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Review

The Opportunity of Valorizing Agricultural Waste, Through Its Conversion into Biostimulants, Biofertilizers, and Biopolymers

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Abstract: The problems arising from the limited availability of natural resources and the impact of certain anthropogenic activities on the environment must be addressed as soon as possible. To meet this challenge, it is necessary, among other things, to reconsider and redesign agricultural systems to find more sustainable and environmentally friendly solutions, paying specific attention to waste from agriculture. Indeed, the transition to a more sustainable and circular economy should also involve the effective valorization of agricultural waste, which should be seen as an excellent opportunity to obtain valuable materials. For the reasons mentioned above, this review reports and discusses updated studies dealing with the valorization of agricultural waste, through its conversion into materials to be applied to crops and soil. In particular, this review highlights the opportunity to obtain plant biostimulants, biofertilizers, and biopolymers from agricultural waste. This approach can decrease the impact of waste on the environment, allow the replacement and reduction in the use of synthetic compounds in agriculture, and facilitate the transition to a sustainable circular economy.

Keywords: sustainability; agricultural waste; biostimulants; biofertilizers; biopolymers

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1. Introduction

1.1. A General Overview of The Subject Addressed in This Review

This review addresses the problems of the valorization of agricultural residues to reduce their environmental impact and obtain new strategic solutions to increase productivity and sustainability of agricultural systems. The motivation for conducting such a study stems from the need to deal critically with some aspects of modern agriculture that can be improved, prompting a sustainable transition of this fundamental activity. In particular, the scientific questions that need to be answered urgently are whether agriculture could find smart and innovative solutions to redesign the use, management, and conservation of natural resources. Over the years, exciting approaches have been studied, such as waste thermal revalorization by the production of bioenergy. With this aim, scientific literature has proposed various studies generally focused on a single possible use of the waste. There is a complete lack of an approach that considers agro-industrial waste in its entirety as a starting material for the diversified production of substances to be used in agriculture but with different objectives. In this context, this review's scientific hypothesis is to investigate the potential of waste for making bio-based materials such as biostimulants, biofertilizers, and biopolymers. The success of the proposed approach is, on the one hand, to indicate sustainable strategies to decrease the pressure due to the disposal of waste. On the other hand, biostimulants, biofertilizers, and biopolymers can increase crop productivity and improve soil health.

1.2. A Look at the Sustainability of Agricultural Systems

Agriculture has significantly increased its productivity in the last 50 years worldwide, reaching 23.7 million tons of food per day, as thoroughly reviewed by Duque-Acevedo et al. [1]. This increase in production has caused intense pressure on natural resources, thus questioning some agricultural sustainability aspects. In addition to food production, agriculture generates significant quantities of biomass that cannot be used for food purposes, and it is therefore considered waste [1]. In this context, some other significant concerns about the sustainability of agro-ecosystems should be cited. Agriculture consumes large amounts of soil and water [2]. Furthermore, it must be considered that in the coming years, there will be a mounting need to increase agricultural productivity to feed the growing world population [3] that has more than doubled since 1960 and is expected to grow faster in the coming decades [4]. Likewise, some forecasts indicate a global population of 9.1 billion people by 2050 [5].

Other issues arise from ongoing climate change. Some anthropogenic activities are the main causes of climate change and the consequent temperature increases recorded from 1951 to 2010 [6]. Since 1980, the temperatures, on a global scale, have evidenced a clear upward trend. Some breaks have been recorded, although very abnormal warming peaks have been recorded in the last years [7]. Greenhouse gases (GHG) emissions (methane, nitrous oxide, and carbon dioxide) are considered responsible for the increases in global temperatures [8]. CO_2 is the main contributor to these phenomena and its release into the atmosphere is mainly due to the combustion of fossil fuels [8]. Global warming will directly affect the water cycle around the world, profoundly altering ecosystems, with wetting regions drying out and dry regions getting wet [5,9]. A higher frequency of heatwaves and low rainfall is expected in the coming years in the Mediterranean area, and also in other regions of the planet [5,10].

Even agricultural systems release harmful substances into soil and water and GHG into the atmosphere [11–13]. As far as GHG are concerned, it has been estimated that agriculture releases about 14% of the world's greenhouse gases [8], having a very high carbon footprint [4]. On the other hand, agriculture is strongly affected by climate change, as it can cause frequent natural disasters, floods, and extreme adverse environmental conditions [5]. In the coming years, climate change will vigorously test the resistance and resilience of agro-ecosystems [5]. It has been estimated that in some regions of the planet, unfavorable environmental conditions could lead to up to 70% of losses in crop production [2,14].

In this context, a more responsible management of water resources is necessary, as the increase in the use of water for irrigation poses some risks for the sustainability of agriculture [15,16]. Reduced rainfall, rising temperatures, extreme events, and evapotranspiration will elevate water requirements for the irrigation of cultivated fields. For these reasons, the factors mentioned above are expected to have a substantial impact on the stability and productivity of agro-ecosystems, especially in arid or semi-arid regions [17]. This extreme environmental pressure is also rapidly reducing the availability of land per capita. In 2015, about 0.25 hectares of land per capita had been estimated, while forecasts indicate that it will be about 0.20 hectares in 2050 [18]. Another direct effect of climate change regards the salinization of the soil in coastal areas [18]. The increasing salinity of soils and lands, due to sea-level rise, flooding, storms, and other movements of saline water, is a long-term process that degrades soil and water quality [19].

Another current issue related to modern agricultural practices is the continuous release (meaning into the environment, soil, surface and groundwater, and marine habitats) of a variety of polluting compounds [12]. These substances can be very harmful to living beings, even at very low concentrations. Indeed, heavy metal, excessive amounts of fertilizers, and pesticides are known for being released from cultivation systems and, thanks to their mobility, reaching non-target organisms and being diffuse in the environment [20–23].

As far as fertilizers are concerned, there is an ever-increasing demand for these essential compounds, which increase at higher rates than crop productivity [24]. In particular, the dependence of agriculture on chemical fertilizers has led to excessive use of these substances [13]. Consequently, some concerns are related to the health and quality of soil, water, and the aquatic ecosystem [3]. Furthermore, chemical fertilization can cause human diseases through the contamination of food and water [3].

1.3. Global Perspective, Policy Orientation, and Opportunities for the Re-Use of Agricultural Waste for the Transition to Sustainable Agriculture

The pressure exerted on the environment by agriculture must be seriously considered, finding solutions to mitigate its effects in the short term. In particular, the high inputs of synthetic products, GHG emissions, and the downstream problem of waste disposal represent the main issues to be addressed and changed in a short time period [25]. More concrete efforts have recently been made to shift policy frameworks towards a more conscious approach that promotes an eco-friendly and resource-conserving culture [26]. The idea and pressing needs for a new green and bio-based economy are emerging and gaining attention as solutions to solve some environmental and socio-economic issues [27]. For instance, in 2015, the "The Paris Agreement", signed by the UN, recalled some measures to contain climate change and GHG emissions, recognizing the importance of safeguarding food security and production [28]. In this document, particular emphasis has been placed on the urgent need to improve the resilience of the ecological systems, also through the development of new technologies and materials with low or no impact on the environment. In December 2019, the European Commission placed particular emphasis and attention on a roadmap to make the EU economy sustainable [29]. The EU has identified agriculture as one of the priority activities to stop climate change and achieve more efficient uses of natural resources, thus moving towards a clean and circular economy [29]. The recommendations provided in the Green Deal were aimed at promoting agricultural systems based on sustainable practices, including improved management of nutrients and water and the reduction of GHG emissions.

In this context, the recycling of agricultural waste is of enormous strategic importance for the transition to a circular economy [30] designed on renewable energy and bio-based products made from biomass feedstock [31]. The main idea of the circular economy is to replace the traditional linear economy, which follows the "take–make–dispose" model, with the use of renewable materials [32]. Indeed, the production approach based on a linear economy is no longer considered sustainable due to the consumption of natural resources and its environmental impact [32]. In this sense, the transition of agriculture towards a circular model, based on the re-use and valorization of waste for the high amount produced, is particularly recommended. Morrison and Golden [33] stated that agricultural systems provide about 570 MT of waste annually worldwide. This large amount of materials has very high potential when processed to obtain bio-based products. Renewable materials can be strategic in reducing the consumption of finite resources [31]. Another reason that makes a circular approach very attractive, socially acceptable, and convenient is the possibility of reducing the impact of waste on the environment and the costs for its disposal [34]. To date, most research has generally considered bio-energy and biogas as an appropriate way to valorize waste in order to break our dependence on fossil fuels, which have a considerable impact on the planet [30]. However, agricultural waste can be processed to obtain other non-energetic materials, which can be used for smart purposes. In particular, waste can be processed to obtain substances employable in agriculture to improve the productivity of agricultural systems, to reduce chemical inputs and the impact of waste on the environment.

In this context, this review addresses the idea of reporting recent studies aimed at obtaining from agricultural waste substances that can be applied to crops to improve their productivity and resistance to environmental stresses and restore soil fertility and nutrient content. Therefore, this review deals with studies aimed at the valorization of agricultural wastes or by-products through their conversion into plant biostimulants, biofertilizers, and biopolymers. For this purpose, Section 3 will treat each of these groups of substances providing definitions, information on raw materials, and describing the advantages of their use.

2. Methodology

The literature was systematically revised, considering the issues addressed, according to a logical progression, starting from a general perspective on the problems related to the current impact of agriculture on the environment. Sections 1.2. and 1.3 were still introductory and were mainly based on the importance given at the European and global level to climate change issues and how agriculture should manage waste more ecologically and sustainably.

Section 3.1 introduces in general terms what is meant by biostimulants, and it is based on a limited number of highly cited reviews that help define what these substances are. This methodology was considered the best way to introduce Section 3.2, which gets to the heart of the possibility of recovering biostimulants from agricultural waste, and it is based on a literature search conducted using Scopus. Specifically, the bibliographic search was done combining the following fields and logical operators: TITLE(by-product) OR TITLE (waste) AND ALL(biostimulant). This search found 88 articles published in the period 1996–2020. Those from the period 2001–2020 were selected if they dealt with the use of agricultural waste to make biostimulant substances, i.e., capable of exerting beneficial effects on the crops studied. The focus was on articles showing that biostimulants stimulated biomass production, photosynthesis, plant nutrition, root development, phytochemicals, and nutraceutical value.

Section 3.3 deals with biofertilizers, particularly on their characteristics and effect on soil, and how it is possible to obtain biofertilizers from agricultural waste. In Section 3.3, the importance of using biofertilizers, and the derived environmental advantages in terms of reduced risk in pollution and the effectiveness of nutrients supply for plants, was highlighted. A collection of literature, reporting the benefits of using biofertilizers, was carried. This research was focused on the main impacts of biofertilizers on soil chemical properties by searching in Google Scholar for "conservative and sustainable agriculture, biofertilizers and nutrients availability, effects of biofertilizers on soil organic matter". Section 3.4 was dedicated to the valorization of agricultural waste as a strategy to obtain added-value products to be reused in agriculture for "closing the loop". The selected articles focused on the valorization of agricultural waste through biological treatments and on the effect of obtained organic fertilizers (digestate and compost) on soil properties. The necessity of using carrier materials to minimize nutrients losses was introduced, highlighting the importance of the combined use of biofertilizers and identification of bio-based materials for ensuring an efficient nutrients release. In this case, the keywords used in Google Scholar for collecting articles were "agricultural waste valorization, preparation of biofertilizer, bio-based fertilizers".

In Sections 3.5–3.7, the bibliographic search was centered on the availability of biopolymeric materials from different biomasses, with specific attention given to the biopolymers that can be obtained by modification of agricultural waste biomass. Additionally, a search on dedicated use of these materials in agriculture was performed. The possibility of considering biopolymers both as biofertilizers and biostimulants has been taken into account, highlighting the specific properties, such as biodegradability and nutrients binding capacity, that those systems have inherently in comparison with polymers from synthetic routes and sources. Special attention has been given to the use of nanotechnology due to the possibility of a precise, dosed, and not harmful delivery that cannot be achieved in the case of commonly used fertilization and stimulation systems. The search in SCOPUS and Google Scholar has been operatively done by combining the following fields and logical operators: TITLE (biopolymers) AND TITLE (agricultural waste), TITLE (biopolymers) AND TITLE (biostimulant), TITLE (biopolymers) AND (biofertilizer) in a time frame 2000–2020.

A schematic overview of the adopted methodology is reported in Figure 1.

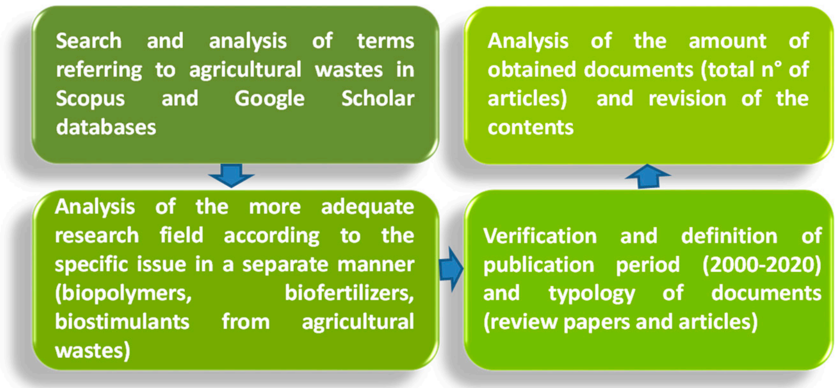

Figure 1. Adopted methodology for literature search and analysis.

3. Results and Discussion

3.1. Biostimulants: General Aspects

Plant biostimulants (PB) are a very complex, heterogeneous, and varied group of substances, which can be obtained from many different raw materials [35]. They are considered an innovative agronomic tool that is gaining more and more attention, as demonstrated by the continuous expansion of their market [36]. PBs improve crops' productivity and, consequently, this also allows us to reduce the input of agrochemicals significantly. Accordingly, this aspect also makes these materials interesting for the possibility of diminishing the environmental pressure of the agricultural systems [37]. Among the beneficial effect on crops, PBs can stimulate the flowering, plant growth and productivity, nutrient use efficiency, and resistance to abiotic stresses. At the same time, they can also allow reducing the use of chemical fertilizers [13,14].

Biostimulants have been defined in various ways over time. Furthermore, countries often do not adopt harmonious and comparable criteria to define these materials [38]. On the other hand, the scientific community over the years has proposed several definitions. In 2014, Calvo et al. [35] provided a broad and new definition of biostimulants that reflected their complexity due to the high number of raw materials from which they can derive. These authors emphasized that biostimulants should impact plant biological functions, improving plant nutrient uptake and utilization, crop quality, and resistance to abiotic stresses. Likewise, rather than classifying biostimulants according to the raw materials from which they derive, the classification of materials as biostimulants should be based on their effectiveness in improving biological functions [35]. More recently, du Jardin et al. [39] made the biostimulant's definition even more precise, stating that this class of compounds must not provide nutrients or target pests or pathogens, but they should have the sole function of increasing crop productivity and resistance to environmental stresses. Rouphael and Colla [37] specified that although biostimulants can derive from a wide range of raw materials, they should be distinguished from other classes of compounds only by the presence of bioactive substances and their beneficial functions in agriculture.

In Europe, the use of biostimulants is legislated at national levels, and regulations can vary from state to state [38]. However, the new European Regulation of 2019 (EU–2019/1009) [36,37] defined PBs as follows: "A plant biostimulant shall be an EU fertilising product the function of which is to stimulate plant nutrition processes independently of the product's nutrient content with the sole aim of improving one or more of the following characteristics of the plant or the plant rhizosphere: (i) nutrient use efficiency, (ii) tolerance to abiotic stress, (iii) quality traits, or (iv) availability of confined nutrients in the soil or rhizosphere". In other countries outside the European community, definitions and regulations of biostimulants may vary, indicating that, to date, there are no harmonic evaluations. For instance, in the USA, biostimulants, whose use is spreading in the last years, are defined as substances that can induce beneficial effects on crops when applied directly to the plant or soil [38]. In Canada, biostimulants are defined as substances whose function is to improve plant growth and crop yield. From the above, there is a need in the coming years for more precise and harmonized definitions and regulations on biostimulants. [38]. This is also necessary because of the increasing popularity of biostimulants in the market.

In general, it has often been stated that a key feature of PBs is that they are used in small or minute quantities. This characteristic emphasizes their effectiveness at very low doses with impressive effects on crops, but, at the same time, it clearly distinguishes PBs from fertilizers and soil conditioners [16,37,40]. It is also essential to specify that these substances do not fall within the regulatory framework of pesticides as they have no effect on pests [35].

PBs can be conveniently grouped by referring to the raw materials from which they are derived: hydrolysates of plant and animal proteins, humic and fulvic substances, seaweed extracts, vegetal extracts, and beneficial microorganisms. PBs often show a multicomponent composition, which may include amino acids, peptides, protein, phenolic compounds, sterols, vitamins, lipids, sugars, mineral, plant hormones, hormone-like substances, etc. [41]. Nevertheless, the impossibility of obtaining a complete identification of the active PBs components does not allow us to define their mode of action. The beneficial effect of PBs probably depends on the combinative action of several substances, with actions that are also synergistic [41]. In this context, the research generally aims to explain the stimulatory effect of PBs on plants, paying more attention to some possible and broad mechanisms of action [41].

The effectiveness of PBs is due to their ability to induce beneficial morphological, physiological, and biochemical responses that enhance crop productivity, nutrient use, and resistance against stresses [35]. PBs can be applied directly onto seeds, immersing them for several hours in a solution containing the biostimulant, either in the early stages of plant development or when crops are fully developed [16]. The best mode of application depends on the species to be treated and the desired results. The identification of the right time and dosage maximizes the effect on plants and minimizes the risk of product waste, avoiding an increase in the costs of the treatments [16].

From an economic perspective, the global market of PBs is proliferating rapidly, reaching 2.24 billion dollars in 2018 [13]. This data demonstrates growing attention to these products. This interest is also confirmed by the high number of new products registered, with an average annual increase of 12.5% from 2013 to 2018 [13]. The European market is very important globally, and in 2013 it reached € 400–500 million [42]. The success of PBs in Europe is presumably due to the growing awareness of the importance of implementing and promoting policies aimed at fostering more sustainable agriculture [43].

3.2. Biostimulants from Plant Biomass Residues

The development of plant biostimulants from agricultural waste or by-products is an environmentally friendly solution that reduces their impact on the environment and provides innovative materials to improve crop performance and stress resistance. Depending on the raw materials, PBs can show very different biological functions. The procedure used to obtain these substances will also profoundly influence the final biological properties. Some studies have examined the valorization of agro-industrial waste to obtain substances to be used as plant biostimulants due to their considerable content of high-value molecules. Indeed, such waste can show elevated amounts of phenolic compounds, phytohormones, protein, and amino acids, which can stimulate beneficial effects in crops and improve some physiological functions. Donno et al. [44] investigated the effect of a hydrolyzed extract derived from apple seeds, rapeseed, and rice husks residues on growth parameters, antioxidant activity, and the ascorbic acid content of kiwi. The extract increased the fruit weight thanks to its considerable content in auxins, gibberellins, and cytokinins, which were mainly present in apple seeds. Rapeseed and rice husks exerted their stimulating effect due to their high content of amino acids, protein, and minerals. The beneficial action of phytohormones and amino acids was found in crops treated with biostimulants, and this effect significantly affected their productivity [45,46]. Another aspect to underline is the possibility of improving the nutraceutical value of crops using PBs. In this context, Donno et al. [42] found that the extract of apple seeds, rapeseed, and rice husks waste ameliorated this characteristic of kiwi, raising, in particular, the content of ascorbic acid essential for human health because of its excellent properties.

Colla et al. [47] studied the effects of another plant-derived protein hydrolate obtained from pea and tomato residues on maize plants, both in the laboratory and greenhouse experiments. The protein hydrolate induced the rooting in biostimulated samples, which showed increases in root dry weight and area. In addition, the extract also positively affected shoot length, total biomass, SPAD index, and nitrogen content. These effects were correlated with the considerable amount of peptides present in the extract, which exerted a phytohormones-like activity. This auxin-like effect, which improved the functionality of the root apparatus, increased the efficiency of the plant in water absorption, leading to an increase in plant productivity and yield [48,49]. Furthermore, the presence of gibberellins in the extract stimulated beneficial effects on plants by inducing the biosynthesis of hydrolytic enzymes during the development of the seedlings. This effect improved the growth, flowering, and fruit set of the biostimulated crop [47]. Finally, the improvement observed in nitrogen metabolism was presumably due to the induction of the enzymes nitrate reductase and glutamine synthetase [50].

The high number and types of agricultural waste allow us to realize and test a vast range of biostimulant substances, widening the possible solutions for their valorization. A recent study was aimed at the valorization of residues of fennel, lemon, and brewer’s spent grain by combining these materials to create a biostimulant extract. The authors thus studied the impact of the material obtained on the agronomic and metabolic performance of tomatoes [51]. This biostimulant improved shoot growth and dry matter, nutrient, and vitamin C content. The analysis of the extract showed the presence of a variety of bioactive compounds: organic acids, sugars, flavonoids, amino acids (particularly proline, glutamine, and asparagine), and phenols. Particularly relevant is the action of some organic acids, which can increase the solubility and bioavailability from the soil of nutrients for plant roots, thus increasing their assimilation by vegetables [52]. Finally, Abou Chehade et al. [51] also pointed out the beneficial effect of phenols present in the extract, as they can exert a stimulating effect on maize plants. In particular, this positive action resulted from the induction of the activity of the phenylalanine ammonia-lyase (PAL), a key enzyme involved in the biosynthesis of phenylpropanoids, flavonoids, and lignin [53].

Choez et al. [54] studied the content of trans-zetain and other phytohormones in maize waste to obtain an extract to be used as a biostimulant. Trans-zetain is a natural phytohormone worthy of attention, as it can promote the development of cotyledons, cell division, and delay leaves senescence [54]. Typically, trans-zetain is obtained from embryos and immature fruit. However, its recovery represents a clear opportunity to valorize maize waste. Choez et al. [54] found that the extract from the agricultural waste had an appreciable content of trans-zetain, and this suggested the possibility of using maize waste as a valuable source of this compound.

Vegetal biomass containing a significant quantity of phenolic compounds has been proposed as a raw material for the production of biostimulants. Phenols are natural antioxidants; promote plant growth, plant water use, stomatal function, photosynthesis, and respiration; and show beneficial effects on humans [55]. In this context, Ertani et al. [56] studied the effect of hawthorn leaf extracts, red grape skin material, and blueberry fruit residues on maize plants. The beneficial effects on plant growth and metabolic pathways and increases in protein, chlorophylls, and nitrogen uptake were associated with the presence in the extracts of plant growth-promoting substances and different phenolic compounds. In particular, the extracts improved the phenylpropanoid metabolism and induced the PAL activity, thus causing the accumulation of some phenols in the maize leaves. Moreover, in addition to the positive effects mentioned above, the increase in the content of phenols can also improve the resistance of plants to environmental stress [57].

Recently, Ceccarini et al. [58] studied the effects of two phenolic-rich extracts, obtained from spelt husks (Triticum dicoccum L.), with the scope of improving maize resistance to saline stress. To this end, two methanolic extracts were obtained from the soluble and insoluble phenolic fractions of spelt husks. The bound and insoluble phenolic fraction was very effective in promoting the recovery of maize subjected to salt stress, stimulating plant growth, pigment content, and antioxidant defenses. Furthermore, maize plants biostimulated with the insoluble phenolic fraction showed reductions in the content of hydrogen peroxide (H_2O_2), malondialdehyde (MDA), glutathione (GSH), and proline. By contrast, H_2O_2 and MDA accumulated in non-biostimulated and salt-stressed maize samples. All the positive effects of the biostimulant were related to the large amount and the different types of phenols present in the spelt husks extract. This study demonstrated how some raw materials could be valorized through the realization of an effective biostimulant, able to improve plant performance and resistance to a variety of prevalent stresses affecting cultivation systems [58].

The use of biostimulants, obtained from plant residues, to improve the performance of crops grown in dry conditions is intriguing. In this regard, Maqbool and Sadiq [59] have shown that phenolic extracts obtained from sorghum leaves can improve maize germination and plant growth in conditions of water deprivation. Very low concentrations of this extract also stimulated the growth of shoots and roots and increased the plant's ability to assimilate CO_2 and some nutrients [59]. The latter effects also increased the photosynthetic activity and counterbalanced the oxidative stress resulting from water shortage [59].

Viticulture is another attractive agricultural sector that produces a high amount of waste, which could cause environmental problems related to its disposal [60]. For instance, vineyards generate a consistent amount of vine-shoot each year, estimated at 1.4–2.0 tons per hectare [61]. The valorization of this waste represents a great opportunity and a strategy to create materials to be used in agriculture. These residues can be used to obtain plant biostimulants, as they generally have a high content of phenolic compounds [62,63]. Furthermore, phenols are also involved in the protection mechanisms activated by plants against insects [64].

Sánchez-Gómez et al. [65] obtained several wine-shoot aqueous extracts by applying some extraction methods and tested the materials thus obtained on Leptinotarsa decemlineata, Lactuca sativa, and Lolium perenne. In lettuce, some stimulating effects were found in terms of radicle elongation. On the contrary, antifeedant and inhibitory effects were exerted by the extract on L. decemlineata and L. perenne, respectively [65]. The different behaviors of the extract on the crop and Lolium were attributed to the allelopathic properties of the phenolic compounds extracted from vine-shoots. In fact, a correct balance between these compounds and the nutrients present in the extracts, in relation to the treated species, may cause positive or negative effects [66].

In addition, other studies addressed the valorization of vine-shoot residues. Pardo-García et al. [62] found that the water extract of vine shoots, applied to the grapevine itself, improved the quality of the wine, its aroma, and its content of volatile and phenolic compounds. Furthermore, these extracts can also increase grape yield and alcohol content [63]. This approach demonstrated how vine-shoots could be properly valorized in the same production chain to improve the quality of the final product, respecting the central concept of the circular economy and sustainable agriculture.

Lignin is another relevant source of potentially bioactive compounds that can assume essential importance in a bio-based and circular economy. In general, lignin residues are considered waste to be discharged or burnt [67]. However, more attention is being paid to the use of lignin residues for obtaining various types of chemicals [68]. Savy et al. [69] investigated the potential as biostimulant of extracts of cardoon, eucalyptus, and black poplar residues on maize plants. For this purpose, these authors extracted lignin with alkaline aqueous solutions and processed the extracts with oxidants in order to obtain well fragmented and oxidized phenols. These extracts positively affected maize germination and seedling development, also promoting, depending on the extract applied, root elongation, lateral seminal root, and coleoptile [69]. The bioactivity was linked to the hydrophilic nature of the lignin extracts. In particular, these effects were correlated with the presence of water-soluble phenols, which have accounted for a hormone-like activity [70]. In a successive study, Savy et al. [71] investigated the effect of water-soluble lignin extracted from Giant Reed on tomato residues seed to ascertain whether or not the hormonal inductive action of the extract was due to an auxin- or gibberellins-like activity. Although no auxinic effect was found, the extract exerted a gibberellins-like action. In particular, this substance stimulated tomato seed development and root length, and such an effect was associated with some phenolic compounds present in the lignin–water soluble extract of Giant Reed [71].

Particular attention was also paid to seaweed biomass residues. Seaweeds are widely employed for the production of food, fine chemicals, alginate, agar, etc. For all these applications, considerable amounts of seaweed wastes are produced annually, which end up being discharged into the landfills. The extracts and processed material derived from seaweed represent an essential category of plant biostimulant due to their richness in the content of compounds that promote plant growth and yield, seed germination, root development, and resistance to abiotic stresses [72,73]. In addition, seaweeds are considered a renewable resource readily available in marine ecosystems [40], and this makes them very attractive from the perspective of a circular economy. Finally, their biodegradability, their non-polluting nature, and the absence of toxic effects on humans and animals are to be emphasized [74].

With the aim of valorizing algal wastes, Zheng et al. [75] studied kelp waste (Laminaria japonica Aresch.) in order to produce PBs to stimulate Pakchoi (Brassia chinensis L.). Kelp is a seaweed massively employed in alginate production. It has been estimated that this process generates a large amount of algal waste every year in China. However, Zheng et al. [75] tested kelp waste extracts on pakchoi and found that at very low concentrations, this material stimulated seed germination and the vigor of seedlings. In contrast, high concentrations of kelp extracts exerted a negative effect on plant germination and growth. However, the right doses of this extract positively influenced root length and weight of pakchoi, as well as increasing the contents of soluble sugars and vitamin C. The beneficial effects on germination were explained as being based on the high content in kelp extracts of soluble sugars and amino acids. The presence of sugars is important in PBs, since they can act as signaling molecules, similarly to hormones, enhancing plant growth [76]. Differently, the protective effects of amino acids were explained for their osmoprotectant function. This beneficial action has been attributed in many studies to proline, the most represented osmolyte in plants [77]. Proline, due to its osmoprotective action, can improve leaf water status and plant transpiration [78]. In addition, proline also shows antioxidant properties, which improve plant resistance to oxidative stress [79].

Very recently, Gebreluel et al. [80] addressed the problems of improving the quality of the extracts obtained from kelp wastes as a crucial point of research in the alginate industry. In particular, kelp waste was subjected to enzymatic hydrolysis, evaluating the quality of the final hydrolate also as the effect of the time, temperature, and pH. Generally, hydrolysis is applied to vegetal waste for improving the efficacy of the derived plant biostimulants [81]. Hydrolysates are very rich in free amino acids and small peptides, which, by acting as signalling compounds, can have a beneficial effect on plants, prompting nutrient use efficiency, metabolic changes, and resistance to oxidative stress [82,83]. Gebreluel et al. [80] found the best results by treating kelp extracts for enzymolysis with cellulose, pectinase, and papain for 3.8 days at 50 °C.

The final part of the present paragraph briefly raises another issue of relevance to be considered when trying to obtain a complete valorization of agricultural waste. In particular, the studies aimed at recovering PBs from plant residues should also evaluate the costs of the treatments, their energy use, and impact on the environment. In this sense, an interesting study conducted by Colantoni et al. [84] investigated the energy use, CO_2 emissions, and water associated with the production of a plant biostimulant through the enzymatic hydrolysis of a vegetal extract of lupin. The impact of this production was estimated by a life cycle assessment (LCA) encompassing all the phases of the process for the biostimulant production, accounting for CO_2 emission (g of carbon dioxide per kg of protein hydrolysate), fossil energy consumption (MJ per kg of protein hydrolysate), and water use (kg employed per kg of protein hydrolysate). The results obtained for this vegetal biomass were compared with those related to the production of a biostimulant derived from leather waste protein hydrolate. In fact, plant biostimulant can also be obtained from animal residues, in particular from the tanning industry [13,35]. This section will not discuss this category of PBs, since they do not derive from green agricultural waste. However, Colantoni et al. [84] found the production of PBs from lupin was characterized by a lower GHG emission (−57%) and energy use (−26%), making the production of the legume-derived biostimulant more economically convenient and environmentally friendly.

3.3. Biofertilizers: Characteristics of Biofertilizers and the Effect of Their Application on Soil

The large scale use in agriculture of chemical fertilizers to support plant nutrition and improve crops' productivity has led to the pollution of the water, air, and soil. Therefore, the implementation of modern agricultural practices must solve the problem of feeding crops, which are facing various environmental hazards associated with the use of chemical fertilizer [85].

The overuse of certain substances is threatening the health of ecosystems and living organisms and can also affect the functionality and diversity of the beneficial microorganisms for plants [86]. In this context, biofertilizers are developed to prevent or reduce the risks of environmental pollution and degradation, for their effectiveness in stimulating plant nutrition, and providing the correct supply of nutrients. To this end, living micro-organisms have been successfully employed to effectively enhance plant growth, performance, and reproduction, and the four major types of biofertilizer formulation are peat, liquid, granules, and freeze-dried powders [86,87]. The correct use of biofertilizers represents a cost-effective, eco-friendly solution for providing plants with nutrients. This leads to an increase in crop production, making it possible to achieve the objective of pursuing the perspective of creating sustainable agricultural systems [86]. A conservation agriculture consists in the application of new tools and techniques, as well as on the application of biofertilizer on soil that improves its properties and biota rather than chemical fertilizers [86]. Indeed, it was studied that biofertilizer regulates the microbial nitrogen transformation, leading to a reduction of nitrogen losses of 54% when the urea is substituted for the 50% [88]. Moreover, the biofertilizers alone or the combined use with organic fertilizers can have positive effects on nutrients availability and organic matter dynamics [89]. The combination of biofertilizers (nitrogen fixing bacterium and phosphate solubilizing bacteria) with 50% of chemical fertilizer improved the essential oil yield in basil, representing also in this case a suitable strategy to reduce the demand of chemical fertilizers and their negative effects on the environment [90]. The term biofertilizer refers to a preparation containing live cells of nitrogen-fixing, phosphate-solubilizing, or celluloytic microorganisms, used for application on seed, soil, or composting in order to accelerate the microbial process and increase the availability of nutrients for plants [86]. Hence, biofertilizers are used to increase crop productivity, and this beneficial action is due to a more considerable increase in the availability of nutrients in the soil through hormonal activity or by decomposition of organic residues [91]. The term "biofertilizer" has been defined in different ways over the past 20 years, which derives from the improved understanding of the relationships occurring between the rhizosphere microorganisms and the plant: in 2005, biofertilizer was defined as "a product that contains living microorganisms, which exert direct or indirect beneficial effects on plant growth and crop yield through different mechanisms" [92]. More recently, Mąciket et al. [93] gave a definition more strictly relasted to the agronomical context, considering the biofertilizer a product composed of strain(s), useful for nutrient mobilization, usable as carrier, and ready to be to applied to the soil or plant. In this view, biofertilizer can also let substances be added that improve microorganisms' activity. Indisputably, the term "biofertilizer" should not be confused with terms such as plant or animal manure, intercrop or fertilizers, or biostimulants derived from microorganisms.

Biofertilizers used in organic agriculture are classified into different types on the basis of the group of microorganisms they contain.The different types of these preparations include nitrogen-fixing, phosporous, and plant-growth-promoting biofertilizers. The atmospheric nitrogen is unviable for plants and needs to be converted to ammonia through the process of biological N fixation. Nitrogen biofertilizers mostly include Rhizobium, Azotobacter, Azospirillum, blue–green algae, and Azolla, which fix atmospheric N in the available forms for plants [86]. Since many soils contain low levels of soluble phosphate, a large amount of P fertilizers is to be applied to cope with its low bio-availability. Consequently, this often leads to P losses in the environment. Indeed, Kang et al. [94] suggested that to prevent the environmental risks linked to P added with manure, it is important to consider the decomposition of organic materials and the competition between P and dissolved organic C for the anions adsorption. P-solubilizing micro-organisms, represented mostly by Pseudomonas and Bacillus and fungi, can efficiently transform insoluble P into soluble forms to make it available to plants by secreting organic and inorganic acids that alter rock phosphate and tricalcium phosphate in soil [86]. Potassium in soil can be present in an easily available form for crops (water soluble and exchangeable) and slowly or non-available K (non-exchangeable and structural forms) [95]. Biofertilizers can also be used to make K more available to plants, enhancing crop yield without causing disturbances to the environment, and this is possible thanks to the activity of K-solubilizing micro-organisms, represented by bacteria (Bacillus mucilaginosus, Bacillus edaphicus, Bacillus circulans, Acidothiobacillus ferrooxidans, and Paenibacillus spp.) and fungi strains (Aspergillus spp. and Aspergillus terreus) [95]. Concerning the effect on soil organic matter, the application of biofertilizer can increase the stable fractions of organic matter, thus improving the capacity of the soil to sequester C [96]. Piotrowska [97], over a three-year period, observed that the application of a commercial biofertilizer increased the soil C content, because of humification of fresh organic matter as straw and post-harvest residues. Hence, it is important to consider the variations of organic matter quality in the soil as changes in the dissolved organic matter (DOM), which represents the most bioavailable fraction of soil organic matter affected by microbial activity [98]. With this regard, Debska et al. [96] observed the decrease of the contribution of DOM in total organic matter and the increase of total organic C and humic acids and humins after the application of a biofertilizer over a three-year period, suggesting its important role in C sequestration in soil. Moreover, it was observed that the application of biofertilizer in combination with vermicompost had a positive effect on stability and organic C content of aggregates, hence improving soil's physical and chemical properties [99].

Moreover, the role of biofertilizer in the bioremediation of heavy metals is known, as well as reducing pesticide contamination and reducing nematode populations [86].

Although the effectiveness of using biofertilizers is well known, there is a need to adopt new strategies to identify suitable carrier material as a delivery vehicle to the field. Hence, it is difficult to identify universal carriers (organic, inorganic, or synthetic) for all biofertilizers, but it is necessary that they have specific properties (non-toxic, easily sterilized, high moisture absorption capability, cheap, etc.) [87]. Although most of the animal, agricultural, and food waste derived from industries can be used as a carrier for biofertilizers, the lack of technology to manufacture biofertilizer products make it more expensive than chemical-based fertilizer [86]. The recovery of nutrients from waste is a valuable solution to substitute the mineral fertilizer with new bio-based materials, with a reduction of 30% in the use of non-renewable resources [100].

3.4. Biofertilizers from Agricultural Wastes

In 2015, a new model of the economy was proposed as part of the "Closing the loop—An EU action plan for the circular economy" [101]. This challenge was aimed at valorizing waste by proposing its use from one sector as input for others. This transition meets the requirements of the proposed new model finalized at promoting a circular chain, which aims to close the loop by recovering the components of potential value from the agricultural waste, co-products, and by-products (AWCB). The objective of this action is based on the concept that waste can be used as substrates and raw materials, to be treated with the scope of originating innovative added-value products [102]. Indeed, most of the organic waste and by-products, derived from livestock manure, agriculture, and food processing industries, can satisfy the requirements necessary to be employed as biofertilizers [103]. Forest and plant residues are sources of cellulose, hemicellulose, and lignin and can be incorporated into a polylactic acid (PLA) matrix, whereas animal manure (pigs, cattle, and poultry) can be employed as a source of N to improve soil fertility and crop production or recovered as substrates for the anaerobic digestion [104,105].

The production of biofertilizers represents a valuable strategy to recover the organic materials from farm livestock, olive milling, and organic by-products of food processing [102,106]. Therefore, organic farming represents a strategic and convenient alternative to the use of chemical fertilizers. In addition, the use of biofertilizer can be seen as a reasonable tool for promoting the development of sustainable agriculture, with low environmental impact, without causing adverse effects on ecosystems [87].

Anaerobic digestion and composting are considered traditional technologies of waste treatments and biomass valorization. These processes have been studied with particular attention and depth, since they deal with waste management from a circular economy point of view [102,107,108]. Agricultural waste and other different organic matrices, such as food waste, can be treated by anaerobic digestion to produce biogas (methane and carbon dioxide) and digestate. The latter is rich in micro and macro-nutrients and considered as a valuable fertilizer for crop nutrition and yield, and also valuable from a climate mitigation perspective [109,110]. Concerning the quality of the organic matter during the anaerobic digestion of pig slurry, and the composting of the solid fraction of digestate, Provenzano et al. [111] observed the consumption of sugars, amino acids, and fatty acids, even if the agronomic re-use of this kind of organic material may affect changes in microbial community structure [112]. However, the digestate from the anaerobic co-digestion of farm and agro-industrial residues and pharmaceutically derived waste can be restricted for its content of heavy metals (particularly Cu and Zn), salinity, phytotoxicity, and hygiene characteristics [109,113]. Even the digestate obtained from the anaerobic digestion of food waste and human excreta reveals the possible presence of pathogens [114]. Thus, further treatments of the digestate are recommended to avoid sanitary risks and reduce the phytotoxic effects [109,114]. Olive milling waste is mostly produced in the Mediterranean area, as olive cultivation is particularly important in these regions. However, olive milling is generally characterized by a significant amount of organic matter. For this reason, this material represents an excellent opportunity to recover precious substances to be re-used in agriculture. In fact, the olive milling is often recovered as a substrate to be composted to obtain a fertilizer [115]. The compost obtained with olive milling waste results in a valuable fertilizer, since it shows decreased amounts of water-soluble organic matter and phenolic and lipidic compounds. Moreover, this end-product shows decreased phytotoxicity if compared to the starting material. This improvement allows obtaining a compost characterized by high quality, for the agronomic properties and for the low or null impact on the environment [115]. Moreover, poultry slaughterhouse represents another waste that could be valorized by composting. In fact, this treatment leads to a compost with a high level of maturity, which does not show phytotoxic effects, improving of 60% all yield parameters of maize [116]. Even if composting can generate greenhouse gas emissions, the positive effects that result from C sequestration should be considered. Finally, such management and recovery of waste allow the avoidance of the environmental impact resulting from their disposal [102].

The combined use of organic fertilizers and/or biofertilizers, along with chemical fertilizers, can be cost-effective and sustainable in terms of crops [52]. However, the best strategy to combine the use of all fertilizers is a challenge, as well as the identification of the carrier materials, characterized by certain properties that have to keep the number of microorganisms inoculants high for a long storage period [52,93]. For these reasons, modern agriculture needs to pay attention to the synthesis of nanomaterials for the production of "nanofertiliser" in plant nutrition, with the aim of generating less waste, minimizing nutrient losses, and ensuring a proper release of nutrients [117].

3.5. Biopolymers from Agricultural Wastes

Finding sustainable useful solutions and potential agricultural waste applications is a current and much-aspired-to research field. Sustainable strategies and innovative concepts for reducing waste, and their use for realizing compounds and products with additional value, can promote the economy and decrease the pressure on the environment. Awareness of the need to minimize losses and waste throughout the whole supply chain is beneficial to farmers and customers [118]. However, the design of adequate value chains and sustainable business models is still a prerequisite for achieving success [119]. Today, in agriculture and food production systems, some challenges have to be overcome. In general, waste has been used for the production of organic fuels, chemicals, animal feed, and many other things [120]. In the current global scenario, considerable importance is given to exploring the effectiveness of such waste. This is with the aim of producing products of value, such as bio-based polymers. Proper modifications of waste and industrial residues (as renewable sources) can lead to new interesting biopolymers. A radical methodology would be assuming a further circular economic model that helps socio-economic and environmental sustainability. In this model, bioplastics are adequate, as they are realized with more eco-friendly biopolymers while still offering the suitability we have to presume from plastic [121].

The word "biopolymers" is, nonetheless, used to define, in general, a range of materials. Biopolymers are polymers that are produced by or derived from living organisms, such as plants and microbes, rather than from petroleum, the traditional source of polymers. The primary sources of biopolymers are renewable. Many, but not all, biopolymers are biodegradable, which means they are capable of decomposing into carbon dioxide, methane, water, inorganic compounds, or biomass by the enzymatic action of microorganisms. Biopolymers can be divided into two main principal categories: (1) polymers that are made by biological systems, such as micro-organisms, plants, and animals and (2) polymers that are chemically synthesized but are the result of biological conversion of amino acids, sugars, natural fats, or oils. Biopolymers could not only be obtained from agro-resource biomass, but also synthesized by means of microbial activity, by chemical modification of monomeric agro-resources fossil resources monomers, Figure 2.

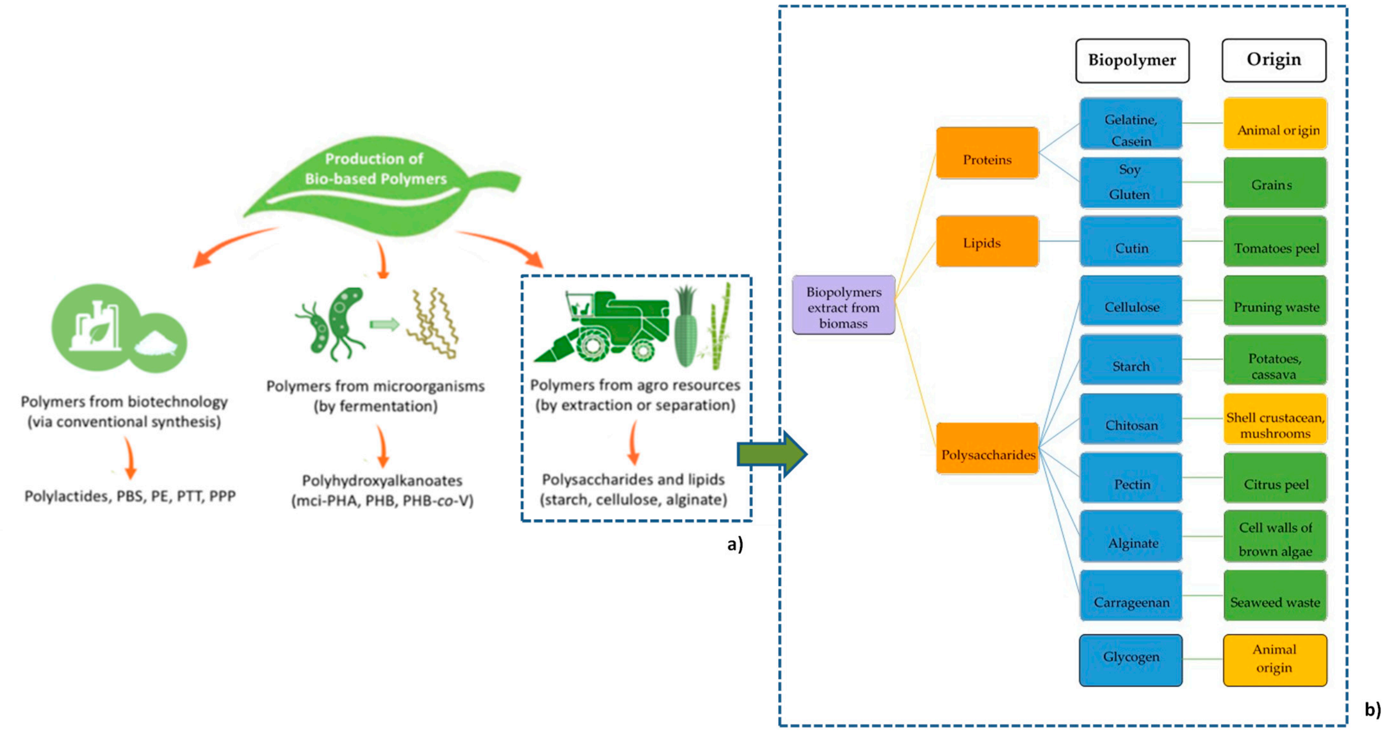

Figure 2. Bio-based polymer manufacturing route **(a)** and examples of biopolymers from agrowastes **(b)**. Adapted and reprinted with permission from [122,123].

In the specific case of biopolymers obtained from agricultural waste, it should be underlined that their production is subjected to the availability of starting material, which should be inexpensive and also prepared in substantial amounts. The quantity of inedible plant residues from crops (i.e. mainly fruit, cereals) annually reaches about 250 million t [124]. For this reason, they can potentially become a source of agricultural waste. This waste shows a high content of many interesting substances (lipids, carbohydrates, and aromatic molecules), which can be utilized to produce polymeric materials. However, agro-waste typically requires chemical processing to extract and obtain certain macromolecules. Particularly attractive are cellulose, lignin, tannins, and terpenes, as these can be used to produce bio-plastics. Belgacem and Gandini [125] carried out an extensive review of the polymers that can be obtained from these resources. Excluding the animal sources and limiting the analysis to agro-resource based polymers deriving from plants or seaweeds, we will limit the analysis here to the re-use of extracted polysaccharides, proteins, and lipids in the agricultural sector. In particular, we will focus our attention on plant/algae sources (polysaccharides, such as starch, cellulose, agar, hemicelluloses, pectin, alginate, carrageenan) and in addition on lignin and lipids and proteins, such as zein or gluten.

In the case of agriculture applications, key polysaccharides are cellulose and starch. However, other natural polymers, such as proteins, can be considered to realize biodegradable materials. A nice overview of the role that natural biopolymers have in the agricultural field is reported in a series of recent works, where the valorization of these different components has been properly reviewed [126]. From a circular perspective, biodegradable products from this specific waste have found wide application and made rapid advances in the agricultural and horticultural sectors. Mulching films, compostable seed belts, and active component capsulations made out of biopolymers are examples of how the theoretical circular approach finds real application in the field. Indeed, a lot of attention has been given to the use of synthetic biopolymers as plant stimulants and fertilizers that have overcome these traditional applications: their use as release coatings and/or plant stimulants has been deeply revised, and the scientific investigation in this field has proceeded fast under this conception [127].

Nevertheless, it should be said that the direct re-use of natural biopolymers from agricultural waste has received limited attention in the literature. Accordingly, in the following paragraph, the role of natural biopolymers extracted from agricultural waste as biostimulants and biofertilizers will be discussed.

3.6. Biopolymers as Biostimulants

In view of the growing consciousness of the adverse effects of agrochemicals, there has been a recent change to “green farming” sustainable methodologies. One feature of green farming is the selection of natural plant biostimulants. These are compounds that, when considered at low concentrations, provoke diverse physiological responses in plants, activating plant growth and defense against environmental stresses. There are different plant biostimulants available, such as seaweed extracts (SWEs), humic and fulvic acid, protein hydrolysates, N-containing compounds, chitosan, and other biopolymers and inorganic compounds [128]. Definitely, seaweeds contain distinctive polymers such as agars, alginates, carrageenans, fucans, and phlorotannins that may possess biological activity, acting as signal molecules to control growth as well as stimulating defence mechanisms in plants.

The beneficial effects of these extracts on plant growth have been extensively studied in a variety of plants. These effects include enlarged germination rates, enhanced shoot and root growth, healthier plant vigour, better nutrient uptake, higher pigment content and photosynthetic rates, high flower and fruit set, and enhanced shelf-life of fruit. These responses are well recognized in a number of reviews [35,40]. A recent application for alginate based compounds has recognized alginate oligosaccharides (AOS), produced by enzymatic depolymerization, as able to tune plant growth and improve resistance to various plant diseases. These effects have been associated to the presence of low molecular weight compounds able to stimulate activities such as plant hormones. Larger bioactive molecules, such as phlorotannins and oligosaccharides, have been also found to alter stress responses by activating molecular and biochemical pathways. Cellulose and hemicellulose can also be found in many types of seaweed, but the use of these polysaccharides as plant biostimulants remain rather unexplored [41]. Quite recently, Kocira et al. [129] considered the use of a biostimulant based on seaweed and amino acids on some soybean cultivars. In particular, they investigated the content of lignin, hemicellulose, cellulose, and fibers, obtaining as a result that the level of fiber fractions and the contents of hemicellulose and cellulose were altered by the biostimulant application.

Lignosulfonates and peptides have also acquired importance as biostimulants for use in agriculture [130]. Lignosulphonates can elicit hormonal activity as auxins or gibberellins, thus significantly increasing maize's biomass [46]. The authors showed that lignosulfonates improved N content in treated plants, thanks to induction of glutamate synthase and glutamine synthase, the key enzymes in N assimilation. Furthermore, lignosulfonates promoted photosynthesis by stimulating the activity of the rubisco enzyme and chlorophylls' biosynthesis. Similarly, Lucini et al. [131] found that using a biopolymeric biostimulant holding lateral root stimulating peptides and lignosulphonates modified the secondary metabolites' profile and the photosynthetic activity. On the other hand, research on lignin's application, especially lignosulfonates, is restricted to its effectiveness in stimulating root development or as a complexant to be used in formulations as fertilizer to be applied on leaves. Differently, scarce information is available on the effect of lignin obtained from different feedstocks on plants and soils. Gebremikael et al. [132] showed that root biomass could be significantly stimulated (62–152%) by directly treating plants with lignin obtained from pruning waste, compared to untreated controls. In general, polyphenols, synthesized in plants as protective agents against pathogens, microfauna, and competitive plants, have been studied for this purpose. For example, it has been seen that hydrolysable tannins can perform as plant biostimulants and regulate nematode populations, as well as inducing root growth and improving culture quality. In the same manner, the wide-ranging antimicrobial activity of flavonoids against fungi and bacteria has been demonstrated in numerous studies, and they could be considered to control plagues that can result in important economic losses [133].

3.7. Biopolymers as Biofertilizers

A feasible and encouraging strategy to optimize agricultural inputs is the practice of considering slow/controlled release systems for nutrients or other active principles. This technology permits the use of a limited product amount, consuming only the amount necessary to assure effect in a certain period and, therefore, guaranteeing better efficiency and minimization of environmental contamination and damaging effects [134].

Synthetic polymers typically used to realize slow and/or controlled release matrices have a tendency to degrade at very slow rates or may show toxicity, generating a predictable soil residue of about 50 kg^{-1} $year^{-1}$ [135]. Growing alarm about the use and disposal of polymeric materials has inspired the research on renewable and biodegradable materials that could diminish the environmental impacts. Natural-based biodegradable polymers, such as polysaccharides, are able to swell and gradually release the nutrients or other active substances in the soil without gathering toxic waste, due to their hydrophilicity. They could also perform as soil conditioners, improving water availability [136].

Agro-industry waste has been regarded as a valued source of naturally based polysaccharides and proteins, with interesting functional properties for food, pharmaceutical, and agricultural applications [137,138]. Examples of how agricultural residues have been utilized as environmentally friendly fertilizers can be found in many works dealing with different cereal straws [139], corn stover [140], and different food waste [141].

Regardless of the synthetic or natural origin, biopolymers serve as soil stabilizers, seed protectors, yield-enhancers, and plant growth regulators. Biopolymers dry quickly, dissolve rapidly in water, form effective water-soluble film, readily adhere to seeds, minimize the required dose of fungicides, and provide excellent control of plant diseases, thereby contributing to enhanced plant productivity [142]. Biopolymers precisely provide early access to each sown seed with nutrients, fertilizers, and pesticides in an accurate and timely manner with long-lasting ingredients. From this viewpoint, an encouraging alternative to commonly used fertilizers may be biological materials that have an intrinsic capacity to bind ions available in micronutrients Figure 3a. It was found that different functional groups (hydroxyl, phosphate, or amino groups) have an affinity for metal cations containing micro-elements, forming metal complexes [143]. This makes the biosorption binding of micronutrient cations to bio-based material an interesting way of producing controlled release fertilizers. Biomass-based fertilizers are also characterized by greater bio-availability and slowed nutrients release to the soil. They are fully biodegradable, reducing the undesirable impact of fertilizers on the environment. In this sense, natural-based polymeric hydrogels, realized by combining synthetic and natural substrates, such as polysaccharides and polypeptides, have been favored, Figure 3b.

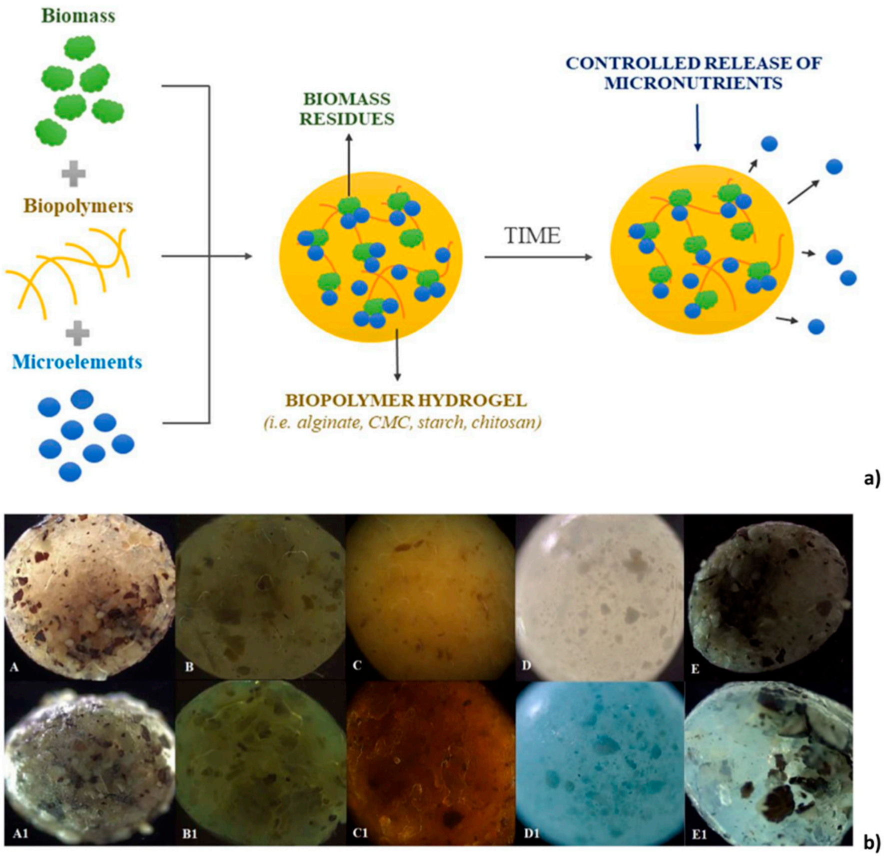

Figure 3. (a) Release of microelements from hydrogels with immobilized biomass and **(b)** immobilized biomass in a polymer matrix as eco-friendly fertilizers produced by biosorption: A–rapeseed meal post-extraction residues, B–alfalfa post-extraction residues, C–goldenrod post-extraction residues, D–eggshells, E–blackcurrant post-extraction residues, lower line with number 1–capsules enriched with Cu^{2+}. Reprinted with permission from [100].

Nanotechnology also has a role in the fertilizer industry, since pesticide or insecticide products designed for plant protection based on nanomaterials, such as pesticides, are becoming progressively widespread. The cause is correlated to the possibility of having accurate and precise dosing, due to the immobilization of fertilizer during nanoparticles formulations. In addition to the several benefits, however, there are also some drawbacks: any micro-element given at high doses may cause phytotoxic effects, regardless of the form of its dosage. It can cause damage to the epidermis covering the roots, slowing down their growth and ultimately weakening the whole plant, causing lower yields [144].

While in the recent past attention was directed towards the use of synthetic polymers, the outlook is, however, now shifting toward natural polymeric nanomaterials. Other areas in which such natural polymers are starting to be considered are, other than for controlled release, even for pesticide encapsulation and as water-retaining agents. Some examples of biopolymers studied for use in controlled release are starch [145], chitosan [146], gelatin [147], lignin [148], cellulose, and k-carrageenan [149]. Chitosan and cellulose are poorly soluble in water, whereas starch can be chemically modified to give new properties, which make them perfect for agricultural uses.

Another sector where polymeric materials are currently employed in agriculture is for water preservation in drought-prone and semi-arid regions. Practically all of the current polymers considered for this purpose are acrylate-based superabsorbent polymers (SAPs). Even though many studies are in progress for the production of smart and semi-synthetic SAPs, some problems arise, such as non-biocompatibility, non-biodegradability, and non-renewal character, leading to the exploration of natural SAPs. Hereafter, significant research has been done to advance in the functional properties of natural hydrogels (chitosan, alginate, pectin, and gellan), with the main aim of substituting synthetic polymers for water retention [150].

Natural polymeric nanoparticles can also be used in varying applications, including nanoherbicides, nanodetectors, and nanofertilizers, to solve limitations in the agriculture sector, such as environmental contaminations and human health concerns. These engineered nanoscaled products can also help to improve, indirectly, food production and nutritional value by improving the quality of pesticides, fertilizers, and growth regulators. For example, nanocarriers can be considered for carrying and delivering pesticides in a controlled way to achieve a "precision farming" model. In this regard, principally nanoparticles resulting from biopolymers are attractive, having biocompatible properties and low impact on human health and the environment. Biopolymeric nanocarriers made up of two natural polymers, chitosan and pectin, were developed by Sandhya et al. [151] to make available a controlled release of encapsulated carbendazim with good bio-efficacy and inhibition against fungi, such as Fusarium oxysporus and Aspergillus parasiticus. Moreover, phytotoxicity studies indicated that carbendazim-loaded polymeric nanoformulation affords better germination and root growth for the seeds of Zea mays and Cucumis sativa [151]. Encapsulation in chitosan alginate has shown to reduce the toxicity by 50% and advance in the efficiency of two herbicides, imazapic and imazapyr, considered to fight weeds in maize and peanut fields [152]. The design of different soft nanomaterials from renewable feedstocks is, consequently, gaining incredible attention for their distinctive properties and safer applications.

All these described studies show the advantages of using nanoformulations in diminishing concentrations and amounts of herbicide or pesticide necessary for effective treatments, thus reducing their impact on non-target species [153]. The numerous advantages and applications of nano systems definitely hold the potential that nanotechnology could theoretically transform the agricultural sector, while helping to resolve major problems such as food scarcity, crop yield, and sustainability. However, the alarms over the safety of nanomaterials directly influence the public acceptance of these technologies, especially in the agri-food sector. The encouraging request for their use, in the case of biopolymeric nanomaterials, comes from the fact that all of them can be easily degraded in the soil, differently from inorganic nanoparticles, which remain in different environments where the toxicity cannot be foreseen. Additionally, considering the number of possibilities where natural biopolymers can be used to substitute inorganic nanoparticles in agriculture, we are forced to move a step toward making nanotechnologies safer and more acceptable to the public, enabling us to gain the full benefits of nanotechnology.

4. Conclusions

More conscious and responsible management of our production system is necessary, since it is imperative to preserve and better manage natural resources. In this context, this review illustrates the possibility of valorizing agricultural waste by converting it into substances and materials thtat can be used to improve crop performance and soil quality.

Such actions are also dictated by precise and globally agreed policy lines, as discussed in detail in the review's introductory section. Such actions address current global food needs, the ongoing climate change, and the need to reduce the environmental impact of production and agricultural activities. Realistically, in the coming years, losses in agricultural productivity of up to 70% are expected for climate change and the progressive degradation of primary resources (mainly soil and water) [14].

Therefore, the originality of the work presented lies in exploring the possibility of using agricultural waste to produce innovative materials (biostimulants, biofertilizers, and biopolymers) that can be used in the same production chain (circular economy), Figure 4.

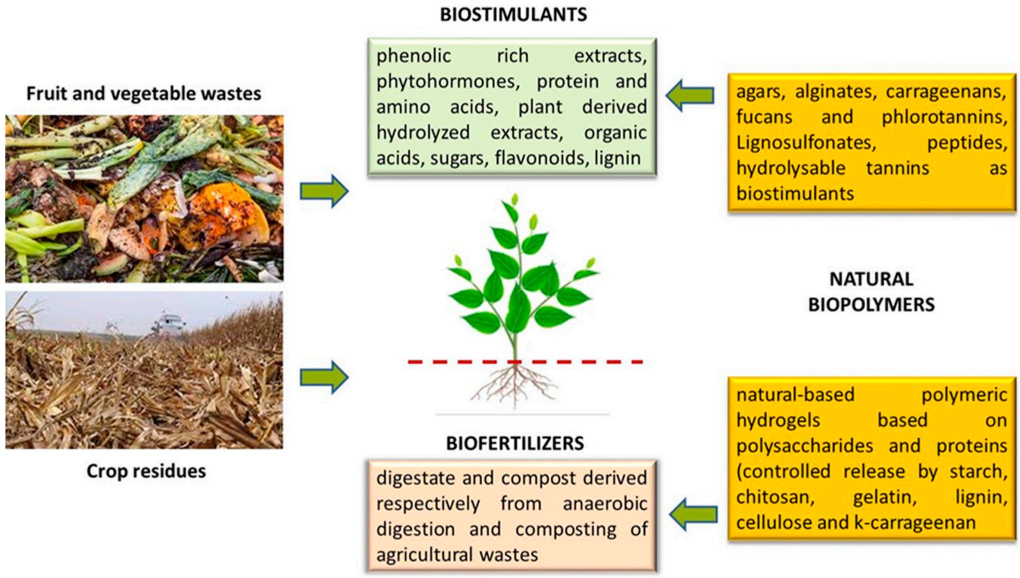

Figure 4. Graphic illustration of how agricultural wastes and their constituents, including biopolymers, can be used as biostimulants and biofertilizers.

Among the benefits of this approach, in addition to the valorization of waste, is the possibility of increasing crop productivity and resistance to stress and restoring and improving soil quality. These ameliorative aspects must be seen as solutions also to be implemented to counteract climate change. Moreover, these innovative substances, particularly biofertilizers, can lead to a progressive reduction in chemical inputs (i.e., synthetic fertilizers) that create many environmental issues by impacting primary resources. Finally, environmental sustainability due to waste valorization allows alternative agricultural waste uses, avoiding its disposal, spreading, and burning.

As far as biostimulants are concerned, from an applicative point of view, this review has collected experimental evidence that demonstrates many positive aspects found by recent studies aimed at valorizing agricultural wastes deriving from very different matrices. Summarizing the novelty of what was presented in Section 3, biostimulant substances from waste biomass have been shown to be able to improve plant biomass production and CO_2 fixation capacity. Another aspect worth mentioning is the effect demonstrated by some studies where biostimulants stimulated root development and, consequently, more efficient plant nutrition. This last aspect deserves attention, as improving plant nutrition allows maximizing plant efficiency in nutrient use and positively affects the environment. Furthermore, another intriguing aspect is that biostimulants have been shown to increase phytochemicals and protein content and enhance the end product's nutraceutical value. Finally, it should be noticed that biostimulants from particular waste can also be employed to improve plant resistance to salinity and drought, which are very current issues directly related to climate change.

The reuse of agricultural wastes is a sustainable solution to recover nutrients and produce biofertilizers from the perspective of a circular economy. It is important to promote the implementation of new technology processes by using bio-based raw materials, i.e., agricultural wastes., to produce biofertilizers. The nutrients recovery directly from these wastes or after their biological treatments (anaerobic digestion and composting) permits the reduction of the use of chemical fertilizer and improves soil physico-chemical properties, in terms of organic matter and nutrients availability for plants.

Biopolymers obtained from agricultural waste, whose production is subjected to the availability of waste raw material, are inexpensive and can also be prepared in substantial amounts. They can work as biostimulants, with beneficial effects on plant growth, germination rates, shoot and root growth, plant vigour, and nutrient uptake. Lignosulfonates and polyphenols in general, chitosan, and peptides have acquired importance as biostimulants for use in agriculture. If considered as biofertilizers, biopolymeric systems are the best solution when slow/controlled, and precise release of nutrients or active principles is required due to their inherent propency to swell, form films, bind ions, and biodegrade in the soil. Biopolymeric nanoscaled products have also gathered attention, due to several advantages, such as diminishing concentrations necessary for effective treatments, even if some drawbacks related to safety are still limiting their widespread use.

In conclusion, the advantage of the approach proposed in this review lies in the possibility of preserving natural resources, reducing or eliminating the impact of waste on the environment, and limiting the use of synthetic compounds in agriculture. Such an approach is in line, therefore, with the transition from a production system based on the "take–make–dispose" model to the recycling of waste, thus satisfying the paradigm of the circular economy.

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