



## Bio-waste valorisation: Agricultural wastes as biosorbents for removal of (in)organic pollutants in wastewater treatment

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### ABSTRACT

The conventional waste management practices dispose or incinerate agricultural and forestry waste, contributing to the environmental pollution while misusing biomass, a valuable resource with a great potential of reuse. In fact, cultivation of agricultural crops and harvesting generate an abundant amount of waste (e.g., stones, shells, straw) that can be used for wastewater treatment. Waste biomass may be used as: (i) an adsorbent in its original, raw form, following ambient drying and grinding; (ii) modified bio-based sorbents; or (iii) a source material for the synthesis of activated carbon adsorbents through carbonization. Despite the numerous publications in this field examining the removal of a wide range of target pollutants (metals, metalloids, dyes, pesticides, as well as emerging contaminants) by several materials, more realistic studies are still required to evaluate the potential to remove residual compounds in complex matrices, by testing natural matrices, i.e., environmental samples without spiking the target compounds.

This perspective paper highlights how an integrated-engineering approach may help solving environmental-pollution issues related to water, solid waste, and air pollution. Chiefly, the application of locally produced bio-waste as an adsorbent for wastewater treatment tackles water contamination, decreases the overall amount of agricultural waste, and reduces the potential gas emissions caused by waste transportation, treatment and/or disposal.

### 1. Introduction

Agricultural production has globally tripled since the 1960s due to the expansion of land used for agriculture, sparked off by the technological innovations of the green revolution which have increased yields to meet the demands of a rapidly growing global population [1]. At current yields, worldwide agriculture produces an average of 23.7 million tons of food per day [2]. The worldwide agricultural production has placed a great pressure in the environment, causing negative

impacts on soil, air, and water resources and thus, jeopardizing the sustainability of ecosystems and the human health [3]. It is estimated that approximately 998 million tons of agricultural waste is produced annually [4]. Moreover, agriculture is responsible for 21% of all greenhouse-gas emissions. Considering world population projected to exceed 10 billion by 2050, a sustainable path for agriculture is yet to be found. Due to constraints on natural resources, this must be achieved by using lower levels of fossil fuels, by lessening emissions, and minimizing solid waste [3]. In the field of solid waste management, the current trend

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is to reduce the amount of waste at the source, or, alternatively, reuse the unavoidable waste material generated. In order to lessen their impact on the environment, the ultimate goal in both agriculture and industry is to create a closed loop by which waste materials are repurposed as a resource stream, thereby having a further knock-on effect of removing their potential transport/storage costs and eliminating their greenhouse emissions. This will contribute to fill the gaps between the current environmental status and the desired climate-neutrality before the end of the century subscribed in the Paris Agreement [5] by 190 countries, including the European Union (EU). Furthermore, it will assist the accomplishment of some goals of the European Green Deal that also ambitions to achieve a climate neutral based on resource recovery and environmental impact minimization, by mobilizing industry for a circular economy and implementing a sustainable product policy for waste reduction [6]. Moreover, this pact establishes a zero-pollution ambition through prevention of pollution and remediation measures.

In the search for economic and eco-friendly biosorption materials for the remediation of water pollutants, many studies have refocused on agricultural waste materials, such as stone fruits, nuts and husks, peels, wood and forest residues, and plants [7–10], owing to their unique chemical composition, abundant availability, renewable nature and low cost. These agricultural wastes are composed by cellulose, hemicelluloses and lignin as major constituents and may possess other functional groups, including hydroxyl, aldehyde, carbonyl, carboxyl, phenolic, and/or ether groups, which are able to interact with pollutants occurring in wastewaters through a range of selective binding mechanisms/interactions [11]. However, the biosorption capacities of raw agricultural wastes are generally lower than those of synthetic commercial adsorbents. Therefore, different pre-treatment methods have been used to improve the sorption properties of raw biomass, thus enhancing their exploitation and utilization in wastewater treatment [12]. These procedures mainly include physical and chemical treatments using organic compounds, oxidizing agents, bases, organic and mineral acids [13]. The chemical reagents commonly used to enhance pollutant-binding capacities of sorbents comprise calcium hydroxide, sodium carbonate, sodium hydroxide, nitric acid, hydrochloric acid, sulfuric acid, tartaric acid, citric acid, formaldehyde, methanol, and hydrogen peroxide [14]. To effectively boost the pollutant removing properties of the biomass, the conditions required for chemical treatment must be identified [15].

Metals are naturally found on the Earth's crust, achieving the water compartments due to anthropogenic activity, namely metal mining and smelting industries, metal-based industries, leaching from landfills, excretion, livestock, automobiles and roadworks, agricultural runoff, but also natural origins like volcanic activity, metal corrosion, soil erosion [16]. Due to their ecotoxicological effects, bioaccumulation and cancerogenic properties, metals pose serious risks to the environment and the human health. Similarly, organic compounds are often toxic, poorly degradable, persistent in the environment and bear a high impact on water pollution [17, 18]. Organic pollutants include natural and anthropogenic substances (e.g., pesticides, pharmaceuticals, personal care products, hormones, and drugs of abuse) and can be sourced by discharge of treated or untreated industrial wastewater, agriculture, livestock, and aquaculture runoff, landfill leaching, and domestic and hospital effluents [19]. The pharmaceutical industry and agricultural production play an important role as sources of pharmaceuticals and personal care products and pesticides, respectively [20–22]. However, the effluents of wastewater treatment plants (WWTPs) are considered the most impactful source of organic micropollutants. Together with industrial chemicals (e.g., flame retardants, plasticizers, and food additives), the organic micropollutants are continuously discharged into the environment at concentrations between ng/L and µg/L, which can result in toxic and adverse effects on ecosystems and consequently on human health [23]. Synthetic dyes and pigments are another class of environmental concern due to their large-scale production, achieving the environment through textile, tannery, plastic and paper industries

[24]. The water pollution by dyes results in reduced dissolved oxygen in water due to the sunlight blockage and increased chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solids (SS) and turbidity, and total organic carbon (TOC), with consequent jeopardizing effects on the environment and human health [25].

This perspective paper seeks to systematize results reported in the literature on agricultural waste valorisation and its further application in wastewater treatment as an added-value bio-waste adsorbent to remove metals and organic pollutants (including dyes) from wastewaters. Comprehensive comparative studies examining materials by type (biosorbent), experimental conditions, target pollutants, sorption capacity, and the overall removal efficiency of pollutants, are discussed in this review (methodology on the literature search is given in Text S1).

## 2. Literature analysis

### 2.1. Agricultural waste

The world's population reached 7.7 billion in mid-2019, having added one billion people since 2007 and two billion since 1994. According to the current projections, the global population is expected to reach 8.5 billion in 2030, 9.7 billion in 2050, and 10.9 billion in 2100 [26]. Fig. 1 shows the projection for world growth population by SDG regions (referred to throughout this report are those used in The Sustainable Development Goals Report) and selected groups of countries, from 2020 to 2100, according to the medium-variant projection [26].

The question is whether this population growth will exhaust the Earth's natural resources or if there is a sustainable way to improve agricultural efficiency. Unfortunately, demands on the environment as well as the pollution caused by the booming global population are pushing the endurance limits of both the environment and humans. Based in the changes of consumption patterns registered over the last three decades, it is predicted that the total production yield of food from chief crops and livestock must increase 53% to 12.160 billion tons by 2050, corresponding to an increase of 4.230 billion tons compared to 2015 production levels [28]. However, according to the statistics of the Food and Agriculture Organization of the United Nations, roughly one-third of food produced for human consumption is lost or wasted globally, which equates to approximately 1.3 billion tons per year (95–115 kg/year in Europe and North America) [29]. This number includes "lost food" that is lost prior to being sold in retail (e.g., during storage or transport) and "discarded (wasted) food", i.e., all edible foodstuffs that are either processed or a primary ingredient that may be further processed, which have been disposed by the consumer or during retail.

In response to this growing crisis, multiple sustainable frameworks have been proposed among supranational, international and national bodies [6], as well as some actions have been taken by private enterprises. The 2030 Agenda for Sustainable Development Goals (SDGs) covers multiple areas related to food waste and loss: SDG2 ("Zero Hunger"; including sustainable agriculture), SDG 6 ("Clean Water and Sanitation"), SDG 11 ("Sustainable Cities and Communities"), SDG 13 ("Climate Action"), SDG12 ("Responsible Consumption and Production"), SDG 14 ("Life below Water"; considering Marine Resources), and SDG 15 ("Life on Land"; considering Terrestrial Ecosystems, Forestry and Biodiversity). As an example, the Agenda 2030 envisages halving the amount of waste per capita by 2030 by adjusting the entire food cycle, from retail food waste to domestically generated waste, as well as regulating losses occurring during transport. To better achieve sustainability of food management during agricultural production and in the whole supply chain, the following questions must be addressed:

- How much is the total amount of food lost and disposed, where are their locations and the reason why for their disposal?
- What is the attributable cause for food loss and where may it be reduced?

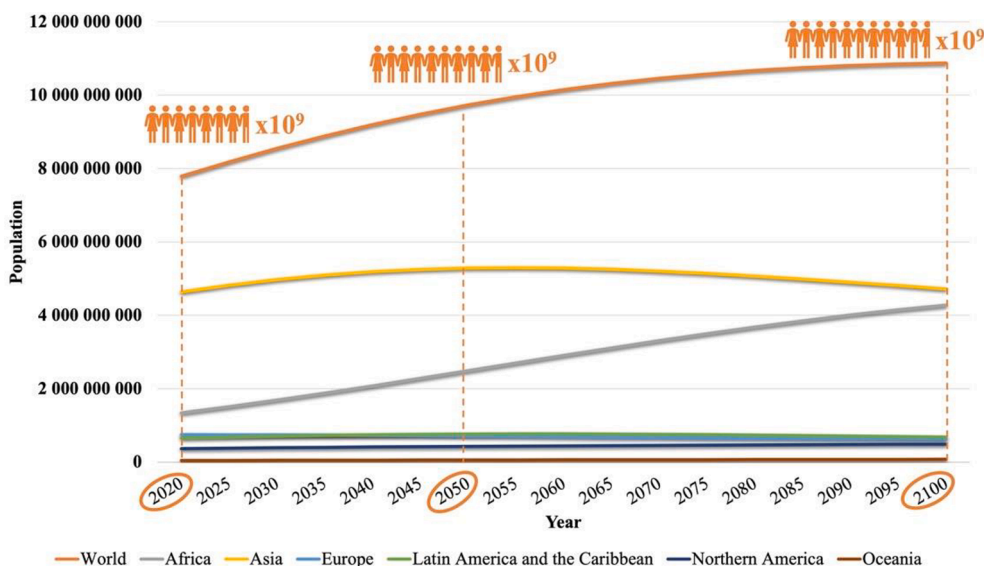


Fig. 1. Projected size of the world’s population, medium variant and momentum scenario, 2020–2100 (adapted from United Nations [27]).

- Which areas of food regulation and safety need to be strengthened?
- Could reducing wasted food or food by-products help to achieve other goals?

In fact, 30% of all land used for agriculture purposes (1.4 billion hectares) is cultivated merely for food that is never eaten [27]. According to the data, 40% of food loss in developing countries occurs at the collection, processing, and preparation stages, whereas in developed countries it occurs mostly at the retail and consumption stages [30]. Economically, 47% of the total value of food waste is reported to be largely an end-user problem [31]. Given the quicker decomposition of dairy products, vegetables, and fruit, in comparison to other food types, these categories account to ca. 50% of wasted food (Fig. 2) [32].

### 2.1.1. Sustainable food waste management

The global food waste management market size was estimated at USD 34.22 billion in 2019, according to the Market Analysis Report [33]. It is expected to expand at a compound annual growth rate (CAGR) of 5.4% between 2020 and 2027, which is attributed to the rising concerns over food waste globally [33]. Food waste represents a substantial loss of itself and also other vital resources, namely land, water, energy,

and labor. Avoidable food waste accounts for approximately 15 million Euros annually, which is equivalent to 76 €/month and 910 €/year in households with children [34]. These amounts are estimated to be equal to six wasted meals per week. In addition to environmental and economic impacts, food waste also includes a social dimension, since 795 million or around 11% of the world’s population suffer from hunger [35].

The cumulative effect of food waste and loss can be better analysed when examining it through production, transport, and consumption (Fig. 3, European Environment Agency, 2020). Due to the diverse nature of agricultural production, which depends on the target crop, it is necessary to distinguish the stages at which food losses most commonly occur:

- The losses within *livestock farms* and agricultural fields can occur due to numerous external factors (e.g., climate, infestation by parasitic or pest species, disease), which may be controlled but are generally unpredictable. Cultivation method, farm management and capacity may be adjusted to better reach yields [37, 38].
- Sufficient *storage capacity* provides the elasticity within supply throughout all steps of the food chain, responding to the needs of

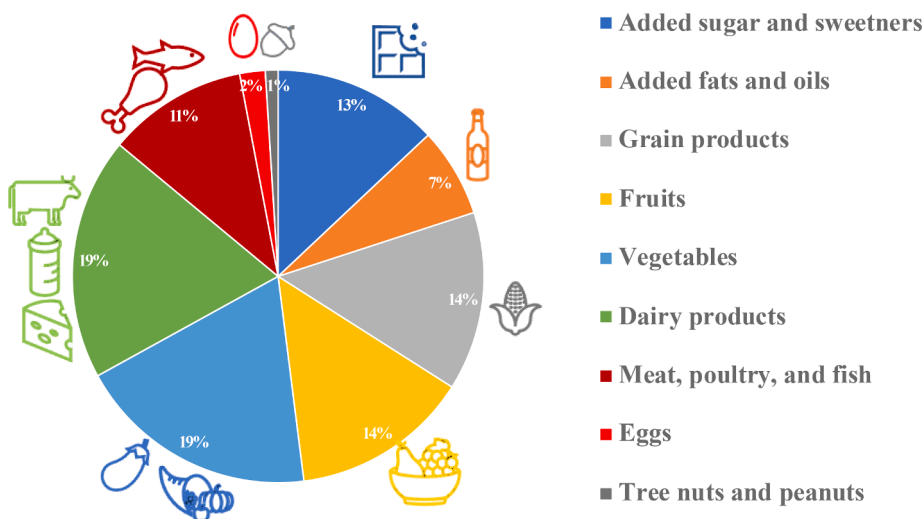


Fig. 2. Estimated proportion of food waste by category in the U.S. (adapted from [32]).

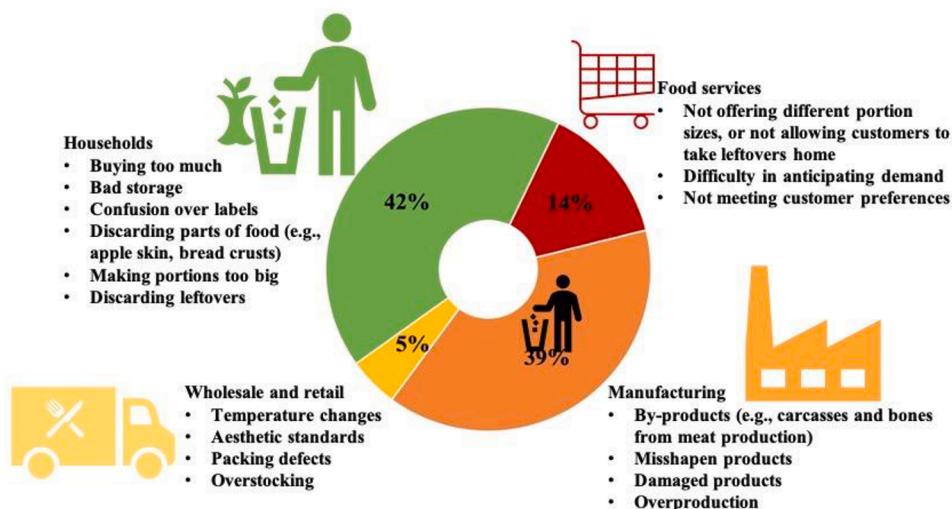


Fig. 3. Total value of food waste by origin and by percentage (adapted from [36]).

consumers and the abilities of producers. Whereas losses may occur due to a lack of storage capacity, the shelf life, the ability to mature after harvesting, and the preservation method (desiccation, freezing, milling, canning, or pickling) determine the longevity of the final product [39, 40].

- c) *Transport* is a limiting factor in the supply chain due to the food exposure to external influences, being fruits and vegetables more prone to losses due to their handling and natural decay [41].
- d) The degree of losses that occur in *food processing and packaging* largely depends on the raw material and the procedure efficiency in the facility. Lower developed countries in terms of overall infrastructure often suffer considerable losses due to the needed complex processing and packaging technology [35, 41].
- e) *Wholesale and retail* facilities have limited available space and storage facilities for perishable foodstuff, thereby affecting limited lifespans [42].
- f) Food waste becomes more significant as living standards rise since higher income levels are related to the accumulated purchase of traditional “luxury” foods, which have higher and quicker spoilage rates due to low shelf lives, being meat, fruit, vegetables, and (to a lesser extent) nuts, most of this waste. A global rise in living

standards is also reflected in more land being cultivated to feed livestock [27].

According to the World Resource Institute’s [43] data from 2011/2012 (Fig. 4), if the quantity of food and organic waste in landfills were calculated as a separate state, it would rank third in terms of mass of carbon dioxide emitted, just behind China and the United States [44]. Food production itself accounts for ca. 26% of the global greenhouse gas emissions. A recent study conducted by Poore and Nemecek [45] found that 24% of food’s emissions come from food that is lost in supply chains or wasted by consumers. Almost 15% of these food emissions come from losses in the supply chain, which result from poor storage and handling techniques, lack of refrigeration, and spoilage in transport and processing. The other 9% come from food thrown away by retailers and consumers. Food waste is therefore responsible for roughly 6% of the total global greenhouse gas emissions. Since this study has the limitation of not including food losses during production and harvesting, this percentage may be even higher [45]. In fact, given that agriculture and disposed food are together one of the main contributors to global pollution, reducing the amount produced through more efficient use of foodstuffs would contribute to the mitigation of greenhouse emissions and to reduce the stress placed onto land and water resources.

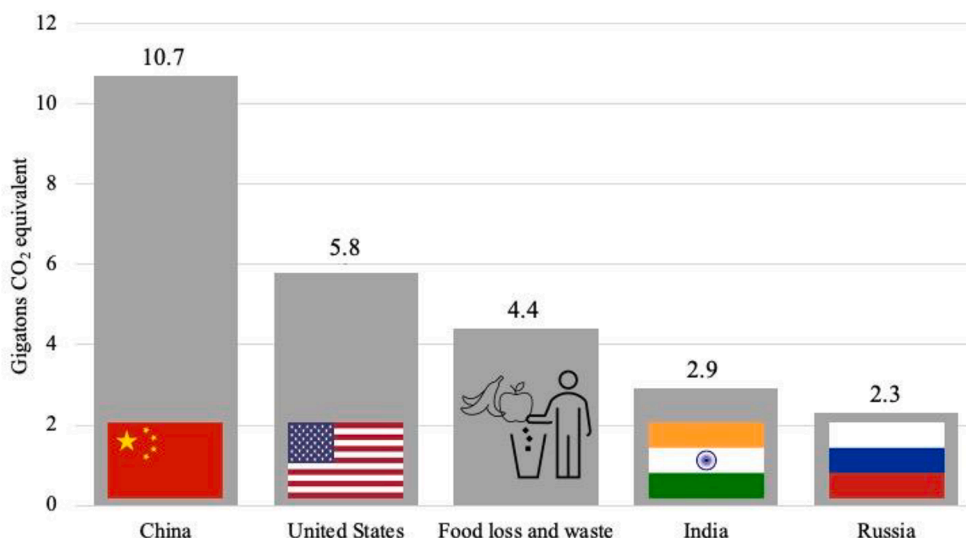


Fig. 4. Amount of CO<sub>2</sub> emitted (in gigatons) (2011/2012) (adapted from [43]).



As part of a new green revolution (e.g., the European Green Deal [20]), implementing new environmental laws would result in a revolution to energy, waste processing, and new sources of base materials that would revolutionize the worldwide economy, driving new areas to help gross domestic product (GDP) growing, creating sustainability and rolling-back damage caused to the environment. For instance, collecting and recovering 1000 tons of food and organic waste would generate 60% more GDP and 40% more jobs than its disposal. Current efforts to collect and recover resources from food and organic waste through household food waste, organic waste, and leaf and yard waste programs support approximately 1700 direct and indirect jobs in Ontario, and generate over \$100 million in GDP [44].

A circular and sustainable economy is a promising solution to solve these growing problems, by applying a system of production and supply in which materials are not thrown away but reused or valorised into new products, while reintegrating them into the market production channels. However, despite its potential, implementing a circular economy is a substantial task that requires both macro- and micro-implementation, as well as vertical and horizontal integration of production and supply chains. In terms of government direction, top-down directives may instruct the stakeholders to reach from central administrative decision-making bodies down to local, municipal ones.

### 2.1.2. Valorization of agricultural waste

Due to the rapid increase in the volume and types of agricultural waste biomass, stemming from population growth and intensive agricultural activities, these wastes are considered an important pollution source with an average annual growth rate of 5–10% [46]. People generate about 150 billion metric tons of agricultural waste biomass annually, according to 2013 data [47]. The accidental abandon and unreasonable utilization of these wastes result in water and soil contamination, local air pollution, climate change, and environmental depletion [46]. Climate change is considered as a major global challenge that has motivated the international community to apply mitigation strategies aiming at limiting the average rising of global temperature. Biomass burning has a significant impact on the chemistry of global atmosphere because it provides large source of atmospheric carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and nitrous oxide (N<sub>2</sub>O) which are the most potent long-lived greenhouse gases (GHG) contributing to global warming [48]. Therefore, much research has been focused on waste

management in the context of five main routes: waste prevention, reuse, recycling, energy recovering, and disposal. The effective transformation of agricultural waste and its recycling and utilization are essential in controlling environmental pollution.

As example, some values of agricultural waste produced at global level (unless otherwise indicated) are listed below:

- 80 million tons of rice husks [49];
- 70–140 thousand tons of potato peels [50];
- 10.6 million tons of bananas, of which 40% are peels [51];
- 55 million tons of corn cob from China [52];
- 300 million tons of rice straw from China [53];
- 10 million tons of plant waste (parts of stems and flowers) of medicinal plants used for traditional medicine [54];
- 47 million tons of citrus fruits in the world, 50–60% of which are peels [55];
- 25 million tons of coconut waste (shell, husks, and coir dust) produced throughout south-eastern Asia and Asia Pacific [56];
- 7180.5 thousand tons from peanuts production in India, of which 20% are waste shells [57].

Fig. 5 outlines the 2018 crop yields of citrus-fruit, banana, rice, plums, and potato crops produced in China, India, Europe, North and South America. Interestingly, by examining the amounts of agricultural products generated worldwide and the wastes that may be disposed in the form of scrap during production, lost during transport to consumers, as well as discharged by consumers, it is clear that there is a constant source of potentially repurposed waste streams [27]. For instance, these crops' raw materials may yield activated carbon [31]. While there is a need to further reduce losses during agricultural production and transport to improve the efficiency of the agricultural system, the inevitable waste product created in production must find a sustainable new application.

### 2.2. Wastewater treatment by biosorption

Considering the serious ecological and health safety concerns related to toxic and persistent pollutants [58], the development of economically profitable and environmentally friendly processes for water purification is crucial. Under this topic, multiple techniques to remove organic and

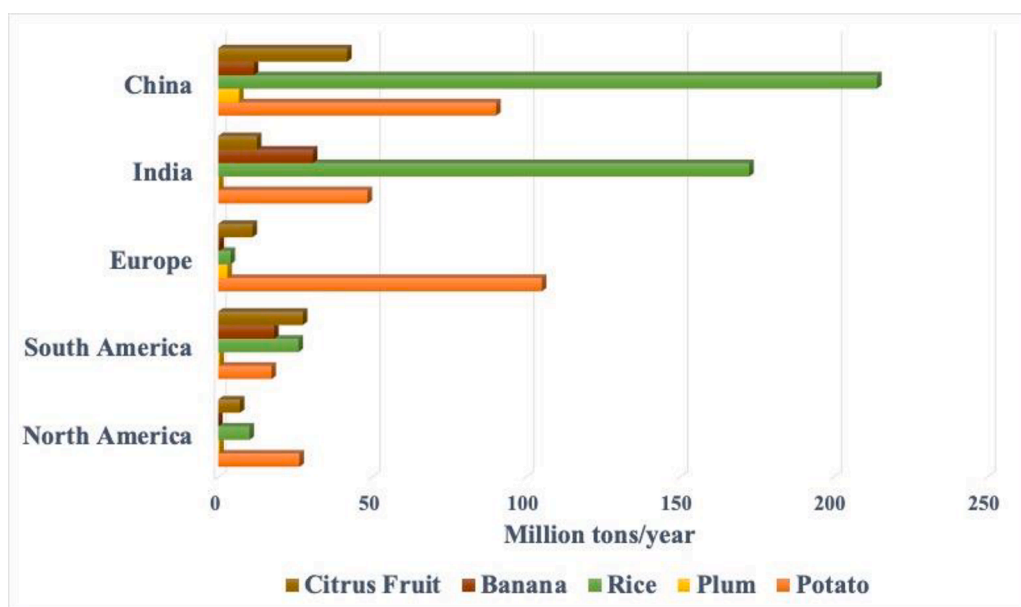


Fig. 5. Total crop yields (millions of tons per year) of citrus-fruit, banana, rice, plum, and potato produced in China, India, Europe, North and South America (adapted from FAO, 2020).

inorganic pollutants have been studied in the last decades. Overall, typical wastewater treatment combines physical, chemical and/or biological processes to remove solids, organic matter, nutrients, inorganic and organic pollutants from effluents. Crini and Lichtfouse [59] classified the available techniques into 3 classes: (i) conventional methods, including coagulation/flocculation, precipitation, biodegradation, sand filtration, and adsorption using commercial activated carbons (CAC); (ii) established recovery processes comprising solvent extraction, evaporation, oxidation, electrochemical treatment, membrane separation, membrane bioreactors, ion-exchange, and incineration; and (iii) emerging removal technologies that include advanced oxidation; adsorption onto non-conventional materials, biosorption, biomass, and nanofiltration. Adsorption/Biosorption offers the simplest method for eliminating organic compounds or metals from wastewaters, before discharging them into the environment [60].

Adsorption/Biosorption is the process of migration and accumulation of dissolved substances on the surface and porous structure of the adsorbent/sorbent/biosorbent, being the concentration(s) of the substance(s) higher in the solution from which they are removed [61, 62]. An ideal biosorbent has high capacity, biosorption rate, selectivity, fast kinetics, and low cost [59]. In fact, the biosorption capacity of the biosorbent depends on the texture, morphology and chemical composition of the material, as well as on its chemical activation/functionalization [63]. Conventional adsorbents that are commercially available include CAC, ion-exchange resins, and inorganic materials (e.g., activated aluminas, silica gel, zeolites, and molecular sieves) [59]. The adsorption onto CAC is currently used after the biological treatment in urban WWTPs, the process being called end-of-pipe technology. For instance, the major application of CAC as non-selective adsorbents has been found to be the post bio-purification (after the main treatment by biological treatment) in the removal of dissolved non-biodegradable organic compounds and refractory residues. However, after material's exhaustion (usage period), these conventional adsorbents are hard to regenerate and replace which increase the total cost of the applied method, limiting their widespread use [59].

The mechanism of biosorption of disparate water pollutants (heavy metals, organic pollutants, and dyes) is crucial for understanding and appraising the efficiency of biosorbents. Up to now, numerous studies have focused on investigating possible biosorption interaction mechanisms. Knowing these solid-liquid interactions is a key for the optimization of the overall removal conditions. The biosorption process is based on the physicochemical features of the biosorbent, which includes: solubility, molecular size, surface charge, chemical composition, reactivity, and hydrophobicity. In general, the presence of numerous functional groups facilitates the sorption process of both metal ions and organics. Commonly, biosorption processes include a combination of several mechanisms: electrostatic interactions, ion-exchange, chelation, complexation/coordination, covalent binding, van der Waals forces, adsorption, aggregation/precipitation (microprecipitation), chemical oxidation/reduction [64]. Physical adsorption takes place because of weak Van der Waals' attraction forces and also because biosorbents have in general low specific surface values and are non-porous, whereas the so-called chemisorption is a result of relatively strong chemical interactions between adsorbates and adsorbent surface functional groups [64].

Novel materials for wastewater treatment have been intensively investigated, especially biosorption on raw and/or modified bio-waste material, as well as on activated carbon synthesized from waste stone fruit, husks, shells, and/or parts of (lignocellulosic) plants [65, 66], which appears as an ecologically method of removing hazardous substances that will be further analysed in this paper. These products are abundant, cheap, and renewable, and contribute to the development of the local economy. However, the selection of the optimal biosorbent to remove pollutants from an aqueous solution is one of the greatest challenges of sorption methods. The type of raw material, the activation method of the material, the target pollutants, the interaction between

the adsorbent and the adsorbate, as well as the method of desorption of the adsorbed substance influence the treatment efficiency [67].

### 2.2.1. Bio-based waste materials as adsorbents

Globally, agricultural waste is mostly disposed through dumping or incineration, which neglects its potential and contributes negatively to environmental pollution [57]. These agricultural waste materials can be used to produce biosorbents, thereby biosorption becoming a more attractive method for wastewater purification. Repurposing waste to improve the biosorption of pollutants from water is a "green technology" that leads to a sustainable and closed blue-green cycle.

Physically and chemically treated agricultural waste crops may be used in the process of removing pollutants from wastewater or for water retention. In addition to the chemical composition greatly affecting the ability to adsorb pollutants, many physical characteristics of the adsorbent (e.g., particle size, density, specific surface area, porosity, pore size, and distribution) are important factors governing the ability to adsorb a diverse range of ions and molecules [66, 68]. The materials selectivity may be 'designed' by proper functionalization, which allows to tailor their affinity for the target pollutant(s), as well as their multifunctional application [69–71]. To illustrate, the biosorption capacities of treated and untreated walnut shells substantially differ due to the functional groups to which metals attach. Following their acid modification, sulfur-containing functional groups build affinity for metals by generating complexes on the surface of the shell [72]. In addition to the sulfur-functional groups contributing to the biosorption capacity, hydroxyl, carboxyl, sulphhydryl, and amino groups are also capable of affecting the affinity for a pollutant.

Another important factor affecting the degree of ionic biosorption from a given solution is the value of  $pH_{pzc}$ , which corresponds to the pH value at which the charge of the adsorbent surface is zero [73]. Cation biosorption is favoured at pH values above the adsorbent's  $pH_{pzc}$ , while anion biosorption occurs at pH lower than the  $pH_{pzc}$  [17].

Ideally, biosorbents are low-cost options, ready to use or requiring a simple modification, being naturally abundant or resulting from an industrial by-product/waste. Numerous approaches have been studied for the development of cheaper and more effective bio-based materials that are aimed to be used as adsorbents for the removal of diverse pollutants from wastewater. These materials are promising alternative adsorbents owing to diverse reactive groups in their macromolecular structures that confer them good physicochemical characteristics, chemical stability, high reactivity and excellent selectivity toward organic and inorganic compounds [74].

### 2.2.2. Chemically and thermally treated bio-based waste materials

The biomass most commonly used to produce activated carbon can be classified into four groups: 1) cereal waste (e.g., wheat, rice, corn straw, and pruning residues); 2) fruit waste (pits, shells, peels); 3) plant waste, including stems and cobs (sugar cane, sugar beet, corn, wheat); and 4) biosorbents (living and non-living biomass: fish oil, animal tallow, algae and special species of tall grasses, and manure) [17, 75]. All these materials have a very high content of cellulose, hemicelluloses, lignin, lipids, proteins, starch, and other organic components, qualifying them as raw materials to produce activated carbon [17]. Polysaccharides contained in these materials generally include: 35–50% of cellulose, 15–30% of hemicelluloses, and 20–30% of lignin. Multiple factors influence the composition, including the plant type and the pedologic conditions under which the plant was grown [68]. Natural inorganic materials (i.e., zeolites, iron oxides – magnetite, goethite, hematite – clays, limestone) are also commonly used as binder materials to enhance the inorganic structure of the hybrid adsorbent [11, 53, 76, 77]. Whether activated carbon can be synthesized is largely determined by the chemical composition of the feedstock and the available adsorption surface; however, the activation process itself is a determining factor to obtain the best adsorptive properties.

The carbonization process is often performed through combining

physical and/or chemical treatments to obtain affordable materials that possess high adsorption efficiency. There are two main processes to manufacture activated carbon: 1) physical pyrolysis at high temperatures; and 2) hybrid processes involving the addition of chemical agents and a slightly lower operating temperature [10]. For example, when synthesizing activated carbon using potato peels, carbonization was performed exclusively at a high temperature of 500 °C for 30 min [50]. However, for walnut shells subjected to a combined carbonization process, the shell is immersed in concentrated sulfuric acid for 12 h at room temperature, after which it is exposed to temperatures lower than 55 °C [78]. Physical pyrolysis is sometimes the only method to carbonize raw materials (when toxic compounds are present in the biomass), while complex chemical reactions may efficiently occur if a mixed carbonization method is used [75]. In general, the best characteristics are obtained through activation with bases, acids, and salts of mineral acids.

Carbon activation through a chemical process involves chemical agents such as KOH, H<sub>3</sub>PO<sub>4</sub>, and ZnCl<sub>2</sub> [75], with changes in the material water sorption, ion exchange, conductivity, hydrophilicity and/or hydrophobicity. The reactions that may occur upon chemical activation include protonation, chemical pyrolysis, saponification, halogenation, oxidation, polymerization, as well as the removal of inhibitory functional groups [17]. The physical or thermal treatment implies annealing at temperatures from 827 to 1027 °C using supercritical CO<sub>2</sub>, air or water vapor, whereas the combined-physical-chemical method necessitates both a chemical and physical process. Physical activation leads to lower environmental pollution and has a smaller impact on the environment, but biosorbents possessing better adsorption properties are generally obtained by chemical activation [17, 75]. Another problematic characteristic is that potential biomass must account for ash residue created after annealing or carbonization, such as for walnut shells used as a precursor in activated carbon synthesis [78]. Nonetheless, by comparing the characteristics of the adsorbent obtained through physical or chemical activation, adsorbents activated through chemical processes are shown to have a specific surface area up to 3000 m<sup>2</sup>/g, usually accompanied by a substantial increase in pore size (from nanometre to micrometre limits), as well as a well-defined pore size distribution and the pore volume from 0.1–2.5 cm<sup>3</sup>/g [79–83].

### 2.3. Examples of pollutant classes

#### 2.3.1. Organic compounds

Urban wastewaters are the major hotspots for a wide range of organic compounds so-called micropollutants, some already prioritized in the EU Directive 2013/39 [84], and many others considered as contaminants of emerging concern (CECs). This term results from the recent recognition of: (i) their potential negative effects to ecosystems and/or humans; (ii) their presence in the environment with the help of contemporary analytical techniques that are available nowadays; and (iii) their occurrence resulting from a new synthetic pathway [23]. Since conventional WWTPs are not designed to remove recalcitrant and toxic organic pollutants [23], the mitigation of the discharge of these pseudo-persistent pollutants as well as their transformation products has been acknowledged as crucial for preserving aquatic ecosystems [85]. In the case of pesticides that can also be sourced by agriculture runoff, determining their content and constantly controlling them in wastewater is highly important due to their diverse chemical nature, their multiple modes of action, biotransformation, excretion, and toxicity [86]. The impact of long-term exposure to pesticide residues can lead to the appearance of malignant diseases, allergies, and damage to numerous vital organs [87]. Also, pharmaceuticals and their metabolites although mostly present in residual amounts in discharged water may have detrimental effects on living organisms and human health [63, 88]. Toxic pharmaceutical by-products can also be formed during abiotic treatments (ozonation, chlorination or ultraviolet radiation) used for disinfection or improved oxidative processes during wastewater treatment [88]. As example, during the treatment of wastewater containing

paracetamol at least two transformation products formed (1,4-benzoquinone and N-acetyl-p-benzoquinone imine) possess higher toxicity than the parent compound [89]. Unfortunately, apart from priority substances regulated in the European Union [84], and CECs identified in the EU Decision 2020/1161 [90], there is no harmonized regulation governing CECs, even for those included in previous watch lists of EU Decisions 2015/495 and 2018/840. However, in terms of wastewater reuse, the European Commission has recently approved for the first time the minimum requirements at European level for reclaimed water to be used for agricultural purposes, in a safe way (EU Regulation 2020/741) [91].

It is known that WWTPs are not designed to remove CECs. In fact, secondary treatment like conventional activated sludge and tertiary (or end-of-pipe) technologies as filtration (sand or sand-carbon) and disinfection (ozone) are not completely effective for their elimination and advanced treatment alternatives have been investigated for their removal from wastewater. These options include either consolidated processes as activated carbon adsorption, advanced ozonation, and membrane filtration or other not intensively implemented technologies such as advanced oxidation processes (AOPs) [23].

Activated carbon is frequently applied as a powdered slurry feed into a contact reactor (powdered activated carbon, PAC) or in a granular form in a packed bed filter (granular activated carbon, GAC). As the adsorption process involves the transfer of CECs from the liquid to the solid phase, competition mechanisms occur, including the direct competition between the organic molecules for the surface sites and pore blocking by the large organic molecules. These competitive mechanisms depend on the adsorbent surface characteristics, the nature of the adsorbed molecules (e.g., chemical structure, hydrophobicity, charge), the wastewater composition, pH, and temperature.

#### 2.3.2. (Azo)Dyes

(Azo)Dyes are common pollutants found in aquatic ecosystems, which can be harmful even at low concentrations [17]. They are used in the textile industry, as well as in leather, cosmetics, paper, and plastics production, accounting for ca. 70% of the dyes used in industry [92]. Industrial footprint related to azo dyes is of extreme relevance considering that a volume of water between 70 and 150 L is required to dye one kg of textile [7] and an average of 100 tons of azo dyes are discharged into watercourses annually [93]. The presence of such dyes in aquatic ecosystems slows down photosynthesis among flora, can damage the epidermal layers of aquatic fauna, and leads to the failure of entire organ systems. Synthetic organic dyes can bioaccumulate through different trophic levels and may cause biomagnification and thus, they are considered as persistent bioaccumulative toxic substances (PBTs). Their toxic effects include disruption of ecological balance and carcinogenicity [24]. Depending on the parent dye, its degradation can originate transformation products that can be more toxic than the original compound, or instead lead to less toxic by-products [24]. The aquatic toxicity of synthetic organic dyes is very diversified, depending on the compound, even within the same chemical class, and also on the organism, with values of LC<sub>50</sub> varying largely [24]. According to the criteria of the European Union for the classification of dangerous substances, azo dyes present low acute toxicity and the values of LD<sub>50</sub> are in the range of hundreds to thousands mg/kg body weight [94]. Some azo basic, acidic and direct dyes can be extremely toxic to fishes, crustaceans, algae, and bacteria, while reactive azo dyes are toxic only at high concentrations (>100 mg/L) [95].

Physico-chemical treatments (including several steps such as oxidation, coagulation, precipitation and flocculation) are used to remove dyes and pigments from wastewaters. Biological treatments (membrane bioreactor) such as aerobic and anaerobic processes, electrocoagulation, adsorption-oriented processes, and filtration membrane can be used to remove dyes from industrial wastewater [96, 97]. However, small industries often do not have the technological and economical capacity to incorporate these purification processes. The application of biosorption

at semi-industrial and industrial scale offers a promising solution for industrial wastewater treatment [98]. Since dyes generally have chemical and photostability, adsorption can be applied as an effective tertiary treatment [7, 93]. According to their chemical structure, dyes are either basic or acidic and thus, binding to adsorbents is largely dependent on the pH value of the adsorbent ( $\text{pH}_{\text{pzc}}$ ).

### 2.3.3. Metals

Unable to degrade under normal environmental conditions, metals such as cobalt (Co), chromium (Cr), copper (Cu), manganese (Mn), molybdenum (Mo), and zinc (Zn), are extremely toxic at high concentrations [17]. Although lead (Pb), mercury (Hg), and cadmium (Cd) have been less used in industry in the last 2 decades, these metals are still of concern for environmental and health assessments [99]. Metals are able to bioaccumulate in flora and fauna and have a negative impact on public health, namely lead (Pb) [100], mercury (Hg) [101, 102], cadmium (Cd) [103, 104], arsenic (As) [105], selenium (Se) [106], chromium (Cr) [107], nickel (Ni) [108], and copper (Cu) [109].

Due to the potential hazards that metals pose to the environment and public health, their concentrations in wastewater are generally stipulated by law [99], their discharge is highly regulated and they are also regularly monitored in air (EU Directive 2010/75) [110]. Lead, mercury, cadmium, and nickel are considered priority substances in the EU Directive 2013/39 [84] in the field of water policy, for which Environmental Quality Standards (annual average and maximum allowable concentration) are set for surface water bodies. Moreover, both cadmium and mercury and their compounds are classified as priority hazardous substances.

Besides adsorption, a diversity of techniques has been proposed to remove metals from aqueous media: biological methods, ion exchange, chemical precipitation, membrane filtration, coagulation/flocculation, solvent extraction, and electrochemical technologies [111]. The selection of the most appropriate approach depends on the efficiency, reliability, feasibility, operation difficulties, costs, and environmental impact [59], the economic constraints being the most important, especially for small industrial structures. The flexibility of operation and design process, as well as its impact on toxicity and transport of heavy metals in wastewater, makes adsorption a very interesting alternative [111].

These contaminants are transported from the aqueous solution to the sorbent surface, then adsorption onto solid surface occurs, followed by transport within sorbent particle. The charged pollutants tend to adsorb on sorbents oppositely charged through electrostatic forces, with heavy metals having a strong affinity for hydroxyl or other functional groups. The reversibility of adsorption allows the regeneration of the sorbent for multiple uses. Thus, this option is considered a cost-effective and high efficiency process to remove heavy metals, aiming to obtain high quality treated effluents [111].

Table S1 summarizes the list of the inorganic and organic pollutants analysed in this review paper, classified into 3 main categories: organic compounds in general, (azo)dyes, and inorganics. Characteristic subgroups of compounds (lanthanides, actinides, and metalloids) and radioactive elements are distinctly noted.

## 2.4. Agricultural waste derived biosorbents

This review has covered a wide breadth of research published from 2015 to 2020 examining wastewater treatment using agricultural waste in its raw and modified forms, which may be utilized in the removal of metals, organic pollutants (e.g., pesticides, pharmaceuticals, carboxylic acids, phenolic compounds, and artificial sweeteners), and (azo)dyes. The removal of a broad spectrum of pollutants from natural and synthetic wastewater samples was reviewed, including data for individual ions (several cations and 3 oxyanions), organic pollutants (pharmaceuticals, pesticides, and industrial chemicals), and (azo)dyes. Studies applied to industrial wastewater emphasize the importance of analysing

sourced samples and monitoring the total dissolved solids (TDS), COD, BOD, SS, total nitrogen (TN), and total phosphorus (TP) in natural samples, to confirm the practical application of the proposed solutions outside of the controlled laboratory conditions.

The biosorbents included in the reviewed literature were grouped according to the origin of the raw waste material into six main categories: stone fruit derived biosorbents (group 1, Table S2); husks and shells derived biosorbents (group 2, Table S3); peels derived biosorbents (group 3, Table S4); plant derived biosorbents (group 4, Table S5); activated carbon sorbents (group 5, Table S6); and biosorbents derived from mixtures of bio-waste and other materials (group 6, Table S7). This group 6 includes mixtures of raw and/or modified biosorbents, combining any material of the groups 1–5 with added natural/mineral materials (zeolite, hematite, limestone, peat), synthesized (cement), and/or industrial waste materials (fly ash, wood chips - sawdust and waste material from tea production).

A comprehensive overview of the biosorbents that have been applied in the last years, including the target pollutant tested and the most relevant experimental conditions (adsorbent mass, initial concentration, initial pH value, temperature, reaction time, and mixing rate) are presented in Tables S2–S7. The sorption capacities and removal efficiencies of the inorganic and/or organic pollutants are detailed in those Tables. The discussion hereafter analyses the adsorbents strengths by the above mentioned biosorbent groups and are given separately in the Tables S2–S7, depending on the bio-waste used. An overview of data concerning the utilization of bio-waste as potential biosorbents based on recent publications is presented in the following sub-sections, which include discussion on biosorption performance, influencing factors, and mechanisms. Although a single and general conclusion cannot be drawn due to the large array of materials overviewed, individual observations, recommendations on the efficiency of biosorbents, and optimal conditions to purify certain types of pollution are highlighted.

### 2.4.1. Stone fruits derived biosorbents

The canned fruit industry has been producing stoneless products for many years with most of these extracted fruit stones being discarded as wastes. Stone fruit derived biosorbents (Table S2) are obtained from raw and modified bones and seeds of fruits, most often papaya, avocado, peach, and apricot (group 1). The potentiality of stone fruits waste as a biosorbent is supported by its properties [112]. In fact, the chemical composition of fruit stone mainly consists of cellulose, hemicelluloses, and lignin. The hydroxyl groups at the surface are the most reactive sites of the material and can be used to incorporate a variety of functional groups. These active functional groups, including carbonyl and hydroxyl groups of the lignocellulosic material, interact with metals ions through biosorption [113]. The biosorption of metal ions  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , oxyanions of As and Cr, and methylene blue onto these materials has been widely tested under laboratory conditions. Although our literature search did not retrieve any study on the use of stone fruit biosorbents for the removal of organic pollutants (Table S2), this subject was already investigated, namely for the removal of antibiotics by  $\text{Fe}_3\text{O}_4$ /graphene oxide/citrus peel-derived biochar-based nanocomposite [114] and for the elimination of 2,4-dichlorophenoxyacetic (2,4-D) acid by using an adsorbent obtained from agricultural waste of yam peels [115]. The pH is a recognized parameter affecting biosorption. The optimal pH value for the biosorption of metal ions  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  onto stone fruit derived materials typically falls within the range of 5–5.5 [116–118], whereas it was estimated to be 6 for As (III) [119] and 2 for Cr (VI) [120]. In the case of the methylene blue dye, the optimal pH for its removal was shown to be 5.5 when using either peach shell or stone [121, 122]. Regarding to the simultaneous biosorption, the lower efficiency obtained for the removal of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions using *Carica papaya* seed modified feldspar clay in comparison to the removals of pollutants from individual metal solutions [123], is a good example of the competitive mechanism (i.e., antagonistic biosorption) that can occur. The percentage removal of both metal ions



decreased with an increase in the initial metal concentration from 100 to 600 mg/L. A decrease from 89.6% to 62.3% and from 94.7% to 68.9% for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ , respectively, was obtained. This decrease is due to the fact that all adsorbents have a fixed number of active sites and at higher concentrations, the active sites become saturated. Those evidences of competitive biosorption are especially significant due to the potential application of waste materials to remove inorganic and organic impurities from sourced wastewater samples [124]. In such cases, competitive co-sorption of adsorbates chemically not related can occur [124]. This fact must be considered when using complex matrices as wastewaters, being crucial to study the removal of representative molecules of all chemical groups targeted. The high efficiency of discarded stones/pits of fruit as bio-waste materials has been confirmed in the removal of methylene blue at a pH 5.5, initial concentration from 200 to 400 mg/L, adsorbent mass from 0.001 to 0.1 g, with the sorption capacities ranging from 178.25 to 444.4 mg/g [121, 122, 125]. In general, biosorbents obtained by chemical or physical modification have also shown improved biosorption than the respective crude biosorbents [116, 117, 120, 125]. Monroy-Figueroa [15] showed comparative results for the biosorption of  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  ions on the crude and chemically modified endocarp of *Byrsonima crassifolia*. It was found that the chemical modification of *Byrsonima crassifolia* biomass with citric acid could improve its biosorption properties for the removal of  $\text{Cd}^{2+}$  and  $\text{Ni}^{2+}$  ions under competitive sorption conditions. This improvement in sorption properties is mainly related to an increment of the acidic functional groups on the biomass surface caused by the chemical reaction between citric acid and the lignocellulosic material. As the Energy Dispersive X-ray (EDX) analysis showed that C, O, and  $\text{Ca}^{2+}$  were the main elements found in the biomass, the biosorption mechanism of heavy metals using modified-biomass could be an ion-exchange process where both the interactions with phenolic, carboxylic, and hydroxyl groups at the sorbent surface and the replacement of  $\text{Ca}^{2+}$  may be involved [15]. In addition to modification using mineral and organic acids [117, 118, 120], basic functionalization may be used to activate the surface of biosorbents, by increasing the number of active sites on the surface of the material while improving the sorption capacity [116]. Peach-activated citric acid may be used to remove  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  with reported sorption capacities of 118.76, 93.4, and 89.6 mg/g, respectively (initial concentration of 200 mg/L and pH 5, and adsorbent mass of 0.1 g) [125]. Avocado pits treated with tartaric, citric, or sulphuric acid had higher sorption capacities for  $\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ , ranging from 3.3 to 21.8 mg/g, in comparison to raw avocado seeds, which ranged from 2.5 to 5.6 mg/g [118]. Apricot stone waste activated using 1.0 mol/L solution of NaOH was efficiently used for the removal of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$  for a metal concentration of 400 mg/L and a pH 5.0, using 0.5 g of biosorbent mass, eliminating the metals by 81, 87, and 97%, respectively [116]. It has also been confirmed that the sorption capacity of alkalinized peach kernels was 2–3 times higher than the same biosorbent in its natural form [116].

#### 2.4.2. Husks and shells derived biosorbents

Table S3 displays several studies conducted over the last years on the application of biosorbents obtained from waste shells and husks, mostly derived from rice husks, walnut shells, almond shells, coconut shells, and waste coconut shell fibres (group 2), in their raw or modified forms. Shells and husks are abundant agricultural residues with great stability, wide specific surface area, and high mechanical strength, and they are mainly composed of lignin and polysaccharides, specifically in the case of walnut shell: 49.7% polysaccharides, 29.9% lignin (Klason lignin, soluble lignin), 10.6% extractives (dichloromethane, ethanol, and water), and mineral components [126]. These materials have been used to remove metals and organic pollutants from wastewaters. Several studies have shown the usefulness of such sorbents under experimental conditions for biosorption of the cations  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{NH}_4^+$ , the oxyanions Cr (VI), many organic compounds (e.g., phenol, lignin, tetracycline, bisphenol A, clofibrac acid, carbamazepine,

naproxen, diclofenac, pyridine, quinoline), as well as for the reduction of COD and the elimination of the dyes rhodamine-B, black 5, crystal purple, diamond green, reactive black 5, reactive yellow 84, acid yellow 23, acid red 18, alkaline purple 10, alkaline red 46 and Congo red (Table S3). The excellent performance of this type of biosorbents has been demonstrated by removals over 90% of metals  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$  on rice husk [127–129], being  $\text{Pb}^{2+}$  the most commonly tested metal [9, 78, 130]. The main biosorption mechanism is chemisorption. The biosorption power of crude [131–133] and modified coconut shells [134], as well as waste coconut fiber [135] have been exploited to remove rhodamine-B (99.2%) [134], Congo red (98.9%) [135], diamond green (85%) [132], phenol (64%) [133], and phosphorus (95.22%) [131] from laboratory spiked wastewater samples. The most remarkable performance shown by this group of biosorbents was related to the treatment of very complex samples like landfill leachate and wastewater effluents, where different pollutants may be removed simultaneously [136–138]. Under experiments where the landfill leachate samples were diluted 5 to 25 times, the efficiency of COD, dye and  $\text{NH}_4^+$  removal using rice husk increased up to 80, 90, and 100%, respectively [136]. When raw coconut shell was used to remove clofibrac acid (CA), carbamazepine (CBZ), naproxen (NAP), and diclofenac (DCF), from both spiked ultrapure water and secondary wastewater effluents [138], the removal efficiencies for CA, CBZ, NAP, and DCF were found to be much lower in sourced samples with adsorbent mass/solution volume of 250 mg/L (26.9; 57.9; 44.7, and 31%, respectively) in comparison to simulated samples with adsorbent mass/solution volume of 133 mg/L (63; 85.5, 79.1, and 68.8%, respectively). The authors ascribed this lower biosorption efficiency to the presence of SS and soluble organic compounds in wastewater and concluded that a further purification is required in a real scenario for this matrix, when using this type of activated carbon to adsorb pharmaceuticals. The overall removal of pollutant(s) in realistic samples is determined by the so-called matrix effect, i.e., the presence of multiple pollutants in multicomponent systems [139, 140]. A high removal efficiency for crystal violet (CV) (97%) and  $\text{Pb}^{2+}$  (86.9%) was obtained by using a modified *Camellia oleifera* shell with citric acid via esterification. These results were carried out with 0.2 g of biosorbent, an initial pollutant concentration of 150 mg/L, at pH 7 and 5 for CV and  $\text{Pb}^{2+}$ , respectively. In addition to the chemical interactions which occurred between the pollutants and the functional groups of biosorbent, in the case of CV, surface adsorption and intra-particle diffusion also played a very important role [60]. Coupling strategies can be used to meet the elimination efficiency required as proposed in a study focused on the removal of (azo)dye from industrial wastewater, using rice husk material as substratum in constructed wetlands augmented with microorganisms, where three processes could occur: biosorption onto the substratum, phytoremediation, and bioremediation [18]. In that work, it was observed that both rice husk and the respective biochar as part of the substratum can enhance the removal of textile dyes, being very dependent on the pH of the pollutant solution. For the biosorption of black-5 azo dye by 0.2 g of biosorbent, using a solution concentration of 100 mg/L, at pH values 4, 7, and 10, elimination efficiencies of 84, 52, and 55% were obtained, respectively, with higher removal efficiency observed at lower pH values, resulting from the negative surface charge of the dye molecules (anionic dye) [18].

#### 2.4.3. Peels derived biosorbents

Biosorbents produced from waste peels (fruit and vegetables) have been largely investigated for pollutants removal (Table S4). While bananas, oranges, lemons, pomegranates, avocados, papayas, pomelos, and pomegranates are the most described in the literature, raw and thermally treated potato peelings also fall into this group. The large number of reports on the use of citrus and other fruits may be attributed to the high market share of these crops globally and their final generation as a bio-waste. Thereby, the price of this type of waste as raw materials for further treatment and application of novel secondary raw materials is highly affordable (see section 3.1). Using such biosorbents,

reports on the removal of at least 33 inorganic and organic pollutants were retrieved from this literature review (Table S4), namely for  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$ , the oxyanions As, As, Cr, Mo, the anions  $\text{SO}_4^{2-}$ , radioactive elements (thorium and uranium), organic compounds (phenol, ciprofloxacin, phenanthrene, fluorene, naphthalene, benzoic acid, salicylic acid, and doxycycline), as well as the dyes methylene blue, rhodamine-B, reactive red 272, reactive yellow C19Y145, alcian blue, diamond blue, neutral red and crystal purple. Biosorbents obtained by chemical [11, 141, 142] or thermal modification [50, 143] showed better biosorption abilities than the respective crude biosorbents. The widest range of applicability has been reported for raw banana peel, which has been used to remove  $\text{Cd}^{2+}$  (97.77%),  $\text{Pb}^{2+}$  (96.9%) and  $\text{Cr}^{3+}$  (98.9%) [144, 145], radioactive elements such as thorium (99.9%) and uranium (70%) [68], some polycyclic aromatic hydrocarbons (PAHs, phenanthrene (98%), fluorene (98%), naphthalene (95%)) [146, 147], phenol (60%) [11, 58], benzoic (88.71%) and salicylic acids (94.2%) [141], and rhodamine-B dye (91.07%) [148] from simulated and real wastewater samples. The simultaneous removal of  $\text{Cd}^{2+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Pb}^{2+}$  ions from real industrial wastewaters at pH 6 (Baghdad, Iran) using banana peel, resulted in quite high biosorption efficiencies of 97.77, 98.9, and 96.9%, respectively [144]. Interestingly, raw banana peel used as separation medium for thorium and uranium was reported as having the same purification efficiency in both laboratory and directly sourced mine wastewater samples from South Africa [149]. Orange peel has also been tested for many applications, namely to remove the metal ions  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  [150], and for the efficient removal (ca. 90%) of methylene blue within 2 h using raw orange peel [151]. An elimination efficiency of 65% has been reported in the simultaneous biosorption of  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  ions from real water samples (pH 5.5) with 0.5 mg of a hybrid sorbent based on orange peel mixed with the fungus *Aspergillus niger* [73]. The use of orange peel reduced TDS and COD in real wastewater samples by 92.3 and 88.8%, respectively [152]. A simultaneous acid-base modification (using NaOH and citric acid as activator agents in moderate conditions) and thermal activation of orange peel was demonstrated to be a very promising option in a study reporting an increase on the efficiency of phenol biosorption by more than 18-fold and an enhancement superior to 6-fold for reactive-red dye (marked RR-272) [142]. For the extremely toxic arsenic anion in both valence states (III) and (V), its binding to lime peel was reported with an efficiency over 86% [153]. All these studies indicated chemisorption as the main interaction to explain the materials performance.

#### 2.4.4. Plant derived biosorbents

As shown in Table S5, rice, wheat, and barley straws are the most often used biosorbents derived from the remains of the body of the plants, together with corn cobs. These residues have attracted a lot of attention as an important by-product during plant growing process, not only due to their vast production but also their easy availability, not to mention their low cost [154]. In 2016, the estimated production of cereal straws in the world was approximately 1580 million tons, mainly from Europe (barley and oat), the United States (corn and sorghum), and China (rice and wheat) [155]. Rich in nitrogen, phosphorus, potassium, calcium, and organic matter, crop straws can be used as valuable biomass resources. Moreover, crude fibres are composed of cellulose, hemicelluloses, and lignin, which are the major constituents of plant cell walls. Because of the large presence of active functional groups (e.g., hydroxyl, carboxyl, carbonyl) on the surface of polysaccharides, chelation, ion exchange, and other reactions (acid-based interactions) may occur with metal ions, thereby being a valuable alternative to eliminate metals from the contaminated environment [156]. The biosorption results of the metal ions  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ce}^{3+}$ , the oxyanion Cr (VI), the organic compounds chlortetracycline and norfloxacin, and some dyes including methylene blue, orange II, methyl-blue, and crystal-purple, were analysed. Raw, chemically, and thermally modified biosorbents have been used to remove pollutants from synthetic and real

wastewater samples, under diverse experimental conditions (Table S5). Amino functionalized wheat straw with nitric acid and tetraethylene-pentamine was applied to remove Cr (VI) from a wastewater sample (pH 2.2) generated from electrical-panel production in China, being achieved a purification level over 90% [157]. In addition, a mixture of wheat straw and weeds (*Eupatorium adenophorum*) showed an adsorption capacity of 89.22 mg/g within 3 h to remove Cr (VI) at pH 1.0 [158]. A barley straw modified through impregnation of phosphoric acid and microwave radiation was tested for the removal of norfloxacin at mg/L levels. The adsorption experiments using 5.0 mg of adsorbent, a pollutant concentration of 100 mg/L, and neutral pH resulted in a sorption capacity of 349, 359, 387, and 441 mg/g at experimental temperatures of 25, 35, 45, and 55 °C [208]. Two waste materials were used to eliminate the organic pollutant chlortetracycline, corn cob, and sugar cane, and the removal efficiency was reported to be over 90% for both biosorbents at an optimal reaction time of 20 h [160]. Certain discrepancies were observed in the optimal pH value for the removal of methylene blue which is expected to be better adsorbed under slightly acidic to acidic conditions. Corn straw modified with citric acid and graphene oxide removed over 80% of methylene blue at pH 8 [53], while treated residue of *Salvia miltiorrhiza Bunge* removed over 90% of methylene blue at pH 7. Combination of biodegradation and biosorption can be a highly efficient method for methylene blue removal from wastewater. Rice straw (1.0 g) combined with the white rot fungus *Phanerochaete chrysosporium* (5 mL spores suspensions) removed 88% of methylene blue for an initial dye concentration of 400 mg/L at pH 5.0. Of the total removed dye, 28.4% was biodegraded by *P. chrysosporium*, and the rest was adsorbed on the biodegraded rice straw and the fungal cells [161]. A similar study was conducted with rice straw and *Bacillus subtilis* [162]. The mixture of 0.5 g of rice straw and 0.2 mL of spore suspensions removed over 90% of methylene blue for an initial dye concentration of 400 mg/L at pH 7.0. *P. chrysosporium* and *B. subtilis* increased the specific surface area of the straw and produced more functional groups on it, which led to the significant improvement in methylene blue removal. Microbial biodegradation also contributed for the dye removal.

The degree of (azo)dyes removed largely falls on the experimental parameters used, most commonly the duration of the reaction. Although the sorption results (i.e., the efficiency of the (azo)dye removal) vary widely, it is important to note that biosorbents derived from plant bodies are highly attractive for further testing due to the large amount of raw material produced worldwide and the consequent low price (see section 3.1). One possible path for future scientific research is the use of waste wood derivatives (i.e., the synthesis of bio-hybrid materials based on lignin, tannins, and cellulose), for further application as both a separation and extraction medium for the simultaneous removal of pollutants [52, 69, 70] and for extraction and pre-concentration of pollutants in sample preparation before high performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS) and gas chromatography-mass spectrometry (GC-MS) analytical methods, as recently reported for cork-based adsorbents [163].

#### 2.4.5. Activated carbon sorbents

The activated carbon is a microcrystalline, amorphous, carbonaceous material with high porosity, physicochemical stability, adsorptive capacity, mechanical strength, degree of surface reactivity, and surface area [164]. Traditionally, typical precursors for activated carbon production were coal, peat, and lignite. However, in recent years, there has been a growing interest in the production of activated carbons from agricultural by-products, industrial and residual wastes. A wide range of waste from agricultural materials has been used as precursors of activated carbon: coconut, walnut and almond shells, banana and cassava peels, corn cobs, wheat and rice straw, pine wood, among numerous others [165]. Agricultural waste materials are rich sources of cellulose material with an average composition of 40–50% cellulose, 20–30% hemicellulose, 20–25% lignin, and 1–5% ash, which makes them an

attractive source for carbon production [166]. The type of precursor plays a primary role in influencing the quality, characteristics, and properties of the resulting activated carbon. Also, the properties of the resulting activated carbon are influenced by the activating reagents, time, impregnation condition, carbonization temperature, inorganic impurities, and others [167].

The activation of a carbonaceous precursor can be performed through physical or chemical activation or a combination of both [168, 169]. The physical activation method involves carbonization of a precursor at elevated temperatures (500–900 °C) in an inert atmosphere. Carbonization is the thermal decomposition and the removal of non-carbon species from raw material. During the carbonization, lignocellulosic contents will be decomposed leading to the elimination of non-carbon elements, particularly nitrogen, oxygen, and hydrogen. Then, deposition of tars takes place. Basically, volatile matter content with low molecular weight will be diffused first, followed by light aromatics and hydrogen gas. At the same time, pore structures start to develop, and the tars produced will fill the pore structures. After carbonization, the charcoal obtained will be activated using oxidizing gaseous to upgrade and enhance the pore structures [170]. In the activation process at high temperatures (800–1000 °C), the oxidizing gas will remove more reactive carbon species, forming pores and vessels. Finally, activated carbon with high porosity will be produced. In general, formation of pores by activating gas consist of three phases, which are opening of previously inaccessible pores, new pore formation, and lastly broadening of existing pores [168, 169].

In the chemical activation method, raw material is impregnated with an activating reagent and the impregnated material is heated under an inert atmosphere. The carbonization step and the activation step progress simultaneously in the chemical activation method [171]. During the activation process, the raw material is impregnated with strong dehydrating and oxidizing chemicals, such as  $H_3PO_4$ ,  $ZnCl_2$ ,  $KOH$ , and  $NaOH$ , and the impregnated material is heated under an inert atmosphere [168, 169]. The common feature of all substances used in the chemical activation process is that they are dehydrating agents which influence pyrolytic decomposition and inhibit the formation of tar, thus enhancing the yield of activated carbon [167].

The advantages of the chemical activation method can be summarized as follows: pyrolysis carried out at lower temperatures; one step procedure; higher throughput than physical activation; and very high surface area activated carbons obtained [171].

Table S6 shows the experimental results of the adsorption of inorganic and organic pollutants onto activated carbon produced from diverse bio-waste (group 5). It includes approximately 40 varieties of activated carbon synthesized from bio-waste mixtures and used to remove ca. 40 inorganic and organic pollutants. These pollutants include the cations  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $NH_4^+$ ,  $Hg^{1+}$ , the oxyanions As (III), As (V), Cr (III), and Mo (VI), the anion  $S^{2-}$ , TN, P, COD, TSS, turbidity, the organic compounds phenol, *p*-nitrophenol, pentachlorophenol, 2,4-dichlorophenol, 2,4-dichlorophenoxy acetic acid, acetaminophen, nitrobenzene, PAHs, carbamazepine, as well as a large number of (azo)dyes, such as methylene-blue, rhodamine-B, neutral red, methyl-orange, orange-G, basic yellow-13, base red-14, reactive red-2, reactive yellow-145A, acridine orange, Congo red, crystal purple and sour orange 10. Son et al. [172] studied a magnetic activated carbon obtained from seaweed algae (originating from Japan) to remove  $Zn^{2+}$ ,  $Cd^{2+}$ , and  $Cu^{2+}$ , showing an average reduction of the concentration of individual metals equal or superior to 90% over 24 h of biosorption [172]. A calcinated magnetic biochar (CMB) biosorbent obtained from banana peels with an amount of 0.05 mg showed high biosorption potential for  $Zn^{2+}$ ,  $Cu^{2+}$ , and  $Hg^{2+}$  (72.8, 75.9, and 83.4 mg/g, respectively) in single systems at pH 6 within 3 h of biosorption. However, biosorption in ternary systems revealed that  $Hg^{2+}$  significantly inhibited the biosorption of  $Cu^{2+}$  and  $Zn^{2+}$  in the multi-component system. However, in ternary systems, CMB has higher biosorption affinity toward  $Hg^{2+}$  than  $Cu^{2+}$  and  $Zn^{2+}$  [173]. Activated

charcoal made from a mixture of cashew shells, millet stalks, and rice pomace, impregnated with a film of  $Fe^{3+}$  ions to improve the chemical affinity was tested for the removal of oxyanion As (V), showing an adsorption capacity between 0.236 and 0.301 mg/g [174]. In addition to the efficient removal of metal ions, activated carbon adsorbents have been used to remove a number of organic compounds, both in laboratory and directly sourced wastewater samples. Although the majority of biosorption experiments have been performed in batch mode, the separation of pentachlorophenol has also been tested using activated carbon obtained from coconut shells as separation medium in a column using simulated (spiked) solutions [175]. The resulting biosorbent had a sorption capacity of 36.82 mg/g, demonstrated at neutral pH under relatively mild and economically viable conditions (i.e., contact time of 6 h and temperature of 37 °C) [175]. Such results encourage the further application of biosorbents for wastewater treatment in real flow systems. Erabee et al. [176] have also examined the adsorption of ammonia nitrogen ( $NH_3-N$ ) and  $S^{2-}$  ions from leachate (Kuala, Malaysia) on coconut shells chemically modified with  $KMnO_4$ , suggesting that the positively charged surface of the sorbent (acidic surface group  $KMnO_4$ ) influenced the efficient binding of neutral molecules ( $NH_3-N$ ) and sulfide anions ( $S^{2-}$ ), with biosorption capacity of 0.1979 and 0.0065 mg/g, respectively [176]. Activated carbon obtained from pine wood was efficient to remove carbamazepine - one of the most frequent pharmaceutical in surface waters - at very low concentrations ( $0.5-20 \mu g L^{-1}$ ) and at a wide range of pH (3.0–8.0) [177]. The results showed that nanobiochar had an adsorption capacity of 0.074  $\mu g/g$  after 3 h of contact time and it was found that increasing pH from 3 to 8 could enhance the adsorption efficiency. The cationic dyes methylene-blue and rhodamine-B supplemented in a simulated laboratory sample (initial concentration of 1000 mg/L) at neutral pH were completely sequestered by 20 mg of hierarchically porous carbon from banana peels with sorption capacities of 744.39 and 520.29 mg/g, respectively [51]. Directly sourced wastewater samples pre-treated with anaerobic bio-filtration with removals of 88% COD, 71% TSS, and 93% turbidity were then subjected to a separation process on activated carbon obtained from rice pomace, showing a reduction of 52% COD and 63% turbidity [178]. A study conducted by Devi et al. (2017) confirmed that powdered activated carbon from walnut shells, used to treat wastewater sourced from a refinery (Sultanate, Oman), achieved an overall reduction in COD of 79% in a slightly acidic environment – pH 6 [179].

#### 2.4.6. Biosorbents derived from mixtures of bio-waste & other materials

Mixtures of crude and modified adsorbents from the groups of biosorbents referred above have been used, by supplementing them with natural, minerals (zeolite, hematite, limestone, and peat), industrial materials (cement), and industrial-waste materials (fly ash, wood chips – sawdust, and waste materials produced in tea production). Such mixtures of biosorbents have been tested for the removal of the metal ions  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ; oxyanions As and Cr; and the azo dyes allura red and twilight yellow. Table S7 compiles studies on biosorption of inorganic and organic pollutants by such materials. Our literature search did not retrieve any study using this type of biosorbent to remove emerging organic pollutants. Based on their promising results for ions and dyes, such materials are required to be investigated under practical applications and using realistic wastewater samples. To illustrate, a hybrid biosorbent composed of cement, rice husk ash, zeolite, limestone, and activated carbon was used to purify a mixture of leachate and municipal wastewater [77]. The metal ions  $Ni^{2+}$ ,  $Cd^{2+}$ ,  $Fe^{2+}$  and  $Mn^{2+}$  were efficiently removed, using 3.24 g of adsorbent and obtaining sorption capacities of 0.386, 0.482, 0.700 and 0.198 mg/g, respectively [77]. In a study conducted by Wang et al. [180], pinewood biomass and natural hematite mixtures were pyrolyzed at 300, 450 and 600 °C under  $N_2$  environment to prepare nanocomposites (HBC300, HBC450 and HBC600). The results showed that the maximum sorption capacities of HBC300, HBC450, and HBC600 were 0.0194, 0.0155, and 0.0146 mg/g for  $Cd^{2+}$ , and 0.0228, 0.0109, and 0.0125 mg/g for  $Cu^{2+}$ , respectively.



Sorption of both  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  was enhanced by increasing the pH from 3 to 5, whereas raising the ionic strength led to a decreased  $\text{Cd}^{2+}$  sorption. Sorption of  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  by HBC300 was accompanied by a cation release of one order of magnitude superior than HBC450 and HBC600, whereas  $\text{Cd}^{2+}$  sorption was diminished by over four times in a binary system (simultaneous presence of  $\text{Cu}^{2+}$ ) [180]. The removal of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Cd}^{2+}$  ions using a mixture of coconut shell biochar and tea factory waste resulted in biosorption capacities at pH 5.5 of respectively 45, 34, and 19 mg/g [181]. The influence of physico-chemical properties on the adsorption capacity was comparable for the three cations. Acidic surface functional groups were found to act as the key property that governed the adsorption capacity of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ . Carboxylic groups played a major role in the adsorption of  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$ , while lactic groups were more important in providing binding sites to  $\text{Cd}^{2+}$  [197]. The sorption performance of different lignocellulosic wastes (jacaranda fruit, plum kernels, and nutshell) to remove  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  from aqueous solutions was investigated by Mendoza-Castillo et al. [182]. The sorption experiments were performed at pH 5.0 and using a sorbent dosage of 1 mg/mL. The nutshell biomass showed the best sorption properties for heavy metals removal, where its monolayer sorption capacities ranged from 1.0 to 7.0 mg/g [182]. Industrial wastewater from automobile production (Tornio, Finland) was also treated with acid-activated peat (modified with HCl) and acid-activated sawdust (modified with citric acid) [159], resulting in the separation of  $\text{Cr}^{3+}$  oxyanion, with sorption capacities of 0.1026 and 0.1320 mg/g for modifications with organic and inorganic acid, respectively, with an optimal material dosage 0.75 g [159]. Perez-Ameneiro et al. [183] examined the removal of amaranth dye from industrial wastewater (wine production) using eucalyptus sawdust and humus composite in batch experiments during only 2 h, obtaining sorption capacities of 0.85 and 0.76 mg/g, respectively, with an optimal adsorbent mass of 0.3 g [183].

### 3. Environmental, Economic and Engineering Implications

#### 3.1. The cost of biosorption application

Biosorption is a technology that presents a great diversity of options and combinations, demonstrating a great flexibility for its application. There is plenty of room for investigation on biosorption since it can only be competitive with a material with adequate properties. Moreover, the individual determination of the properties of a possible biomaterial needs to be compared to other already established commercial sorbents, allowing to conclude that this new material is a better alternative. There are several challenges of biosorption application at industrial level: the development of large-scale procedures, greater commercialization, and, in general, its application in real conditions. Although the advantages of biosorbents are evident, primarily their economic feasibility, only a few biosorbents are currently marketed [184].

The techno-economic analysis is one of the most important criteria for the selection of the most adequate wastewater treatment. The cost of adsorption mainly depends upon the price of the adsorbent used for the removal of pollutants from wastewater. Although activated carbon is one of the most common and efficient adsorbents, its high cost is a significant disadvantage. Hence, low-cost materials comparable to activated carbon in terms of adsorption capacity are greatly needed [185]. In the study of Praveen et al., 2021, an economic assessment of biochars derived from agricultural wastes (coconut shell, groundnut shell, and rice husk) for the removal of Basic Red 09 from wastewaters was carried out. The cost of the biochar processing is a core component for its marketing and industrial use, which includes costs of manufacturing, maintenance, feedstock, transportation, labor, and distribution. There is currently no major industrial biochar market from which biochar price and cost data can be obtained for a comprehensive estimation [186]. Until 2018, a total of 91 companies have reported the sales of biochars across the world. Globally the mean price of biochar

was 2.13 €/kg, from 0.072 €/kg in the Philippines to 7.11 €/kg in the United Kingdom [187]; while in India, the mean price of the blended biochars ranges from 0.064 €/kg to 10.83 €/kg [188].

The cost of collection of feedstock and transportation, pyrolysis, drying and grinding, labor cost, and all other miscellaneous were included in the overhead cost for the biochar production. From the cost analysis, it was estimated that the cost of 1 kg of adsorbent is 0.52 €, 0.49 €, and 0.49 € for coconut shell, groundnut shell, and rice husk, respectively. It was found that the cost for groundnut shell per gram of Basic Red 09 removal is 0.01 €, which is the least when compared to the other two biochars. Groundnut shell biochar showed high adsorption capacity (46.29 mg/g) when compared to other synthesized biochars (10 mg/g for coconut shell biochar, and 44 mg/g for rice husk biochar). The cost of coconut shell and rice husk per gram of Basic Red 09 removed was 0.052 € and 0.011 €, respectively [186]. The economic feasibility of commercial adsorbents (granular activated carbon – GAC, Zeolite 13 ×, and Zeolite 4A) to remove fluoxetine was examined by Silva et al., 2020 [189]. Comparative results of the cost of biosorbent/commercial adsorbents per gram of removed Basic Red 09 and fluoxetine in these two studies are shown in Table 1.

Conventional (waste)water treatment processes generally merge technically extensive and chemically intensive technologies. Some of these traditional processes rely on high economic costs, including high energy consumption and carbon emissions [23]. Considering that (waste)water treatment may lead to various types of waste generation (wastewater sludge, adsorbents) or carcinogenic byproducts (disinfection) [190, 191], a need for improved water treatment is directed to multidisciplinary and sustainable solutions.

#### 3.2. Further investigations

Despite the fact that agricultural waste derived biosorbents possess lower sorption capacity in comparison with current commercial adsorbents, a proper **chemical modification** can considerably improve the adsorptive properties of a given material [192]. The chemical functionalization is a necessary step of 'material design' to provide the biosorbent with a high target selectivity. In addition, more investigations are needed to test the utilization of a **bio-sorbent derived from various agricultural wastes** since each waste type has special functional groups and chemical character, and thus, several types of appropriate biosorbents can be combined for gaining better removal efficiency. Moreover, the use of efficient hybrid biosorbents composed by biosorbents in synergy with natural and widely available mineral raw materials, including zeolites [77, 193], clay [123, 194], hematite [180], and limestone [77], has been reported. These materials, when combined with a mixture of bio-waste and industrial waste material such as fly ash [195, 196], iron oxides [197, 198], concrete [199], and/or sawdust [8, 200], may be applied in sustainable engineering practices.

Most pollutants may be successfully removed or at least significantly reduced using thermally activated bio-waste (activated carbon), as an efficient and non-selective adsorbent for the removal of metals, organic

**Table 1**

The comparison of the cost of biosorbent/commercial adsorbent application.

Type of biosorbent/adsorbent	Cost (€/kg)	Cost of biosorbent/adsorbent for removal of 1 g of pollutant (€)	Reference
Groundnut shell biochar	0.49	0.01 <sup>a</sup>	[186]
Coconut shell biochar	0.52	0.052 <sup>a</sup>	
Rice husk biochar	0.49	0.011 <sup>a</sup>	
GAC	250	1.07 <sup>b</sup>	[189]
Zeolite 13 ×	100	3.13 <sup>b</sup>	
Zeolite 4A	150	6.85 <sup>b</sup>	

<sup>a</sup>Basic Red 09.

<sup>b</sup>Fluoxetine.



compounds, and dyes. Although many investigations have been focused on heavy metals removal, more scientific effort has to be performed on industrial dyes, organic pollutants, and phosphate and nitrate discharged from agricultural and industrial areas. Considering that the biosorption efficiency of metal ions is generally extremely high, the best option should be selected depending on the least polluting material and procedure. Furthermore, more research should be done for **simultaneous removal of (in)organic pollutants**, especially in real wastewater samples. Moreover, a number of studies has shed light onto the mechanism of biosorption (adsorbate - adsorbent interaction) [192], but there is a limited number of studies highlighting the importance of **modeling of engineering design** [201], which would provide the nexus between mechanism identification and engineering application. Gifford et al. have proposed Simultaneous Removal Capacity Index as a tool to evaluate and quantify the ability of heterostructured mineral sorbents to treat a mixture of pollutants [202]. One possible path for future scientific research is the use of waste wood derivatives (i.e., the synthesis of bio-hybrid materials based on lignin, tannins, and cellulose) for the simultaneous use of a single material as a **separation and extraction medium** for the removal of pollutants as a separation medium [52, 69, 70] and for extraction and pre-concentration of pollutants as a sample preparation adsorbent for further high performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS) or gas chromatography-mass spectrometry (GC-MS) analytical methods, as recently reported for cork-based adsorbents [163].

There are only few studies which have investigated the removal of pollutants onto agricultural waste derived sorbents in a **column mode** [203–205]. The future perspective of agricultural biosorbents must be reflected into the continuous column performance and semi/industrial application [201, 206]. Moreover, a sustainable **regeneration process of pollutant-loaded biosorbents** can reduce the costs of the overall water/wastewater treatment (in terms of chemical stability and physical durability of material tested). Biobased materials have specific features that bring challenges to the **lifecycle assessment (LCA) methodology**, gathering the balance of biobased carbon and reuse, recycling, or energy/material recovery [207]. The holistic material characterization has recently increased more scientific attention [201], but most of these advanced techniques tend to evaluate only the material before its use. As a result, many researchers have directed their efforts towards improved novel biosorbents, without understanding the impact of potential **leaching performances** and the whole life cycle that may detrimentally affect the application of the material. Further research in this direction may introduce the regeneration or replacement methods, allowing for a higher recycling rate and less requirement of long-lasting sorbents. Besides, **safe disposal of exhausted (spent) bio-sorbent** should be deliberately considered in future studies, promoting the concept of agricultural waste valorization.

Concluding, the use of agricultural waste biosorbents for the treatment of industrial and municipal wastewater is currently an attractive solution that reduces the overall footprint of pollution, by treating one waste (water) using another (solid) waste. Although further research and breakthroughs are needed, the production of activated carbon as a highly efficient biosorbent based on agricultural waste material is a promising green-technological solution, while meeting the requirements of a sustainable economy and effective engineering practices.

#### Declaration of Competing Interest

The authors declare no known competing financial interests or personal relationships affecting the research or conclusions of the work published.

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#### Supplementary materials

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