, Cu, Hg and Pb content [33]. In Thoothukud's water, they found a higher concentration of heavy metals, than in water samples from Vizhinjam city [34,35]. The order of bioaccumulation factors was also determined as follows: Pb > Cd > Cu > Hg [36–38].

3. Comparison of Different Adsorption Surfaces

However, due to the frequently varying reaction conditions in soil environments (SOM, soil organic matter), the equilibrium assumption may not be appropriate for metal adsorption and desorption reactions [39,40]. The modeling approach based on instantaneous equilibrium was not able to describe the time-dependent metal adsorption/desorption reactions in soil [40–42]. Among all SOM binding sites, the carboxylic and phenolic sites are two of the most important functional groups controlling metal binding. Each type of site, or binding sites formed through various combinations of those two, have thermodynamic properties, such as proton and metal binding constants [43,44]. The "WHAM 7" product provides the mechanistic description of metal binding to various binding sites of SOM [45,46]. In this study, the kinetics of heavy metal adsorption and desorption on 10 natural soil samples were studied under various reaction conditions for multiple heavy metals (Cd, Cu, Ni, Pb, and Zn), that all have different metal binding strengths with SOM and metal (hydr)oxides [47,48]. Therefore, to conduct a better risk assessment and design of remediation techniques for contaminated sites, a quantitative understanding of the kinetics of heavy metal adsorption and desorption reactions in soil under varying environmental conditions is required. This provides a basis for further predicting dynamic behavior of heavy metals in coupled chemical and physical processes in SOM [49]. So far, it is unknown how those individual SOM binding sites control both the adsorption and desorption rates of various heavy metals under various reaction chemistry conditions. This limits our ability to accurately predict the dynamic behavior of heavy metals in soil (SOM) [50,51].The transformation of each isotherm is very important, in order to determine the best adsorption method of each heavy metal in SOM. Figure 2. presents the mathematical transformation of isotherms. The decision of best adsorption solution could be the basic process for modeling heavy metal adsorption and comparing the isotherm models.

	Original form	Linearized form
1. Langmuir model:	$q = \frac{q_m . K_L . C}{1 + K_L . C}$	$\frac{C}{q} = \frac{1}{K_L . q_m} + \frac{1}{q_m} . C$
2. Freundlich model:	$q = K_F . C^{\frac{1}{n}}$	$\log q = \log K_F + \frac{1}{n} . \log C$

Figure 2. The transformation of each adsorption isotherm from original to linearized forms [51].

In these equations, the adsorption process is a potent and adaptable method for treatment of heavy metals at very low metal concentration. In combination with the desorption process, it can help solve sludge disposal problems [52]. In order to optimize the conditions for efficient adsorption of heavy metals to melanin, the kinetic and thermodynamic parameters of the adsorption process are studied, and different experimental models are analyzed to understand the nature and behavior of adsorption [53]. Synthetic eumelanin synthesized by tyrosine catalyzed polymerization of L-dopa and eumelanin extracted from human hair were used as adsorbents to remove Pb(II) from the aqueous medium [54]. Usually, the heavy metal-contaminated groundwater is a little acidic (to near neutral pH range) and thus the groundwater in this pH range has to be treated and have the heavy metal content removed [13,53]. Melanin is recently scrutinized for its various biological features, like metal ion adsorption properties, anti-oxidant activity, free radical scavenging behavior and photoprotection [54]. Metal ions could easily be bound to the functional groups of melanin due to the chemical charge, as well as a high surface area of the melanin [55]. The melanin pigment synthesized using tyrosine enzyme exhibited the capability to efficiently remove the uranium from an aqueous solution [56]. Researchers have investigated various techniques (such as reduction) for the removal of heavy metals from wastewater. Heavy metals, such as Cu(II), Pb(II) and Cr(VI) precipitates at a pH value of near, or higher than neutral pH value, and become inseparable from solutions at lower concentrations [54,57]. This study makes use of biosynthesized melanin nanoparticles extracted from the bacterium *Pseudomonas stutzeri* for efficient removal of Hg(II), Cr(VI), Pb(II) and Cu(II) from the aqueous material [56,58].

Considering hexavalent chromium's highly toxic potential, a number of studies have been devoted to its removal by using a kind of liquid extraction, membrane transport processes or sorption processes via various sorbents [58,59]. Since plasticizers are rather expensive, the manufacturing of solid polymeric sorbents like PIMs (polymer inclusion membranes) without added plasticizers that possess good sorption and reuse properties, could result in a good sorbent for the removal of Cr(VI) ions [57]. The aim of the cited papers is to prepare solid sorbents similar to non-plasticized PIMs, based on polyvinyl chloride (PVC), together with the extracting agent Aliquat 336, and also the evaluation of their efficiency in the removal of Cr(VI) ions from aqueous solutions [54,57,60]. In previous studies, the sorption and membrane transport processes of Pb(II) ions used non-plasticized PIMs containing PVC and the extracting agent [61]. However, the synthesized sorbents like modified zeolites, polymeric and composite materials, ionic hybrids and different resins (functionalized or not) have a higher fabrication cost, but instead possess very good sorption capacities, high selectivity, and also good reusability capacities [61,62]. Although the majority of the studies regarding heavy metal separations by PIMs are membrane transport processes, a few studies reported the sorption of some heavy metals on PIMs, such as: Cd(II) and Cu(II), Co(II) and Ni(II), Zn(II), and Pb(II) [13,63,64]. Moreover, the membrane characterization study highlights that the Aliquat 336 also acts as a plasticizer of the PVC polymer matrix [64]. Thus the sorption processes are widely used for the heavy metal removal, both because these methods are easy to handle, and because they allow the use of a plethora of natural and synthetic sorbents [65]. PIMs—which are used in this paper as synthesized sorbent—are thin and stable films obtained by dissolving a polymer [66].

Heavy metal ions, except copper ions, mean biosorption energy which could be calculated using the Dubinin–Radushkevich isotherm models. The biosorption of Se^{4+} and Sb^{3+} ions onto a biomass was determined by an ion exchange mechanism [64,66]. Biomass is caused by interactions between metal ions and functional groups, such as carboxyl groups, on the surface of the bioadsorbent. He and Tebo 1998 [65] used oak sawdust to adsorb Cu^{2+} and noted that Cu^{2+} ions were bound to that active surface on the sawdust by O^{2-} ions, and this action released H^{+} into the solution [65].

The environmental and health challenges posed by toxic heavy metal pollution are increasing. As the advancement of industrialization reaches further heights, developing economies demand that more investigations be carried out with respect to the use of commercial activated carbon adsorbents for heavy metal ions that are prevalent in these countries [66,67]. Activated carbon has gained widespread use for the treatment of heavy metal ions and other pollutants because of its inherent physical properties, such as large surface area, porous structure, high adsorption capacity and large reactive surface [67]. Some of these compounds are known as priority pollutants in many waste streams, such as those originating from industrial activities relating to petroleum production, refining and petrochemicals, pulp and paper manufacture, battery manufacture, tanneries, paint and pigment industries, fertilizer, herbicide and pesticide industries, as well as mining and metallurgic plants [67,68]. Lead metal is used in the construction and building industry as a component of metal alloys, and in the nuclear industry as a radiation shield [68]. These properties of activated carbon are generally controlled by the manufacturing process, which depends on the nature of raw materials, activating agents, and conditions of activation [68]. Therefore, this study is designed to provide information on the use of a commercial activated carbon adsorbent, for the removal of two prominent heavy metals that are toxic, and are prevalent in developing economies because of their drive towards industrialization [69].

While leached dissolved organic matter (DOM) concentrations are usually not measured in studies of heavy metal adsorption to natural sediments, it was found that even a low concentration of leached DOM (10 mg/dm^3) could decrease heavy metal adsorption, and that neglected DOM could substantially increase predictions on heavy metal adsorption [69,70]. When natural sediments are exposed to water, cations, anions and natural organic matter in the sediment are susceptible to leaching by desorption and dissolution [69–71]. Aqueous concentrations of leached materials are governed by factors such as the speciation and abundance of the species in the sediment, the sediment-to-water ratio, the sediment grain size, sediment–water contact time, temperature, and water chemistry [71]. To quantify the influence of leached cations and DOM on heavy metal adsorption, knowledge of aqueous concentrations of the leached species is necessary. The objective of this cited paper is to investigate the leaching of major multivalent cations and DOM from a natural sediment, and quantify the effects of these leached species on the adsorption of Cu and Zn using experimental and surface complexation modeling methods [71]. The influence of leached multivalent cations and DOM from natural sediments on heavy metal adsorption is not fully examined. The potentially inexpensive and abundant remediation option is the adsorption of dissolved heavy metals by natural minerals and sediments. In other studies, the effects of leached Ca and Mg on heavy metal adsorption were simulated by model calculations using total exchangeable Ca and Mg concentrations extracted by $BaCl_2$ [72].

One problem with bark- and tannin-containing materials is the discoloration of water from soluble phenols [73]. Zaini et al., 2010 [74] also presented a study with peanut skin, polymerized with formaldehyde to prevent leaching of color and disintegration upon prolonged contact with water. While pretreatment will increase cost, some pretreatment may be necessary for controlling color [74,75]. Ion exchange takes place as metal cations displace adjacent phenolic hydroxyl groups, forming a chelate compared bark adsorption to that of peanut skins, walnut expeller meal and coconut husks, and showed their capacities to be comparable [75].

In the adsorption process, the heavy metal ions appear to react with calcium ions to form a metal-alginate. In the experiment by Tifoghy and Mohammadi in 2011 [76], and that of Bulgariu and Bulgariu in 2012 [27], the brown seaweeds, *Fucus serratus* and *Laminaria digitata*, outperformed other biological materials such as fungi, green seaweed and unicellular green algae for Cd and Hg removal [76]. The modifications included formaldehyde cross-linking, glutaraldehyde cross-linking and polyethylenimine embedding. The maximum adsorption capacity for the seaweed is approximately 67 mg Cd/g. Alginate, a polysaccharide-based biosorbent, is formed from algin by replacing protons in the carboxylic groups with metal ions [76,77]. Experiments by Visa et al. in 2010 [77] used the brown marine algae, *Ascophyllum nodosum*, in sorption columns to remove Cd. A material derived from the processing of brown seaweed is algin, a high-molecular-weight polymer [77].

Table 1 shows the overview and summary of presented literature sources in a comparison of each type of heavy metal adsorption technique used. There are sample groups of each field of adsorption research, and all of them combined with sample literatures. Table 1 seems to be useful to decision of better adsorption technique application.

Table 1. Listed literatures grouped by adsorption research fields (edited by authors).

Research Fields of Adsorption Techniques	Number of Relevant Cited Literatures	Listed Literatures (With Citation Numbers—Listed in "References" Section)
Studies of adsorption kinetics (isotherms, modelling, process analyses and thermodynamics)	22	[1–3,7,9,10,13,23,26,28,36,37,41,42,58,61,67,69,75,78–80]
Adsorption by biosorbent materials	22	[4,17–19,22,25,27,29,30,36,45,46,49,50,53,56,60,70,71,81,82]
Algal biosorbent adsorptions	19	[19,27,46,49,69,83–96]
Adsorption processes in microbiological ways	5	[65,66,76,77,97]
Physical and chemical quality of several adsorbents	14	[5,24,37–40,43,47,48,55,63,64,77,79]
Unique adsorbent materials (such as industrial waste and bentonites) *	24	[6–16,20,21,30,33–35,42,64,68,71,73,98,99]
Biopolymers, nanomaterials and composite adsorbents	14	[31,32,41,44,51,52,54,57,59,72,74,76,100,101]

* This is the most researched field in our cited literatures.

Table 1 shows the relevant research fields in the focus of cited literature sources. The application of several unique adsorbent materials (such as industrial waste, modified cellulose and bentonites) seems to be an effective way of heavy metal adsorption. According to number 22 of the cited articles, the adsorption method and usage of biosorbent materials (meaning biological adsorbents) could be the two future scientific ways, but the process analyses will be described in the Conclusion. Due to the success of algal biomass adsorbent utilization, we focused on this research are to develop the water footprint and water allowance coefficient (WAC) calculation process (see Sections 4.1 and 4.2 points).

Table 2 shows a comparison of each adsorbent by heavy metal adsorption efficiency (with gray colored cells and italic numbers of efficiency in percent). We collected efficiency data from the cited literature and linked into the table to help the utilization of them for further adsorption research. The best adsorption efficiency was presented by the algal biosorbent (more than 90%). The microbiological and biopolymer adsorbents presented the same adsorption efficiency range (between 70% and 95%). The unique adsorbent materials (mostly artificial materials, such as industrial wastes and gel-based chemical materials) presented the lowest adsorption capacity, but they are more than 60%.

Table 2. Comparison of each adsorbents by heavy metal adsorption efficiency (edited by authors).

Adsorption Efficiency of Each Adsorbents [in %]	Algal Biosorbent	Microbiological Adsorption Processes	Biopolymer Adsorbents	Unique Adsorbents (Artificial Materials)
60–70%				60%–
70–80%		70%–	70%–	
80–90%				90%
90–95%	90%–	–94–95%	–94–95%	
95–(~)99%	–98–99%			

Figure 3 also shows a kind of collection of cited literature sources. The diagram presents the number of relevant literature sources by year, and expresses the current improvement direction of the adsorption research field (because most of the relevant sources were from the last few years).

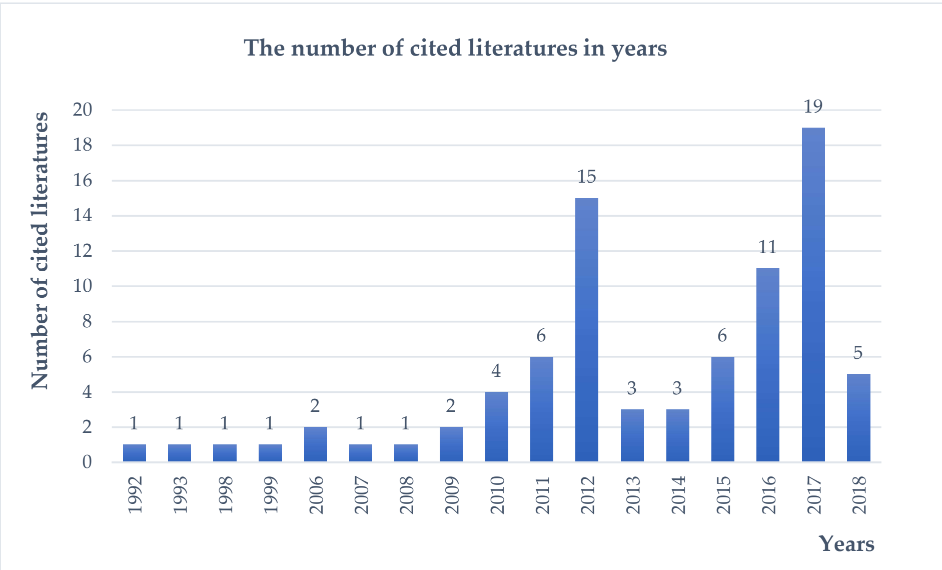

Figure 3. The number of cited literature sources in target years (Data collection from cited literatures—edited by authors).

4. Environmental Economics Concepts Related to Practical Application

Algae are capable of supporting the cleaning processes even in a deceased state, to a varying degree of efficiency. This is notable because not all contexts that need to be processed can serve as an environment for the cells in question to multiply, be those either cells or algae, or even bacteria [94–96,102]. In the case of producing micro-algae in an open area, using an open water system, a significant part of the water footprint comes from the evaporation of the water body's surface area, and the water supplementing the loss. In both cases, this is added to the blue water footprint value (ground, or subterranean water usage). In order to estimate this, we need to consider a multitude of geographic, climate, and weather factors. By contrast, the closed water system process is less sensitive to the ever-changing risks of the environment. It can be operated more safely, and with a higher income, but may have further technical costs, which have to be included in the calculations as a correction water footprint factor. In the case of algae used for bio-adsorption of heavy metals, the harvesting phase of the microalgae has the highest water requirement. However, this water can be fed back into the production phase [103].

4.1. Biosorption of Heavy Metals and Water Footprint Calculation through the Example of Algae

Researching the water footprint of producing algae is important for third-generation bio-fuel production nowadays. This is redefining the question of "drinking and/or driving". (Alternatively, according to earlier research, "eat, drink and/or drive" as related to fuel production, further questions on soil usage, foodstuffs production and air pollution/greenhouse gas (GHG) emissions, also arise) [83,84,104,105]. The first phase of such estimations deals with the water footprint of algae production or harvesting in either closed or open methods. This is a general starting point. Among the estimations' results, there are differences by area, and in process, but as a base value, we can accept the water footprint of bio-fuel production from microalgae to be 3494 kg water for each kg of bio-fuel, if we do not feed the water back. This value improves by 39.4% with 50% of water fed back, while it produces 93% better results when all water is fed back [85–89,106]. One of the most notable advantages of using microalgae in our current study is that producing it is not dependent on freshwater, and it can be done using contaminated water just as well [90].

If our starting point is the aforementioned research, we can state that re-feeding technological solutions based on the principle of circularity may offer new perspectives for the biological water treatment of heavy metals. In order to make circular system planning for this field as well, in order to optimize water usage, we suggest the following factors for the planning process of adsorbing heavy metal content from wastewater:

- Exact comparative analysis of the water footprints of chemical-based heavy metal adsorption water treatment methods;
- Comparative analysis of the water footprints of heavy metal binding biosorbent planning methods, with additional field comparison;
- Application of water availability indicators for production fields of heavy metal binding biosorbent;
- Application of circular economy value (CEV) indicator for comparing chemical-based and biological-based heavy metal adsorption methods.

These can be done with the assistance of specific central and economic actors, and by conducting precise, field-specific research using the already introduced, but extendable circular economy evaluation, water footprint calculation and energy efficiency methods [107,108].

For algae resulting from the wastewater treatment process, further considerations for opportunities of manufacturing biofuel after (partial) heavy metal adsorption have to be made. This is due to international studies stating that the efficiency of the process goes way beyond that of other plants' bio-fuel use production in terms of water footprint [86].

4.2. Water Allowance Coefficient—A Tool for Expressing the Water Value of Heavy Metal Adsorption

The waater allowance coefficient (WAC) is an environmental economic indicator based on the water footprint. It uses the water footprint to express absolute water consumption with both its direct and indirect components, supplemented by local water availability. A general conclusion is that the lower the product's water footprint is, the better the utilization of available water as a natural resource. For algae, the environmental economic analysis of biosorbents in relation to heavy metal adsorption from wastewater using WAC uses the following equation (Equation (1)):

$$WAC_i = 100/WF_{algae,i}\ \% \tag{1}$$

where

WAC_i = water allowance coefficient, based on algae water footprint changes at region i.

$WF_{algae,i}$ = changes of algae water footprint at region i, %.

The WAC value we get as a result will also consist of green, blue and grey components due to the base water footprint calculations, which offers a better estimation of algae production's and its water requirement's monetary value, supplemented with the actual prices. The higher the algae's WAC coefficient is, the higher monetary investments, costs needed to produce it in the target field. The methodological basics of the WAC calculation is detailed by Fogarassy et al., 2014 [109].

5. Conclusions, and Additional Scientific Value

According to our review results, we can determine an additional scientific value of this research: ways of developing heavy metal adsorption experiments. Most of the cited literature sources describe new scientific results with many adsorbent materials. As Table 1 shows, the most researched field is adsorption with several unique adsorbent materials. Some literature sources describe the kinetics of adsorption, and determine the adsorbing process with thermodynamics and modifying the Langmuir and Freundlich isotherm models. All of this research together expresses both the study of adsorption kinetics and the process analyses of unique adsorbents. These two fields seem practically to be enough to describe the whole process of heavy metal adsorption from several wastewater samples. Industrial waste sometimes contains polluting materials in high concentrations. Although these contaminations are either pollutant or toxic in nature, in this case they could be useful for heavy metal adsorption because there could be a metal-complex material production with physical-chemical processes and chemical boundaries. These complex chemical materials could not accumulate by organic-life compounds of natural rivers in the environment naturally. This is the reason why natural rivers have the lowest pollution level, although this pollution contains metal compounds.

Table 1 also shows other important results. Although more literature sources (22) describe the adsorption process with unique adsorbents, similarly many cited papers (20) express the biosorbent research. The biosorbent materials seem to be adsorbents applicable to heavy metal treatment. The biochemical process produces organic compounds, which can be seen in later parts of wastewater treatment yards. The biological sorbent materials can bind heavy metals efficiently, but this adsorption works in two ways simultaneously. The first process is the monolayer adsorption with strong chemical boundaries. This is a one-step process, and all of the heavy metal ions could adsorb. There is no later regeneration with light techniques (such as opposite-way water treatment). This chemical adsorption could work with low-concentration heavy metal pollution, because higher concentration adsorbed with a multilayer process. This type works with van der Waals boundaries, and there is an opportunity to regenerate the adsorbent. We could eliminate the last heavy metal layer, and produce a new metal pollution in wastewater. All of this type of adsorption seems to be the part of the biosorbent treatment process. The biosorbent materials produce organic compounds in later parts of the process, and could disturb the control (analytical chemical) measurements of the wastewater processing. The efficiency of this adsorption type seems to be higher than the widely used chemical methods. Although the biological treatment could be a success, there is an additional process to eliminate the additional organic compounds (e.g., with oxygen-intensive treatment and microbiological processes).

The unique adsorbents mean artificial materials because all adsorbents are made from non-organic chemical and physical components. They could be regenerated successfully, and more efficiently than the biological materials. This is the reason for the increased number of literature sources, which present artificial material adsorption research. There will be a two-stage research experiment in the future, because there could be a solution for organic pollution of wastewater systems after biosorbent usage.

This review paper presents an overview of different adsorption techniques of heavy metal treatment from several wastewater samples. We collected the references from the adsorption literature to show the wide range of heavy metal elimination methods. There are physical-chemical and microbiological techniques to conduct treatment effectively. We presented the average isotherm models, which seem fit to visualize the adsorption process. These isotherms can show the maximum adsorption capacity of each adsorption surface. In this paper, we presented a short summary of new thematic research fields of heavy metal adsorption studies (in collection of related research fields and research years). In addition, before the final chapter of the paper, we have shown that the cost of heavy metal cleaning using algae and the WAC are in direct relation to each other employing as practical methods.

Author Contributions: C.F. and M.C. had the initial idea for the manuscript. M.C. and I.F. designed the manuscript. M.C. processed the literature materials. C.F. and E.N. performed the methods and harmonized them with the literature materials. M.C. wrote the manuscript with the support from E.N. C.F. supervised the project. All authors provided critical feedback and helped shape the result.

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

Appendix A

Figure A1 presents the sample process of heavy metal treatment from each wastewater sample by cellulose adsorption (chemical method).

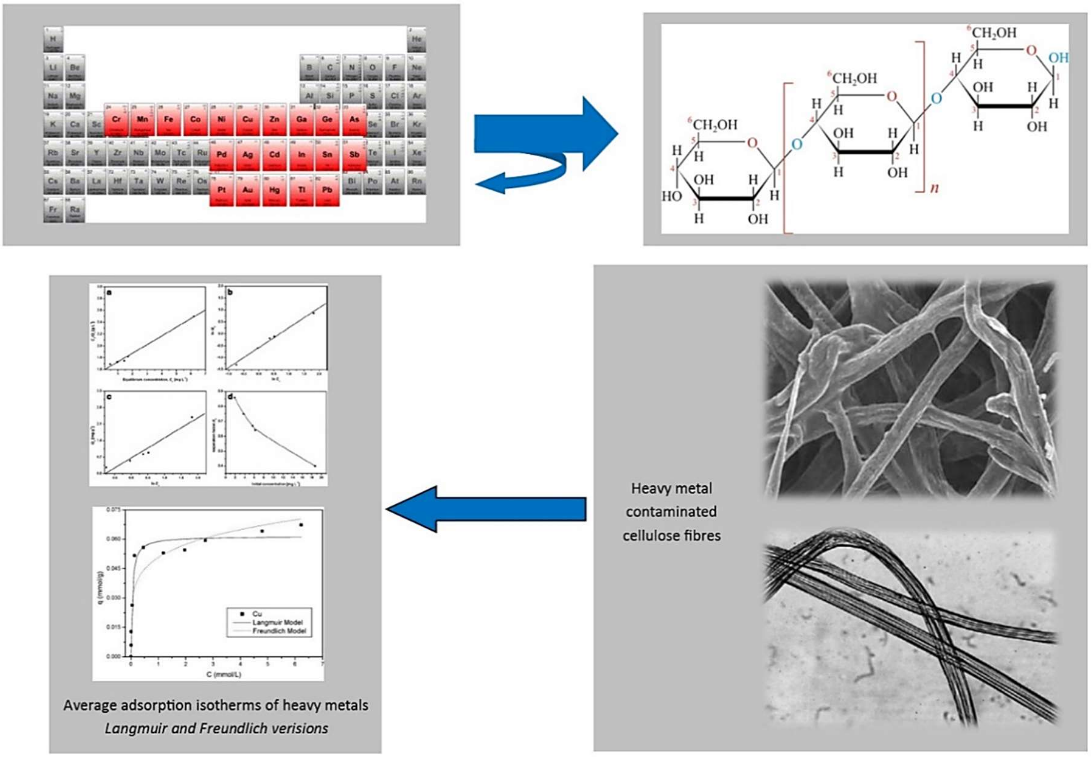

Figure A1. Sample of heavy metal treatment process from each wastewater sample by a typical cellulose adsorption method (Source: edited by authors).

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