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Removal of Heavy Metals from Aqueous Solutions with the Use of Lignins and Biomass

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Abstract
The overproduction of pollutants resulting from the development of industry causes the deposition of large amounts of toxic and carcinogenic substances, including heavy metals, in the aquatic ecosystem and other ecosystems. This is a civilisation problem of the present times, posing a serious threat to the natural environment, including humans. For this reason, it has recently become extremely important to develop effective methods to minimise the concentration of heavy metal ions in the aquatic systems and thus reduce their negative impact on the environment. One such technique is adsorption, which is believed to be an effective method of removing contaminants such as heavy metal ions from aqueous solutions. Looking at the available literature of the last few years, it can be concluded that adsorbents of natural origin are becoming more and more important. These are agricultural waste, all kinds of biomass, and waste from various industries. The study attempts to present and evaluate the sorption capacity of materials of natural origin, including oat bran, chitosan, alginate, tree bark, coconut fibre, and lignin. The use of such biosorbents is more friendly for the environment compared to their synthetic counterparts and perfectly fits the concept of sustainable development and the circular economy.

Keywords
heavy metals, adsorption, biosorbents, lignin.

1. Introduction

The rapid urbanisation and industrialisation in the last decade have made water pollution a huge global problem [1-3]. There may be various types of contaminants in water, such as viruses, bacteria, organic particles, dyes and heavy metal ions, e.g. Cu^{2+}, Cr^{6+}, Pb^{2+}, Co^{2+}, Cd^{2+}, Zn^{2+}, As^{3+}, Ni^{2+}, and Hg^{2+} etc. Among heavy metals, zinc, due to its wide application in various industries, is frequently present in sewage. The zinc (II) content in water may vary from a few to several hundred $\mu g/dm^3$ [1]. What distinguishes heavy metals from other toxic substances is their persistence in the environment (they are not biodegradable) and the possibility of their accumulation in living tissues, leading to their concentration in the food chain. The accumulation of heavy metals in the human body can cause very serious adverse effects, such as skin diseases, brain damage, anaemia, liver damage, kidney failure, ulcers, and hepatitis [4]. Heavy metals are also carcinogenic and even their trace amounts can lead to many health problems in humans [5,6]. Moreover, the presence of these pollutants in groundwater and wastewater used for the irrigation of agricultural land contributes to their increased content in soil and vegetables, causing negative health effects for their consumers [7]. There are various sources of heavy metals entering water and the environment, including waste from manufacturing batteries, fertilizers, pesticides, as well as from the petrochemical, pharmaceutical, metallurgical, mining, pulp and paper industries [6,8]. Water pollution caused by the presence of heavy metal ions makes the lives of millions of people vulnerable to disease and even death. Moreover, the presence of contaminants in water constantly reduces the availability of drinking water [6]. By the year 2050 the gross per capita water availability is projected to decline and the total fresh water demand will increase sharply, leading to water shortage [8].

Concern for the natural environment is becoming the driving force behind the development of "green" industrial technologies through, inter alia, product waste management and forces scientists to seek and develop innovative, relatively available materials and techniques that will reduce the excessive accumulation of heavy metals in the environment in the future. For these reasons, the search and acquisition of new, cheap adsorbents for the removal of heavy metals from water is becoming a priority. The adsorbents often used are materials that have high mechanical and chemical resistance, such as synthetic ion exchange resins and chelating resins. Due to their strength properties, their disposal after use is relatively troublesome, which makes them unfriendly to the environment [9]. In recent years, an important and widely analysed issue has become the search for new, environmentally friendly sorbents. The heart of the problem is to replace expensive traditional sorbents with cheap ones, which can often be made from waste materials and by-products. Such natural sorbents do not require regeneration and after use can be burnt, glazed or composted [9, 10]. Some agricultural waste i.e palm oil waste, is produced in millions of tonnes per year [6]. Therefore, this review addresses the topic of unconventional, ecological and economical methods of purifying water from heavy metal ions, and also shows the need and possibilities of waste biomass management.

2. Mechanism of biosorption

Effective wastewater treatment is carried out using various physical, chemical, and biological processes. They may vary according to the type of wastewater treated. Other processes and devices are used for household wastewater than for industrial wastewater, in which the treatment called ‘water renewal’ is aimed at the removal of residual impurities, which occur mainly in the form of true and ionic solutions [1,5,8]. In the chemical technology of water and wastewater treatment, different methods are used to purify wastewater, such as the precipitation of some soluble compounds, electrocoagulation [11]. and sorption on activated carbon. Adsorption and ion exchange methods [12] are successfully used as well as membrane filtration [13], coagulation-flocculation, flotation and chemical precipitation [14]; however, these methods are unfortunately relatively expensive [1,5,8,15].

Among the methods mentioned above adsorption is the most common and efficient method of removing heavy metals from wastewater. This process is based on the retention of molecules, atoms, or ions at the surface or interface of physical phases [16]. It involves a solid phase (sorbent) and liquid phase (solvent) containing dissolved substances to be sorbed. Due to the high affinity of the sorbent to metal ions, they are attracted and bound by a rather complex process affected by several mechanisms involving chemisorption, complexation, adsorption on surface and in pores, ion exchange, chelation, adsorption by physical forces, and entrapment in inter and intrafibrillar capillaries and spaces of the structural polysaccharides network as a result of the concentration gradient and diffusion through the cell wall and membrane [17]. Surface functional groups, mainly oxygen-containing groups, such as carboxyl -COOH and hydroxyl –OH groups as well as acetamide, carbonyl, phenolic, amido, amino and sulphydryl groups, structural polysaccharides, and esters present on the sorbent surface may have a strong interaction with heavy metal ions. In water systems, the sorbent surface takes on a negative charge, which is important for the adsorption of positively charged metal ions from model solutions [16, 17]. These groups have an affinity for metal complexation. Some biosorbents are non-selective and bind to a wide range of heavy metals with no specific priority, whereas others are specific for certain types of metals depending upon their chemical composition [17].

In order to determine the effectiveness of sorbents, kinetic tests are carried out. The experimental data are tested with pseudo-first and pseudo-second order kinetic models. Understanding the kinetic parameters of the process allows for an in-depth assessment of the sorption capacity of the materials used and to determine whether in the sorption process there are reversible interactions between the liquid and solid phases at equilibrium, or chemical interactions leading to the binding of metal ions on the adsorbent surface according to the mechanism based on ion exchange or complexation [18-22]. Thermodynamic studies are often performed to determine the effect of the process temperature on the sorbent capacity because the basic thermodynamic parameters such as free energy (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o) depend on temperature [23,24].

On the basis of the results obtained, it is possible to determine an appropriate model of the adsorption isotherm in order to determine the relationship between the amount of substance adsorbed and the equilibrium concentration of the solution. Analysis of the isotherms obtained allows to obtain a lot of valuable information on the mechanism of the sorption process, its nature, and the type of interaction of the adsorbate with the adsorbent [25].

3. Examples of biosorbents used in the removal of heavy metal ions from aqueous solutions

The topic of the article is taken up due to the need to solve three important issues in the field of environmental protection: I - removal of heavy metal ions present in surface waters, II - management of by-products and waste products used as a sorbent, III- replacement of existing petrochemical sorbents with natural, fully ecological sorbents.

The adsorbents presented in the article belong to a group of low-cost adsorbents that can be an alternative to conventional sorbents.

The use of a wide range of adsorbents of natural origin makes it possible to design simple, modern and low-energy technological installations, and ultimately reduces the costs of the wastewater treatment process. The adsorbents used may be of significant importance in industrial wastewater treatment plants and, above all, become the basis for low-budget and waste-free technologies.

3.1. Rice bran

Rice bran, a by-product obtained from the outer layers of rice grains, is highly attractive because of its abundance, environmental friendliness, and low cost [26]. Chinese researchers demonstrated the ability to adsorb zinc ions on raw and chemically treated rice husks. The process reached its equilibrium within 30 min. and the zinc removal rates after 0.5 and 1.5 h of the process were 52.3% and 95.2%, respectively, with a initial zinc concentration of 25 mg/dm3 and optimum pH of 4.0 [27]. Another study concerned the evaluation of heavy metal ion adsorption by cellulose, hemicellulose, and lignin fractions as the main components of rice bran. The study showed that rice bran cellulose showed a better ability to adsorb heavy metal ions than hemicellulose and lignin [26]. In subsequent research on heavy metal ion adsorption by raw and defatted rice bran, the results obtained were 80% and 87%, respectively [28, 29].

3.2. Chitosan

Chitosan, a natural polymer with sorption abilities, can also be used to remove toxic Ni^{2+}, Cd^{2+}, and Pb^{2+} ions. It is obtained by the heterogeneous

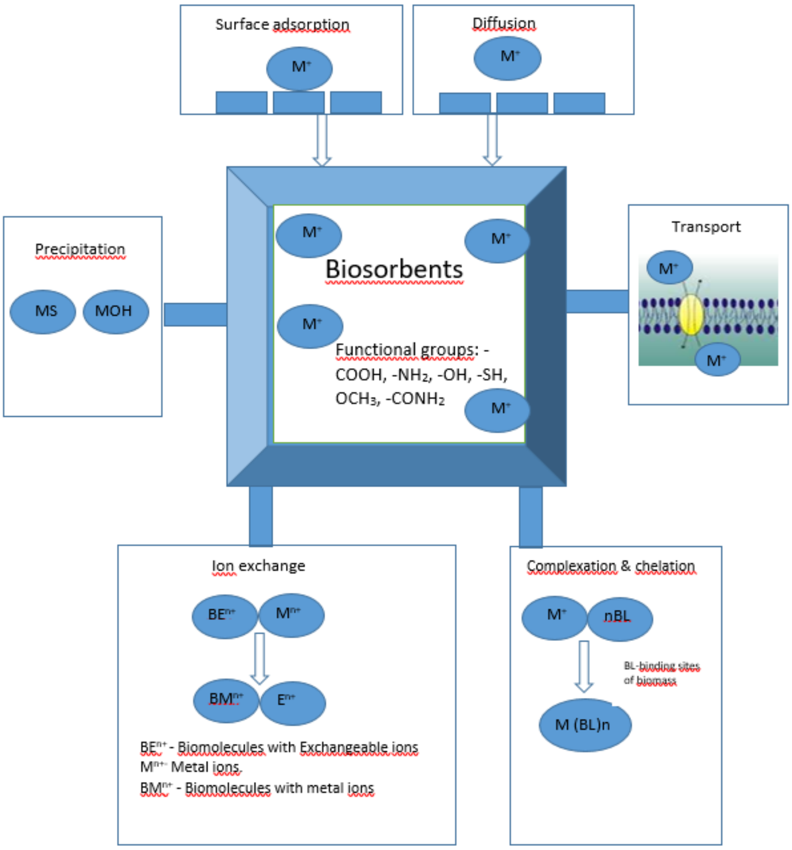


Fig. 1. Plausible mechanism of biosorption based on [17]

enzymatic or chemical deacetylation of chitin in concentrated alkaline solutions. The most common source of chitin is the shells of marine animals (crabs, shrimps, krill). Chitosan can chelate several times more metal ions than chitin due to free amino groups exposed as a result of deacetylation [30-36]. Iranian scientists tested a composite consisting of, among others, chitosan and hydroxyapatite. The data obtained indicate that it was able to remove 50.39% and 74.77% of Zn^{2+} and Cu^{2+} ions, respectively, from an aqueous solution at room temperature [37]. In another study, chitosan-coated permutite granules were prepared as a new adsorbent and used to remove zinc and copper ions from water for watering plants. In this trial, 58.8% and 50.2% of zinc and copper ions were removed, respectively, within 30 minutes [38]. Seyedmohammadi et al. investigated the removal of zinc ions by chitosan macro- and nanoparticles. The sorption capacity was shown to be 90.80 and 99.10%, respectively, at an ion concentration of 10 mg/dm^3 at a temperature of 25 °C [39].

3.3. Alginates

Alginates are widely known polysaccharides obtained from marine algae, mainly brown algae and seagrass, or produced extracellularly by some bacteria, such as *A. vinelandii, P. aeruginosa,* and *P. fluorescens*. Alginates are copolymers consisting of β-D-mannuronic (M blocks) and α-L-guluronic acid (G blocks) residues linked together by glycosidic bonds. Among biopolymers, they are considered to be a good sorbent for heavy metals from low concentrated aqueous solutions [40-45]. In Poland, the process of biosorption of three bivalent metal ions - nickel, lead, and zinc by calcium alginate from an aqueous solution in one-component systems was investigated. It was found that the removal of metal ions by calcium alginate increased with the increasing dose of the adsorbent and reached its maximum at a dose of 8g/100 cm^3 [46]. In another study, a solid residue obtained after alginate extraction from *Sargassum filipendula* algae was used as Zn biosorbent. The role of the ion exchange mechanism was observed in kinetic studies with a predominance of external diffusion. The possibility of using the material tested to remove zinc ions was confirmed [47]. Modified sodium alginate showed an excellent adsorption capacity towards Cu(II), Zn(II), and Pb(II), which can be attributed to the presence of a large amount of amino and carboxyl groups on the adsorbent surface and in the porous structure. Moreover, a study on the adsorption-desorption cycle showed that this kind of sorbent can be successfully regenerated in appropriate solutions [48]. Other plant-based sorbents, including tree bark, cork tissue, fibre obtained from coconut palms, and activated carbon produced from coconut shells, also have an affinity for heavy metal ions.

3.4. Plant bark

Plant bark is one of the low-cost biomass materials most frequently used in research on the removal of pollutants from water media [49]. The sorption efficiency of tree bark is related to the high content of tannins, whose adsorption properties are attributed to their polyhydroxy and polyphenolic groups [50-52]. Studies on *Platanus orientalis* bark showed maximum removal of Cr(VI) ions of 89.6% for unmodified bark and 90.7% for modified bark. In contrast, the maximum nickel removal of 74.5% and 56.5% was obtained for unmodified and modified bark, respectively [53].

3.5. Coconut fibers

Coconut fibers from *Cocos nuciferato*, were used to remove zinc ions and metallic copper from aqueous solutions. Periodic experiments were carried out on Zn(II) and Cu(II) in order to quantify the ion sorption kinetics. Unmodified coconut fiber was used. The ion removal was 91% for zinc and 97% for copper, and the optimum pH was 4.5 and 3,. respectively 5 [54]. Further studies [55] show that coconut fibre, both modified and unmodified, is an effective adsorbent for removing various toxic as well as valuable metals from industrial wastewater at a level of about 70%.

3.6. Agricultural waste biomass

Agricultural waste biomass [56-58] from soybean [59], egg shells [60,61], olives [62], bagasse [63], dried ground castor leaves *Ricinus communis L.* [64], fruit e.g. banana and orange peels, [65], as well as ash from incinerated sewage sludge [66], may be used as natural biosorbents. Modified starches may show high adsorption capacity towards some dyes and heavy metals due to the replacement of hydroxyl groups with other chemically active groups [67,68]. Moreover, the use of wheat bran [69] and mango peel [70] resulted in the sorption of zinc ions at the level of 16.40 mg/g and 28.21 mg/g, respectively. Scientists were also interested in the use of corn cobs to remove nickel and zinc ions from water, and observed that the percentage adsorption was 72% for zinc and 82% for nickel [71]. Thakur and Parmar studied the adsorption of zinc using the waste from a tea factory, and the results obtained showed 90% removal efficiency [72].

3.7. Thallus and microbial biomass

Also, the use of seaweed thallus, mould, yeast, and other dead microbial biomass and agricultural waste for the removal of heavy metals was investigated [73]. Already in the 90s of the last century, scientists got interested in the use of mycelium for the sorption of metal ions. Luef et al. demonstrated the usefulness of *A. niger* treated with NaOH for the removal of zinc from contaminated waters in Austria [74]. The results of the research provided by other scientists from Pakistan show that the mycelium of *P. chrysogenum, A. niger, and R. oryzae* has the potential to remove copper and zinc ions from electroplating waste at the level of 50.9% and 71.2%, respectively, at a temperature of 40 °C [75]. Other researchers used biomass from the thallus of *Pseudevernia furfuracea* and obtained the maximum bio-sorption efficiency for zinc of 92%. They confirmed the effective uptake of the metal cations by chelation and/or electrostatic interactions [76].

3.8. Activated carbon

Activated carbon is characterised by the highly developed specific surface area and porosity, and thus by a high capacity to adsorb chemicals from gases and liquids. Activated carbon belongs to the category of porous carbon materials. The production of activated carbon is based on natural organic raw materials with a polymeric structure. The main raw materials used for the production of activated carbon are wood (35%), coal (28%), lignite (14%), peat (10%), and, locally, also some waste such as nut shells and fruit stones (10 %) [77].

Literature also describes studies on the production of activated carbon from various biomass raw materials of agricultural origin, including eucalyptus biomass and peanut shells [78,79]. In the studies described in [80], the degree of zinc ions removal by activated carbon was determined. The affinity of the adsorbent to the zinc ions was independent of temperature, and Zn removal was up to 75 mg/dm^3 [80].

All this makes sorbents of natural origin potential substitutes for expensive synthetic adsorbents, as they are readily available, cheap, abundant in nature, or are by-products or waste from various industries [52].

4. Characterisation and importance of lignin

The combination of lignin with selected natural biosorbents of plant origin in various combinations will contribute to obtaining a system with a definitely better sorption capacity than those of the separately used precursors.

There is great potential in the pulp and paper industry to produce high-value products other than pulp and paper. The implementation of new technologies available in pulp and paper mills could further improve the use of renewable resources, such as lignin recovered from black liquor.

Pulp and paper mills are currently operating in a closed loop with a focus on the recovery of pulping chemicals from black liquor. An important aspect is the energy gain resulting from the fact that the dry substance of black liquor is flammable due to the high content of organic compounds. Black liquor combustion products are carbon dioxide and water, and the heat produced is used to generate heating steam, which, to a greater extent, covers the heat demand of cellulose mills. The excess black liquor generated in pulp mills can now be used as a substitute for water during the pulping process. The use of black liquor as make-up liquid reduces water consumption, but at the same time increases the amount of lignin in the pulping process, and thus affects the load on the soda boilers. Removal of part of the lignin from black liquor is a favourable process for many reasons: it will reduce the heat load on the recovery boilers, which will increase the pulp yield. The separated lignin can be used as a biofuel to replace e.g. oil or natural gas in lime kilns or can be burned in power boilers, and the surplus energy produced can be exported to other users. In addition, the separated lignin can be used as a raw material in the chemical industry. For these reasons, it is worth paying special attention to so many areas of lignin applications and distinguish it among the other biosorbents described.

Lignin is also an example of a biosorbent, which is mainly a by-product in the pulp and paper industry. Lignin is a biopolymer found in the cell wall of plants and ranks as the second most abundant natural polymer on the planet. Besides cellulose and hemicelluloses, it is one of the components of wood biomass. Its content in wood varies, depending on the type of plant (lower values in tropical and subtropical trees, and higher in conifers), and on average is at the level of 20% of the total weight of wood, [81-83]. Lignin can be extracted from plant raw materials by indirect or direct methods. Extracted lignins are not identical to native lignin, and they differ from each other depending on the chemical compounds used and the reaction conditions [83].

This biopolymer, whose complex structure is still not fully understood, is currently becoming the subject of the intense research of a number of scientists. Numerous current literature reports indicate a research trend related to the use of lignin as a precursor to create new materials applicable in various industries [83,84]. Annually, between 50 and 70 million tonnes of lignin are produced [85], and only about 2% of this amount comes onto the market in the form of chemicals [86]. The unique feature of lignin as a chemical compound is the variability of its monomeric units and the multitude of the types of inter-monomeric bonds. Investigations of softwood lignins revealed the chaotically branched structure of the macromolecules. Hardwood lignins have the properties of star-shaped polymers. It has been suggested that cereal lignins are composed of linear macromolecules. The wood lignins most studied come from pine, spruce, birch and aspen. The structural features of lignins extracted from agricultural plants, including cereals, have been investigated much less frequently [87]. Lignin is isolated from black liquor, which is a by-product in the wood pulping process. This lignin is called technical lignin [88,89].

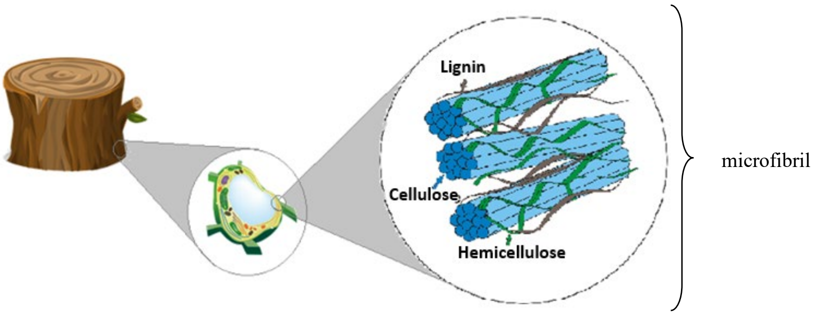


Fig. 2. Schematic structure of lignocellulosic biomass

4.1. Type of the lignins

In general, lignins can be divided into four categories (Kraft lignin, lignosulphonates, sodium lignin and organosolv lignin) depending on the application of sulphur-using or sulphur-free processes [90].

Alkaline lignin (sulphate lignin, Kraft lignin) is obtained by the alkaline digestion of wood consisting in the separation of lignin from lignocellulose by breaking the bonds holding the phenylpropane units together in the presence of NaOH and Na_2S. In this process, free phenolic hydroxyl groups are formed, increasing the hydrophilicity of alkaline lignin, which, in turn, increases its solubility in water/alkaline solutions, resulting in black liquor. Alkaline lignin contains only a small amount (<1.6 wt.%) of sulphur in the form of thioether bonds, while most of the lignin backbone is sulphur-free, allowing the removal of lignin from black liquor by acidification and precipitation. Sulphate lignins from hardwood and softwood are commercially available.

Lignosulphonates are obtained in the sulphite process of wood digestion by separating lignin from the biomass in the presence of sulphur dioxide and sodium, magnesium, ammonium or calcium hydroxides. The lignosulphonate obtained contains about 6.5% of elemental sulphur, which is present in the form of sulphonate groups of the lignin macromolecule. Lignosulphonate is water soluble, thus it cannot be applied to adsorb heavy metals from water.

Soda lignin differs from Kraft lignin and lignosulphonates in that no sulphur-containing reagents are used for wood digestion, which makes the lignin sulphur-free. The relatively severe digestion conditions make lignin rather condensed and resistant. Like Kraft lignins, sodium lignins contain low amounts of ash and carbohydrates, and are of low to moderate purity. In contrast to Kraft lignin and lignins extracted in an acidic environment, vinyl ethers can be found in sodium lignins. Commercially available sodium lignins are obtained from annual crops and, to some extent, from hardwood.

Organosolv lignins are of high purity, containing very little carbohydrates and ash. They are more homogeneous than other lignins in terms of overall structure, i.e. they are characterised by lower molecular weight and polydispersity, and can be equally chemically resistant as sodium or sulphate lignins. This type of lignin is separated from the biomass with the use of organic solvents such as ethanol, methanol, formic acid or acetic acid in the presence of an acidic or basic catalyst. The organosolv method is essentially environmentally friendly and does not require the use of toxic sulphides or extreme temperatures and pressures as it belongs to the alkali or sulphide methods. Organosolv lignins may be extracted both from hardwood and softwood. Organosolv lignins obtained on a laboratory scale under mild conditions are most similar in structure to native lignins [91-95].

Most of the lignin is burned for energy production due to its high calorific value and only 5% of industrial lignin is used for the production of value added products. Currently, lignosulphonates hold a 80% share in the market; however, sulphate lignin production is expected to increase in 2023-2028, competing, to some extent, with lignosulphonates due to its lower cost and higher reactivity [90]. Strategies for the use of lignin residues from industrial processes are well assessed in terms of green chemistry and biotechnology. In 2018 the global recovery of sulphate lignin in pulp mills was 265,000 tonnes [96].

Sulphate lignin has a high adsorption affinity for Pb(II) (49.8 mg/g at neutral pH), and this process can be reversible by adjusting the pH level, making sulphate lignin a promising industrial Pb(II) adsorbent with regenerative abilities [97].

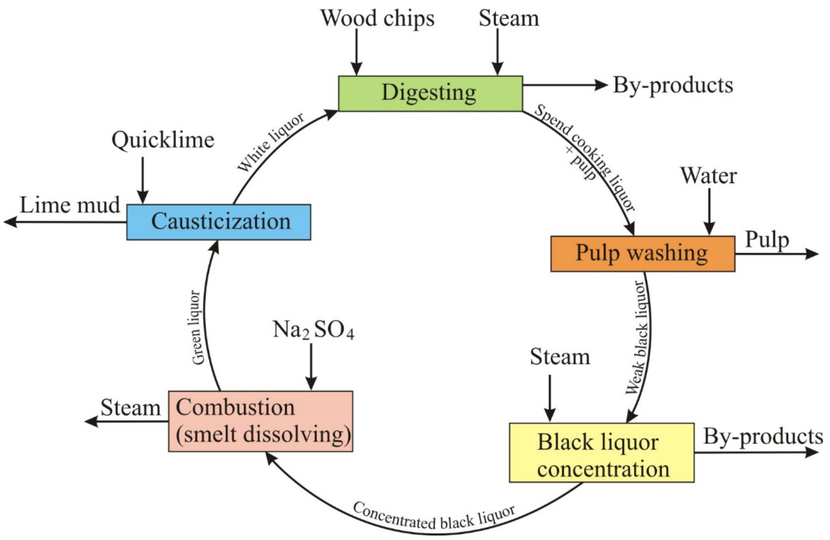


Fig. 3. Scheme of black liquor formation, based on [87]

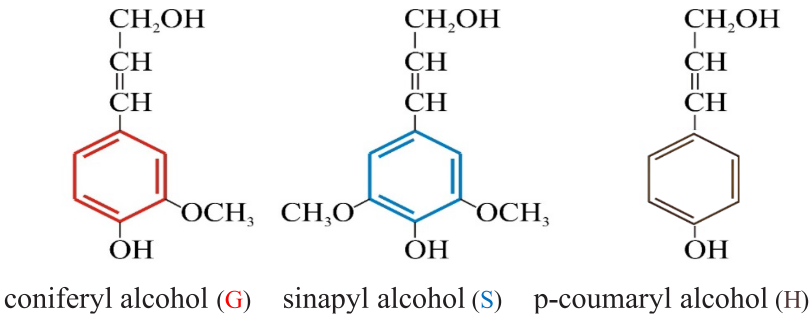


Fig. 4. Lignin precursors, often referred to as phenylpropanoid units

	 Hardwood	 Softwood	 Grass
Lignin content [99]	18-25%	27-33%	17-24%
Lignin building block composition [91]	**G+S**	**G**	**H+G+S**

Table. 1 Approximated lignin content and lignin building block composition in different raw materials

5. Structure of lignin

In terms of its chemical structure, lignin should be classified as a polymolecular compound. Its backbone structural elements are phenylpropane derivatives, which occur in lignin in three basic structural forms: p-hydroxyphenyl propane, guaiacyl and syryngil propane. Typical representatives of these structures in lignin are as follows: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. In lignin, macroparticles are bound by various ether bonds and carbon-carbon bonds [83, 84, 92].

The chemical composition of lignin varies depending on the type of wood, processing conditions, and extraction methods [98]. The figure shows the approximate content of lignin in different types of plants and the main lignin building blocks.

This biopolymer forms a three-dimensional amorphous network that provides the plant with mechanical strength and acts as a binder between cellulose and hemicellulose in the cell walls.

6. Sorption properties of lignin

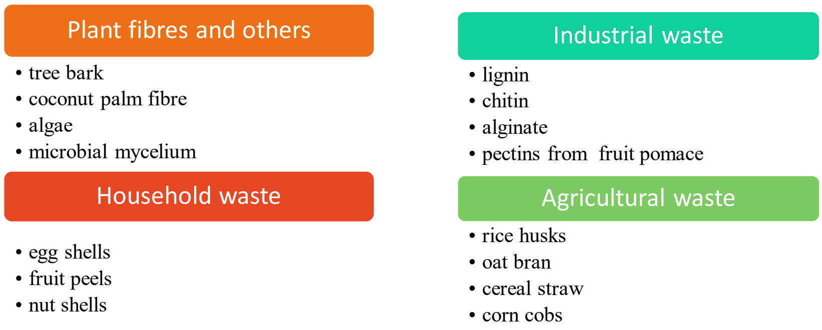
The sorption process is a method that has many advantages, including low cost, the possibility of managing waste and by-products, the storage of which is a big problem, and the possibility of biodegradation of the biomass used.

Lignin is characterised by a large number of functional groups influencing its reactivity, including methoxy, hydroxyl, carboxyl, phenol, ether, carbonyl, and ketone groups. That is why lignin can be one of the potential, cheap, and easily available biosorbents of metal ions harmful to the environment.

Numerous studies have indicated the possibility of using lignins as enterosorbents capable of binding, among others, radionuclides and estrogens [82, 87, 100]. The mechanism of ion adsorption on the lignin surface is based on the reaction of functional groups that have the ability to bind metal ions by donating an electron pair and thus form complexes or new chemical bonds with the adsorbate [101-103].

By reviewing the available literature, it can be concluded that lignin-derived adsorbents can provide significant environmental benefits due to their stability, biocompatibility, and wide availability. In addition, owing to the extensive structure of lignin, a significant part of the functional groups is present on its surface, which enables the permanent capture of harmful metal ions and effective removal from the polluted environment [81, 104,105].

Biosorption is a relatively innovative process that significantly contributes to the issue of removing pollutants from aqueous solutions. It is an environmentally



Plant fibres and others

- tree bark
- coconut palm fibre
- algae
- microbial mycelium

Household waste

- egg shells
- fruit peels
- nut shells

Industrial waste

- lignin
- chitin
- alginate
- pectins from fruit pomace

Agricultural waste

- rice husks
- oat bran
- cereal straw
- corn cobs

Fig.. 5. Adsorbents of natural origin

friendly technique for removing certain types of biologically inactive or dead biomass from dilute aqueous solutions. This review discusses the bio-sorption of toxic metal ions, mainly zinc, using inexpensive, natural, or waste-derived efficient bio-sorbents as an alternative to existing conventional systems. The use of bio-sorbents is currently highly encouraged as they are relatively cheap or even free, readily available, renewable, compostable, and have a high affinity for heavy metals. Available popular science literature indicates a new emerging trend in the modification of adsorbents to increase the effectiveness of metal ion removal.

7. The influence of chemical and geometric modifications of lignin on the sorption properties of heavy metal ions

Numerous examples of starch [106], chitosan [107], sodium alginate [108], and lignin modifications can be found in the literature. Lignin can be modified, for example, by its functionalisation with amine and sulphone groups (ASL) [109], with amine groups (A-LMS) [110] or with crown ethers [111]. In such a way, lignin with a high sorbing efficiency can be obtained. The latest research shows that lignin can also be modified by giving its particles a special geometry (bowl shape). Recently, bowl-shaped and concave sorbent particles have attracted a lot of attention due to their good mass transport properties, rheological properties, and large adsorption surface [112]. Scientists from Finland and China synthesised multifunctional hybrid magnetic nanoparticles based on lignin with an ultrafast Pb^{2+} and Cu^{2+} adsorption capacity. Abundant active sites in modified lignin enabled high adsorption efficiency driven by ion exchange, hydrogen bonding, and electrostatic attraction [113]. Polish scientists successfully combined lignin with silica, creating a multifunctional material with a significant sorption capacity of Pb(II) ions from aqueous solutions. The maximum sorption value obtained was 89.02 mg/g [114]. In other research lignin-PEI composite was obtained from a cross-linked lignin matrix based on enzymatic hydrolysis and branched poly(ethylene imine). A test of the adsorption of Cr(VI) was carried out with a satisfactory result [115]. In another study, lignin was combined with chitosan to create a lignin-chitin film [116] or 50:50 composite [117]. In the first case, the adsorption of Fe(III) and Cu(II) cations from aqueous solutions was investigated, and it was observed that the maximum adsorption capacity was 84 % for Fe(III) and 22 % for Cu(II). According to the authors, such a sorbent can be regenerated by ion desorption within 48 hours by direct soaking of the adsorbent foil loaded with metal ions in water at room temperature. In the second case, a composite was used to remove harmful elements present in wastewater. The composites were characterised by weak interactions between the β-1,4-glycosidic bond, amide, and hydroxyl groups of chitosan and the ether and hydroxyl groups of alkaline lignin. The experiment showed the effective percent removal of anthraquinone dye, Remazol brilliant blue, and Cr(VI) ions. In China, a hydrogel based on lignin isolated from wheat straw was obtained for the removal of Cu(II) ions. As a result, a product capable of binding copper ions at the level of 74,359 mg/g was obtained. From the comparison of the results obtained with other Cu-absorbing sorbents described in the literature, such as carbon, Kraft lignin, and amine lignin, it can be concluded that a new superabsorbent was produced [118]. Despite the great interest, bio-sorption requires further research into modelling of the process, bio-sorbent regeneration increased efficiency, and metal ion recovery.

8. Summary and Conclusions

A review of the results listed in Table 2 perfectly illustrates the sorption potential of the sorbents presented in the article. By analysing the research results, it can be concluded that chitosan absorbs Zn(II) and Cu(II) ions are best. Rice hulls have the highest sorption for Zn(II) and Cd(II) ions, where the adsorption of Zn(II) ions reaches up to 95%. In addition, alginates are characterised by an excellent sorption of Cu(II), Cd(II), Pb(II) and Zn(II) ions, exceeding 90%. Lignin best sorbs Cu(II), Cd(II), Pb(II) and Cr(VI) ions. On the other hand, coconut fibre absorbs Zn(II), Cu(II) ions, agricultural waste Zn(II) and Ni(II) by over 80%.

The present article shows that the knowledge of the market needs as well as trends and directions of development of new technologies show the need for full management of waste materials and/or by-products from various industries, including the pulp and paper industry, for potential processing using environmentally friendly methods in order to obtain new products intended for mass use.

The research described in this article belongs to the area of advanced technologies and is in line with the principles of sustainable development and the circular economy [120], the economic concept of which assumes that products, materials, and raw materials remain in the economy for as long as possible, and waste should be minimised as much as possible. In a circular economy, it is important that

Biosorbents		Metal ion	Results	Reference
Chitosan	chitosan / hydroxyapatite / nanomagnetic composite	Zn	50%	[37]
		Cu	80%	
	permutite with chitosan	Zn	58,8	[38]
		Cu	50,2	
	chitosan micro and nanoparticles	Zn	>90%	[39]
Rice bran		Zn	95,22	[27]
		Cd	>80%	[29]
		Cr(VI)	40-50%	
		Zn(II)	87%	
		Cr(VI), Ni(II)	40–50%	[17]
Alginate		Cu	>90%	[48], [44]
		Cd		
		Pb, Zn		[54]
Coconut fibers		Zn	91%	[54]
		Cu	97%	
		Cr(VI)	>80%	[17]
Agricultural waste biomass	corn cobs	Zn	72%	[71]
		Ni	82%	
	waste from tea leaves	Zn	90%	[72]
		Ni(II)	86%	[17]
	mango wood sawdust	Cu(II)	60%	
Lignin		Cu, Cd	90-95%	[119]
		Pb	>90%	[114]
		Cr(VI)	85%	[115]
Lignin-chitin composite		Fe(III)	84%	[116],[117]
		Cu(II)	22%	

Table 2. Summary of work done by different researchers using different waste materials to remove heavy metal ions

waste - if it has already been generated - is treated as secondary raw material. That is why lignins from, for example,. waste biomass from forestry and by-products of the pulp and paper industry, precipitated as black liquor sediment fit perfectly with the above assumptions. The lignin obtained from plant waste, which can effectively remove heavy metals from aqueous solutions is quite inexpensive since the raw material is easily available and has low or almost no economic value [121]. Moreover, the use of sorbents based on biomass will allow in the future to increase the agricultural and natural management of polluted waters, and even industrial wastewater.

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