

Review

Sustainable Use of Cruciferous Wastes in Nanotechnological Applications

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Abstract: Over the last few years, new nanoparticle preparation methods have emerged by replacing the usual reagents with plant extracts obtained in different conditions. An example of a natural plant extract is those of cruciferous vegetables, to obtain the new bio-nano-coatings. Given the composition of cruciferous extracts and large amounts of wastes produced all over the world, they can be successful substitutes to replace conventional coatings and extend the possibility of “smart coatings”. The present review aims to be a critical discussion regarding the application of cruciferous waste in nanotechnological applications. This review paper can be a starting report for different researchers who intend to use this sustainable approach “from green to nanotechnology” to transpose manufacturing from laboratory to industry. Applying this approach to obtain nanostructures with plant waste highlights the importance of minimizing and re-utilizing residues from primary and secondary processing via chemical and social intervention, in order to contribute to the sustainability needs of the planet and its inhabitants.

Keywords: *Brassica* genus; cruciferous; nanocoating; antimicrobial; antioxidant



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1. Introduction

In the last decade, nanomaterials have been considered a pivotal tool for different domains such as healthcare, food and agriculture, and the environment. To use nanoparticles in chemical reactions, adequate preparation methods are needed. As these materials are diversified in morphology and chemical composition, various methods have been developed, such as sol–gel, spinning, chemical vapor deposition, and microemulsion or microfluidic methods [1]. These methods require expensive equipment and environmentally hazardous reagents. Mostly, metal salts are reduced using sodium borohydride, citrate, ascorbates, and glucose, and the type of the reducing agent determines the size of the nanoparticles [2]. The bigger particles are produced by the strong reducing agents, while nanoparticles with smaller dimensions are produced by the mild reducing agents; by utilizing appropriate surfactants, particle morphology control is achieved [3,4]. Lately, new nanoparticle preparation methods have developed by replacing the classical reagents with plant extracts obtained in different conditions. An example of a natural plant extract is those of cruciferous vegetables, to obtain the new bio-nano-coatings. As observed from Figure 1, there has been an annual increase in the rate of papers from 2011 to 2019, with two exceptions in 2014 and 2018. Compared to other publications, their number is not large and, for this reason, this review is important to bring scientists’ attention to the usage of cruciferous vegetables in nano-coatings considering their properties.

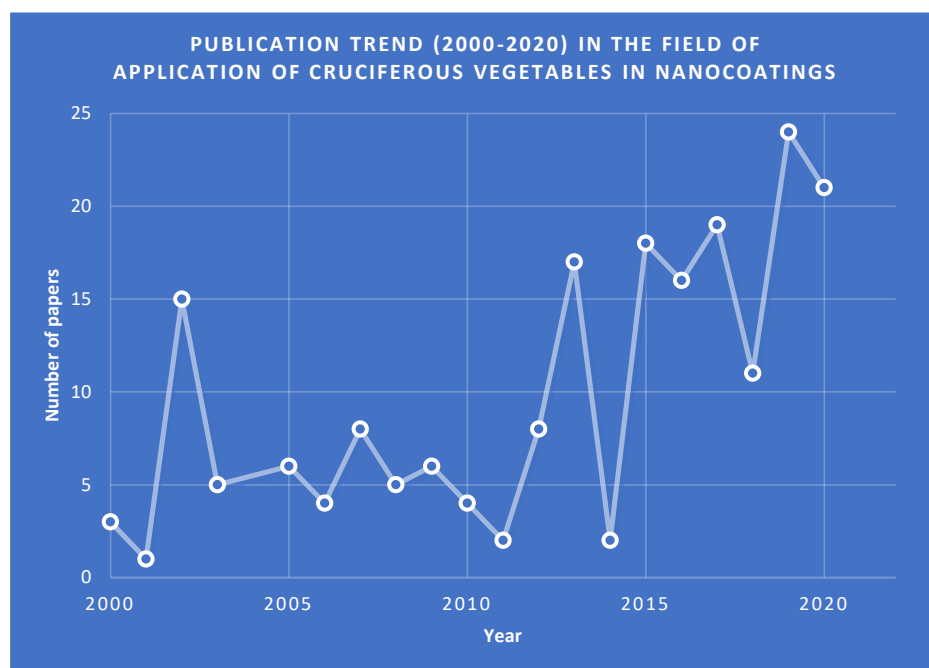


Figure 1. Publication trend (2000–2020) in the field of application of cruciferous vegetables in nanocoating (source of data: <https://www.sciencedirect.com>, accessed on 28 April 2022).

At the international level, only during 2019, the production of cabbage and other related brassicas was 97 million tons with a proportional amount of waste (leaves, roots, some stems, a.o.) [5]. In the last ten years, bioeconomy strategies and policy-related bioeconomy initiatives have been developed all over the world (Figure 2). Europe’s strategy addresses the sustainable production of renewable biomass, value-added products, bioproducts, and bioenergy from different type of wastes through an efficient transformation.

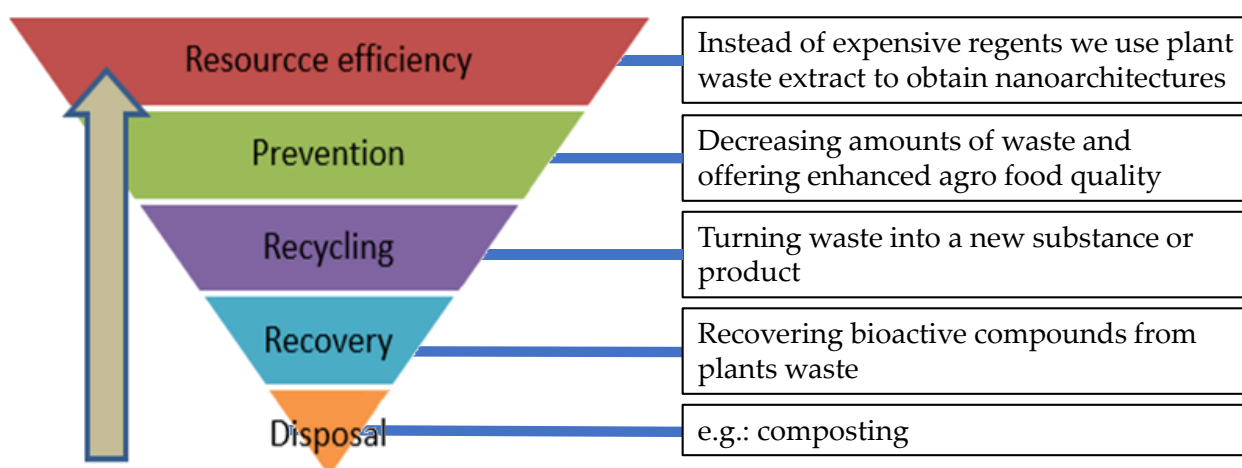


Figure 2. Current bioeconomy approaches of the cruciferous vegetables waste in nanocoating.

Hayek and Schultz [6,7] were the first researchers who published information about the origin of Brassicaceae. *Brassica* is a genus of plants in the Brassicaceae family (the cabbage and mustard family). The members of the *Brassica* genus are known as cruciferous vegetables and *Brassica* spp. (Table 1) is generally classified into three groups: mustards, coles, and rapeseeds [8]. The name comes from the shape of the flowers that are in the shape of a cross. They have been cultivated for centuries, mainly in Europe and Asia, and there are several varieties that belong to this large family of crucifers.

Table 1. Classification of Brassicaceae family (main species, subspecies (ssp.), and varieties (var.)) [5,8–11].

Species	ssp./var.	Common Name
<i>Brassica rapa</i> L.	<i>japonica</i>	Curled mustard
	<i>rapa</i>	Turnip broccoli
	<i>rapifera</i>	Turnip
	<i>chinensis</i>	Pak-choi, Chinese mustard
<i>Brassica napus</i> L.	<i>pekinensis</i>	Chinese cabbage
	<i>napus</i>	Rapeseed
	<i>napobrassica</i>	rutabaga
<i>Brassica oleracea</i> L.	<i>italica</i>	Broccoli
	<i>gemmifera</i>	Brussels sprouts
	<i>capitata capitata f. rubra capitata f. alba</i>	Cabbage Red cabbage White cabbage
	<i>botrytis</i>	Cauliflower
	<i>alboglabra</i>	Chinese kale
		Radish
<i>Raphanus sativus</i> L.		Radish
<i>Brassica alba</i> /Sinapis alba, <i>Brassica hirta</i>		White or yellow mustard
<i>Brassica nigra</i> /Sinapis nigra		Black mustard
<i>Brassica juncea</i>		Brown mustards
<i>Raphanus raphanistrum</i> L.		Wild radish
<i>Eruca sativa</i> Mill.		Rucola
<i>Diplotaxis muralis</i> L.		Wall rocket

The present review aims to be a critical discussion regarding the application of cruciferous waste in nanotechnological applications. It contains general information regarding the composition of the Brassica genus, the application of the Brassica genus in green nanotechnology, and conclusions and future perspectives.

2. General Composition of Brassica Genus

Crucifers contain a lot of nutrients and are beneficial to the body, from vitamins, minerals, and proteins to carbohydrates and fats. They are rich in vitamin A, vitamin C, folic acid, and fiber, with a low caloric content. Ideally, a person should eat at least three servings of cruciferous vegetables a week, and to retain as much of the beneficial nutrients of these vegetables as possible. These should be eaten as fresh as possible. A diet rich in cruciferous vegetables is also good for detoxifying the body and strengthening the immune system, with some studies suggesting that these vegetables also contain certain anticancer substances [8,12].

The genus *Brassica* is very important from an agricultural and horticultural point of view. Cruciferous vegetables including cabbage, broccoli, turnip, and radish are among the agricultural crops produced in the largest quantities, and their residues (leaves) have become a burgeoning environmental problem. Nonedible cruciferous vegetable residues are bio-convertible into other valuable products, providing a way to reduce pollution and to obtain value-added products, eliminating other problems such as handling and storing Cruciferous vegetables such as radish, cauliflower, cabbage, mustard, carrot, and turnip are edible plants that are high in fiber, rich in vitamins and minerals, and have physiologic effects in humans [8–13]. Most of the plants listed above are seasonal plants (annuals or biennials), while some are small shrubs.

There are over 30 wild species and their hybrids plus many controlled cultivated varieties. Due to their high importance in agriculture, *Brassica* plants have been the subject of numerous publications [14–18].

Plants in the *Brassica* genus contain several phytochemical compounds such as glucosinolates, glucosides, phenolic acids, erucic acid, polyphenols and tocopherols, carotenoids, flavonoids, alkaloids, terpenoids and terpenes, phytoalexins, and Phyto steroids with diverse biological activities, mainly antimicrobial and antioxidant effects, but also act against some herbivores [19–23].

Some important enzymes such as chitinase, glutathione transferase, and epoxide hydrolase are also found in cruciferous vegetables [24,25]. Indole and isothiocyanate, enzymatic products of myrosinase from glucosinolate found in cauliflower and cabbage, lower the incidence of tumor formation, and have an antioxidative effect [26]. There are also antimicrobial components such as iprodione [27], chitosan [28–30], and a peptide [31] in cruciferous vegetables.

Nowadays, as noted in the references mentioned above, the cruciferous vegetables are becoming more and more present in restaurants because they are very healthy (Figure 3). The following is a summary of the healthiest crucifers in terms of their chemical composition and the benefits they bring to human health [8,12–31].

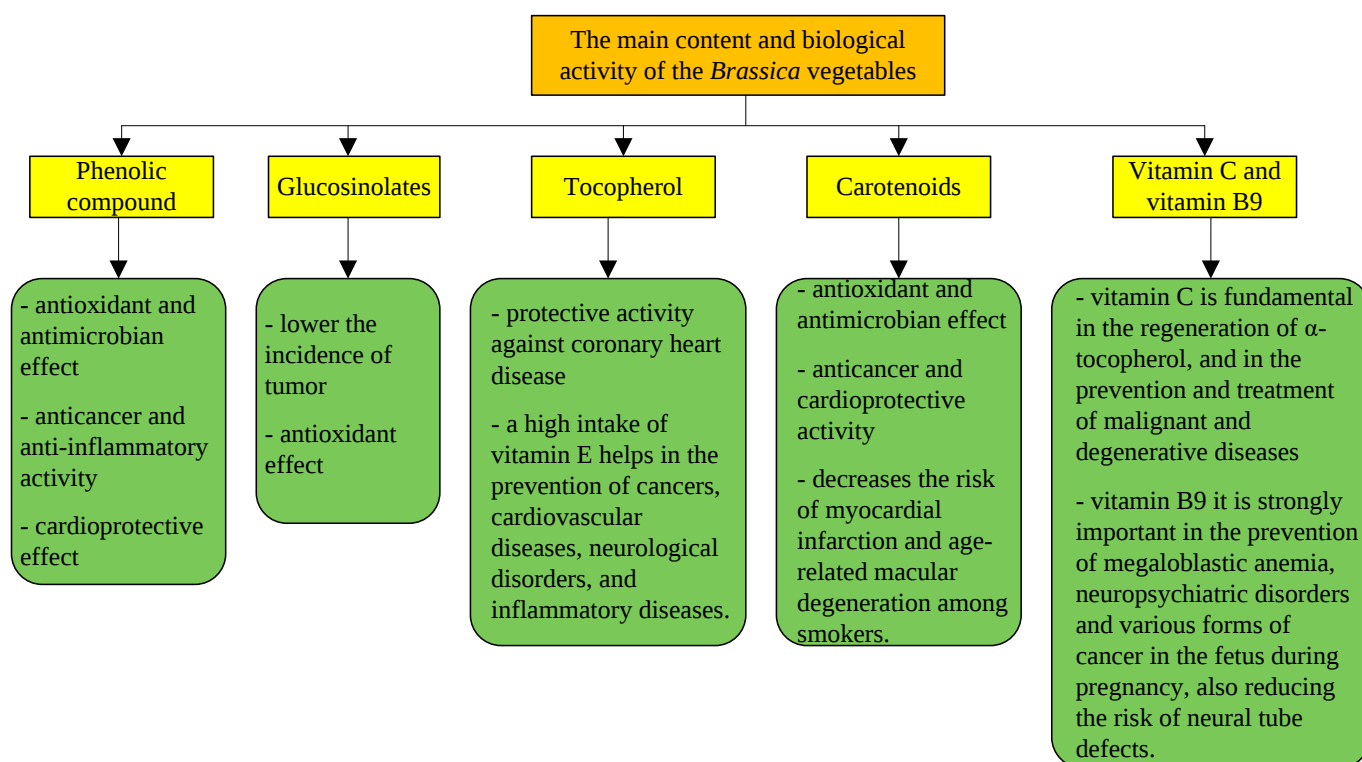


Figure 3. Main biological activities of *Brassica* vegetables.

Arugula is a plant native to the Mediterranean area, related to kale and cauliflower. The arugula leaves have a specific, peppery, slightly bitter, and intense taste, which fits perfectly in any salad, in combination with other green leaves. Arugula has antimicrobial properties and stimulates immunity, supporting the body in the transition periods between the cold and hot seasons. Being an excellent source of vitamin A, together with the flavonoids in the composition, it supports eye health and helps maintain healthy skin. Fresh arugula contains a significant amount of vitamin C, which has an anti-inflammatory effect and protects against the harmful effects of free radicals [32,33].

Broccoli is a vegetable with an exceptional nutritional value, which can help maintain a long and healthy life. Broccoli contains a significant amount of glucosinolate, which is converted in the body into sulforaphane, a substance that has a proven effect in stopping the growth of cancer cells [34]. Sulforaphane also has the effect of removing toxins from lung cells, eliminating harmful compounds from pollutants and cigarette smoke. Both the stem

and the fluorescence of this vegetable are rich in nutrients and are edible. When cooked, certain substances such as carotenoids become more concentrated, but the number of glucosinolates decreases. These losses can be avoided if it is steamed instead of boiled [35].

Brussels sprouts, the relative of ordinary cabbage, looks like a miniature cabbage. It is very rich in nutrients, being primarily a good source of vitamins C and K. It is composed of mineral salts (especially manganese, potassium, calcium, iron), folate, vitamin A, and B vitamins, all accompanying a large amount of fiber [36]. Brussels sprouts can help prevent or alleviate many ailments: rheumatoid arthritis, cardiovascular disease, digestive disorders. As with other cruciferous vegetables, they contain sulforaphane [37].

Cabbage is a vegetable with a very low caloric content. It is one of the vegetables with the highest vitamin C content (the richest are the leaves on the outside). Cabbage is also very rich in vitamin E. Provitamin A (or carotene, which is converted to vitamin A in the body) is also very well represented [37]. Cabbage also contains B vitamins. Dietary fiber is abundant in cabbage, being composed mostly of cellulose and hemicellulose, which explains some intestinal intolerances. Dietary fiber can stimulate the gut and prevent constipation. The most popular varieties of cabbage are white cabbage and red cabbage. All these varieties of cabbage are eaten raw, cooked, or added to pickles [38].

The cauliflower head consists of hundreds of white bouquets that are attached to a single stem. In addition to the well-known white cauliflower, on the market you can find dark green varieties (which are obtained by crossing with broccoli), purple or orange varieties, and cauliflower of the variety “Chartreuse Romanesco” (Roman cauliflower) [39]. Cauliflower contains significant amounts of vitamin C, B-complex vitamins such as folate, pantothenic acid (vitamin B5), pyridoxine (vitamin B6), and thiamine (vitamin B1), niacin (B3), and vitamin K. These vitamins are essential as the body needs external input to restore the reserves needed for proper functioning. It can be a reliable ally in the body’s fight against toxic substances, which helps reduce the risk of various forms of malignancy. It also helps prevent cardiovascular disease by lowering triglyceride and cholesterol levels [40].

Kale cabbage, also known as “borecole” or “farmer’s cabbage”, has been grown for more than 2000 years. Over time, it has been widely consumed, especially in Europe, due to its resistance to frost and the fact that these crops can be harvested late at the end of the year. Kale cabbage has a sweet and slightly pungent aroma, with an astringent flavor, due to its high iron content. The different types of kale cabbage also have different tastes: red kale is suitable for salads, for a fine taste, and has a pungent taste, while kale palm has a sweet taste [41]. The smaller kale leaves are generally thinner and sweeter than the larger ones. Kale can act as an anti-inflammatory due to its high content of omega-3 and fatty acids, which are essential in the fight against rheumatoid arthritis, asthma, or autoimmune diseases. Kale also contains a significant amount of vitamin K [42].

Kohlrabi is a vegetable with a sweet and delicate aroma, between radish and cabbage, whose origins are in northwestern Europe. Although it appears to be a root that grows in the ground, Kohlrabi grows on the surface of the soil. These vegetables are an excellent source of vitamins C, A, E, B, and K, minerals such as phosphorus, iron, zinc, potassium, magnesium, calcium, and copper, folic acid, lutein, but also fiber. Kohlrabi contains over 90% water. Glucosinolate determines the characteristic aroma and taste, known to have anticarcinogenic activity [43,44].

Mustard Leaves

Research has shown that mustard originated in ancient Egypt, and the population here combined meat with mustard seeds. In the Greeks, mustard was also used for meat, while the Romans used it as an antidote to snake bites, muscle fever, and even plague. Not only are the berries from this vegetable used, but also the leaves. They are an excellent source of vitamins A, C, and K. With a strong taste, mustard leaves are preferably eaten cooked and not raw [45,46].

Radishes have been consumed since ancient times and have been mentioned in Chinese history since 2700 BC. The Egyptians cultivated these vegetables before the period when

they built the pyramids. Radishes are distinguished by their antibacterial and antifungal action, abundance of vitamins and minerals (vitamin C, vitamin B complex, magnesium, potassium, sodium, etc.), and low cholesterol and calories. Significant amounts of dietary fiber and folic acid found in radishes are recommended for daily consumption in a balanced diet [47]. Although most of us are familiar with red radishes, white radishes from Asia and black radishes grown in Spain are part of the same family. Radishes are eaten raw, in salads, in garnishes, or can be added to soups and other dishes [48].

Turnip began to be widely cultivated during Greco-Roman Antiquity, after the 15th century BC, and seems to have been originally discovered by the Asian civilization. The root of this plant is used primarily, but its leaves are not left out either, being highly valued in traditional medicine or as a substitute for spinach leaves in culinary preparations [49]. Small varieties are intended for human consumption, while larger ones are used as feed. Fresh turnip root is an excellent source of vitamin C, but the leaves of the plant have a higher content of antioxidants and nutrients. An excellent source of vitamin K, Omega-3, and vitamin A, turnip leaves have an anti-inflammatory role and protect the body against cardiovascular disease [50].

Horseradish is appreciated for its sweet and very hot taste, being frequently used with beetroot salad (it is a combination that brings valuable nutrients to the body during the winter), but also together with meat dishes. From horseradish, the young leaves and root can be used. Horseradish root is very rich in vitamin C, mineral salts, enzymes, amino acids, moderate amounts of B-complex vitamins, and carotenoids. Horseradish has effects on the respiratory tract due to volatile compounds, is very rich in vitamin C, has antibiotic and stimulating properties on the metabolism of the adrenal glands, lowers blood pressure, and has a deworming and diuretic effect. Due to its effects, horseradish is recommended in respiratory infections, asthma and allergies, urinary tract infections, to regulate metabolism and digestion, in hypertension, asthenia, and fatigue [51].

As noted in the references mentioned above, in the case of *Brassica* spp., nutritional quality is given by the presence of molecules such as phenols, vitamin C (antioxidant compounds), or nonantioxidant compounds such as glucosinolates and minerals.

Antioxidant compounds that are found in *Brassica* spp. are of two types: lipo-soluble antioxidants and water-soluble antioxidants. Lipo-soluble antioxidants (carotenoids such as β -carotene and xanthophylls) are responsible for the yellow, orange, and red pigmentation of some cruciferous plants. Through the metabolic processes that take place in the body, β carotene is transformed into lutein, zeaxanthin, and vitamin A. Many epidemiological studies show that the use of lutein and zeaxanthin reduce the risk of cataracts and maculodystrophy, two of the leading causes of vision loss and blindness. In addition to the many benefits it brings to the human body, beta-carotene helps prevent cardiovascular disease and reduces the risk of heart attack [50–53]. Beta carotene is converted to vitamin A in the body and is the most important source of provitamin A in food. It acts as an antioxidant together with vitamins E and C and can reduce the risk of chronic diseases. Beta carotene also plays an important role in protecting the skin from the harmful effects of ultraviolet radiation [52]. According to Podsedek, kale is the cruciferous with the highest content of lutein and zeaxanthin (3.04–39.55 mg/100 g) [53]. Muller [54] reported the decrease in the total carotenoid content of some cruciferous species as follows: Brussels sprouts (6.1 mg/100 g), broccoli (1.6 mg/100 g), red cabbage (0.43 mg/100 g), and white cabbage (0.26 mg/100 g).

In addition to carotenoids in the category of lipo-soluble antioxidants, vitamin E plays an important role in the composition of cruciferous plants. As with beta carotene and vitamin E, it prevents cardiovascular disease (inhibition of LDL oxidation), cancer, and inflammatory and neurological diseases. Vitamin E is a major lipo-soluble antioxidant responsible for protecting membranes from lipid peroxidation [52]. The antioxidant properties of vitamin E that act on free radicals could slow down the biological aging process. In humans, vitamin E deficiency can cause neurological and cardiovascular dysfunction [55]. Vitamin E is formed by tocopherols and tocotrienols; in cruciferous plants,

α -tocopherol is the main compound except for the cauliflower where γ -tocopherol is found in its composition [56].

In addition to the lipo-soluble antioxidants in *Brassica* vegetables, we also find water-soluble antioxidants. This category includes phenolic compounds (flavonols, flavones, anthocyanins), vitamin C (ascorbic acid), and vitamin B9 (folic acid). Polyphenols are one of the most numerous and important substances that have their origin in the vegetable kingdom. Along with vitamins C, E, and A, they are considered compounds that give fruits and vegetables all those well-known properties, beneficial for the human body [50–56]. According to Moreno et al. and Heimler et al., kale and broccoli have the highest quantity of phenolic compounds [57,58]. In addition to its antioxidant properties, polyphenols also hide other secrets, fulfilling complex functions regarding the immune system, more precisely in the prevention of tumors, inflammatory processes, and cardiovascular pathologies. The main beneficial activity for the health of the human body is represented by the antioxidant action. In fact, polyphenols can neutralize free radicals, reducing inflammatory processes and the effects of cellular aging [59]. Certain types of polyphenols (procyanidin) also promote the death of irreversibly “damaged” cells, thus preventing the formation of cancer cells. Specifically, polyphenols manage to reduce the buildup of cholesterol located especially on the walls of blood vessels (the anti-atherogenic action) [60].

Flavonoids are the most important phenolic compounds found in *Brassica*; these phenolic compounds possess many properties such as antioxidant and antimicrobial activity [61], and a capillary protective and inhibitory effect [53,59,62].

The most common flavonoids in *Brassica* are: flavonols, flavones, and anthocyanins. Anthocyanins, which have very high antioxidant activity, are present only in colored vegetables such as purple broccoli and red cabbage. In herbal medicine, anthocyanins have long been used to treat many ailments (including high blood pressure, colds, and urinary tract infections). Recent research suggests that anthocyanins may also help alleviate major health problems, including heart disease and cancer [63–65]. As with the anthocyanins presented above, flavones also show antioxidant activity through apigenin and luteolin (the only flavones found in the cruciferous composition) [66]. Medical studies conducted in recent years on the properties of flavonoids were aimed at anti-inflammatory, antioxidant, antimicrobial, antiviral, antitumor, antihemorrhagic, and antiallergic [60]. The whole set of benefits attributed to flavonoids depends largely on their ability to block the damage caused by free radicals, associated with various chronic degenerative diseases: considered powerful antioxidants, they successfully intervene in the proper functioning of the liver, capillaries, and immune system; contribute to the prevention of many pathologies of cardiovascular origin and inflammatory diseases; with the ability to boost the immune system, these substances manage to counteract some forms of tumor; diets rich in flavonoids help prevent cardiovascular disease and reduce the risk of early death; these chemicals in plants are able to act on cholesterol and other factors that affect the health of the circulatory system. The most represented flavonols in cruciferous vegetables are quercetin, up to 23 mg/100 g of fresh product in kale, and the second most common flavonoid is found in broccoli (Kaempferol 3-O-sophoroside) [67–69].

Sanlier et al. and Blažević et al. [70,71] showed that among Brassicaceae, kale is the richest in almost all the main macro and micro elements. The high capacity of *Brassica* to accumulate the metals present in the soil is considered a very good metal hyperaccumulator. Macronutrients (nitrogen, phosphorus, potassium) help plants in essential structural and energetic roles, and the minerals such as copper, iron, zinc, and selenium are required by plants in very small quantities and are so-called microelements.

In addition to the components mentioned above in *Brassica*, there are also glucosinolates and isothiocyanates [71,72]. Glucosinolates are glucosidic compounds (with sulfur) derived from amino acid biosynthesis, and the concentrations vary according to the developmental stage and environmental factor. They serve no direct function to human health, but the health effects are fulfilled by the hydrolysis breakdown products, the isothiocyanates. They are responsible for the typical and spicy aroma of cruciferous vegetables.

The most used isothiocyanates is sulforaphane [73], which is found in large quantities in broccoli and Brussels sprout; sulforaphane acts as a catalyst in the stimulation of the cellular antioxidant system and some enzymes against tumoral cell proliferation [74].

3. Application of *Brassica* Genus in Green Nanotechnology

Considering the data presented in the previous section, cruciferous vegetables contain many substances that have antimicrobial and antioxidant activity [48], making them ideal candidates for use in the phytosynthesis of metallic nanoparticles for the nanocoating's purpose.

In the 21st century, finding new “green” materials with potential applications in various fields is an important goal. The use of these materials and the real interest in their research is due to green synthesis methods that have considerable advantages such as avoiding toxic chemicals, high cost, and severe reaction conditions [75]. Even direct precipitation, the sol–gel method, reverse micelles, thermal decomposition, or the solvothermal method was successfully used for the obtaining of metallic nanoparticles; “green methods” (with biological sources such as bacteria, fungi, yeast, actinobacteria, and plants) can be used as well (Figure 4).

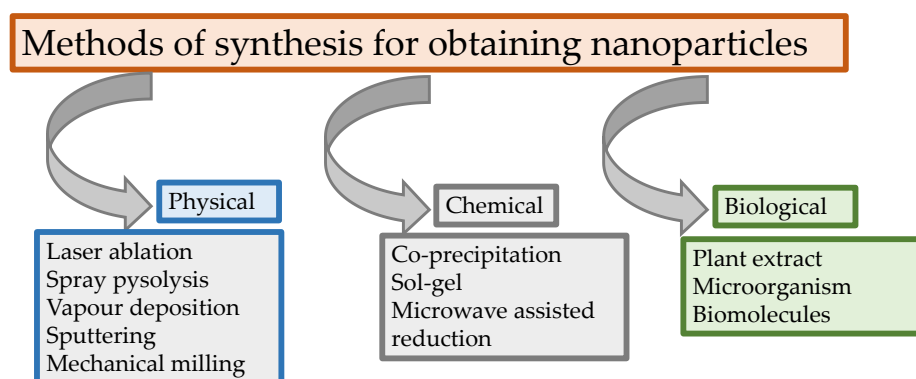


Figure 4. Methods of synthesis for obtaining nanoparticles.

The recent pandemic of the COVID-19 virus has demonstrated that costs in both human life and economic terms can be very high if the spread of the infection is not controlled [76]. Therefore, it is very important to have measures to minimize this spread of infection.

Nano-coatings containing nanoparticles, such as metal nanoparticles, metal oxide nanoparticles, carbon nanotubes, or various heterostructures have been shown to be up to 99.99% effective against many microorganisms [77]. Inorganic nanomaterials are stable at high temperatures and have a long shelf life, and they also show anti-microbial and antiviral activities compared to organic nanomaterials [78]. Future research needs to focus on new antiviral and antibacterial nanocoatings for a wide range of applications, especially for so-called high-traffic objects (e.g., hospitals, schools, door, and window handles in public places; public transport) and/or coatings for textiles (e.g., face masks, laboratory coats).

Sharma and coworkers [79] showed that the antibacterial activity against *Escherichia coli* of biologically synthesized AgNPs (silver nanoparticles, via *Brassica oleracea*) are more pronounced than chemically synthesized AgNPs. Ansar et al. also demonstrated that the green synthesis of AgNPs via *Brassica oleracea* has antimicrobial, antioxidant, and anti-tumor activities [80].

Pandit [81] reported that the green synthesis of AgNPs from seed extract of *B. nigra* possess antimicrobial activity; these nanoparticles can be successfully incorporated into antimicrobial coatings.

In addition, it has been observed that metallic nanoparticles can be synthesized with the vegetal material extract or can be formed in situ in different plant organs [82]. Moreover, if the nanoparticles are calcinated at enhanced temperatures (from 100 to 900 °C), they lose their beneficial properties, and the properties gradually decrease with increasing calcina-

tion, due to the increase in particle size [83]. Green synthesis is the use of bio-reduction that is 100% eco-friendly and is energy-saving and economically viable [84]. Plant extracts can offer a complex matrix of chemical compounds and secondary metabolites acting as natural reducing agents as well as a capping agent [85]. AgNP applications are numerous, and there is strong potential for continuous growth in this area (Table 2). They can be used as active compounds for medical applications (wound healing, drug carrier, and as a material for medical diagnostics), personal care products, food and feed industry, environmental applications, or sensors [86–88]. Following the aspects of global solid waste management and the ecofriendly green synthesis approach, Umamaheswari and collaborators evaluated the anticancer property of ZnO nanoparticles obtained from *Raphanus sativus* var. *Longipinnatus* leaves extracts using A549 cell lines. IC₅₀ was found to be 40 µg mL^{−1}, explaining that the higher surface area-to-volume ratio of these small particles may be responsible for the enhanced cytotoxic effect [89]. More studies have focused on the effect of metallic nanoparticles as antifungal agents. Spherical ZnO nanoparticles can be efficient against *Escherichia fergusonii* and *Escherichia coli* (approx. 15 to 23 mm inhibition zone, depending on the strain) [90]; meanwhile, spherical AgNPs are efficient as antibacterial agents against *Bacillus subtilis* (MTCC 441) (IZD = 23 mm); *Staphylococcus aureus* (MTCC 740) (IZD = 12 mm); *Escherichia coli* (MTCC 443) (IZD = 34 mm); *Serratia marcescens* (MTCC 97) (IZD = 36 mm) [91] and CuI nanoparticles can be successfully used against *Escherichia coli* (ATCC 443) and *Staphylococcus aureus* (ATCC 96) [92]. The complex matrix of the extract and plant moieties on the surface of NPs can change the charge of the particles, enhancing the potential effect, and offering multiple applications (medical and environment protection) [93].

Table 2. Application of *Brassica* genus in green nanotechnology.

Vegetal Material	Extraction Method	NP	NPs Characteristics	NPs Applications	Ref.
Medical Applications of Metallic Nanoparticles					
<i>Raphanus sativus</i> var. <i>Longipinnatus</i> leaves	Boiling; solvents: water, dichloromethane and ethanol; t:15 min; 10 g fresh vegetal material	ZnO	The average size —209 nm (DLS); Z potential—−13.7 mV NP—spherical, hexagonal ZnO NPs—66.43 nm (XRD)	Evaluation of anticancer property in A549 cell lines; IC ₅₀ —40 µg mL ^{−1}	[89]
<i>R. sativus</i> root extract	Fresh juice	ZnO	40 nm, Spherical shape,	Activity against <i>Escherichia fergusonii</i> and <i>Escherichia coli</i> (15–23 mm inhibition zone)	[90]
<i>R. sativus</i> leaves	Fungal fermentation of <i>Alternaria</i> sp. isolated from fresh leaves; Inoculation of <i>Alternaria</i> sp.: conical flasks containing 200 mL of fermentation medium (Potato dextrose broth); incubation: T = 28 °C, t = 72 h; Percolation treatment: 10 g of washed and filtered fungal biomass, 100 mL double distilled water, t = 2 h;	AgNP	The average size: 4–30 nm (TEM and AFM), ~80 nm (DLS); Z potential: −16.8 mV NP—spherical shape	Evaluation of antimicrobial effects against <i>Bacillus subtilis</i> (MTCC 441) (IZD = 23 mm), <i>Staphylococcus aureus</i> (MTCC 740) (IZD = 12 mm); <i>E. coli</i> (MTCC 443) (IZD = 34 mm); <i>Serratia marcescens</i> (MTCC 97) (IZD = 36 mm);	[91]
<i>R. sativus</i> roots	Boiling; Solvent: 100 mL water; Vegetal material: dried and powdered;	ZnO	The average size: 15–25 nm (XRD); 25–40 nm (HR-TEM); Z potential: −33 mV; NP—mixed morphology (TEM)	Notable antimicrobial activity against toward microbes isolated from diabetic foot ulcers: <i>Pseudomonas aeruginosa</i> ATCC 27853, MDR— <i>E. coli</i> , <i>S. aureus</i> ATCC 29213, MDR—MRSA, <i>E. coli</i> 36 ATCC 25922, <i>Enterococcus faecalis</i> ATCC 29212, MDR— <i>P. aeruginosa</i> , and MDR— <i>Acinetobacter baumannii</i>	[94]
<i>Brassica oleracea</i> var. <i>botrytis</i> (Cauliflower head and <i>Raphanus sativus</i> tuber	20% (w/v) aqueous extract: vegetal material grounded; solvent: deionized water; Agitating: t = 1h; centrifugation: 10,000 rpm, t = 15 min, T = 4 °C	AgNP	The average size: 4–18 nm (TEM); NP—monodisperse and spherical shape;	Strong antimicrobial activity against Gram-positive and negative bacteria;	[91]

Table 2. Cont.

Vegetal Material	Extraction Method	NP	NPs Characteristics	NPs Applications	Ref.
<i>R. sativus</i> var. <i>longipinnatus</i> Bailey (red radish, GC.Herb.Bot.3296) <i>R. sativus</i> (white radish, GC.Herb. Bot. 3297) <i>B. rapa</i> (turnip, GC.Herb.Bot.3298) <i>B. campestris</i> var. <i>sarson</i> Prain (Saag, GC.Herb.Bot.3299) <i>B. oleracea</i> var. <i>botrytis</i> (Cauliflower, GC.Herb.Bot.3300)	Maceration: 10 g of seeds; solvent: 100 mL of deionized water; T = room temperature;	ZnO-NP	The average size: 50–150 nm (XRD) NP: spherical shape (XRD)	Evaluation of antimicrobial activity against bacterial strains: <i>B. subtilis</i> , <i>S. aureus</i> , <i>Salmonella typhimurim</i> and fungal strains: <i>Aspergillus niger</i> , <i>Fusarium oxysporum</i> and <i>Penicillium digitatum</i> ; Range of IZD: 10–20 mm	[95]
<i>B. oleracea</i> var. <i>capitata</i> f. <i>rubra</i>	5 g of cabbage flakes boiled in 100 mL distilled water.	CuI	Spherical shape, 77.5 nm, band gap energy—2.75 eV	antibacterial activity against <i>E. coli</i> (ATCC 443) and <i>S. aureus</i> (ATCC 96) > 50 µg/mL catalytic activity in Hantzsch reaction- higher yield of 0.9 g of 1,4— dihydropyridine derivatives	[92]
<i>B. oleracea</i>	1 g of vegetal material powder in 90% ethanol (200 mL) at 37 °C, 12 h	Au NPs Ag NPs	Triangular, rod, spherical shaped morphology 24–38 nm (Au), 30–45 nm (Ag)	Inhibition the growth of the tested bacterial and fungal pathogens at the concentration of 50 µg/mL (<i>Salmonella typhi</i> , <i>B. subtilis</i> , <i>E. coli</i> , <i>S. aureus</i> , <i>Pneumocystis</i> sp.)	[96]
Environmental Application for Metallic Nanoparticles					
<i>Brassica oleracea</i> var. <i>capitata</i>	500 mg vegetal material; heated at 60–65 °C for 30 min in 25 mL water	AgNPs	Spherical, polydisperse, and size range between 15 and 80 nm	Catalytic performance of AgNPs by the reduction of 4-Nitrophenol (4-NP) into 4-Aminophenol (4-AP) in the presence of NaBH ₄ in 60 s	[97]
<i>Brassica oleracea</i> var. <i>Capitata</i> F. <i>rubra</i>	100 g vegetal material, microwave extraction, P-900 W; time-2 min.	AuNP	The average size 25 nm; Narrow size distribution and spherical shape	Conversion of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP)	[98]
Multiple Application of Metallic Nanoparticles					
<i>Thlaspi arvense</i> L.	20 g vegetal material; 220 mL de-ionized water; 60 °C; 45 min.	Zinc Oxide nanoflow-ers	70–90 nm (DLS)	Antibacterial properties against <i>E. coli</i> (Gram-negative bacteria)—inhibition zone of 20 ± 0.6 mm Photocatalytic by reducing 4-nitrophenol and methylene blue. Antibacterial activity against <i>E. coli</i> and <i>S. aureus</i>	[93]
Kimchi cabbage	10 g vegetal material in 100 mL double distilled water	AgNP	The average size 10 to 30 n; spherical size	Electrochemical supercapacitor applications: specific capacitance of 424 F/g with an energy density of 14.04 Wh/kg and a power density of 6.41 kW/kg	[99]
In Situ Formation of Metallic Nanoparticles					
<i>B. juncea</i> root	In situ formation	AuNP	5–10 nm Spherical, hexagonal, Triangular		[82]
<i>A. thaliana</i> root	In situ formation	AuNP	20–50 Spherical, triangular		[100]

In addition, Zandi et al. [101] recently published a study about an active coating containing radish leaf extract and can be used as an effective strategy for sweet lemon preservation.

Other types of nano-coatings in which crucifers are used are the following functional antimicrobial and anticorrosion coatings.

Given the composition of cruciferous extracts, they can be successful substituted to replace conventional toxic inhibitors and extend the possibility of “smart coatings” by inducing a response in the coating and/or substrate to improve the inhibition of corrosion.

Li et al. [102] studied a green *Brassica oleracea* L. extract as a novel corrosion inhibitor for Q235 steel in two typical acid media. This extract also had very good results in the inhibition of pipeline steel and mild steel and zinc in acidic media [103,104].

In addition to the extract of *B. oleracea*, it proved to be a good corrosion inhibitor, as well as the extract from *B. campestris*. Caseletto et al. showed that the eco-friendly extract of *B. campestris* is capable of inhibiting Cor-Ten steel corrosion in HCl and NaCl solutions [105].

Lately, with the use of facemasks and visors, eyeglasses become are fogged, and these cause a major challenge in several optical applications that require excellent light transmission characteristics. Ren et al. [106] studied a bioinspired coating with antifogging capabilities. The bioinspired adhesive was based on tannic acid, which is also found in rapeseed but also in other crucifers [107].

Starting with tannic acid, too, Behboodi-Sadabad et al. studied the biomimetic surface coatings base of combinations of polyphenols and catecholamines (e.g., dopamine) from plants [108]. Dopamine is found in different parts of plants of *Brassica species*: broccoli (*Brassica oleracea* var. *italica*) (1 µg/g FW) and Brussels sprouts (*Brassica oleracea* var. *gemmifera*) (1 µg/g FW); in addition, polyphenols are found in abundance in the genus *Brassica* as we showed in the previous chapter; thus, crucifers are a serious candidate for their use for obtaining the biomimetic surface coatings such as anti-fouling coatings referring to the solid surfaces repelling liquids [109], and is related to the chemical composition and the coatings morphology; they have a high potential in various domains such as the food industry.

Anti-fouling coatings [110] in food technology are very useful to reduce or prevent cross-contamination and in marine anti-fouling applications. Zulkifli et al. [111] studied the potential of *B. oleracea* as an anti-fouling agent for mild steel in seawater and, in conclusion, the cabbage extract has potential as an additive in paint.

4. Conclusions and Future Perspectives

In recent years, developing a sustainable use of wastes has gained great interest and has become an attractive research topic all over the world. Moreover, the discovery of new applications of these residues led to new opportunities for plant-derived natural compounds as drug agents with diverse chemical structures and novel mechanisms of action, new approaches for environmental applications, or for other industries. Green synthesis is using bio-reduction that is 100% eco-friendly and is energy-saving and economically viable. This review is useful for developing a new nano-bio-coating with increased antioxidant, antimicrobial, and other important qualities, according to the end users' needs. If the final users and the manufacturer are aware of the main biological activities of *Brassica* vegetables, they will act accordingly considering the final goal.

The biggest challenges for the synthesis of new compounds based on plant extracts are related to the obtaining of controlled morphologies for the nanoparticles, lower minimum inhibitory concentrations for medical applications, decreased toxicity, and bioavailability. The phytosynthesis of nanoparticles usually leads to a reduced toxicity of the NPs and to lower MIC values, due to the contribution of the bioactive compounds acting as capping agents. According to the presented data, metallic nanoparticles presented notable medical applications, such as antimicrobial activity against different bacterial lines or efficiency in environmental approaches. As such, the evaluation of different plant materials is necessary, as different plants can lead to different results regarding the NPs properties. At the same time, the evaluation of plants wastes is promising, both from the nanotechnological point of view, as well as from the perspective of environmental protection and wastes reduction.

Future perspectives must be targeted toward the scale-up processes, from the laboratory level to industry, under the conditions that some extraction methods of bioactive compounds responsible for NP synthesis are already scaled up. In addition, research must be conducted in order to obtain stable formulations with no or less toxic by-products with efficient cost, energy, and reagents consumption. The scale-up of phytosynthesis procedures using cruciferous vegetables wastes would represent a valuable approach for the development of tailored nanomaterials, as the slight modification of the phytosynthesis parameters can lead to the achievement of the desired properties. These approaches will have great promise considering large amounts of wastes produced all over the world due to increased population and globalization.

Overall, major emphasis must be oriented toward the design of the next generation of nanoparticles with special properties and applications, as well as for their application

in day-by-day products. Given the importance of this application field, the research and development of nanocoatings based on natural extracts has been continuously increasing. However, advances related to nanomaterials biofunctionalization are crucial to achieve a further high specificity in different areas.

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Abbreviations

spp.	subspecies
var.	varieties (in Latin: varietas)
LDL	low-density lipoprotein
COVID 19	Coronavirus disease 2019
AgNPs	silver nanoparticles
ZnO	zinc oxide
MTCC	Microbial Type Culture Collection
IZD	inhibition zone diameter
IC50	the half maximal inhibitory concentration
A549	cell lines
CuI	copper iodide
XRD	X-ray diffraction analysis
nm	nanometer
TEM	Transmission electron microscopy
HR- TEM	High-resolution transmission electron microscopy
AFM	Atomic force microscopy
DLS	Dynamic light scattering
Z potential	zeta potential
°C	degrees Celsius
h	hours
mL	milliliter
mV	millivolt
MDR	multidrug-resistant
w/v	mass concentration of solution is expressed as % w/v for weight per volume
rpm	rotation per minute
min.	minutes
eV	electron Volt
Au	gold
Ag	silver
NaBH ₄	Sodium borohydride
W	Watt
<i>E. coli</i>	<i>Escherichia coli</i>
<i>S. aureus</i>	<i>Staphylococcus aureus</i>
AuNP	gold nanoparticles
µg	microgram

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