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Review

Coffee Industry and Ways of Using By-Products as Bioadsorbents for Removal of Pollutants

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Abstract: As a result of anthropological activities, various pollutants, for example heavy metals, enter the environment in significant quantities. They have the potential to accumulate in living organisms and are not biodegradable in the environment. This poses a major threat to the health and life of living organisms and the environment. Therefore, the search for effective technologies to reduce anthropic pollutants in the environment is so important. Currently, membrane techniques, chemical precipitation, electrolysis, coagulation, ion exchange and adsorption, among others, are used to remove heavy metal ions. The most versatile method is adsorption on adsorbents. It is a relatively simple method, but very expensive. This prompts a constant search for new, effective and inexpensive adsorbents. Coffee is one of the most important foodstuffs and agricultural commodities in the world. From the point of view of the circular economy, by-products from the processing of coffee beans have become a valuable raw material in other areas of life. An important way to manage waste from the coffee bean processing industry is to produce adsorbents using it. There are data from laboratory studies indicating that it is possible to produce effective and low-cost adsorbents using by-products from the agro-food industry to remove pollutants from the aquatic environment and wastewater. Laboratory studies prove the high efficiency of heavy metal removal when using coffee-processing waste as adsorbents. However, data from real-world studies are still lacking. In addition, there is a lack of data from analyses on the impact of alternative adsorbents on economic, environmental and social aspects.

Keywords: circular economy; raw materials; food industrial waste; coffee waste; coffee; by-products; adsorption; pollutant impact

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1. Introduction

Coffee is considered one of the top agri-food commodities on the world market. The value of the coffee market ranks high, along with that of oil, copper, aluminum, flour and cereals, and its annual turnover in 2008 exceeded USD 70 billion [1,2]. Among coffee-producing countries, Brazil, Vietnam, Indonesia, the Philippines, Mexico and Colombia are the leaders. These countries supply more than 60% of the world's production of the commodity, which is due to optimal climatic conditions—the soil composition, air quality, degree of sunshine, intensity of rainfall and other environmental factors [3,4].

The first coffee plantations appeared in the 6th century in the Abyssinian Highlands and the Somali Peninsula. Coffee drinking was initiated by the Arabs between the 11th and 12th century. [5]. By the 15th century, coffee was grown in Yemen's Arabia, while by the 16th century it was cultivated in Persia, Egypt, Syria and Turkey. Travelers coming from Europe traveling to the Middle East began to tell stories about the unique dark-black drink. In the 17th century, coffee reached Europe and became popular across the continent [6].

Table 1 shows world coffee consumption in 2020, based on a report by the International Coffee Organization; at that time, a total of 166,346 thousand bags of coffee (the unit of measurement used in coffee marketing, equivalent to 60 kg) were put on the market [7].

Table 1. World coffee consumption in thousand 60 kg bags. Own elaboration based on literature data [7].

	2017/18	2018/19	2019/20	2020/21	CAGR (2017/21)
World	161,377	168,492	164,202	166,346	1.0%
Europe	53,251	55,637	53,372	54,065	0.5%
Asia and Oceania	34,903	36,472	36,002	36,503	1.5%
North America	29,941	31,779	30,580	30,993	1.2%
South America	26,922	27,156	26,898	27,180	0.3%
Africa	11,087	12,017	12,024	12,242	3.4%
Central America and Mexico	5273	5431	5327	5364	0.6%

Over the past 40 years, global coffee consumption has doubled, from 4.2 million tons in 1970 to 8.7 million tons in 2015. The value of the global coffee market is estimated at USDS 81 billion. In 2014, global coffee trade turnover reached USD 31.7 billion [4]. Most coffee is grown in subtropical developing countries and processed and consumed in industrialized countries. Coffee is mainly grown in South America, sub-Saharan Africa and Asia. The International Coffee Organization estimates that coffee is grown in more than 70 countries around the world, and its sales reach the highest turnover in world trade after oil. Coffee cultivation is a labor-intensive business. According to some estimates, about 17–20 million households are involved in coffee cultivation, and about 100 million people worldwide benefit directly from the coffee trade [4,8]. In African countries, such as Ethiopia, Rwanda and Uganda for example, coffee accounts for more than 50% of the source of foreign exchange earnings [9].

Euromonitor data shows that in 2015, the value of the coffee market in Poland exceeded PLN 5 billion. Forecasts for the near future predict a steady growth of more than 1% per year [10]. The value of the coffee market in Poland in 2020 is estimated at around PLN 6 billion. According to Mintel data, 94.4 million kg of coffee worth PLN 4.03 billion (retail sales) were sold in Poland last year. More than 66% of Poles drink coffee regularly, and half start their day with it (from Food Research Institute data). In 2019, imports to Poland amounted to 181 thousand tons, worth USD 577.9 million (EUR 516.26 million). This included 56.6 thousand tons (worth EUR 285.5 million) of roasted coffee (31% of total imports). Coffee was mainly imported from Germany (74.2 thousand tons, 42.7% of the value of Polish imports), Italy (10 thousand tons, 13.4% of the value of Polish imports), Vietnam (46.6 thousand tons, 13% of the value of Polish imports) and Brazil (19.7 thousand tons, 7.7% of the value of Polish imports). The largest coffee producing and exporting countries in 2019 were Brazil (USD 4.5 billion), Vietnam (USD 2.4 billion) and Colombia (USD 2.3 billion). In contrast, the largest importing countries were the United States (USD 5.8 billion), Germany (USD 3.2 billion) and France (USD 2.7 billion). World coffee production amounted to 169.34 million bags in the 2019/2020 season, 2.2% less than in the same season a year earlier [11].

Coffee supply chains can be so complex that beans change hands more than a dozen times on their way from farmer to consumer. The global supply chain has long been dominated by a handful of multinational coffee trading and roasting companies. Three companies—ECOM, Neumann and Volcafe—control about half of the world's coffee trade, while another ten, including Nestle and Jacobs Douwe Egberts, are responsible for roasting nearly 40% of the coffee consumed worldwide [4]. The ways of processing coffee beans since the turn of the century are constantly being modified due to the development of technology, and as a consequence, the amount and nature of the by-products are also changing. This affects not only the coffee industry but also other industries; this is due to the expanding knowledge of the properties of coffee beans and the potential for their use [12]. From the point of view of a circular economy, by-products from coffee bean processing have become a valuable raw material in other industries. Solid wastes from coffee bean processing have found applications, for example, as biosorbents for heavy metal removal, as fertilizer additives, for the production of biodegradable materials, and as additives in cosmetics. In addition, biologically active substances that are used in the pharmaceutical and cosmetic industries can be extracted from coffee-bean-processing waste [13,14]. Therefore, the purpose of the presented work is to review the literature related to the methods of processing coffee beans and managing the resulting waste.

2. Characteristics of Coffee

The main coffee species in the world include Arabica and Robusta, in addition to which Excelsa and Liberica are found in smaller quantities in the trade [15]. The main components of coffee are caffeine, tannin, solid oils, carbohydrates and proteins. Coffee contains 2–3% caffeine, 3–5% tannins, 13% proteins and 10–15% solid oils. In coffee beans, caffeine occurs as the salt of chlorogenic acid. Coffee beans also contain oil and wax [16]. The main chemical components found in coffee beans are caffeine, thiamin, tannin, xanthine, spermidine, guaiacol, citric acid, chlorogenic acid, acetaldehyde, spermine, putrescine and scopoletin [16,17].

Coffee beans have an extremely complex chemical composition depending on the origin of the beans, cultivation method, location of cultivation, soil quality, method of cleaning, as well as the degree of roasting, among other factors [18]. In the 21st century, the total area under coffee cultivation is about 10 million hectares located in about 80 countries. Of this group, about 50 countries' coffee exporters are economically significant [19].

Coffee is a complex beverage that contains many plant substances, many of which have high biological activity. Among the most important of these are:

a. Alkaloid caffeine (which has, among other things, properties that stimulate the nervous system);
b. Trigonelline (which, under the influence of smoking, is converted into nicotinic acid);
c. Theobromine;
d. Diterpene alcohols (caffeoyl and caffestol-affecting lipid metabolism);
e. Chlorogenic acid (with antioxidant properties);
f. Organic acids (malic, citric, phosphoric);
g. Phenolacids (caffeic acid and its esters with quinic acid);
h. Tannins;
i. Carbohydrates (sucrose);
j. Proteins;
k. Lipids (present in small amounts) [20,21].

B vitamins (especially vitamin B3-niacin) and minerals, especially magnesium and potassium, can also be found in coffee. The energy density of coffee (without additives) is low, at about 2 kcal per 100 mL of drink [22].

Caffeine is considered the best-known bioactive compound found in coffee, as well as the best scientifically studied [18]. Caffeine is also responsible for the organoleptic properties of coffee [20]. The average caffeine content in a cup of coffee is 60–135 mg, again depending on how it is prepared, the strength of the drink and the species of coffee plant [23].

3. Coffee Beans Processing Technologies

Coffee is a widely distributed and traded commodity on the world and Polish markets. Two species of coffee are of the greatest commercial importance, usually known as Arabica and Robusta—Coffea arabica and Coffea canephora. Although coffee (according to coffee researchers) originated in Ethiopia, its production and consumption has spread around the world [24].

Coffee is among the world's most traded commodities, and consequently generates large amounts of by-products/residues during processing from fruit to cup. Coffee cherries are typically harvested after 5 years of coffee trees when the bean fruit turns red [25]. A schematic view of a coffee cherry is shown in Figure 1. The coffee bean is the seed of a cherry-like fruit. These cherries consist of an outer skin and the exocarp or shell. Beneath this is the mesocarp—a thin layer of flesh—followed by a mucilaginous layer called the parenchyma. The grains themselves are covered by an envelope—the endocarp, more commonly known as "parchment". Inside the parchment, two beans lie side by side, each covered separately by another layer of thin membrane called the speroderm. Coffee plantations are found mainly in tropical countries that export coffee to other countries after a process used to remove the exocarp and parenchyma, also known as hulling. The removal of the endocarp precedes the roasting process. The lignocellulosic endocarp is a useless by-product of coffee bean processing that is discarded or burned. However, its composition leads us to think that this by-product may have great potential for conversion into cheaper activated carbon, for example. In addition to endocarp, coffee husks, coffee grounds and coffee beans are also used to produce activated carbon [26–34].

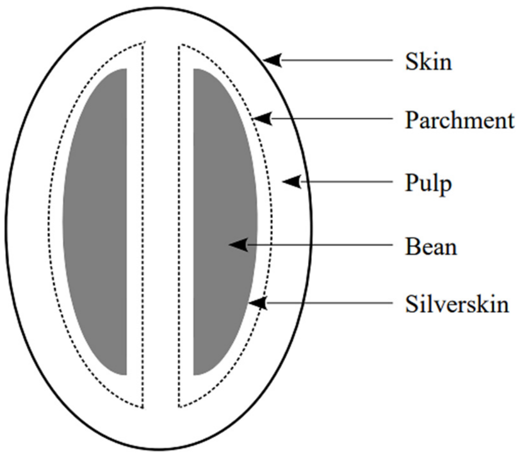

Figure 1. Schematic view of a coffee cherry. Own compilation based on literature data [34].

The processing of coffee beans leads to the production of coffee-based products such as instant coffee. Coffee-based beverages are created through a series of technological processes that begin in the field and end in the cup. After the coffee fruit is harvested, it undergoes pre-processing, in which three methods are distinguished—dry, wet and semi-dry. In the case of the dry method of processing coffee beans, the whole cherries (beans, mucilage, pulp and husk) are dried in the sun or in mechanical dryers until the dry husk (shell) can be easily removed mechanically. The drying process can be carried out by "natural" or "artificial" methods. Natural or sun drying is the method commonly used on large farms. In the wet process, the fruit is mechanically crushed, and the remaining mucilage (pectin and sugars) is removed by microbial fermentation, washed and dried, similar to the dry method. Finally, in the newer semi-dry method, the fruits are crushed, but the fermentation stage is skipped; then, they are dried with the mucilage residue [12]. Figure 2 shows a diagram of the post-harvest handling of coffee cherries, highlighting the stages that contribute the most solid waste. Several washing stages also produce huge amounts of contaminated water, which has a high carbon load and thus a large environmental impact. Other minor wastes can include damaged green coffee beans and coffee tree leaves during harvesting [35].

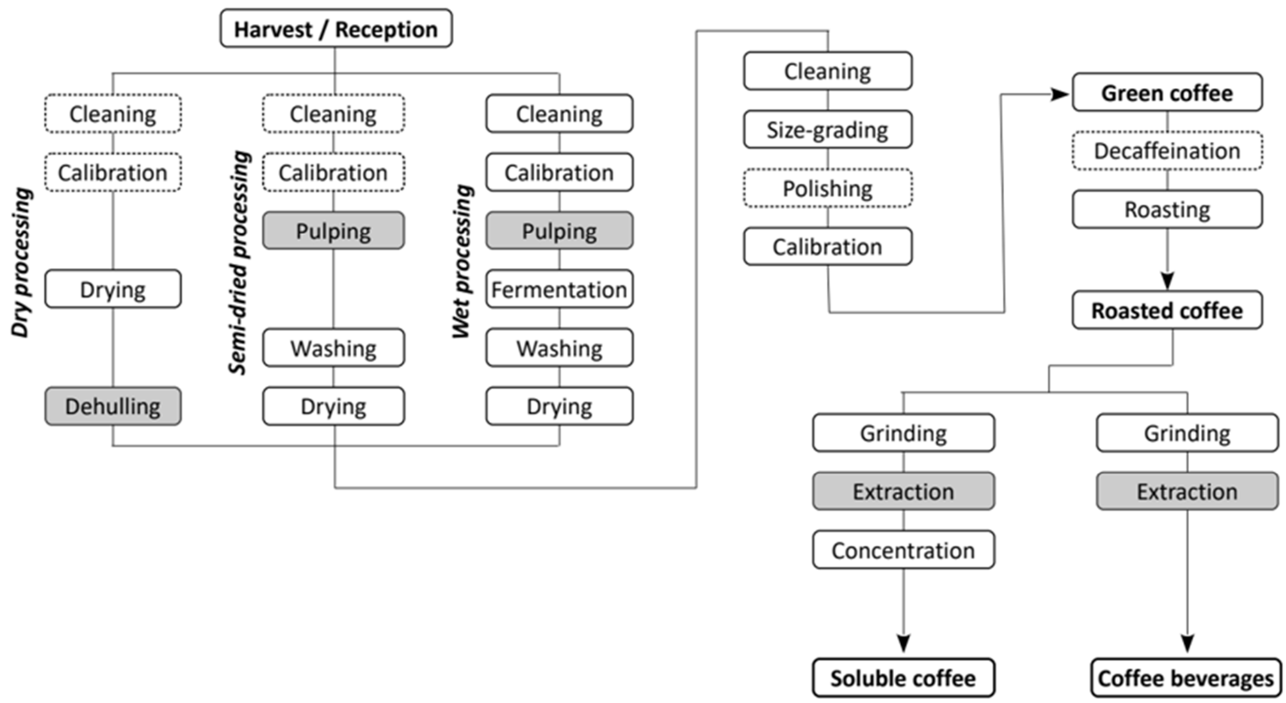

Figure 2. The life cycle of coffee products and residue generation steps. Grey boxes indicate major steps of coffee solid residue production. Own compilation based on literature data [35].

3.1. Dry Coffee Processing Method

The dry processing method of coffee beans, which is the oldest way of processing beans, does not use water. The cherries, which are harvested from the coffee plants, are directly placed on special tables in strong sunlight. The coffee dries on the tables for about a month. After this time, the skin and residual pulp are removed in a dry mill. Then, as in the wet method, they are segregated and evaluated. Although this process seems extremely simple, in reality it faces many problems. First of all, the harvested fruit must be perfectly ripe but also not overripe. Once the coffee lands on the tables, it is necessary to regularly stir and turn it. This is because drying must take place evenly. Fermentation must not be allowed. Thus, in the dry (natural) method, coffee beans are subject to numerous defects. Dry-processed coffees are characterized by an intense, sweet, heavy aroma and notes of tropical fruits, mango, passion fruit, pineapple, berries and even chocolate or cocoa [36]. The advantage of this method is that it does not require advanced and complicated equipment or a large amount of energy. It does, however, require large drying areas. The process is slow, taking three to four weeks, and the berries are usually spread thinly to avoid fermentation. Frequent raking is also required to avoid the appearance of mold and to ensure uniform drying conditions. Artificial drying can be used as a substitute or supplement to natural drying. Several types of equipment are used, including static, rotary, horizontal and vertical dryers, and the process can be carried out continuously or in batches [12,37]. Depending on the chosen method of processing previously extracted coffee beans, different residues can be obtained. Dry processing can produce only one type of coffee residue peelings. The aforementioned skins consist of the outer skin, pulp and parchment. They account for about 12% of the fruit on a dry weight basis. It is worth mentioning that 1 ton of fresh coffee fruit yields about 0.18 tons of husks, from which about 150–200 kg of commercial green coffee is obtained [34]. Coffee husks consist of 58–85% total carbohydrates, 8–11% proteins and 0.5–3% lipids [34,38]. Small amounts of bioactive compounds, such as caffeine and chlorogenic acids, are also present in this residue [34,38]. Many possibilities have been explored for using coffee husks as a substrate for biogas and alcohol production, as a biosorbent for removing cationic dyes from aqueous solutions, for processing into fuel pellets or for extraction to recover bioactive substances.

Gouve et al. (2009) investigated ethanol production through the fermentation of coffee husks by *Saccharomyces cerevisiae*. Batch fermentation studies were conducted using whole and ground coffee husks and an aqueous extract of ground coffee husks. The results indicate that coffee husks show excellent potential for residue-based ethanol production [34,39–41]. Coffee husks additionally show potential for more direct use as a substrate for edible mushroom production or composting. Fan et al. (2000) conducted a study to evaluate the feasibility of using coffee industry residues, i.e., coffee husks, coffee leaves and spent ground coffee beans, as substrates in solid fermentation to grow *Pleurotus edible* fungi. Eight strains of *Pleurotus ostreatus* and two strains of *Pleurotus sajorcaju* were tested on a medium prepared from aqueous coffee-husk extract and agar. The results of the study demonstrated the feasibility of using coffee husks and spent coffee as substrates without any pretreatment for the cultivation of edible fungi in solid fermentation, and represented one of the first steps toward the economic use of these otherwise unused or poorly utilized residues [42]. The results of a study by da Silva et al. (2012) show the great potential of coffee husks in the production of selenium-enriched mushrooms and demonstrate the ability of the fungus *Pleurotus ostreatus* to absorb and biomagnify selenium. Coffee pulp and husk, which are the main by-products produced during coffee processing, are discharged into arable land and surface water. Consequently, the mentioned by-products are responsible for environmental pollution and should be disposed of in an environmentally friendly way. Hence, composting is an environmentally friendly option for using coffee processing by-products [43]. The aim of Kassa et al. (2012) was to evaluate the properties of compost from coffee processing by-products and analyze the changes in physicochemical properties during the composting process. The physicochemical parameters at different composting times indicate that composting coffee-processing by-products yields high-quality compost. The results additionally indicate that it is better to supplement coffee by-products with organic material before composting to improve the quality of the compost [44].

3.2. Wet/Semi-Dry Coffee Processing Method

The wet processing of coffee beans does not involve drying the cherries themselves. In the wet processing method, the coffee cherries initially go into a special machine that resembles a water mill. In the machine, the coffee is stripped of its skin. The fruit then flows in water through special channels, where it is washed. At the same time, the pulp is removed. The dried and spoiled cherries are fished out. Subsequently, the beans go into a drum, which is a kind of grater, which strips them of the remaining pulp. Again, through special channels, the coffee is transported to the fermentation tank, where it steeps for about a day. Finally, the treated beans go to dry on tables exposed in well-sunlit places. The operations performed after the coffee husks/pulp are removed are called drying and include the cleaning, size grading, density sorting, colorimetric sorting and storage of the green coffee beans. Electronic color sorting is the main procedure used to separate defective and non-defective coffee beans. In electronic sorters, coffee beans pass, one by one, through an electronic eye or camera system, and depending on the wavelength measurements, the beans are either passed through or shot out with an air jet into a pile of waste. This discarded pile will be separated as a mixture of defective (low-quality) coffee beans before entering the external market; such a mixture is usually dumped on the Brazilian internal market, being used by the coffee roasting industry in blends with good-quality coffee. Once separated from the export portion, such beans can account for more than 50% of the coffee consumed in Brazil. The presence of defective beans results in a significant decrease in the quality of the beverage. Coffees subjected to this method are the most valued in the world [12,36,39,45,46]. The semi-dry processing method of coffee beans is a variation of the wet processing method, in which the coffee fruit is stripped of its pulp, but the fermentation process takes place directly on the platform [47]. The first by-product of wet and semi-dry coffee processing is coffee pulp, which accounts for 29% of the dry weight of the whole cherry. For every 2 tons of commercial green coffee produced, 1 ton of coffee pulp is obtained [34,48]. Coffee pulp consists of the mesocarp (the fleshy part) and the exocarp (the outer skin). Coffee pulp is rich in carbohydrates (32%), proteins (5–13%) and minerals (9%), and contains significant amounts of caffeine, polyphenols and tannins [49]. Like coffee husks, coffee pulp has been investigated for reuse in mushroom production, composting, biosorbent and bioactive compound extraction purposes (as soluble and bound hydroxycinnamates) [34,50].

4. By-Products of Coffee Bean Processing

Waste generation is inherent in any manufacturing sector. Coffee is the second largest commodity sold in the world, so the coffee industry is responsible for generating a large amount of residue [26]. After going through pre-processing, green coffee can be subjected to a roasting process that will completely change its physical and chemical composition and, consequently, the by-products produced. Coffee processing by-products are produced immediately after roasting and after the preparation of the beverage in industrial settings or in cafes/households [35]. Figure 3 graphically shows the by-products of coffee bean processing and their main components.

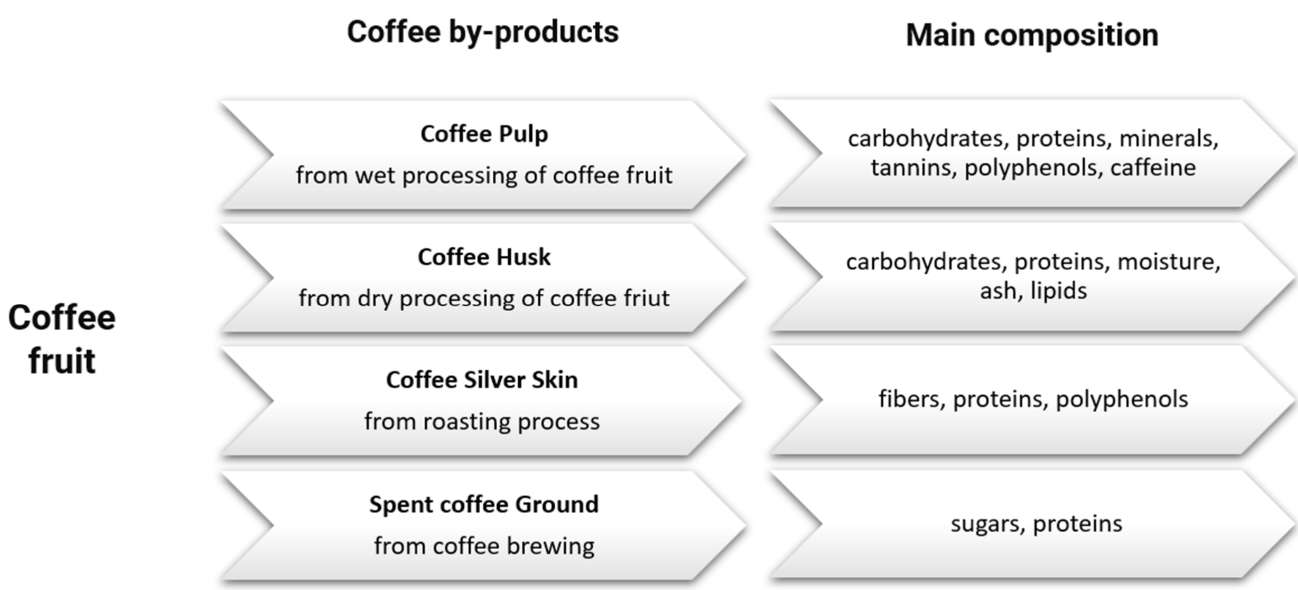

Figure 3. Schematic representation of coffee by-products and their main components. Own compilation based on literature data [14].

4.1. Coffee Husks and Pulp

Coffee husks and pulp consist of the outer skin and attached pulp residue, and these solid residues are obtained after hulling coffee cherries during dry or wet processing, respectively. The moisture content varies depending on the type of processing. The moisture content of dry-processed coffee husks ranges from 7 to 18%, with such a wide range due to differences in processing and storage conditions [51–56]. Wet-processed coffee husks (coffee pulp) contain about 75% moisture and are usually allowed to dry to about 13% moisture [57,58]. The average chemical composition values (per dry weight) of coffee husks and pulp are shown in Table 2. Coffee husks and pulp are rich in organic nature and nutrients, and also contain compounds such as caffeine, polyphenols and tannins. Due to the presence of the latter compounds, the aforementioned solid residues are toxic in nature, which not only increases the problem of environmental pollution but also limits their use as animal feed [57,59].

Table 2. Chemical composition of coffee husks and pulp (g/100 g dry basis). Own compilation based on literature data [53–55,57–61].

	Coffee Husks (Dry Processed)	Coffee Pulp (Wet Processed)
Protein	8–11	4–12
Carbohydrate	58–85	45–89
Lipids	0.5–3	1–2
Minerals	3–7	6–10
Tannins	~5	1–9
Caffeine	~1	~1

Coffee husks and pulp are rich in potassium and other mineral nutrients, which has prompted research into using these solid residues as organic fertilizers without any treatment or after composting. Using coffee husks directly as a soil cover is a good solution for potassium-poor soils and can be used for a variety of crops, including coffee. They promote erosion control, and reduce temperature fluctuations and water loss through evaporation [62].

4.2. Defective Coffee Beans

The removal of defective coffee beans is the final processing step for obtaining good quality coffee drinks. Defective beans are usually associated with certain problems during harvesting and post-harvest processing operations and have a negative impact on the quality of the beverage. The most important types of defects are known as black, sour and unripe. Black beans result from the death of the beans inside the coffee fruit or from beans that fall naturally to the ground as a result of rain or over-ripening [63,64]. The presence of sour beans is usually associated with "excessive fermentation" during wet processing [63] and improper drying or harvesting of overripe cherries [63,65]. Although defective beans are mechanically separated from those that are not defective before entering international markets, they are still marketed in Brazil and other coffee-producing countries. In order to eliminate these defective beans from the commercial market and improve the overall quality of the beverage consumed worldwide, several studies have recently been conducted on alternative uses for such beans [39,66]. Oliveiry et al. (2008) investigated the possibility of producing biodiesel using oil extracted from defective coffee beans [39]. In order to make coffee oil-based biodiesel production an environmentally friendly process, alternative proposals for managing the resulting solid residues are needed. In this regard, a paper by Nunes et al. (2009) investigated the potential of the resulting solid waste as a feedstock for the preparation of activated carbons [66].

4.3. Coffee Silver Skin

Among the by-products of coffee bean processing, silver skin and spent grounds are generated in large quantities, and consequently should be given special attention [67]. Coffee silver skin is the layer covering coffee beans separated during the roasting process. Coffee silver skin is the first residue of the coffee industry produced in consuming countries. Coffee silver skin is rich in soluble dietary fiber (54% of total dietary fiber) and compounds with antioxidant properties (such as phenolic compounds) [17,67]. However, most of these residues remain unused, burned for elimination or discharged into the environment, which is not an environmentally friendly solution. These discharges into the environment cause serious problems such as environmental contamination and pollution due to their toxic nature [42,68], and incineration produces carbon dioxide, a greenhouse gas [67].

The published literature's data on the reuse of coffee silver skin is scarce. Few studies on the composition of coffee silver skin reveal that the mentioned residues are rich in phenolic compounds [17]. Moreover, several of these phenolic compounds from coffee beans may have important biological functions and may have antioxidant potential, which may be of interest to the food and pharmaceutical industries [69]. In some countries, coffee silver skin can be used as a soil fertilizer additive or as a fuel [70]. In addition, coffee silver skin can be used as a source of nutrients during the production of fructooligosaccharides and β-fructofuranosidase by *Aspergillus japonicus* under solid-state fermentation conditions. Coffee silver skin is used as a feedstock for fuel ethanol production or as an ingredient in anti-aging cosmetics and is a functional food additive [71–73]. Solid-state fermentation is a valuable alternative for the reuse of agricultural and agro-industrial residues, as it can be used to produce and/or extract compounds such as enzymes, flavors, pigments and organic acids [74,75].

4.4. Spent Coffee Grounds

The preparation of coffee-based beverages typically uses Arabica coffee or blends of Arabica and Robusta from one or different geographic regions, available to consumers as roasted beans, whole or ground, or even in the form of instant coffee. The term "spent coffee grounds" can include grounds generated after brewing coffee in cafes or at home and those obtained from the production of instant coffee [17]. According to the 2019 European Coffee Report on the soluble coffee trade in Europe to and from non-European destinations, imports of soluble coffee (instant coffee) in 2018 amounted to 47 tons. Several coffee-producing countries have a sizable instant coffee production and are major exporters of the product. Brazil is at the top of the exporters; its sales to the European Union increased slightly in 2018 to 10 tons. Instant coffee imports in 2018 from India amounted to 8 tons. The export of instant coffee from the EU to destinations outside the EU in 2018 was 48 tons [76]. High consumption is accompanied by high waste production in the instant coffee industry. It is estimated that the industrial production of coffee grounds is 6 million tons per year, as for every 1 kg of instant coffee produced, there are about 2 kg of wet grounds [17].

Among the by-products, in addition to coffee silver skin, significant amounts of spent grounds are produced, and for this reason special attention should be paid to them [67]. Coffee grounds resulting from the production of instant coffee are a coffee by-product with fine particles, high organic charge, high moisture content (80–85%) and high acidity [17]. Due to its chemical properties, direct disposal of coffee grounds into the environment is not advisable. In recent years, many environmentally friendly solutions have been proposed. For example, they can be used directly as a fuel for combustion in the solvent industry and for the production of biodiesel and fuel pellets; as a source for the production of low-cost carbon dioxide adsorbents, dyes or heavy metals, or other value-added products such as ethanol (Figure 4); and as a substrate for the production of edible mushrooms [77–81]. Spent coffee grounds can be used as fuel in industrial boilers of the same industry, due to their high calorific value of about 5000 kcal kg^{-1} [82]. In addition to the aforementioned potential uses of spent coffee grounds, several studies describing their bioactivity, amino acid and sugar content have also been conducted to find alternatives for reusing these residues [17]. Numerous studies on the composition of spent coffee grounds reveal that the aforementioned residues are also rich in phenolic compounds [83].

A schematic of the industrial instant coffee production process is shown in Figure 5. The industrial coffee grounds produced during instant coffee production are chemically different from those obtained in coffee shops/households. In fact, the components of industrial coffee are extracted more efficiently, resulting in a more chemically depleted residue compared to coffee obtained after brewing in cafes/households [35].

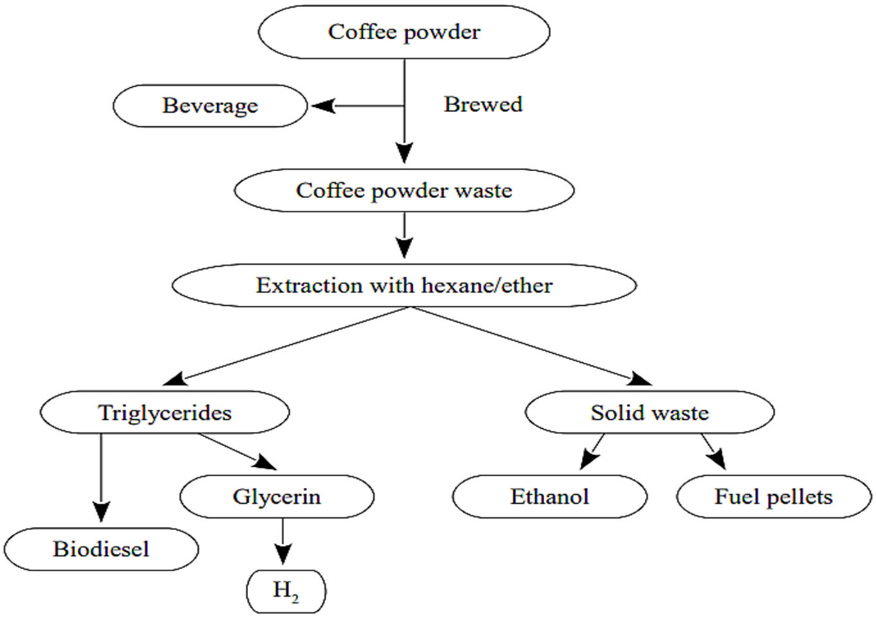

Figure 4. Schematic presentation of biodiesel and fuel pellet production process from spent coffee grounds. Own compilation based on literature data [78].

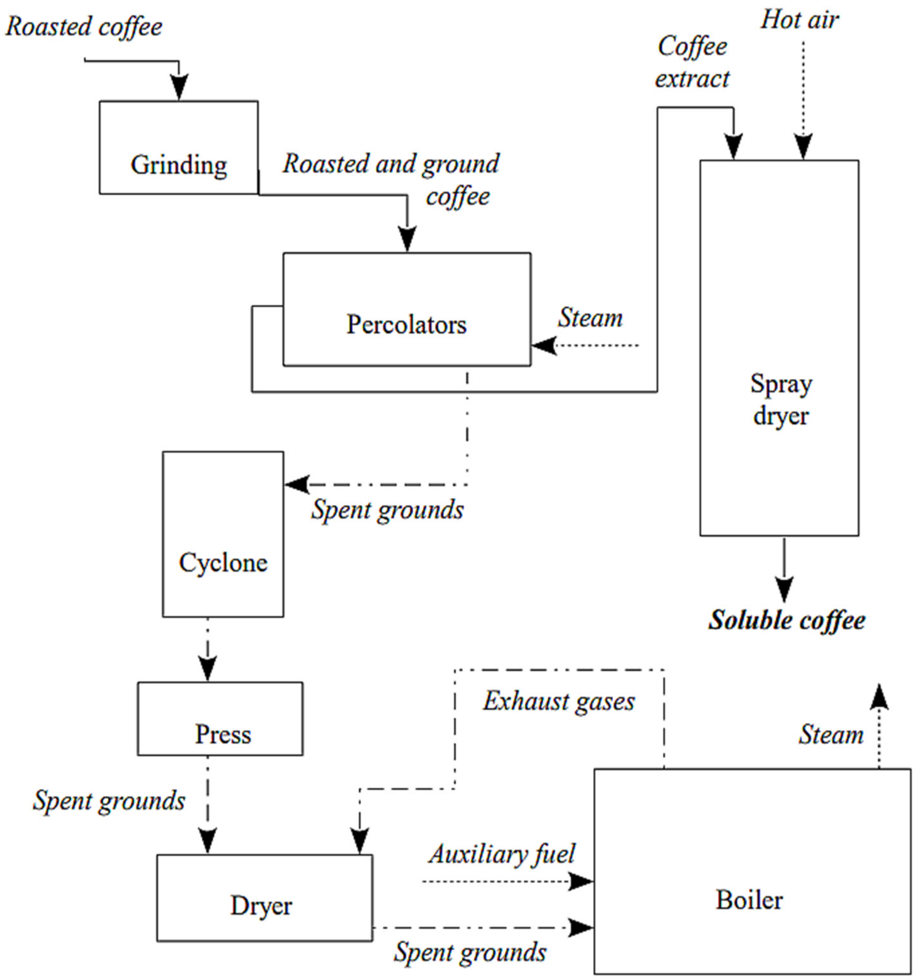

Figure 5. Scheme of the industrial production process of soluble coffee. Own compilation based on literature data [82].

5. Management and Use of By-Products from Coffee Bean Processing

In the past years, climate change has become more pronounced; hence, new environmentally friendly solutions are being sought to reuse industrial and food residues [14]. Increasingly, the world is moving towards a closed-circuit economy, which is an alternative model of economy based on the principle of closing the cycle of a product's life cycle. The circular economy involves minimizing the use of natural resources and minimizing the generation of by-products/waste. This economy has been adopted by the European Union as a solution to achieve its adopted environmental goals. The adopted circular economy additionally aims to increase the competitiveness of the EU economy in the global market [84].

Waste from the agro-food industry is considered a good source of renewable raw materials. It is estimated that about 100 million tons of food waste is generated annually in the EU, of which an average of 30% comes from the agro-food industry. Such high volumes of waste have a significant negative impact on the environment, which translates into a carbon footprint, among other things. Global agri-food waste production is expected to increase to more than 200 million tons per year by 2050. As a result, sustainable management of by-products is necessary [14].

The main priorities in Europe for a circular economy are the reuse of the waste generated, recycling and environmental sustainability. In recent years, citizens have paid more attention to producing innovative materials from waste. This translates into an increased interest toward sustainability education [14]. Given that coffee is the second largest commodity sold in the world and its global production reaches 105 million tons per year worldwide, the industry is responsible for generating a significant amount of waste from the processing of the picked coffee fruit to the cup of coffee in the home/cafe [26,85]. The annual amount of waste from coffee bean processing is expected to exceed 23 million tons per year. As mentioned earlier, by-products of coffee bean processing are mainly created by removing the husks and mucilaginous parts from the fruit, and depend on the coffee processing technology used (dry, wet, roasting, brewing). Solid residues include coffee husks, coffee pulp, coffee silver skin and spent coffee beans (Figure 3). According to the available literature and physicochemical analyses performed, residues from coffee bean processing show great potential for the production of high-value compounds/materials [86,87].

Solid waste fractions (from coffee bean processing) such as coffee grounds, coffee pulp and coffee husks are wastes enriched in organic acids, polyphenols and carotenoids [14]. Currently, there are studies available indicating that roasted coffee grounds can be used as a bioplastic enhancer for biodegradable poly(butylene adipate-co-terephthalate) (PBAT) without the need for a compatibilizer, resulting in innovative food packaging with low toxicity. In addition, other studies indicating the use of solid waste fractions from coffee bean processing to produce biocomposites are noted [88–91]. In addition, the use of the aforementioned solid waste from coffee bean processing for biofuel production has been reported. A study by Dadi et al. (2018) investigated the production of bioethanol from various coffee waste fractions using hydrolysis [92]. A similar study was conducted by Procentese et al. (2018), and the results encourage further research into the reuse of coffee silver skins for solvent production in fermentation processes [93]. Table 3 presents some examples of the valorization of coffee bean processing by-products in energy production, the methods used and the secondary products obtained.

The biocarbon derived from coffee-bean-processing waste (coffee grounds and parchment) has been shown to immobilize heavy metals in contaminated soil, although there are few studies in this area. As previously mentioned, the coffee industry generates a huge amount of waste, which shows potential toward a circular economy and environmental sustainability [94]. Additionally, spent coffee grounds can also be used as an insect repellent (Figure 6) [95].

Table 3. Examples of the valorization of coffee processing by-products in energy production. Own compilation based on literature data [14].

Coffee By-Product	Methods	Fuel	Secondary Products
Defatted spent coffee grounds	Pyrolysis	Bio-oil	Biochar
	Hydrolysis/fermentation	Bioethanol	Fuel pellets
Spent coffee grounds oil	Enzymatic conversion	Biodiesel	Glycerin to bio-hydrogen
	Chemical conversion/enzymatic/in situ	Biodiesel	Glycerin to bio-hydrogen
Spent coffee ground	Pyrolysis	Bio-oil	Biochar, syngas
	Hydrolysis/fermentation	Bioethanol	Fuel pellets

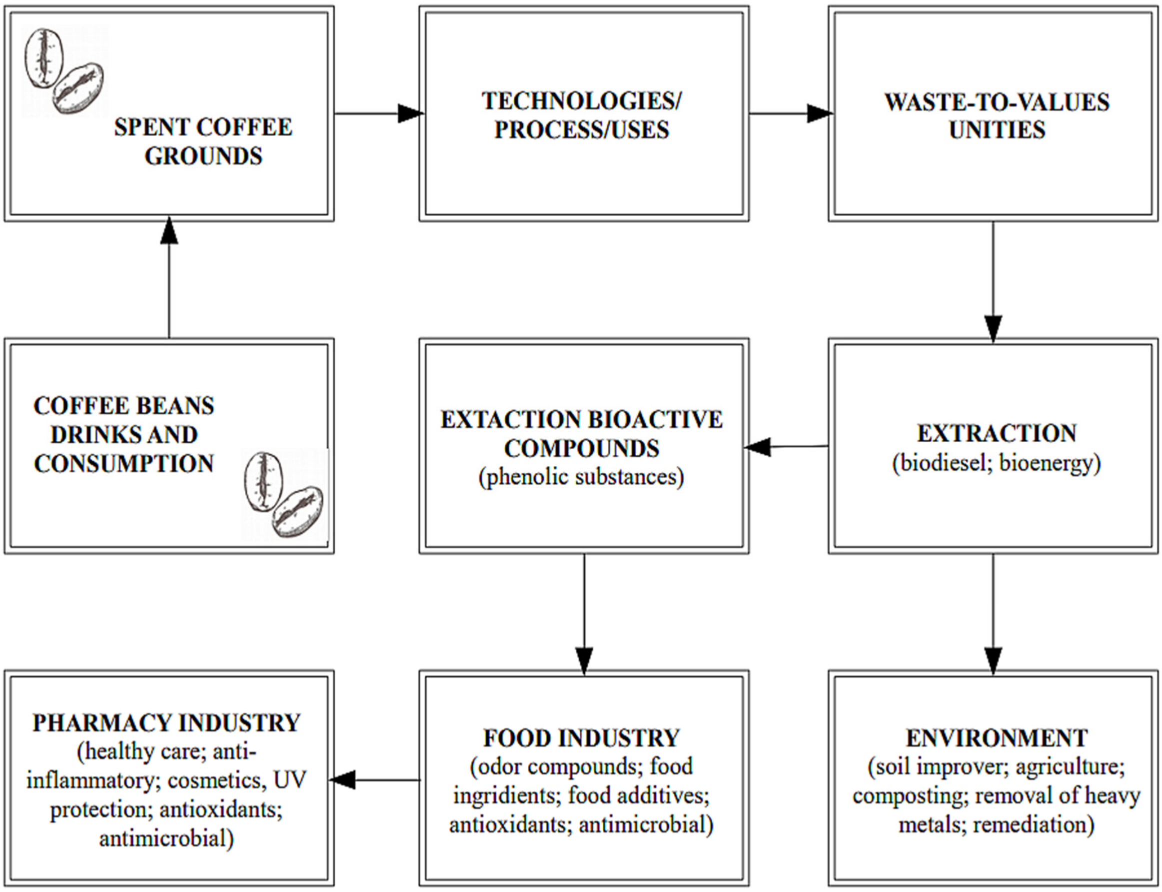

Figure 6. Overview of potential usages of spent coffee grounds. Own compilation based on literature data [95].

The widespread use of synthetic herbicides to remove weeds and maximize yields is not a friendly solution for the environment or human health. As a result, innovative and sustainable solutions are being pursued through the introduction of natural alternative herbicides, which further promotes a circular economy. A study by Lorenzo et al. (2022) found that spent coffee grounds reduced the biomass of all naturally occurring weeds and stimulated crop growth under low rainfall and higher temperatures. However, the effect varied under different environmental conditions. Spent coffee grounds can partially control weeds in the field, consequently becoming a bioherbicide and contributing to sustainable agriculture [96]. Research by Budžaki et al. (2022) indicates the possibility of converting agri-food waste into carriers for enzyme immobilization (Figure 7). Converting coffee-industry waste (spent grounds) into low-cost enzyme carriers can contribute to the development of immobilized enzymes with desirable operational properties and reduce the price of immobilized enzymes for use in biocatalytic production [97]. A study by Goiri et al. (2020) points to the antimicrobial and antioxidant properties of spent coffee grounds, which contributes to their potential as an ingredient in ruminant diets [98].

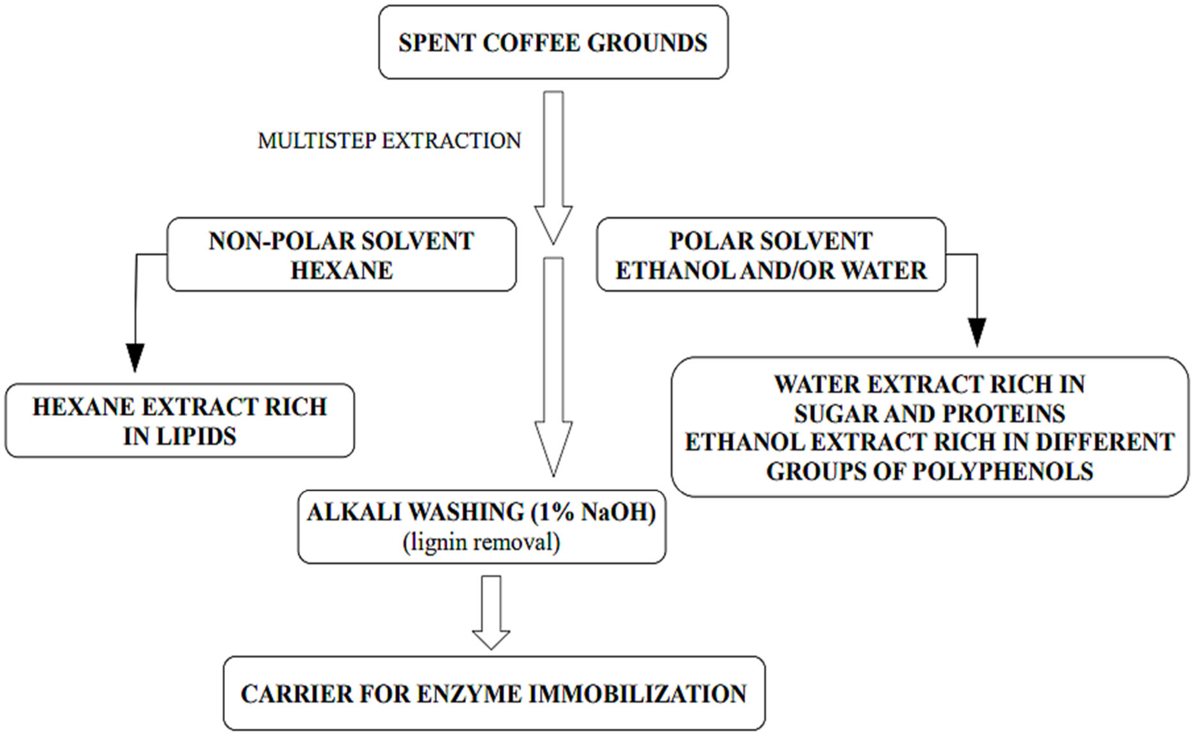

Figure 7. Schematic representation of the transformation of spent coffee grounds and brown onion-skins into high-value biological compounds and lignocellulosic material. Own compilation based on literature data [97].

6. Coffee-Processing Waste as Biosorbents

Pollutants from various industries, mining or electroplating enter the environment in significant quantities as a result of anthropological activities. Among the pollutants, heavy metals such as cadmium, copper, lead and zinc stand out. Heavy metals have the ability to easily accumulate in living organisms and the ecosystem and are not biodegradable in the environment. This contributes to their elevated concentration in the environment. This poses a major threat to the health and life of living organisms and the environment. Heavy metals are most often found in the soil and water phases, but can also migrate into the atmosphere, where they often combine with dust particles [99].

Effective technologies are constantly being sought to enable the reduction of heavy metals in the environment. For example, flotation, ion exchange, chemical precipitation, coagulation, membrane filtration and adsorption are used as technologies that enable the reduction of heavy metals in the aquatic environment and wastewater. The aforementioned technologies are unfortunately costly and can generate nuisance by-products. Hence, adsorption on adsorbents has been considered a versatile and cost-effective method of removing heavy metals from the environment. This is a relatively simple method of removing heavy metals from the aquatic environment by a process of adsorption on the surface of materials serving as adsorbents, followed by removal of the adsorbents from the water. This results in a reduction in the concentration of heavy metals in the water environment under study. Adsorption involves the phenomenon of external absorption of whole substances, liquids, vapors and gases. The material absorbed during the adsorption process is distributed over the entire surface of the adsorbent. Nowadays, activated carbon is most often used as an adsorbent material because of its remarkable properties. The high efficiency of activated carbon for the elimination of heavy metals from the aqueous environment is due to the large number of functional groups and micropores on the large adsorption surface [99–101]. Unfortunately, due to the high cost of producing activated carbons from materials such as lignite or wood, alternative low-cost and local materials are being sought from which adsorbents with the desired properties can be easily produced [102,103]. Figure 8 shows the types of sorbents [104].

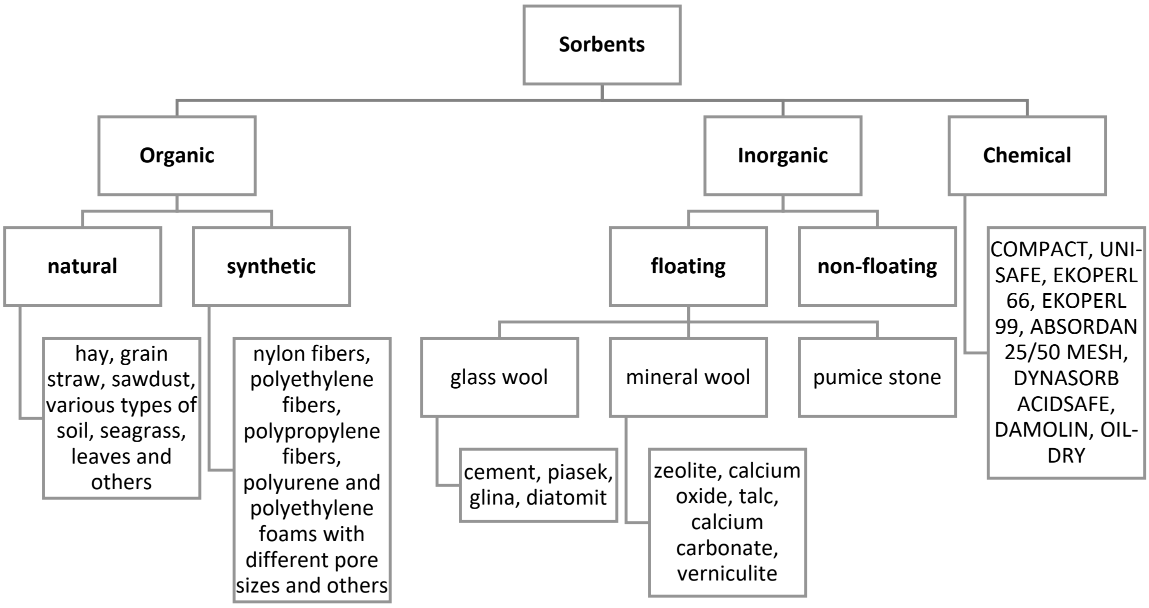

Figure 8. Types of sorbents. Own compilation based on literature data [104].

There is a constant search for alternative, low-cost and effective adsorbents. Demirbas (2008), for example, pointed out the possibility of producing adsorbents using by-products from the agri-food industry, including waste from fruit (skins, husks), tea and coffee (spent beans, skin, pulp) to remove heavy metals from contaminated aquatic environments [105].

Coffee is the second largest agri-food commodity sold on the international market, and as a consequence, large amounts of coffee bean processing by-products are generated [26]. According to the available literature data and physicochemical analyses performed, by-products from coffee bean processing show great potential for the production of high-value compounds/materials [86,87]. Coffee-bean-processing wastes—mainly coffee grounds—are used to extract biologically active compounds and produce bioenergy and valuable materials such as composites and plastics [106]. Research on the production of adsorbents from waste from the coffee bean processing industry for the removal of heavy metals from the aquatic environment is still sparse. However, published literature data indicate their potential as adsorbents, due to their structural properties (small size ≈ 20 µm), are composed of high-molecular-weight lignin and fibers (>50%) and have a large surface area (7.5 m^2 g^{-1}) [106–109].

6.1. Spent Coffee Grounds as Biosorbents

Among the previously mentioned by-products of coffee bean processing, it is the spent coffee grounds that make up the bulk of coffee waste. Spent coffee grounds are organic residues in the form of powder formed after the extraction of coffee beans under high pressure and hot steam. Today, spent coffee grounds are most often used as a raw material for bioenergy production, extraction of biologically active substances or as a raw material for high-value composites and plastics. Although spent coffee grounds show potential as an adsorbent material, there is little research into their use for removing heavy metals from contaminated environments. Spent coffee grounds are characterized by their small size, porosity and large specific surface area; they consist of lignin, and additionally contain tannin material (polyhy-droxy polyphenol functional groups), which translates into the fact that heavy metals can be effectively adsorbed by complexation [106,109].

Kim et al. (2020) conducted a study to determine the potential of spent coffee grounds as an alternative adsorbent for removing cadmium (Cd) from aqueous solutions. For the study, they used spent coffee grounds obtained from a local coffee shop located in Seoul, Korea. They subjected the extracted coffee grounds to an air-drying process for a period of two weeks. The dried grounds were sifted through sieves (0.5 mm) and stored in polyethylene bottles until they were used in the study. Importantly, the spent coffee grounds were not subjected to any chemical or physical pre-treatment before being used for testing. For comparison, zeolite, as a well-studied adsorbent, was used to determine the adsorption efficiency. Zeolites are alkaline minerals characterized by a high adsorption capacity. They are commonly used to remove numerous pollutants, including heavy metals. The zeolite used in this study was obtained from a local horticultural market (Seoul, Korea). The particle size of the zeolite used was <0.5 mm, while the surface area was 38.91 $m^2\ g^{-1}$. The stock solutions of Cd (1000 mM) used in the study were prepared by dissolving $Cd(NO_3)_2 \cdot 4H_2O$ in distilled water, while test solutions of Cd ranging from 0.1 to 120 mM were prepared by appropriate dilution. During the tests, the ionic strength of the solutions used was controlled with $Cd(NO_3)_2 \cdot 4H_2O$, while a parameter such as pH was controlled with a 28% ammonia solution and dilute nitric acid. After preparing the adsorbents and reagents for the study, the selected physicochemical properties of the spent coffee grounds and zeolite were determined. The selected physicochemical properties of spent coffee grounds and zeolite are presented in Table 4 below. The spent coffee grounds were found to be rich in organic matter (94.65% of total weight) compared to zeolite (1.31%). The higher amount of organic functional groups in spent coffee grounds relative to zeolite indicates that Cd adsorption is more efficient with spent coffee grounds [99].

Table 4. Selected physicochemical properties of zeolite and spent coffee grounds. Own compilation based on literature data [99].

Adsorbent	pH	Electrical Conductivity	Loss-On-Ignition	Trace Elements (mg kg^{-1})					
		(mS m^{-1})	(%)	As	Cd	Cu	Ni	Pb	Zn
Zeolite	7.3 ± 0.1	74 ± 8	1.3 ± 0.2	4.3 ± 0.1	0.39 ± 0.02	19.9 ± 0.4	17.3 ± 0.7	15.6 ± 1.8	43 ± 2.3
Spent coffee grounds	5.2 ± 0.1	185 ± 11	94.7 ± 0.5	Not detected	0.01 ± 0.00	12.6 ± 0.3	0.4 ± 0.05	1.1 ± 0.1	6.2 ± 0.2

Wastewater often contains electrolytes, including various ionic species. Numerous reports indicate that the presence of coexisting ions and salts can negatively affect the sorption kinetics of selected metal ions due to the competition for adsorption sites. The aforementioned Kim et al. (2020) investigated the effect of ionic strength on Cd adsorption on spent coffee grounds at background electrolytes with concentrations of 0, 2, 20 and 200 mM $Ca(NO_3)_2$ and pH 6. The study indicated that the amount of Cd adsorbed by the spent coffee grounds and its affinity significantly decreased with increasing ionic strength ($p < 0.01$). In addition, coexisting ions compete with Cd for the adsorbent surface area, which reduces the adsorption capacity of spent coffee grounds. In addition to ionic strength, the adsorption capacity of spent coffee grounds was also affected by the pH of the test solution. This is because the pH of the solution strongly affects metals and their precipitation. The effect of pH on the adsorption of Cd by spent coffee grounds was investigated by adjusting the initial pH of the solution from two to ten. The results show that the amount of Cd removed using coffee grounds increased as the initial pH increased. In addition, the rate of Cd removal was regulated by the final pH of the solution. The maximum degree of Cd adsorption (71.90%) on spent coffee grounds was demonstrated at pH 6. In addition, Kim et al. (2020) investigated the effect of solid-to-solution ratio on Cd adsorption. As predicted from similar studies, the Cd removal rate decreased from 91.04% to 15.14%

with an increase in SSR (Solid/Solution Ratio) from 1:4 to 1:400 while maintaining the Cd concentration in the SSR. It was observed that at a solid/solution ratio of 1:10, the maximum Cd removal rate is obtained with the minimum amount of coffee grounds consumed [99].

An extremely important relationship indicating the effectiveness of adsorbents is the adsorption isotherm. These well-known isotherm models have been used for equilibrium adsorbance studies: Freundlich, Langmuir, Dubinin-Radushkevich and Temkin. Table 5 shows the models of the mentioned isotherms with linearized expression [110].

Table 5. Linearized models of isotherms. Own compilation based on literature data [110].

Langmuir	$\frac{1}{qe} = \frac{1}{q_m} + \frac{1}{K_L q_m} \times \frac{1}{Ce}$	qe = adsorption capacity determined at equilibrium (mg·g^{-1}); q_m = maximum adsorption capacity in mg·g^{-1}; K_L = langmuir constant in L·mg^{-1}
Freundlich	$\ln qe = \ln K_f + \frac{1}{n} - \ln C_e$	K_f = adsorption capacity; n = intensity of adsorption
Dubinin-Radushkevich	$\ln(qe) = \ln(q_s) + K_{ad}\, \varepsilon^2$	qe = amount of adsorbate adsorbed onto the adsorbent at equilibrium (mg·g^{-1}); q_s = theoretical isotherm saturation capacity (mg·g^{-1}); K_{ad} = the Dubinin–Radushkevich isotherm constant (mol^2·J^{-2}); ε = the Dubinin–Radushkevich isotherm constant $\varepsilon = RT \ln(1 + 1/C_e)$
Temkin	$qe = B_T \times lnA_T + B_T \times lnC_e$	B_T (heat of adsorption in J·mol^{-1}) = RT/b_T; A_T = equilibrium-binding constant of the Temkin isotherm in Lg^{-1}; b_T = the Temkin isotherm constant; R = universal gas constant taken as 8.314 J·mol^{-1} K^{-1}; T = temperature taken as 298 K

Table 6 shows the adsorption parameters of zeolite and spent coffee grounds for Cd, fitted to the Freundlich, Langmuir and Dubinin-Radushkevich equation. The results indicate that the adsorption capacity of spent coffee grounds for Cd was higher compared to zeolite [99].

Table 6. Adsorption parameters of zeolite and spent coffee grounds for Cd. Own compilation based on literature data [99].

	Freundlich			**Langmuir**			**Dubinin-Radushkevich**		
	1/*n*	***Kf***	***R*²**	**q_m (mg g^{-1})**	***K* (L mg^{-1})**	***R*²**	**q_m (mg g^{-1})**	***E* (kJ mol^{-1})**	***R*²**
Zeolite	0.39	0.10	0.87	13.91	<0.01	0.92	14.48	16.44	0.81
Spent coffee grounds	0.32	0.85	0.95	19.32	<0.01	0.96	19.79	14.08	0.96

A study by Kim et al. (2020) indicates that spent coffee grounds not subjected to any physicochemical pretreatment have a higher Cd adsorption capacity (19.32 mg g^{-1}) than a commonly used conventional absorbent such as zeolite (13.91 mg g^{-1}). In addition, the study indicates the great potential of spent coffee grounds as an alternative, low-cost adsorbent that can replace conventional materials. The use of waste from the coffee industry as an alternative and low-cost adsorbent material promotes the concept of implementing a closed-loop economy. However, further research should be conducted in this area under more complex conditions (multiple metals in the tested solution) so that the mentioned solution can be applied on a larger scale in the future [99].

Table 7 shows for comparison the maximum Cd adsorption capacities (q_m, mg g^{-1}) of spent coffee grounds calculated from the Langmuir isotherm and other agro-waste materials reported in the literature.

Table 7. Comparison of maximum Cd adsorption capacity (q_m, mg g^{-1}) of spent coffee grounds and other agro-waste reported in literature.

Type	Biosorbents	Maximum Adsorption Capacity	References
Agro-waste	Rice husk	14.40	[108]
	Grape stalk waste	13.93	[111]
	Corn starch	8.88	[112]
	Physic seed hull	11.89	[113]
	Peanut hull	5.96	[114]
Coffee residues	Spent coffee grounds	19.32	[99]
	Coffee	6.47	[100]
	Exhausted coffee grounds	11.60	[115]
	Untreated coffee grounds	15.65	[109]
	Degreased coffee beans	6.72	[116]
	Coffee husks	6.85	[117]
	Spent coffee grounds	4.34	[118]

Similarly, Azouaou et al. (2010) noted that untreated coffee grounds have potential as a cheap and effective adsorbent for cadmium removal. They conducted kinetic and equilibrium studies to determine the effects of adsorbent dose, contact time, initial pH, particle size, initial temperature and initial cadmium concentration on the adsorption process using untreated coffee grounds. The following adsorption isotherm models were used to analyze the equilibrium data: Langmuir, Freundlich and Dubinin-Radushkevich. The results obtained indicate the great potential of coffee grounds as an alternative raw material for the production of effective and economical adsorbents for cadmium removal. The authors of the paper additionally reported a comparison of the adsorption capacity of spent coffee grounds with different adsorbents [109]. Table 8. compares the adsorption capacity of different adsorbents with coffee grounds.

There are also examples in the literature of the use of coffee-processing waste to remove heavy metals (e.g., arsenic, cadmium, lead) from the aquatic environment. Due to their ease of dispersal, non-biodegradability and ability to accumulate, heavy metals pose a serious threat to aquatic organisms and human health. Hence, the removal of heavy metals is a constantly important issue for many scientists. The conventional methods of removing such contaminants are costly. Therefore, research into the use of biomaterials such as coffee as a low-cost raw material for adsorbents is promising. Coffee grounds are a porous material with a networked structure, so they absorb other substances such as certain gases or elements. Nam et al. (2017) in their study investigated the possibility of removing arsenic (As) from wastewater using untreated coffee grounds. For the study, coffee grounds were collected directly from two companies located in South Korea. The biomaterial was rinsed three times with distilled water and dried in an oven at 100 °C for 24 h. Structural characterization of the coffee waste was carried out and compared with activated carbon and CMK-3 carbon (Table 9) [119].

Table 8. Comparison of adsorption capacity of different adsorbents with spent coffee grounds. Own compilation based on literature data [109].

Adsorbents	Maximum Adsorption Capacity (mg g^{-1})
Olive cores	12.56
Olive cake	10.56
S. anthophorbium	18.90
L. arboresens	11.50
Olive wastes	6.56
Degreased coffee beans	6.72
Bagasse fly ash	6.19
Commercial activate carbon F.400	8.21
Oxidized granular activated carbon	5.73
Coffee grounds	15.65

Table 9. Structural characteristics of coffee waste, activated carbon and CMK-3. Own compilation based on literature data [119].

Adsorbent	Total Surface Area (m^2/g)	Pore Volume (cm^3/g)	Medium Pore Size (Å)
CMK-3	1508	0.86	39
Activated carbon	1212	0.60	3
Coffee waste	0.047	0.000935	292.92–427.97

Preliminary results obtained by Nam et al. (2017) indicate the potential of untreated coffee grounds to remove arsenic from wastewater. Higher potential occurred in acidic and alkaline environments than in neutral pH environments. The maximum adsorption concentration of arsenic (As) on 1 g of spent coffee grounds was 6.44 mg/L at 1 mM arsenic solution at pH 7 [119].

In addition to removing heavy metals from the aquatic environment, spent coffee grounds are also used as adsorbents to remove organic compounds, pharmaceuticals and pesticides. Zungu et al. (2022) investigated the possibility of producing biocarbon from coffee grounds by pyrolysis and its potential ability to remove pharmaceuticals from water. Spent coffee grounds were found to be a relatively inexpensive and effective adsorbent to complement conventional purification techniques to remove emerging contaminants from waste by modifying coffee grounds into useful biocarbon. The biocarbon was prepared by pyrolysis under argon gas conditions. The kinetic results confirm the potential of biocarbon produced from coffee grounds to help mitigate environmental pollution by increasing the removal of pharmaceuticals from conventional wastewater treatment plants, thus minimizing their potential risk in the environment. Table 10 shows a comparison of adsorption data in selected isothermal models [120].

The coffee grounds' biocarbon created in the study by Zungu et al. (2022) showed the potential to remove dissolved pharmaceutical impurities and caffeine from aqueous solutions. The study showed that the adsorption capacity of the tested materials increased with the length of contact time (salicylic acid, diclofenac and caffeine were 40.47, 38.52 and 75.46 mg g^{-1}). The tested biocarbon was characterized by a microporous surface structure, high carbon content and enhanced oxygen functional groups on the surface, and negative residual surface charge. All these features caused the studied biocarbon to show a high potential for removing pollutants in wastewater; consequently, it contributes to minimizing environmental pollution by anthropogenic pollutants [120].

Table 10. Parameters obtained by fitting adsorption data in selected isothermal models. Own compilation based on literature data [120].

	Freundlich			Langmuir			Temkin	
	1/*n*	***Kf***	R^2	q_m (mg g^{-1})	*K* (L mg^{-1})	R^2	K_T (L mg^{-1})	R^2
Caffeine	1.98	1.41	0.975	16.46	−0.03	0.915	0.03	0.9996
Diclofenac	0.41	1.75	0.832	35.86	−0.03	0.925	0.03	0.9999
Salicylic acid	0.90	1.60	0.990	25.80	−0.03	0.964	0.03	0.9997

Valorization of coffee-processing waste by modification to activated carbon is being considered as a low-cost alternative to commercial adsorbents. So far, there are few studies on the valorization of coffee parchment into activated carbon. Figueroa et al. (2021) investigated the possibility of preparing activated carbons from spent coffee grounds and parchment and evaluated their adsorption capacities. A co-calcination process with calcium carbonate was used to produce the activated carbons, and their adsorption capacities for organic acids, phenolic compounds and proteins were evaluated. The results confirm the potential value of parchment and coffee grounds as activated carbons and their use as low-cost adsorbents for the removal of organic compounds from aqueous solutions [121].

6.2. Coffee Beans as Biosorbents

The elimination of contaminants such as heavy metals from the aquatic environment and wastewater is an important issue affecting human health and the ecosystem. Although pollutants are most effectively removed using the adsorption process, the conventional adsorbent materials used (e.g., activated carbons, membrane filters, chelating and ion exchange resin, and porous polymer beads) are very expensive. Therefore, alternative, cheaper adsorbent materials are constantly being sought [100].

Minamisawa et al. (2004) investigated the possibility of adsorbing Cd(II) and Pb(II) using the following biomaterials as adsorbents: activated carbon, chitosan, zeolite, coffee beans, black and green tea, aloe vera, yuzu and coarse tea. The goal of their research was to explore the possibility of using biomaterials as alternative, lower-cost raw materials to produce adsorbents with high heavy-metal removal efficiency. The coffee beans used in the study were sourced from KEY Coffee Ltd. (Minato, Japan). The coffee blend was prepared from four varieties of coffee beans: Colombian, Brazilian, Guatemalan arabica coffee and Indonesian robusta coffee. The coffee beans were pre-treated at different temperatures and roasting times: light roast (190~215 °C) for 10 min, medium roast (190~215 °C) for 15 min, city roast (200~230 °C) for 15 min, full city roast (200~240 °C) for 15 min and French roast (200~250 °C) for 18~20 min [100].

The adsorption experiments carried out were performed using the batch method. To 200 mL of a 10 mg L^{-1} solution of Pb(II) or Cd(II) nitrate, 1 g of each adsorbent was added. The metal-containing solutions were pH 2, 4, or 6.5–6.7. The suspension was stirred for 24 h using magnetic stirrers and separated using membrane filters (0.45 µm). The magnitude of Pb(II) and Cd(II) adsorption on the adsorbents used was measured using a spectrophotometer [100].

Table 11 summarizes the obtained parameters from both isotherms. The Langmuir and Frendlich adsorption isotherms show an approximately linear relationship for all biomaterials. The value of K is large, while $1/n$ is 0.1–0.5, which shows that the studied adsorbents have a high adsorption capacity [100].

Table 11. Selected parameters of Pb(II) and Cd(II) adsorption on studied biomaterials. Own compilation based on literature data [100].

Adsorbents	Pb(II) pH 4				Cd(II) pH 6.7			
	Parameters							
	Langmuir		Freundlich		Langmuir		Freundlich	
	K/L mol^{-1}	b/mol g^{-1}	k/mol g^{-1}	$1/n$	K/L mol^{-1}	b/mol g^{-1}	k/mol g^{-1}	$1/n$
Coffee	5.48×10^4	5.76×10^{-5}	1.06×10^{-3}	0.36	4.14×10^4	7.98×10^{-5}	7.45×10^{-3}	0.53
Tea	2.61×10^4	1.01×10^{-4}	4.09×10^{-3}	0.47	1.93×10^3	8.61×10^{-4}	3.32×10^{-3}	0.42
Green tea	2.92×10^4	5.67×10^{-5}	3.33×10^{-3}	0.48	6.10×10^4	1.16×10^{-4}	3.83×10^{-3}	0.43
Coarse tea	3.46×10^4	6.55×10^{-5}	9.46×10^{-3}	0.34	4.52×10^4	1.02×10^{-4}	3.65×10^{-3}	0.46
Yuzu	1.62×10^4	2.67×10^{-5}	5.38×10^{-4}	0.39	2.94×10^4	6.60×10^{-5}	2.55×10^{-3}	0.48
Zeolite	6.18×10^4	4.63×10^{-5}	3.62×10^{-4}	0.27	6.73×10^3	9.96×10^{-4}	5.79×10^{-2}	0.61
Aloe	69.38	9.28×10^{-4}	0.17	1.11	1.29×10^4	8.60×10^{-5}	3.98×10^{-3}	0.51
Chitosan	4.43×10^3	3.16×10^{-4}	5.79×10^{-2}	0.72	1.57×10^4	1.16×10^{-4}	3.76×10^{-2}	0.71

The experiment confirmed that selected biomaterials extracted from plants by hot water extraction can effectively remove Cd(II) and Pb(II) from aqueous solution. Coffee showed the highest complexation capacity with the selected heavy metals. The study indicates that the adsorption capacity of the biomaterials was comparable to zeolite, activated carbon and chitosan. The adsorption capacity of the biomaterials was influenced by the pH and variety of the plant used. The results indicate the great potential of the studied plant biomaterials, which are discarded in large quantities and can be valuable raw materials for low-cost adsorbents for heavy metal removal [100].

Coffee beans have the potential not only to remove heavy metals from the aquatic environment but also dyes. This was proven by Sawalha et al. (2022), among others, who treated model wastewater containing a dye (methylene blue) using locally available waste as an adsorbent. In the study, they used coffee beans, almond shells, pistachio shells, sunflower shells, date seeds, jute sticks, peanut shells and vine sticks. In this experiment, the aforementioned biomaterials were used to produce natural adsorbents, activated carbon and biochar. Table 12 shows the efficiency and maximum adsorption rate for activated carbon and biochar prepared using various natural plant wastes. The results of the study confirm the technical feasibility of adsorption technology for the treatment of dye-containing wastewater using locally available biomass wastes [122].

Table 12. Comparison of efficiency and maximum adsorption rate for activated carbon and biochar prepared using various natural plant wastes. Own compilation based on literature data [122].

	Activated Carbon		Biochar	
Type of Adsorbent	Removal Efficiency (%)	Rate of Adsorption (L/min)	Removal Efficiency (%)	Rate of Adsorption (L/min)
Coffee	80	0.572	90	0.0865
Almond shells	100	0.8503	89	0.0836
Peanut hulls	100	0.9911	99.6	0.0944
Date pits	100	0.951	77.2	0.084
Pistachio shells	100	0.9956	98.6	0.0978
Grape vine sticks	100	0.9994	99.6	0.0988
Sunflower shells	100	0.996	99.64	0.094
Jute sticks	100	0.9945	99.94	0.099

6.3. Other Coffee Waste as Biosorbents

According to a review of the literature, waste from the agri-food industry, which includes coffee-processing waste, can find application as alternative, low-cost adsorbents for the removal of problematic environmental pollutants such as heavy metals. Gómez-Aguilar et al. (2022) conducted preliminary studies on the desorption process of coffee pulp without physicochemical modification, used as a sorbent for Cr(III and VI) ions in synthetic wastewater. Currently, there are few studies related to the desorption of coffee-grown materials. As for adsorption and desorption mechanisms, they are mainly related to electrostatic interactions, oxidation–reduction reactions and ion exchange. It is also related to the physicochemical composition of the materials. As Gómez-Aguilar et al. found, coffee pulp without any physicochemical modification had removal efficiencies of 93.26% and 74.80%, respectively, from synthetic Cr(III) and Cr(VI) wastewater. They investigated the desorption efficiency of four eluting agents at selected concentrations (0.10 M)—EDTA, HCl, HNO_3 and H_2SO_4—over a period of 1 to 9 days. Using H_2SO_4 0.10 M, the highest percentage of desorption was determined to be 45.75% Cr(VI) and 66.84% Cr(III) at 5 and 9 days at room temperature and 100 RPM stirring. In conclusion, coffee pulp can be used to effectively remove Cr(III) and Cr(VI) from wastewater [123].

The results of Gómez-Aguilar et al. (2021) indicate the possibility of Pb biosorption using coffee pulp as a biosorbent in synthetic waters. Tables 13 and 14 provide the summarized results of the studies conducted, respectively [124].

Table 13. Maximum adsorption capacity of selected coffee wastes without modification. Own compilation based on literature data [124].

Biosorption Characteristics			
Lignocellulosic Wastes Derived from Coffee Crops	pH	Capacity of Maximum Adsorption (Q Max.) ($mg \cdot g^{-1}$)	Q Max. Interval
Spent coffee powder/coffee grounds	4.5	66.30	49.73–159.50
	3.5	49.73	
	3.5	159.50	
	4.0	158.70	

Table 13. *Cont.*

Biosorption Characteristics			
Lignocellulosic Wastes Derived from Coffee Crops	**pH**	**Capacity of Maximum Adsorption (Q Max.) (mg·g^{-1})**	**Q Max. Interval**
Coffee waste (instant coffee beans)	5.0	9.70	9.70
Coffee shell/pulp	5.0	54.05	4.80–230.00
	N/A	37.04	
	4.5	4.80	
	0.5–9.0	7.20	
	0.5–9.0	230.00	
	2.0–9.0	50.80	
	2.0	24.10	
Raw coffee beans	6.0	61.60	22.90–61.60
	5.0	22.90	
Spent coffee beans	3.0–4.0	87.02	87.02–159.54
	2.0–12.0	93.24	
	2.0–12.0	159.54	

Table 14. Maximum adsorption capacity of chemically modified coffee waste. Own compilation based on literature data [124].

Biosorption Characteristics			
Lignocellulosic Wastes Derived from Coffee	**pH**	**Q Max. (mg·g^{-1})**	**Chemical Modification**
Spent coffee powder/coffee grounds	3.5	159.50	Citric acid
	4.0	158.70	Citric acid
Coffee waste (instant coffee beans)	5.0	54.05	Pyrolysis

Another study by Gómez-Aguilar et al. (2020) on the process of Zn(II) biosorption in synthetic wastewater used three agro-food wastes (coffee pulp, corn cobs and banana pseudo-stalks). The results of the study indicate that coffee pulp was a material showing a high removal efficiency of Zn(II) ions—63.58% at an optimum pH of 5.0. The authors note that this coffee waste can be used as a green technology in wastewater treatment, especially in the removal of the aforementioned heavy metal contamination [125].

Frezzini et al. (2019) investigated the feasibility of using agri-food waste (potato peels, banana peels, lemon peels, apple peels, carob peels, decaffeinated coffee waste, coffee waste and grape waste) to produce low-cost adsorbents for the removal of aromatic and aliphatic volatile organic compounds (VOCs) from wastewater. The results indicate that coffee waste has great potential as low-cost adsorbents for removing aliphatic and aromatic volatile organic compounds (VOCs) from wastewater [126].

7. Conclusions

A variety of pollutants enter the environment in significant quantities due to anthropological activities. Pollutants such as heavy metals accumulate in living organisms and the ecosystem and are not biologically decomposed in the environment. This poses a major threat to the health and life of living organisms and the environment. Therefore, it is important to search for effective technologies to reduce anthropological pollution in the environment. Currently, membrane techniques, chemical precipitation, electrolysis, coagulation, ion exchange and adsorption, among others, are used to remove heavy metal ions. The most versatile and cost-effective method is adsorption on adsorbents. It is a relatively simple method. At present, activated carbon is most often used as an adsorbent material because of its remarkable properties. Commercially used activated carbon used to remove heavy metal ions from the aquatic environment and wastewater is often very expensive and difficult to regenerate. In addition, commercial activated carbon has a relatively low ion-exchange capacity, and there is a diffusion limitation on the ion-exchange rate. This prompts a constant search for new, effective and low-cost adsorbents.

Coffee is one of the most important foodstuffs and agricultural commodities in the world. In terms of value, the coffee market takes the top spot, right next to the oil market. The ways of processing coffee beans at the turn of the century are constantly being modified due to the development of technology, and as a consequence the amount and nature of the by-products are also changing. This affects not only the coffee industry but also other industries; this is due to the expanding knowledge of the properties of coffee beans and the potential for their use. From the point of view of a circular economy, by-products from coffee bean processing have become valuable raw materials in other areas of life. An important way to manage waste from the coffee bean processing industry is to produce adsorbents using it.

There are laboratory research data indicating that it is possible to produce effective and low-cost adsorbents using by-products from the agri-food industry, including such wastes as coffee waste, to remove heavy metals from polluted aquatic environments. That said, there are several limitations to the use of coffee-processing byproducts as raw materials for the production of new, low-cost and effective adsorbents for the removal of environmental nuisance pollutants such as heavy metals. There is a lack of data from real-world studies where a wide variety of heavy metals and other pollutants are present in the studied environment. In addition, there is a lack of data from studies on the impact of alternative adsorbents on economic, environmental and social aspects.

The described cases of using coffee-processing wastes as alternative adsorbents for pollutant removal mainly concern laboratory-scale studies. Coffee-processing waste usually finds its recipients locally and is used, for example, as an additive in composting or as a fertilizer. Unfortunately, the resulting coffee-processing waste does not find much use on a commercial scale, especially as adsorbents. It is a waste with great potential and for the time being is used primarily as an additive to fertilizers. The literature shows many possibilities for the use of coffee-processing waste; in practice, however, only a few methods of managing this waste are used.

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