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Green synthesis of nanoparticles from olive oil waste for environmental and health applications: A review

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ABSTRACT

Environmental degradation is a growing concern, driving researchers to explore eco-friendly nanoparticle (NP) synthesis, for diverse applications. Within this context, the employment of olive oil waste (OOW) as a green source for the synthesis of NPs has emerged as a viable alternative to conventional techniques. The olive industry has a significant impact in the Mediterranean region, and alongside it, comes the OOW, where most of it cannot be left untreated. In the present review, a comprehensive overview of the NPs' green synthesis derived from OOW and its potential applications in both environmental and health areas have been assessed, outlining its major challenges and potential outcomes for future research. Both principles and methods of green NPs synthesis were also explored, focusing on the unique properties of OOW as an effective agent for reduction and stabilization, as well as the characterization techniques used for characterizing the synthesized NPs. The OOW-derived NPs can have a wide variety of environmental applications including water purification, pollutant degradation, and remediation of contaminated environments. In the health field, the OOW applications include drug delivery systems, antimicrobial activity and cancer therapy. These OOW NPs have been successfully used as efficient drug delivery vehicles to cancer cells, enhancing treatment outcomes and potentially minimizing side effects. However, it is imperative to point out the importance of performing in-depth toxicity assessments, particularly at higher concentrations of NPs.

1. Introduction

In recent years, there have been growing concerns over environmental degradation, which led researchers to explore innovative approaches for more sustainable practices, like the synthesis of nanoparticles (NPs), which has gained significant attention due to its potential for addressing pressing environmental and health challenges [1,2]. Nanotechnology and green chemistry have aligned, utilizing renewable resources to produce advanced nanomaterials with a wide range of applications [3,4], in a process called "green synthesis". In it, organic compounds and their biological pathways are used to create nanostructured materials without toxic waste, offering several benefits like reduced environmental impact, cost-effectiveness, and biocompatibility, making them a promising alternative for sustainable nanomaterial production [5,6].

The olive oil industry, particularly in the Mediterranean region, produces a substantial amount of waste. It is estimated that for every litre of olive oil produced, around 1.1–1.3 litres of olive mill wastewater (OMWW) and 0.5–1 kg of solid waste (pomace) are generated [7,8]. This waste poses environmental burdens due to its high organic content and potential toxicity. However, olive oil waste (OOW) can be used as a green source for nanoparticle synthesis [4,9–11]. These extracts contain valuable components, such as polyphenols, lipids, and other bioactive compounds, which can serve as effective reducing and stabilizing agents for nanoparticle formation [12–14]. Ultimately, merging green synthesis methods with waste valorisation can lead to more sustainable and

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environmentally responsible technological advancements that positively impact human health and the planet.

Conventional methods for synthesizing NPs typically involve chemical and physical processes, such as chemical vapour deposition (CVD), sol-gel methods, and ball milling. While effective, these methods often require high energy inputs, hazardous chemicals, and generate significant waste, posing environmental and health risks [15,16]. Green synthesis offers a promising alternative by using benign reagents, renewable resources, and energy-efficient methods, thus minimizing adverse environmental effects and aligning with sustainability principles [17,18].

Despite the promising potential of OOW in NP synthesis, there is a notable gap in the comprehensive understanding of the mechanisms by which these bioactive compounds function in NP formation. Additionally, there is a need for standardized protocols and scalable methods to ensure consistent and reproducible results. This study seeks to fill these gaps by providing detailed insights into the underlying mechanisms, optimizing synthesis processes, and exploring the diverse applications of OOW-derived NPs.

The primary objective of this review is to provide a comprehensive overview of the green synthesis of NPs from OOW and to explore their potential applications in environmental and health-related fields. By examining the principles and methods of green synthesis, the unique properties of OOW as reducing and stabilizing agents, and the characterization techniques used to analyse synthesized NPs, the present work aims to highlight the advantages and challenges of using OOW in NP synthesis. Additionally, it also discusses the practical applications of OOW-derived NPs in water purification, pollutant degradation, drug delivery systems, antimicrobial activity, and cancer therapy.

2. Green synthesis of NPs

In recent times, with a growing focus on sustainable and eco-friendly methods, the process of synthesizing NPs has made significant progress [3], with green synthesis being an innovative and sustainable alternative for creating nanoscale materials with minimal ecological and health impacts [19,20]. In this method, sustainable and environmentally friendly techniques are used to fabricate different materials, including NPs [21,22]. Its primary goal is to limit the environmental impact of the synthesis process by using eco-friendly reagents, renewable resources, and energy-efficient methods and reducing or eliminating the generation of hazardous by-products [5,23].

2.1. Principles of green synthesis

Green synthesis aligns with sustainability principles, aiming to satisfy current needs while safeguarding the capacity of future generations to meet their own [24]. These principles involve using resource-efficient utilization and minimizing waste [18]. Furthermore, it emphasizes using renewable and sustainable resources, such as plant extracts, microorganisms, or agricultural waste, as raw materials for synthesis, as these resources are readily available and do not deplete finite reserves [25,26]. Green synthesis methods are designed to minimize adverse environmental effects, including reducing energy consumption, lowering greenhouse gas emissions, and minimizing the generation of toxic waste products [27]. Their methodologies prioritize safety by replacing toxic or hazardous chemicals with environmentally benign alternatives while safeguarding the health of researchers and reducing the risk of environmental contamination [17,18]. Green synthesis key principles are summarized in Fig. 1.

Conventional synthesis methods often yield hazardous by-products that pose risks to human health and the environment [15,16]. For example, using strong reducing agents like sodium borohydride can lead to the release of toxic gases and hazardous waste disposal challenges [28–30]. In contrast, green synthesis methods prioritize the use of benign, like water or ethanol, which have low toxicity and are biodegradable, or naturally derived reducing agents (such as plant extracts or microorganisms) to convert metal ions into NPs [31–33]. These agents play a dual role, reducing metal ions to form NPs and stabilizing them to prevent aggregation [34,35]. For instance, plant extracts rich in polyphenols or microbial cells can effectively reduce metal ions to NPs without producing harmful by-products. This minimizes waste disposal's ecological and health risks [36,37].

Fig. 1. Key principles of green synthesis.

Green synthesis advocates the use of renewable resources as raw materials. These resources are abundant, sustainable, and do not deplete finite reserves [38,39]. This emphasis on renewability aligns with the principles of circular economy and responsible resource management [40]. Conventional synthesis often relies on the extraction or use of non-renewable resources, such as petroleum-derived chemicals or rare metals [27], which can lead to resource depletion and environmental degradation [41,42]. In turn, green synthesis values the use of renewable resources. For example, agricultural waste, such as rice husks or fruit peels, can serve as abundant and sustainable sources for nanoparticle synthesis [43,44]. Moreover, microbial organisms like bacteria and fungi play pivotal roles in green synthesis. They possess the natural ability to reduce metal ions and participate in the synthesis of NPs, all while operating within the boundaries of sustainability [5,45,46].

2.2. Methods of green synthesis

NPs synthesized through a biological system offer several advantages, including non-toxicity, high-yield production, ease of scaling up, and well-defined morphology [47] and are, consequently, emerging as an innovative method for nanoparticle production. This green synthesis technique has proven effective in producing NPs that are safe, eco-friendly and easy to handle [48–52]. Based on the nanoparticle formation method, green nanoparticle synthesis can be classified into two categories, known as the "top-down" and "bottom-up" approaches, as seen in Fig. 2. In the "top-down" approach, NPs initially have larger dimensions, which requires mechanical methods or the addition of acids to reduce their size. Typically, the top-down approach necessitates sophisticated techniques such as thermal decomposition, mechanical/ball-milling methods, lithographic methods, laser ablation, and sputtering [53–55]. In contrast, the "bottom-up" approach starts at the atomic level, with the formation of molecules, offering a fundamentally different approach, and its methods are carried out using

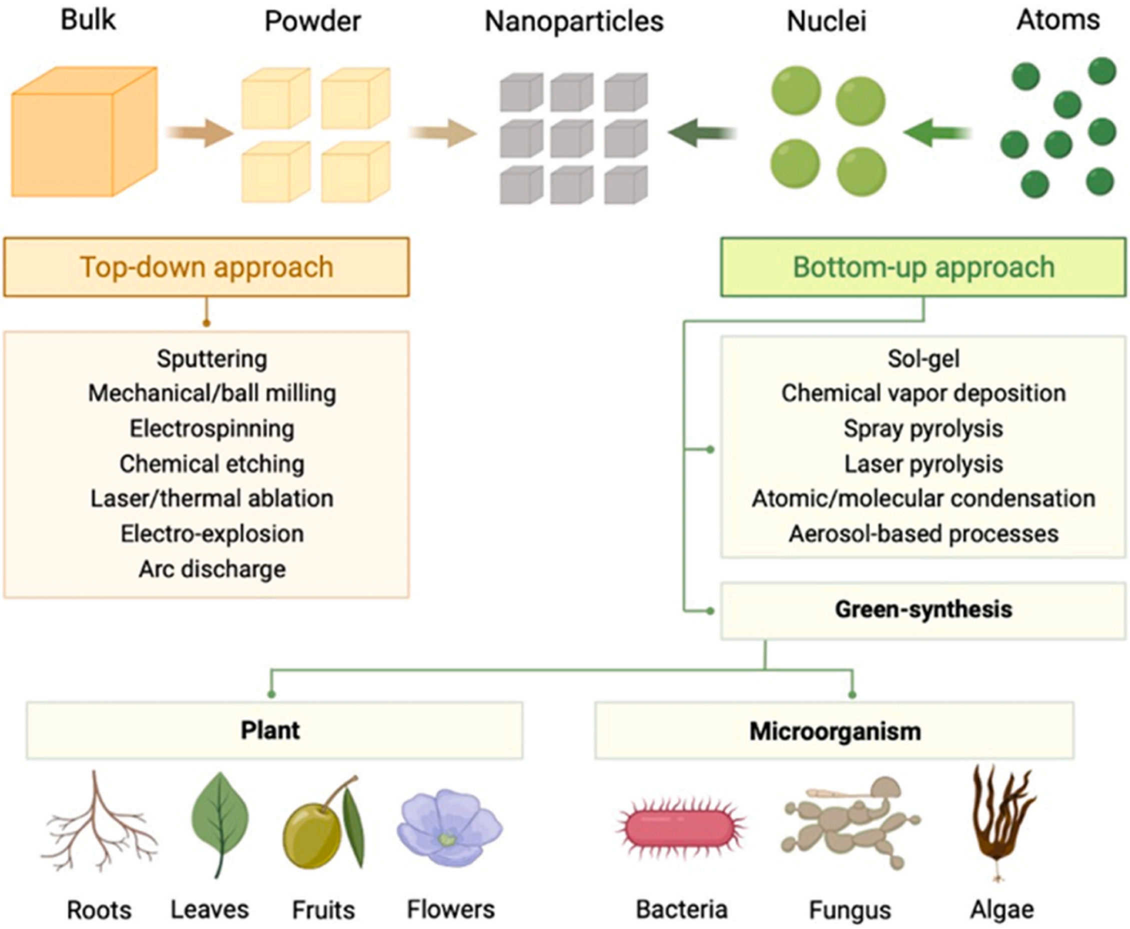

Fig. 2. Summary of the top-down and bottom-up approaches to synthesising NPs.

various techniques, including chemical vapor deposition (CVD), sol–gel methods, spinning, and pyrolysis [48,56,57].

Green synthesis comprises diverse approaches, which include biological, chemical, and physical methodologies [58,59]. This diversity within green synthesis gives researchers flexibility in the synthesis process, enabling them to create nanomaterials with several properties (such as composition, shape, and size). Furthermore, each approach can use different renewable resources, allowing the selection of the most environmentally friendly method for a given application.

2.2.1. *Biological approaches*

Biological methods have gained prominence in green nanoparticle synthesis due to their inherent eco-friendliness and versatility [59–63]. These approaches harness the capabilities of living organisms, or their components, and natural extracts for nanoparticle production [60,64]. Those include:

- **Microorganisms:** Microorganisms like bacteria and fungi are employed as eco-efficient nano factories. Enzymatic processes can be used to convert metal ions into NPs. This biological synthesis route offers precise control over nanoparticle size and shape and ensures excellent stability, making it a preferred choice for various applications [65–67].
- **Plant Extracts:** Plants are nature's treasure troves of bioactive compounds, notably polyphenols. These extracts serve a dual role as effective reducing and capping agents. When incorporated into the synthesis process, they facilitate the controlled formation of NPs with tailored characteristics. Beyond their synthesis capabilities, plant-derived NPs often exhibit biocompatibility, opening doors to various biomedical applications [68–70].

Fig. 3 is a schematic illustration of NPs' green synthesis from different living organisms. Plant extracts are utilised in the 'Plant Synthesis' pathway, offering a 'green' approach to nanoparticle production. The 'Bacteria Synthesis' method capitalizes on bacterial cultures, crucial in reducing metal ions to obtain NPs. On the other hand, the 'Fungi Synthesis' process leverages fungal hyphae in growth media to facilitate the reduction of metal ions. All these routes culminate in a common pathway termed 'Synthesis of Metal NPs,' symbolizing the convergence of these natural agents. This unified pathway ultimately produces stable and capped NPs with high yield, highlighting the immense potential of biologically mediated nanoparticle synthesis methods.

2.2.2. *Chemical approaches*

Chemical approaches in green synthesis emphasize replacing conventional hazardous substances with eco-friendly alternatives derived from renewable sources. This transition represents a pivotal step in minimizing the environmental footprint of nanoparticle production [27,71]. Some strategies include:

- **Greener chemicals:** Green synthesis employs eco-friendly chemicals that reduce the toxicity associated with conventional synthesis. For instance, natural sugars, such as glucose or starch, can serve as reducing agents for metallic nanoparticle synthesis. These renewable resources facilitate the reduction of metal ions and the overall environmental impact [48,71].

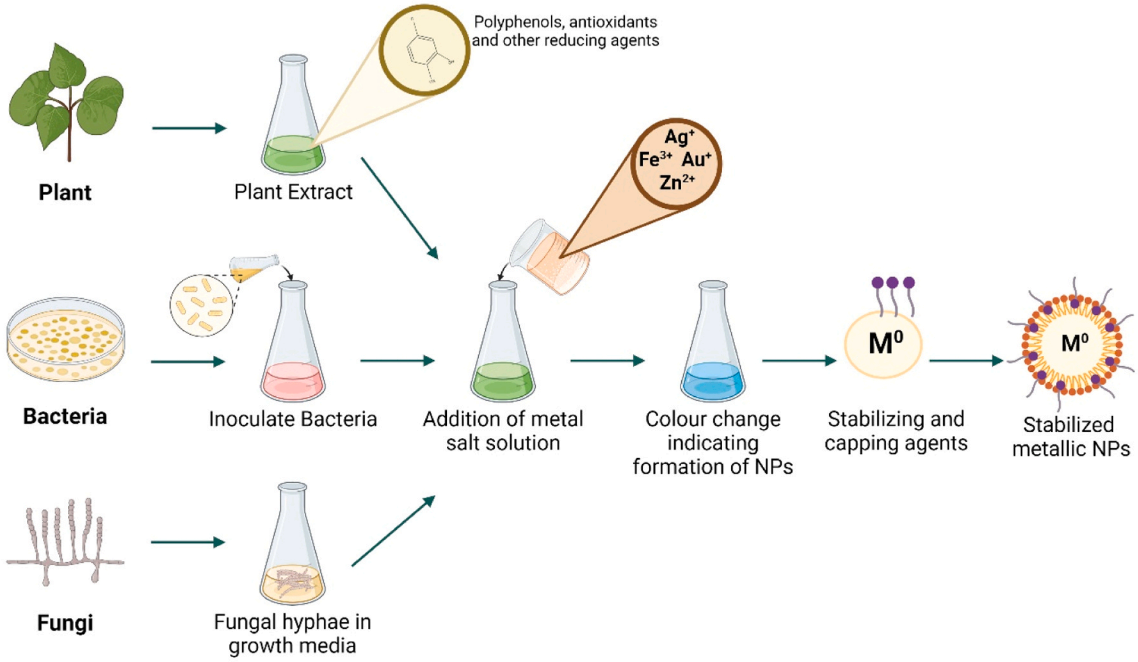

Fig. 3. Schematic representation for green synthesis of metallic NPs from different living organisms.

- **Biodegradable solvents:** Hazardous organic solvents are replaced with biodegradable options like water or ethanol. This substitution not only enhances the safety of the synthesis process but also contributes to reducing the release of volatile organic compounds (VOCs) into the environment [72]. For instance, in the green synthesis of silver NPs (AgNPs), water is used as a solvent where the polyphenols present in olive mill wastewater (OMWW) act as reducing agents, transforming Ag^+ ions into AgNPs while stabilizing the formed particles [73]. Similarly, in the synthesis of copper oxide NPs (CuO), ethanol serves as a solvent, where bioactive compounds from olive pomace reduce copper ions to CuO, with ethanol facilitating in maintaining colloidal stability [74].

2.2.3. *Physical approaches*

Physical methods in green synthesis prioritize energy efficiency and sustainability, leveraging innovative technologies to produce NPs with minimal environmental impact [75]. Some examples of those methods include:

- **Microwave irradiation**: Microwave-assisted synthesis is an energy-efficient approach that selectively heats reaction mixtures, reducing the energy required for heating the entire system. This technique accelerates reactions, leading to shorter synthesis times and lower energy consumption [76].
- **Ultrasound-assisted synthesis**: Ultrasound waves induce cavitation in liquid media, enhancing mixing and mass transfer rates. This results in the rapid and uniform synthesis of NPs. Ultrasound-assisted synthesis is energy-efficient and offers precise control over particle size and morphology [77].

2.3. *Characterization techniques*

Regardless of the green method used to create NPs, their characterisation is critical in determining their attributes and quality. Spectroscopy, microscopy, diffraction, and magnetic resonance procedures are examples of characterisation techniques. The data they provide is critical for assessing the physicochemical and structural aspects of NPs, allowing for a better understanding of the mechanisms behind nanoparticle creation employing organisms [78,79]. As a result, in Table 1 are represented some extensively used characterisation approaches and the information they provide.

A schematic illustration of the steps involved in the green synthesis of silver NPs from vegetable peels is shown in Fig. 4. To determine the suitability of silver particles for their final applications, the silver NPs undergo a series of characterization techniques following their synthesis, including UV-Vis spectroscopy, FESEM, XRD, and ATR-IR analysis [91].

2.4. *Advantages and disadvantages*

Table 2 presents a comprehensive overview of the main pros and cons of green synthesis, with their source Reference (Ref.). Its main advantages include minimized waste generation, lower energy consumption, and using renewable resources. Nonetheless, it is crucial to recognize that green synthesis has inherent challenges, including variability in outcomes and limitations in scalability. It is also noteworthy that the advantages and disadvantages are context dependent. Factors such as the specific green synthesis method, the materials involved, and the intended application can shape the perception of the pros and cons. Ultimately, researchers choose green synthesis when the benefits of reduced environmental impact, safety, and sustainability outweigh any potential drawbacks.

The advantages of green synthesis for NPs are notable, providing sustainable and efficient approaches to advanced material production. However, to focus on the advantages inherently linked to waste utilization, it's crucial to highlight this approach's pivotal role in optimizing natural resource use and reducing environmental impact. The transformation of waste, such as olive oil, into valuable NPs represents a step toward sustainability that deserves special attention. Despite these gains, the utilization of waste for nanoparticle synthesis also presents challenges, such as the need for process optimization and obtaining high-quality waste to ensure the purity of the resulting NPs.

3. Olive oil waste in nanoparticle synthesis: multifunctional roles

The processing of olive oil is a meticulous and time-honored tradition that involves several steps [97]. It begins with the delivery of the

Table 1
Techniques commonly used to characterize the NPs.

Technique	Purpose	Outcomes	Ref.
Attenuated Total Reflectance Infrared Spectroscopy (**ATR-IR**)	Studying chemical composition and surface properties	Information about functional groups, chemical bonds, surface modifications and the presence of organic coating and treatments	[80]
Brunauer, Emmett and Teller Theory (**BET**)	Surface area measurement Pore size distribution Surface porosity characterization Adsorption isotherm studies	Specific surface area; Pore volume; Pore size distribution curve; Adsorption isotherm data	[81]
Dynamic light scattering (**DLS**)	Particle size measurement Hydrodynamic radius determination Aggregation and stability studies Polydispersity analysis	Particle size distribution; Hydrodynamic radius data; Intensity autocorrelation function; Stability assessments	[82]
Energy Dispersive X-ray Spectroscopy (**EDX**)	Elemental analysis; Chemical characterization.	Elemental composition; Qualitative and quantitative analysis	[82]
Field Emission Scanning Electron Microscopy (**FESEM**)	High-resolution imaging	Visualization of surface morphology, topography, and features like roughness and porosity.	[83]
Fourier Transform Infrared Spectroscopy (**FTIR**)	Analysing surface chemistry	Chemical composition, identification of functional groups on the surface, bonding, and molecular interaction; Surface modifications	[84]
Photoluminescence (**PL**)	Studying the optical properties and electronic structure	Emission spectra; Information about electronic states; Defect analysis	[85]
Scanning Electron Microscopy (**SEM**)	Imaging of nanoparticle morphology	Surface imaging, analysis of external features, size distribution, and surface characteristics of NPs	[86]
Transmission Electron Microscopy (**TEM**)	Visualizing NPs at high resolution	Individual nanoparticle visualization; Structural characterization (size, shape, and morphology)	[87]
UV-Visible Spectroscopy (**UV-Vis**)	Determining optical properties	Study of electronic transitions, plasmonic properties. Measurement of absorbance, extinction, and wavelength-dependent behaviour	[88]
X-ray photoelectron spectroscopy (**XPS**)	Surface analysis, element identification, interface characterization, oxidation state investigation	Photoelectron spectra; Elemental identification, depth profile; Qualitative and quantitative chemical analysis	[82]
X-ray Diffraction (**XRD**)	Determining crystalline structure	Identification of crystalline phases and lattice parameters through analysis of X-ray diffraction patterns	[89]
X-ray Fluorescence (**XRF**)	Determining the elemental composition of materials	Elemental composition; Qualitative and quantitative analysis	[90]

harvested olives to the processing facility. Once received, the olives undergo washing to remove any debris or impurities. The cleaned olives are then crushed into a paste, which is subsequently malaxed, or mixed, to facilitate the coalescing of the oil droplets [97,98].

The extraction of olive oil primarily employs three distinct processes: the two-phase decanter, the three-phase decanter, and the traditional press method [97]. In the two-phase decanter, water is added to the paste, and the resulting mixture is centrifuged to separate the oil and water from the solid residue [99,100]. On the other hand, the three-phase decanter incorporates an additional step, which involves the separation of oil, water, and solid residue [101]. Lastly, the traditional press method relies on mechanical pressure to extract oil from the olive paste [102]. Throughout these extraction processes, various waste and by-products are generated [103]. In the two-phase decanter, the solid residue contains water and some residual oil, typically used as animal feed or fertilizer [104]. In the three-phase decanter, the solid residue, which is drier than the one found in the two-phase process, still serves as a valuable by-product for agricultural use [101]. Nevertheless, the olive mill wastewater (OMWW) generated during this procedure presents environmental challenges due to its considerable organic content and demands appropriate treatment. The traditional press method yields a wetter solid residue with higher oil content, which can be utilized similarly to the by-products of the other processes [105]. Fig. 5 demonstrates the olive oil processing and the by-products produced during it.

The production of olive oil produces significant waste, consisting of pomace, olive mill wastewater, and leaves, collectively known as olive oil waste (OOW) [107]. Within this unassuming waste lies a wealth of untapped potential. It is rich in polyphenols, lipids, and bioactive compounds [108–110]. Fig. 6 illustrates the compositions of various by-products of olive oil production, detailing the percentage of water, organic compounds, and inorganic compounds. For instance, olive mill wastewater (OMWW) comprises 82–95 % water, 1.5–18 % organic compounds (including polyphenols, flavonoids, and tannins), and 3 % inorganic compounds (like potassium, sodium, and phosphates). Olive pomace contains 60–70 % water, 25–35 % organic compounds (such as polyphenols, fatty acids, and terpenes), and 5–10 % inorganic compounds. Olive leaves have 50–60 % water, 30–40 % organic compounds (including polyphenols, flavonoids, and terpenes), and 5–10 % inorganic compounds. Olive oil residue contains 40–50 % water, 45–55 % organic compounds (like fatty acids and polyphenols), and 2–5 % inorganic compounds. These constituents, typically discarded during olive oil extraction, have recently emerged as invaluable resources at the nexus of sustainability and nanotechnology. Researchers have harnessed the diverse composition of olive oil waste extracts, turning them into key players in the NPs' green synthesis. Serving as reducing and stabilizing agents, these compounds breathe new life into what was once considered waste material, offering a sustainable and eco-friendly avenue for tailoring NPs with precise characteristics for various applications.

As mentioned, olive oil production generates substantial waste, rich in potentially valuable components [102]. Of particular interest are polyphenols, lipids, and other bioactive compounds within these waste extracts [112]. Roselló-Soto et al. [97] have reviewed the high-added values compounds from the various by-products obtained during the production of olive oil.

Polyphenols, abundant in olive oil waste, are particularly

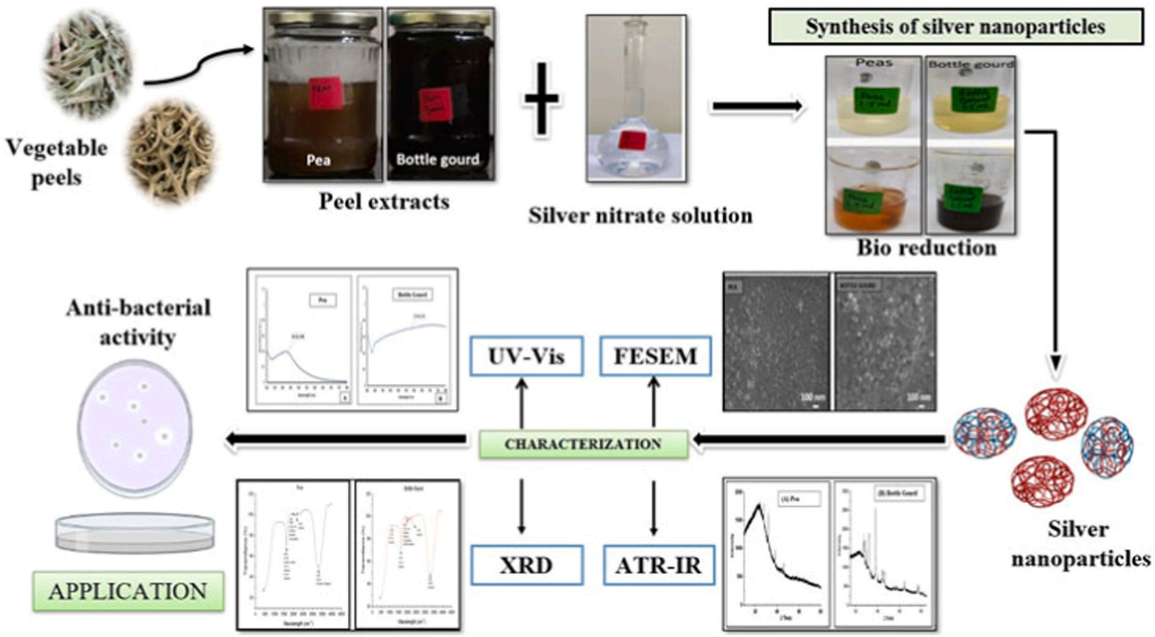

Fig. 4. Illustration of the synthesis, characterization, and antibacterial activity of silver NPs obtained from the peels of peas (*Pisum sativum*) and bottle gourds (*Lagenaria siceraria*). Obtained from [91].

Table 2
Advantages and disadvantages of NPs green synthesis.

Advantages	Ref.	Disadvantages	Ref.
Environmentally Sustainable: Reduces environmental impact by using renewable resources and eco-friendly reagents.	[23]	Variability in Outcomes: Green synthesis can sometimes lead to variable nanoparticle properties due to the natural variability of bio-derived agents.	[37]
Reduced Energy Consumption: Energy-efficient methods and lower reaction temperatures minimize energy demands.	[92]	Limited Scalability: Scaling up green synthesis for industrial applications can be challenging, and the process may not be as easily adaptable as conventional methods.	[93]
Minimized Waste Generation: Produces fewer by-products and reduces the burden on waste disposal systems.	[94]	Longer Reaction Times: Green synthesis methods may require longer reaction times than conventional methods, affecting production efficiency.	[95]
Biocompatible and Non-Toxic: Utilizes natural reagents and solvents, making the resulting NPs safer for environmental and health applications.	[72]	Limited Range of Materials: Some materials may not be suitable for green synthesis, limiting the choice of NPs that can be produced.	[71]
Potential for Multifunctionality: Green synthesis can yield NPs with unique surface properties suitable for multifunctional applications.	[33]	Need for Optimization: Green synthesis methods often require optimization for specific applications, which can be time-consuming.	[96]
Enhanced Sustainability: Aligns with sustainability goals and reduces the overall ecological footprint of nanoparticle production.	[37]	Complex Characterization: Characterizing NPs synthesized through green methods can be more difficult due to the involvement of biological or natural agents.	[95]

noteworthy for their potent antioxidant properties [113]. In green synthesis, these compounds stand out as efficient reducing agents. Polyphenols initiate redox reactions when introduced into a reaction mixture of metal ions [114]. They act as electron donors, facilitating the reduction of metal ions to their metallic state, a critical step in nanoparticle formation. The versatile nature of polyphenols allows them to modulate the size, shape, and characteristics of the NPs being synthesized [115,116]. Beyond their reducing prowess, polyphenols play an equally crucial role in nanoparticle stabilization. They form a protective layer on the nanoparticle surfaces, preventing agglomeration and ensuring colloidal stability [117,118]. This dual functionality makes polyphenols invaluable contributors to the green synthesis process. A study conducted by *Orive et al.* [13] discovered that a highly rich polyphenols extract (up to 17.73 mg g^{-1}) can easily be obtained from extracted olive pomace (EOP) by using water as a unique solvent at ambient temperature, which is an advantage for further food, nutraceutical and pharmaceutical industry applications.

Lipids, another prominent component of olive oil waste extracts, complement polyphenols in nanoparticle synthesis [119]. While polyphenols focus on reduction and surface stabilization, lipids are effective capping agents. The unique amphiphilic nature of lipids, characterized by hydrophilic and hydrophobic regions, makes them adept at forming a protective shell around NPs [120]. In this arrangement, the hydrophilic heads of lipids interact with the surrounding aqueous environment, while the hydrophobic tails orient themselves towards the nanoparticle core. This self-assembly creates a stable bilayer or shell around the NPs, preventing their uncontrolled aggregation [121]. Furthermore, lipids in the reaction mixture offer opportunities for controlled growth and morphology control of the synthesized NPs, enhancing their versatility in various applications [120].

In addition to acting as reducing and stabilizing agents, compounds found in olive oil waste can also function as catalysts in the synthesis of NPs. The presence of polyphenols, for example, can enhance the catalytic activity during the formation of NPs, facilitating the process without altering the oxidation state of the metal ions involved [44]. This catalytic role is crucial as it allows for more efficient and controlled synthesis of NPs, which is particularly important in applications requiring precise nanoparticle characteristics.

Olive oil waste, such as olive leaf extracts and olive pomace, contains bioactive compounds like polyphenols, flavonoids, and terpenoids. These compounds often play dual roles. While they are efficient reducing agents, they also act as stabilizing agents, forming a protective layer around NPs to prevent agglomeration and maintain colloidal stability. For instance, silver NPs (AgNPs) synthesized using olive leaf extract leverage these bioactive compounds for both reduction and

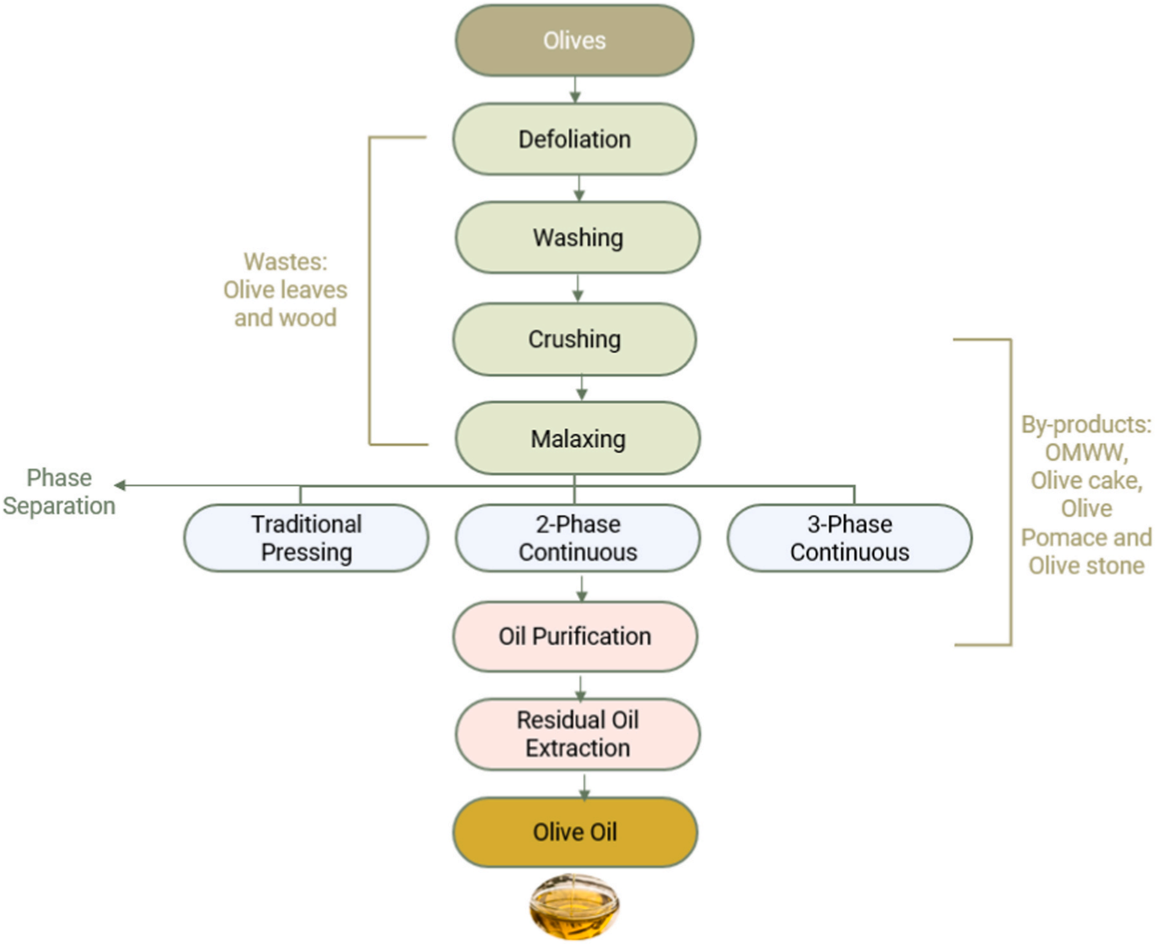

Fig. 5. The residues and by-products produced during the olive oil manufacturing process. Adapted from [106].

stabilization, ensuring efficient synthesis and stability of the NPs [122]. Additionally, olive oil industry residues were utilized to create Fe-supported catalysts for Fenton-like treatment of olive mill wastewater, showcasing promising catalytic performance and potential for circular economy integration [123].

Table 3 describes the various sources of olive oil waste, their phytochemical composition, the mechanisms involved in NP's synthesis, their roles in the synthesis process and their physical-chemical properties. Their main phytochemical groups include polyphenols, flavonoids, terpenoids, and organic acids [124]. Polyphenols, such as oleuropein and hydroxytyrosol, are abundant and act as potent antioxidants and reducing agents. Flavonoids, including quercetin and luteolin, contribute to the reduction and stabilization of NPs. Terpenoids, found in smaller quantities, also aid in stabilization and provide unique surface properties to the NPs [54]. Additionally, organic acids like oleic and linoleic acids serve as capping agents, enhancing the colloidal stability of the synthesized NPs [125]. This diverse phytochemical composition, their high antioxidant activity and lipid content make OOW a versatile and valuable resource for the eco-friendly synthesis of NPs.

OOW may contain other bioactive compounds, including vitamins, organic acids, and minor phytochemicals [12]. While their roles in nanoparticle synthesis are still under exploration, these compounds contribute to the reaction mixture's overall reducing capacity and stability. Some may act as synergistic agents, enhancing the reduction kinetics and influencing the characteristics of the resulting NPs [139]. As research advances, a more comprehensive understanding of these additional bioactive components will likely emerge, further enriching the potential of olive oil waste in green nanoparticle synthesis.

Table 4 lists various NPs synthesized from OOW, detailing the source of waste, methods used, size and morphology of the NPs and their main applications. These NPs exhibit a variety of sizes and morphologies, predominantly spherical. Their main applications include antimicrobial treatments, water purification, soil enhancement, drug delivery, and energy storage.

4. Environmental applications

This section explores the environmental applications of green NPs synthesized from olive oil waste. These innovative nanomaterials are a significant promise to pressing environmental challenges, such as water pollution and contamination. By harnessing the unique properties of these NPs, we can advance sustainable solutions for environmental remediation. Fig. 7 summarizes the main applications that will be discussed in the next sections where, based on the NPs from OOW properties, different applications will be developed for water purification and pollutants degradation and remediation of contaminated environments.

4.1. Water purification and pollutant degradation

NPs derived from olive oil waste extracts offer a sustainable approach to water purification. Their inherent properties, such as size and surface chemistry, effectively remove contaminants from water sources. They also exhibit catalytic and photocatalytic properties, which can play an essential role in the degradation of environmental pollutants, including persistent organic pollutants (POPs) and hazardous chemicals (see Fig. 7).

Ramazanli and Ahmadov [132] studied a novel approach to synthesising silver NPs (AgNPs), which have unique properties and

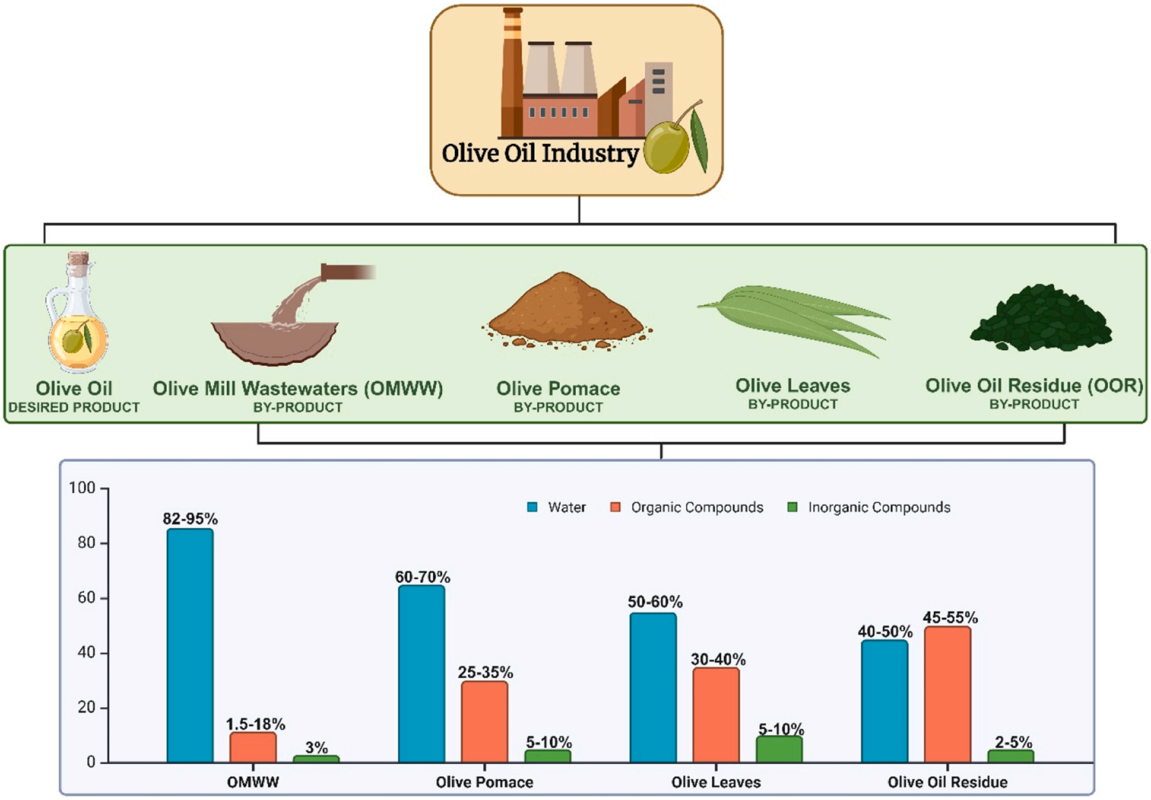

Fig. 6. Composition and by-products of the olive oil industry. Adapted from [111].

Table 3

Composition, Mechanisms, and Properties of OOW in Green Synthesis of NPs.

OOW	Phytochemical Groups	Synthesis Mechanisms	Role in Green Synthesis	Functional Properties	Ref.
Olive Mill Wastewaters (OMWW)	Polyphenols (e.g., hydroxytyrosol, tyrosol, verbascoside), flavonoids (luteolin, apigenin), organic acids (oleic acid, linoleic acid), tannins	Redox reactions, chelation, stabilization	Reduction and stabilization of metal ions to form NPs	High antimicrobial and antioxidant activity; Moderate acidity; Rich in organic content	[126–128]
Olive Pomace (OP)	Polyphenols (oleuropein, hydroxytyrosol), flavonoids (quercetin, rutin), terpenoids, fatty acids (oleic acid, palmitic acid), sterols (β-sitosterol)	Reduction, stabilization, capping	Acts as a reducing agent and stabilizer in NP synthesis	High organic content; Moderate to high lipid content; Fibrous texture	[74,127, 129]
Olive Leaves (OL)	Polyphenols (oleuropein, hydroxytyrosol), flavonoids (luteolin, apigenin), tannins, oleuropein, secoiridoids	Reduction, capping, chelation	Provides reducing agents and capping agents for NPs	High phenolic content; Rich in flavonoids and terpenes; Significant antioxidant properties	[130–132]
Olive Oil Residue (OOR)	Polyphenols (oleuropein, hydroxytyrosol), fatty acids (oleic acid, linoleic acid), squalene	Reduction, stabilization, capping	Functions as a capping agent and in the reduction of metal ions	High lipid content; Rich in polyphenols and fatty acids; High viscosity	[7,130]
Olive Cake (OC)	Polyphenols (oleuropein, hydroxytyrosol), fatty acids (oleic acid, palmitic acid), sterols (β-sitosterol), terpenoids	Reduction, chelation, stabilization	Acts as both reducing and stabilizing agent for NPs	High fiber and lignin content; Moderate to high lipid content; Rich in sterols and terpenes	[109,133, 134]
Olive Stones (OS)	Lignin, cellulose, hemicellulose, phenolic compounds	Carbonization, pyrolysis	Used for carbon-based nanoparticle synthesis	High cellulose and lignin content; Rigid structure; Rich in phenolic compounds	[135]
Olive Leaf Extract (OLE)	Polyphenols (oleuropein, hydroxytyrosol, tyrosol), flavonoids (luteolin, apigenin), tannins, secoiridoids	Redox reactions, chelation, capping	Reduction of metal ions, providing stability to NPs	High phenolic and flavonoid content; Significant antioxidant properties; Moderate acidity	[74,136, 137]
Extracted Olive Pomace (EOP)	Polyphenols (oleuropein, hydroxytyrosol), lignans (pinoresinol, acetoxypinoresinol), secoiridoids (oleuropein aglycone)	Reduction, stabilization, chelation	Reduction and capping in NP synthesis	High in lignans and secoiridoids; Rich in polyphenols; Moderate lipid content	[129,138]

potential to remove pollutants from water sources, using olive leaf extract as a reducing agent. The authors investigated the impact of varying the extract-to-$AgNO_3$ (silver nitrate) ratio on nanoparticle synthesis. It was determined that the optimal ratio for synthesizing AgNPs was 1:3. Also, a colour change in the solution was observed throughout the synthesis process, which is associated with forming AgNPs. Furthermore, UV-Vis spectroscopic analysis confirmed the successful synthesis, as it revealed absorption peaks within the 405 nm – 425 nm range, allowing for quantitative monitoring of the NPs. Subsequent SEM analysis offered a closer look at the synthesized AgNPs, unveiling spherical shapes, polydispersity, and sizes ranging from 7.12 nm to 18.8 nm (Fig. 8). This approach has immense potential in green

Table 4
NPs Synthesized from Olive Oil Waste.

NPs	Source of waste	Methods	Size (nm)	Morphology	Applications	References
Ag	Dry olive leaf extract	Green synthesis	20–25	Spherical	Antimicrobial	[140]
Ag	Extra Virgin Olive Oil	Green synthesis	25.45–42.30	Semi-cubic	Antimicrobial	[141]
Ag	OLE	Green synthesis	7.12–18.8	Spherical	Antimicrobial, Water purification	[132]
Ag	OLE	Green synthesis	5–14	Spherical	Antibacterial, Antioxidant, Cytotoxic, Nutraceutical	[142]
Ag	OLE	Green synthesis	28	Spherical	Antimicrobial, Anticancer	[143]
Ag	OLE	Green synthesis	257	-	Drug delivery, Anticancer	[144]
Ag	OMWW	Green synthesis	30, 50	Spherical	Biomedical	[145]
Ag	OMWW, Olive stone extract	Green synthesis	12.87	Spherical	Antibacterial	[128]
Ag	OMWW extract	Green synthesis	-	Spherical	Biosynthesis of AgNPs	[146]
Ag	OP	Green synthesis	20–25	Spherical	Antioxidant, Antimicrobial	[147]
Au	OMWW	-	5–20	Spherical	Extraction of bioactive compounds	[148]
Au	Olive solid waste	-	0.9–2.8	Spherical	Catalytic activity	[149]
Carbon-encapsulated iron (CE-nFe)	OMWW	Hydrothermal carbonisation	4	Spherical, surrounded by a thin layer of carbon (1 nm)	Removal of heavy metals from water	[150]
CuO	OLE	Green synthesis	-	Oval-shaped	Solar cells, Photocatalysis, Superconductivity, Solar energy harvesting, Energy storage (lithium-ion batteries), Antimicrobial devices	[74]
Fe	OMWW	Hydrothermal carbonisation	100–200	Spherical	Water remediation	[151]
Fe	Olive Oil coating	Green synthesis	37.8–77.6	Spherical	Heavy metal ion removal	[152]
MgS	OMWW	Green synthesis	86.3	Spherical	Soil enhancement, Bio-nano fertilisers	[11]
NiO	OLE	Green synthesis	13.85 and 32.94	Asymmetrical	Antiparasitic, Antimicrobial	[153]
Se	Olive pomace extract	Green synthesis	53.3–181.7	Spherical	Drug delivery, Antioxidant	[154]
SiO_2	Olive residue ash	Green synthesis	30–40	Spherical	Anticancer	[155]
Solid lipid NPs (SLNs)	OOW	-	141–173	-	Drug delivery, Antioxidant	[156]
TiO_2	OOW	Hydrolysis	30	Spherical	Biodiesel production	[157]

nanotechnology, as it provides a sustainable and cost-effective method for synthesizing AgNPs, demonstrating their potential applications in various fields.

Another work discussed the potential applications of pyrolysis, particularly in water purification and the remediation of contaminated environments [158]. Pyrolysis, a thermal decomposition process, was employed to convert olive oil residue (OR) biomass into valuable products. What makes this study particularly noteworthy is the integration of bulk and nanosized metal oxide catalysts into the pyrolysis process. These catalysts, particularly MgO and ZnO, played a crucial role in enhancing the efficiency of the pyrolytic conversion. The researchers synthesized nanosized versions of these metal oxides using a hydrothermal method, focusing on their unique properties, such as their large surface areas and reactivity. Including nanometal oxides significantly altered the product distribution and composition of the pyrolysis process. Notably, the presence of nanosized MgO, with its increased surface area and basic character, substantially increased the synthesis gas production (comprising hydrogen and carbon monoxide). Additionally, these nanocatalysts effectively reduced CO_2 emissions, making the pyrolysis process more environmentally friendly.

Yiamsawas et al. [159] found that Kraft lignin, derived from olive oil and also found in olive oil waste, possesses remarkable potential for applications in water treatment. Traditionally, lignin, an abundant biopolymer, has been primarily utilized for energy production. However, this study revealed an innovative approach by modifying Kraft lignin through esterification with methacrylic anhydride. This process resulted in the creation of lignin nanocarriers with diverse morphologies, including porous NPs. These porous lignin NPs, when carbonized, exhibited an impressive surface area, measuring 552 m^2/g. More importantly, they demonstrated efficient adsorption capabilities, particularly with methylene blue, a typical water pollutant. The porous lignin NPs have the potential to serve as effective adsorbents capable of removing harmful substances from water sources.

In turn, Mahmoud et al. [160] evaluated the potential of Olive Mill Solid Residue treated with water (OMSR-W) as a cost-effective bio-sorbent for efficiently removing heavy metal ions, including Cd^{2+}, Cu^{2+}, and Pb^{2+}, from aqueous solutions. Comparative evaluations with untreated OMSR (OMSR-U) and OMSR treated with n-hexane (OMSR-H)

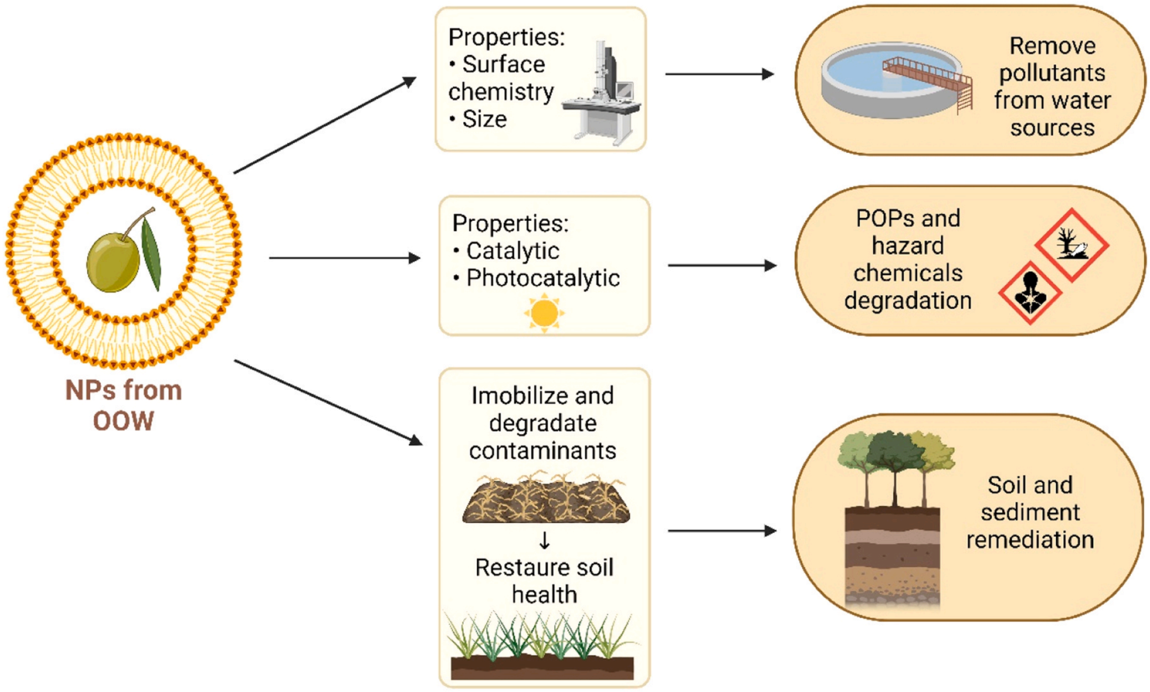

Fig. 7. Environmental applications of OOW.

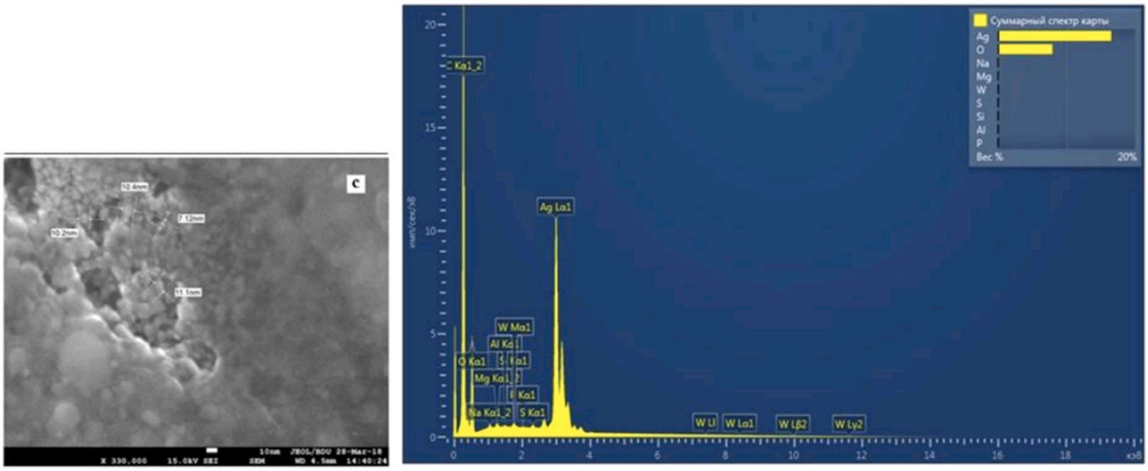

Fig. 8. SEM pictures of Ag NPs synthesized through the extract of olive leaves. Obtained from [132].

affirm OMSR-W as the most effective treatment, exhibiting superior metal uptake capabilities and minimal leaching of organic matter, as evidenced by its lower Chemical Oxygen Demand (COD) value. OMSR-W's performance likely stems from its capacity to expose more available binding sites for metal bio-sorption while eliminating surface impurities from the biomass. Intriguingly, this bio-sorbent's metal uptake efficiency is influenced by various parameters, including pH, bio-sorbent concentration and contact time. Equilibrium sorption data analysis employing the Langmuir isotherm model highlights the remarkable maximum uptake values, with Pb^{2+} closely followed by Cd^{2+} and Cu^{2+}. Notably, OMSR-W, an economically viable option, showcases the potential for treating wastewater contaminated with heavy metals. However, further investigations involving actual wastewater samples and exploring the bio-sorbent's reusability are imperative to validate these findings and potentially implement this approach on an industrial scale.

4.2. Remediation of contaminated environments

The remediation of contaminated environments, such as soil and sediments, is a complex challenge with far-reaching environmental implications. NPs from olive oil waste extracts offer a sustainable alternative for remediating such sites. This section explores their applications in soil and sediment remediation, focusing on their ability to immobilize and degrade contaminants, restore soil health, and mitigate environmental damage (Fig. 7).

Es'haghi et al. [152] investigated a novel approach for the remediation of contaminated environments, specifically focusing on efficiently extracting nickel (Ni) from various real samples. The methodology employed magnetic NPs coated with olive oil, harnessing the precision of nanotechnology to control particle size and surface properties. The innovative technique, dispersive solid-liquid phase microextraction (DSLME), showcased remarkable performance. This technique, in addition to being high-speed, is innovative because MNPs- olive oil acts as a sorbent. Moreover, it boasted a low detection limit (LOD) of 0.821 ng/ml, a wide linear range from 1 ng/ml to 5000 ng/ml, and impressively low relative standard deviations (RSD) at 0.196 % [152]. Comparative analyses with existing methods demonstrated competitive or superior results, reaffirming the method's efficacy.

Furthermore, DSLME offers several advantages, such as reducing extraction time over traditional methods, making it economical and user-friendly [152]. This approach's simplicity, cost-effectiveness, and rapid extraction capabilities position it as a promising solution for efficiently mitigating Ni contamination. Notably, the potential applicability of DSLME extends beyond Ni, making it a valuable tool for addressing a wide range of environmental pollutants in diverse matrices. This advancement holds great promise for the broader goal of remediating and safeguarding ecosystems, aligning with the critical objectives of environmental science and sustainability efforts.

Galloni et al. [111] discussed a compelling avenue for addressing environmental pollution by integrating magnetic NPs into photocatalysts. Various magnetic NPs, including γ-Fe_2O_3, Fe_3O_4, and MFe_2O_4 (where M = Mg, Ni, Zn, Cu, Co), have been skilfully incorporated into photocatalytic materials [111]. This innovation has yielded composite materials with magnetic properties, enabling the separation of photo-induced charge carriers, and significantly enhancing light absorption capabilities. These advances have been pivotal in the quest for effective solutions to combat pollution in wastewater. For instance, *Shen et al.* [161] devised Fe_3O_4@TiO_2@Ag-Au microspheres with remarkable magnetic and photocatalytic properties, demonstrating the potential of such materials in water treatment. *Singh et al.* [162] took a novel approach by immobilizing a BiOI/ Fe_3O_4 photocatalyst on graphene oxide to degrade 2,4-dinitrophenol effectively. The exploration of various magnetic composite photocatalysts, such as $Cu_2V_2O_7$/Co-Fe_2O_4/g-C_3N_4, Mn Fe_2O_4/SnO2, and MoO_3/$CoFe_2O_4$, has further expanded the possibilities in this field. These magnetic photocatalytic materials hold immense promise for environmentally friendly wastewater decontamination, a vital step towards a cleaner and healthier planet.

In turn, *Calderon et al.* studied an innovative solution to the challenges of contaminant remediation. They focused on addressing the limitations of nanoscale zero-valent iron (nZVI), a promising yet costly and unstable option for addressing environmental contamination [150]. Hydrothermal carbonization (HTC) using olive mill wastewater as a sustainable carbon source successfully encapsulated nZVI within carbon spheres, forming thin-shell carbon-encapsulated iron NPs (CE-nFe). This approach not only improved the stability of the NPs but also made the synthesis process more cost-effective [150]. The resulting nanomaterial exhibited a high surface area and ability to efficiently remove heavy metals from water. What sets CE-nFe apart is its carbon layer, which prevents the release of heavy metal ions back into the water, overcoming a challenge associated with the ageing of traditional nZVI. When the authors evaluated the application for heavy metal remediation of contaminated water, represented in Fig. 9, it became evident that the encapsulated NPs, CE-nFe and CE-nFe-P600, effectively prevented the ageing effect typically observed in conventional nZVI. This ageing effect involves re-releasing heavy metal cations into the water after initial removal. Conventional nZVI and CE-nFe-P600 achieved the highest degradation efficiencies, with conventional nZVI initially outperforming the others but eventually releasing contaminants back into the water due to oxidation.

In contrast, the encapsulated NPs consistently improved removal efficiency with time, reaching degradation percentages greater than 99 % for most heavy metals [150]. Only Ni showed a slightly lower removal efficiency of 97 %. This study suggests that encapsulated nZVI, such as CE-nFe, could effectively prevent the release of contaminants, making them highly promising for applications involving extended reaction times, like the remediation of contaminated soils and aquifers.

Hamimed et al. described an innovative and eco-friendly approach to addressing the environmental challenges posed by OMWW, which contains high levels of pollutant compounds, particularly polyphenols [11]. By extracting these polyphenols, researchers could utilize them as reducing, stabilizing, and capping agents for the biosynthesis of magnesium sulfide NPs (MgS NPs). Various characterization techniques confirmed the successful synthesis of MgS NPs, characterized by specific peaks and with an average crystalline size of 86.3 nm. These biogenic

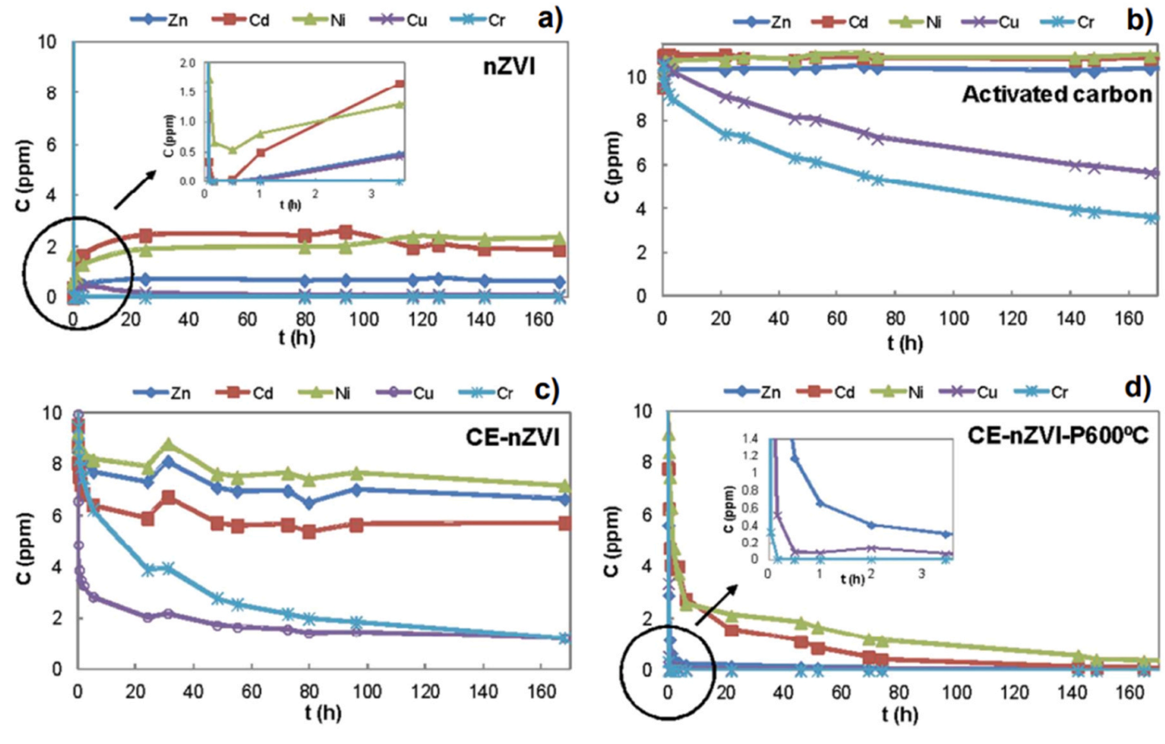

Fig. 9. Removal of heavy metal cations with time, using: a) conventional nZVI; b) AC-P600; c) OMW-CE-nFe; d) OMW-CE-nFe-P600. Obtained from [150].

MgS NPs demonstrated remarkable potential in both agriculture and soil biology and significantly promoted the germination and growth of old pea seeds, indicating their potential as bio-nano fertilizers. The MgS NPs were also found to enhance soil bacteria's growth, further highlighting their potential applications in agroecological systems. A more detailed examination of MgS NpS utility in sustainability agriculture and environmental management was prompted by the study's findings.

Biodiesel produced from olive oil waste was also studied using TiO_2 NPs as a catalyst [157]. Biodiesel is recognized for its renewable nature, biodegradability, and low emissions profile, making it an attractive alternative to traditional fossil fuels [163]. Besides its superior combustion performance, it lacks sulphur and aromatic compounds and is easier to store and manage. However, the viscosity of pure vegetable oil, a common feedstock for biodiesel, poses challenges such as clogging fuel lines, injectors and fouling piston heads. To overcome these issues, researchers have explored various techniques, including blending it with petroleum diesel, pyrolysis, emulsification, and transesterification, to reduce the viscosity of triglycerides [164–166]. Their research highlights the potential of TiO_2 NPs, known for their stability, large surface area, non-toxicity, and cost-effectiveness, as a catalyst for transesterification in biodiesel production, since their study yielded a biodiesel conversion rate of 91.2 %, achieved in just four hours at a temperature of 120°C [157]. This method offers a variety of benefits, including a clean and noncorrosive reaction environment, high biodiesel yield, straightforward experimental procedures, and easy catalyst recycling, all contributing to more sustainable and cost-effective biodiesel production.

5. Health applications

This section explores several health-related applications of NPs synthesized from olive oil waste extracts. Through the processing of olive oil, primary residues like olive pomace, olive cake, and OMWW can be used to recover target compounds, such as polyphenols. These compounds find application in health-related fields, including drug delivery, antimicrobial resistance treatment, cancer treatment, and cardioprotective effects (Fig. 10) [167]. The leverage of these NPs' properties can enhance human health and well-being.

5.1. Drug delivery

NPs synthesized from olive oil waste have tuneable properties, such as size, surface charge, and controlled release capabilities, making them ideal carriers for pharmaceutical compounds [117,143,155,168]. This section explores the use of these NPs in drug delivery systems, emphasizing their ability to improve drug solubility, enhance bioavailability, and target specific tissues or cells.

The increase in drug solubility is directly related to the reduced size of the NPs and increased area-to-volume ratio, which increases the surface energy and the corresponding dissolution rate [169]. Also, the size effect results in a greater ability of NPs to, for instance, enter the pulmonary system, cross the tight junctions of endothelial cells, and cross biological membranes more easily [170]. In cancer therapy, particularly, the increased bioavailability of drugs at the target site is related to the proven effect of enhanced permeability and retention (EPR) in solid tumours. The EPR Effect results from increased pore size of neo-vasculatures found in tumours and poor lymphatic clearance of tumours, allowing preferential accumulation of NPs [171].

Furthermore, the natural functionalization of NPs with bioactive compounds helps to increase stabilization and, in turn, the circulation time in the bloodstream and respective bioavailability.

Silver NPs (AgNPs) synthesized using olive leaf extracts have demonstrated potent antibacterial, antifungal, antiviral, and anticancer properties. These AgNPs leverage the polyphenols, flavonoids, and terpenoids in olive leaves to reduce Ag^+ ions and stabilize the resulting NPs, ensuring efficient drug delivery and improved therapeutic outcomes. Additionally, the bioactive compounds in OLE encapsulated in NPs improve their stability and bioavailability, making them effective in targeted drug therapy [172].

Leong et al. [173] studied the encapsulation of artemether, an

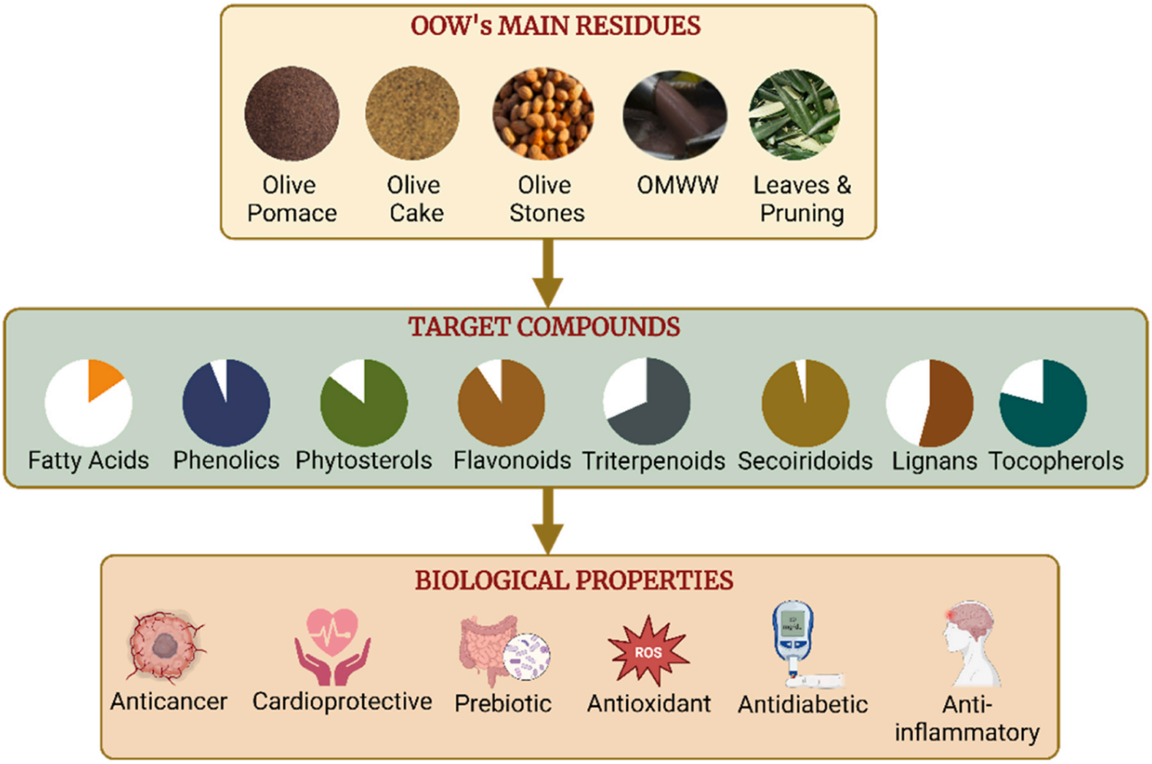

Fig. 10. Main residues, target compounds and main biological applications derived from OOW. Adapted from [167].

antimalarial agent, into chitosan-chondroitin sulphate NPs. As detailed in [168], this encapsulation strategy has promoted advanced drug delivery strategies, particularly in treating acute malaria. Through the ionic gelation technique, positively charged chitosan and negatively charged chondroitin sulphate synergistically form NPs. These NPs exhibit desirable properties, including reduced toxicity, exceptional stability, high encapsulation efficiency, and substantial loading capacity—key attributes for efficient drug delivery systems. Olive oil as a permeation enhancer has been explored, showcasing its potential to increase drug permeability through the skin. This innovative approach holds promise for malaria treatment and exemplifies the broader potential of nanotechnology in drug delivery. Notably, the *in vitro* drug release studies revealed a notable contrast: a high cumulative drug release at a pH of 7.4 and a controlled release rate at a pH of 5.5. This underscores the versatility of this delivery system for targeted therapeutic interventions.

Furthermore, the integration of olive pomace extract (OPE) into the synthesis of selenium NPs (SeNPs) holds significant promise for advancing drug delivery systems [154]. This research conducted by *Galić et al.* [154] successfully harnessed OPE as a surface modifier, optimizing the green synthesis process and yielding stable spherical nanosystems with controlled particle sizes suitable for peroral administration. This achievement is crucial in drug delivery, where nanoparticle size highly influences drug release and bioavailability. Another remarkable outcome of this research was the enhanced bioaccessibility of SeNPs functionalized with OPE [154]. Bioaccessibility, referring to the ability of NPs to release their contents under specific conditions, is a critical factor in drug delivery, enabling the controlled and effective release of therapeutic agents. The findings indicated that OPE positively improved bioaccessibility, which is promising for designing drug delivery systems that require precise control over drug release. Finally, biocompatibility studies revealed that SeNPs functionalized with OPE exhibited lower toxicity than conventional selenium compounds, such as sodium selenite.

De Matteis et al. [145] also tapped into the waste product of OMWW, rich in polyphenols, to serve as a reduction agent for silver nanoparticle (AgNP) production. This sustainable approach yielded AgNPs of two distinct sizes, 30 nm, and 50 nm, with promising implications for therapeutic applications. The biocompatibility of these AgNPs was assessed through testing on human monocytic cells. The results indicated that both sizes of AgNPs exhibited minimal inflammatory responses when exposed to macrophage cells, making them potential candidates for various biomedical applications. Silver NPs are well-regarded for their potential role in drug delivery systems, where they can act as carriers for various therapeutic agents. The biocompatibility of these AgNPs with the OMWW, especially the larger ones with minimal inflammatory responses, positions them as promising candidates for drug delivery vehicles.

5.2. Antimicrobial activity

The global health challenge posed by the rising threat of antimicrobial resistance is of paramount concern. NPs derived from olive oil waste extracts exhibit inherent antimicrobial properties attributed to their composition. As a result, this section discusses their potential in combating microbial infections, addressing biofilm formation, and reducing the spread of resistant pathogens.

Benincasa et al. [174] explored the improved upgrading of the compound hydroxytyrosyl oleate from olive oil and its by-products. In their research, hydroxytyrosyl oleate, a natural polyphenol found in olive oil, was investigated for its antioxidant and skin regenerative properties and their results demonstrated an efficient elimination of this compound obtained from olive oil by-products, contributing to the sustainable use of this waste. Moreover, hydroxytyrosyl oleate was explored in the context of cosmetic and pharmaceuticals, as well as skin health. These findings have significant implications for the economic and ecological exploitation of olive oil by-products and on the development of skin care products based on natural antioxidant compounds. In another study conducted by Nardi et al. [156], researchers also explored the potential of hydroxytyrosyl oleate derived from olive oil and its by-products, focusing their investigation on olive phenolic compounds, known for their potent antioxidant properties and associated health benefits. Additionally, a number of epidemiological studies have highlighted the role that olive oil consumption has in reducing the risk of various diseases, including certain types of cancer and cardiovascular conditions, likely attributed to the protective effects of olive phenols that are present in it [175–178].

Nonetheless, the limited absorption of these compounds has posed a challenge to unlocking their full bioactivity. To address this, the researchers turned to solid lipid NPs (SLNs), offering improved drug stability and the capacity to encapsulate lipophilic and hydrophilic substances. Specifically, hydroxytyrosol oleate based solid lipid NPs were synthesized and meticulously characterized. Notably, these formulations exhibited excellent loading efficiency and fell within a 141–173 nm size range. Furthermore, the study also unveiled that these nanoformulations significantly enhanced the antioxidant activity of encapsulated olive phenolic compounds, effectively reducing reactive oxygen species (ROS) formation when tested in a biological environment. This breakthrough in augmenting olive phenols' bioavailability and antioxidant potential through SLNs holds promise for future *in vivo* applications.

Moreover, *Afonso et al.* [102] explored the latent antimicrobial potential inherent in OMWW content in total phenolics, antioxidant activity and the antimicrobial activity of the olive mill wastewaters obtained from two different olive oil extraction methods. When comparing the phenolic content, there were slight variations between the traditional discontinuous press and 3-phase centrifugal olive oil extraction methods. The traditional press had higher values and demonstrated greater antioxidant potential. OMWW, traditionally deemed an environmental challenge, has been revealed to possess a robust inhibitory effect against various pathogenic bacteria, notably *Klebsiella pneumoniae*, *Staphylococcus aureus*, *Proteus mirabilis*, and *Enterococcus faecalis* [102]. The authors' conclusion states that OMWW exhibits antibacterial properties both in its undiluted liquid form and when diluted to a concentration of 50 % or higher. This discovery carries profound implications for research into NPs synthesized from olive oil waste, as it underscores the potential to harness OMWW-derived components or insights to bolster the antimicrobial attributes of such NPs.

In turn, *Russo et al.* [179] introduced a novel approach to addressing olive mill wastewater's environmental and economic challenges. The authors employ a sequence of three membrane-based strategies, including microfiltration (MF), reverse osmosis (RO), and vacuum membrane distillation (VMD), to isolate and characterize different fractions from OMWW. The research revealed that the eight distinct OMWW fractions exhibited varying levels of antioxidant activity and total polyphenol content, which were correlated with their unique qualitative compositions, as confirmed through infrared (IR) analyses. This study is especially significant because it investigates the antibacterial potential of OMW samples, considered whole mixtures. Except for one fraction (ROp1), all analysed samples showed substantial antibacterial activity against clinically relevant Gram-positive and Gram-negative pathogens. The MD2 fraction emerged as the most active sample [179].

Additionally, the portions that were tested demonstrated effectiveness in inhibiting the growth of *Pseudomonas Syringae pv. tomato*, a seed-borne pathogen responsible for bacterial speck disease in tomatoes. Importantly, this study implies that the combined phenolic compounds within OMWW extracts may have more activity when used as extracts instead of in their purified form, providing new opportunities for their application in different fields.

Silver NPs were also synthesized by utilizing extra virgin olive oil (*Olea europaea L.*) and sunflower oil (*Helianthus annuus L.*) and then subjected to characterization via UV–vis spectroscopy, XRD and SEM [141]. The resulting solutions of olive oil NPs (EVOO-NPs) and sunflower oil NPs (SFO-NPs) exhibited distinctive brown colouration, displaying characteristic absorption peaks at 418 nm and 434 nm, respectively. XRD and SEM measurements revealed that the extra virgin olive oil NPs are semi-cubic in shape with an approximate size of 23.45 nm to 42.30 nm. Sunflower oil NPs have a size of 42.30 nm. The antimicrobial properties of crude extra virgin olive oil (EVOO) and crude sunflower oil (SFO) were investigated against different human pathogenic strains using EVOO-NPs and SFO-NPs synthesized from these oils. As compared to EVOO and SFO, the synthesized NPs from each oil exceeded the crude oils by an increase of 81.14–174.65 % and 111.65–192.31 %.

This type of NP was also produced using biological molecules extracted from Olea europaea leaves (OE-Ag NPs) and can be used in a variety of biological and nutraceutical applications, but further investigations are warranted to determine dose-dependent biocompatibility *in vitro* and *in vivo* [142].

In another research, the dry olive leaf extract (DOLE) and its active compound oleuropein (OLE) were employed as reducing and stabilizing agents to synthesize colloidal Ag NPs with sizes ranging from 20 to 25 nm [140]. These Ag NPs were characterized through TEM, XRD, and absorption spectroscopy. The study investigated the toxic effects of coated silver NPs (Ag NPs) and their organic and inorganic components on trophoblast cells, human peripheral blood lymphocytes (PBLs), and various microorganisms, including Gram-positive and Gram-negative bacteria, as well as yeast. Compared to Gram-positive bacteria, the antimicrobial effect of Ag/DOLE was substantially higher on yeast and Gram-negative bacteria. These results imply that Ag/OLE has the potential as a potent antimicrobial agent. Subsequently, is important to think about the possible risks associated with exposure to high concentrations that cause cytotoxicity in human cells that are in good health.

5.3. Cancer therapy

The NPs made from waste extracts derived from olive oil have unique characteristics that could be used to treat cancer. The adaptability of these nanomaterials allows them for the selective targeting of cancer cells, the delivery of therapeutic agents, and the improvement of treatment results. This section discusses their use in cancer therapy, including photothermal therapy, drug delivery, and their ability to reduce side effects.

Alhajri et al. [144] employed a green biosynthesis approach to synthesize harmless silver-functionalized multi-walled carbon nanotubes (SFMWCNTs), using water-soluble organic materials in olive oil plants to convert silver ions into Ag-NPs. The study recognized the medicinal properties of olive-leaf extracts and explored the potential of combining them with Ag-NPs to enhance drug delivery, particularly for treating cancer cells in vitro. The green synthesis process involved the extraction of various compounds, like Hydroxytyrosol, Tyrosol, and Oleuropein, from the olive plant, resulting in a natural polymer used to create a thin film. The SFMWCNT nanocomposites displayed an absorption peak at 419 nm in their UV–Vis spectra, and their morphology was investigated through SEM and EDS. An MTT assay was performed on different types of cancer cells, namely MCF7 (human breast adenocarcinoma), HepG2 (human hepatocellular carcinoma), and SW620 (human colorectal cancer), to assess their effectiveness in inhibiting cancer cell viability. SFMWCNTs demonstrated meaningful inhibition of cell viability, highlighting their potential as a treatment option for in vitro cancer cells. The study also emphasized the possibility of future in vivo studies to assess the feasibility of using these NPs in developing new nanomedicines.

Meanwhile, Alowaiesh et al. [143] synthesized AgNPs from olive leaf waste extract (OLWE), where the AgNPs, coated with bioactive groups from the OLWE, exhibited excellent cytotoxicity against multiple cancer cell lines, including breast (MCF-7), cervical (HeLa), and colon (HT-29) cancer cells, surpassing the potency of conventional chemotherapy drug doxorubicin (Fig. 11). The high cytotoxicity resulted in a significant reduction in cell viability (79–82 %), underscoring these AgNPs' potential for effective cancer treatment. Furthermore, their small size facilitates cellular entry, enhancing their anticancer efficacy [180,181]. Additionally, the AgNPs demonstrated superior antioxidant properties and antimicrobial activity, adding to their multifaceted potential as safe and environmentally friendly candidates for cancer therapy. These findings demonstrate the promise of OLWE-derived AgNPs as innovative and sustainable tools in the fight against cancer, providing a non-toxic and effective alternative for medical formulations with potential implications in cancer treatment strategies.

In addition to AgNPs, silica NPs (SNPs) have also been identified as candidates for anticancer agents. The research conducted by *Rezaeian et al.* [155] focused on the green synthesis of SNPs derived from olive residue ash (ORA). In this study, SNPs were prepared with a standard diameter of 30–40 nm, establishing their effectiveness for biomedical applications. What distinguishes these SNPs is their remarkable selectivity in cytotoxicity. Notably, they exhibited lower cytotoxicity towards normal fibroblast cells while demonstrating significantly higher cytotoxic effects on breast cancer cells. Intriguingly, these SNPs demonstrated enhanced cellular uptake in cancer cells, which correlated with an elevated production of ROS. This unique combination of selective cytotoxicity and enhanced intracellular activity positions them as promising candidates for targeted cancer therapy. These findings shed light on the potential of ORA-derived SNPs as effective and safe agents for combating cancer.

Boss et al. [137] studied olive leaf extract (OLE), enriched with diverse polyphenols not found in comparable quantities in olive oil, for its potential to combat cancer. Cell models and animal studies have provided compelling evidence of OLE's ability to modulate critical molecular pathways, particularly its anti-inflammatory properties that inhibit the NF-κB pathway and reduce the expression of pro-inflammatory molecules [137]. These effects create an inhospitable tumour microenvironment that hinders cancer progression. Moreover, OLE's structural resemblance to estrogen raises the possibility of interaction with estrogen receptors, potentially reducing the incidence and progression of hormone-related cancers. Notably, epidemiological evidence points to lower cancer rates in populations adhering to the Mediterranean diet, which features OLE-rich olive leaves. While these findings are promising, it is important to emphasize that translating them into concrete human cancer therapies necessitates rigorous clinical trials to confirm OLE's efficacy in preventing and treating various cancer types.

6. Current challenges and future directions

One of the main challenges encountered for the NPs green synthesis from Olive Oil Waste is their natural variability in achieving consistent NP synthesis outcomes. Variations in the composition and properties of these extracts can impact the shape, size, and stability of the produced NPs. Developing strategies for standardization and quality control is essential to overcome this challenge.

While green synthesis methods show promise on a laboratory scale, scaling up the synthesis process for industrial applications remains challenging. Researchers must devise scalable and cost-effective strategies to meet large-scale production demands while adhering to sustainability principles.

NPs green-synthesized are often considered for both environmental and health applications. Real-world case studies and successful practical implementations of NPs derived from olive oil waste in various industries, such as water treatment and drug delivery systems, can provide tangible insights into the benefits and challenges of applying these technologies. Addressing concerns related to their biocompatibility and potential toxicity is critical. Rigorous assessment, including toxicity studies and risk mitigation strategies, are necessary to ensure the safe

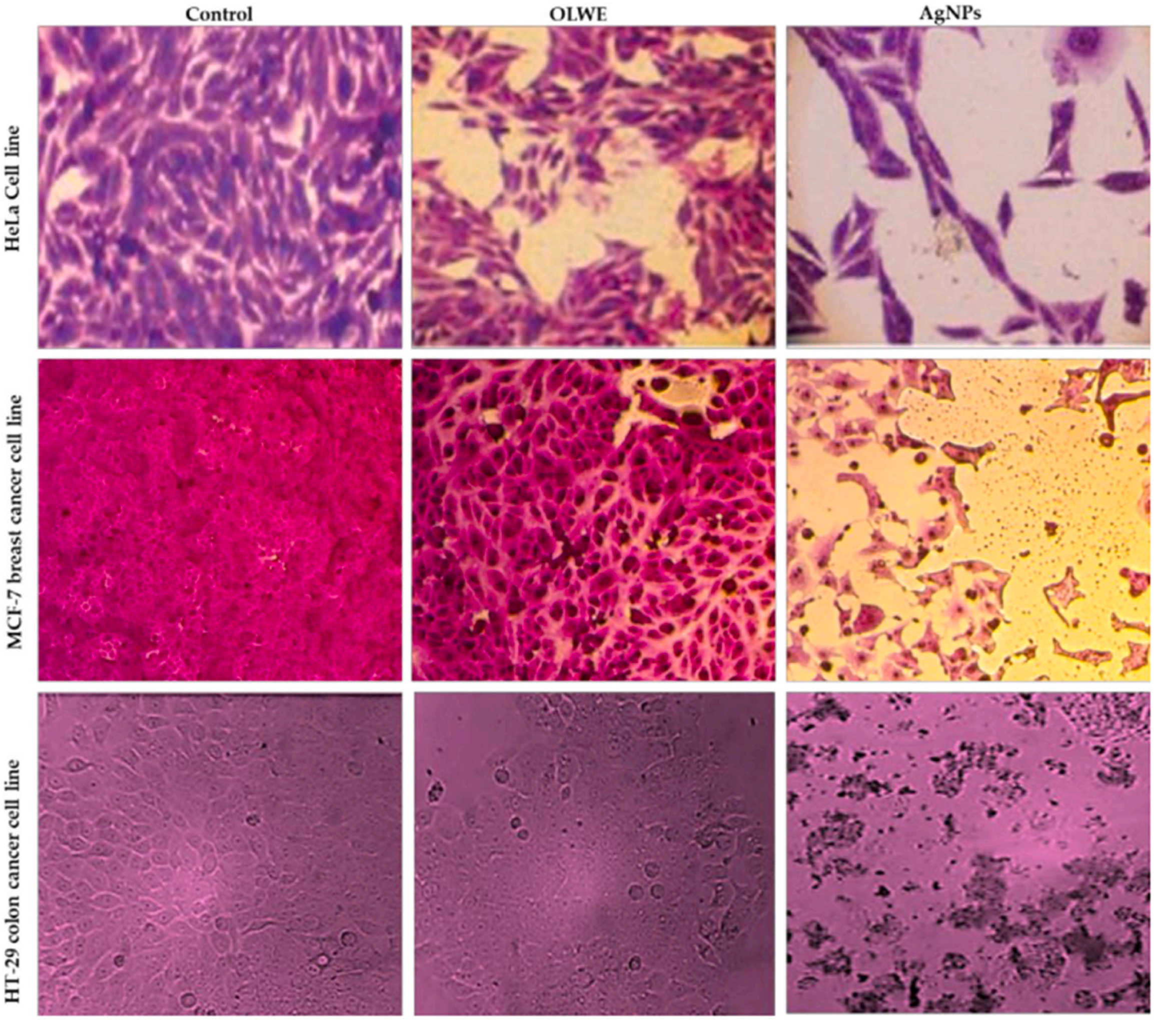

Fig. 11. The cytotoxic effect of AgNPs and OLWE against the cancer cell lines (MCF-7, HeLa, and HT-29). Obtained from [143].

use of these NPs.

The NPs aggregation, sedimentation, stability and longevity are crucial factors for their practical use. NPs must maintain their properties and effectiveness in various environments and applications from nanomedicine to renewable energies [146]. Hence, it is crucial to ensure NPs long-term stability for their reliability in water purification, pollutant degradation and medical applications.

7. Conclusions

This review describes the most recent and relevant findings of green synthesis using olive oil waste (OOW) to produce NPs, focusing on their environmental and health applications. Based on this review, several noteworthy implications have emerged:

- green synthesis methods provide advantages over conventional approaches, including reduced environmental impact and enhanced biocompatibility, where characterization techniques allow for in-depth analysis of NP structure, size, shape, and composition, aiding in optimization and performance evaluation;
- that biocompatibility was seen numerous times in the olive waste NPs, particularly with minimal inflammatory responses when exposed to cells. This discovery is essential as it identifies these NPs as highly promising contenders for various biomedical applications, such as drug delivery nanocarriers and cancer therapy. Additionally, the health benefits associated with olive-derived polyphenols, which can be harnessed through these NPs, suggest implications for improving overall well-being;
- the conversion of OOW into NPs demonstrates a change in basic assumptions about waste management within the olive oil industry. This eco-friendly approach reduces waste accumulation, mitigates environmental impact, and opens the way for sustainable waste valorisation;
- the unique properties of OOW, such as polyphenols and lipids, make them effective reducing and stabilizing agents for NPs synthesis, which offer a sustainable and eco-friendly alternative for various applications from nanomedicine to renewable energies;
- numerous examples of olive waste NPs combined with silver NPs are reported in the literature. This synergy has revealed remarkable properties where, for example, AgNPs synthesized using olive mill wastewater (OMWW) as a reduction agent have exhibited biocompatibility and potential applications in drug delivery systems;
- the inherent antimicrobial properties of OOW NPs offer a powerful tool for combating microbial infections. These NPs have shown promise in inhibiting the growth of various pathogenic bacteria, including multidrug-resistant strains, shedding light on innovative solutions to the global health challenge of antimicrobial resistance. These NPs, especially when enriched with bioactive compounds from olive leaf waste extract (OLWE), have demonstrated exceptional antioxidant properties, which hold immense potential for addressing oxidative stress-related health issues and present new opportunities for nutraceutical and pharmaceutical product development;

- researchers have successfully used these nanomaterials for targeted drug delivery to cancer cells, enhancing treatment outcomes and potentially minimizing side effects. The utilization of OOW-derived NPs in cancer therapy demonstrates their potential in selectively targeting cancer cells and improving therapeutic efficacy;
- throughout the exploration of health applications, it has become evident that while olive waste-derived NPs show promise in various therapeutic areas, the issue of potential toxicity must be approached with care. While some studies have demonstrated minimal inflammatory responses and enhanced biocompatibility, there are instances where toxicity concerns have been raised, particularly at higher concentrations. This duality underscores the importance of performing in-depth toxicity assessments for the application of this kind of NPs in nanomedicine.

CRediT authorship contribution statement

Beatriz Cardoso: Writing – original draft, Validation, Data curation, Conceptualization. **Inês S. Afonso:** Writing – original draft, Methodology, Data curation, Conceptualization. **Rui A. Lima:** Writing – review & editing, Supervision, Project administration, Funding acquisition. **João E Ribeiro:** Writing – review & editing, Validation, Supervision, Resources, Funding acquisition. **Graça Minas:** Writing – review & editing, Funding acquisition. **Glauco Nobrega:** Writing – original draft, Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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