RCMOS – Multidisciplinary Scientific Journal of Knowledge.
ISSN: 2675-9128. São Paulo-SP.
Year V, v.1, n.1, Jan/July 2025. | submission: 2025-03-10 | accepted: 2025-03-12 | publication: 2025-03-14

BIOSYNTHESIS OF METAL NANOPARTICLES FOR ELECTRODE APPLICATIONS: A SYSTEMATIC REVIEW

BIOSYNTHESIS OF METALLIC NANOPARTICLES FOR ELECTRODE APPLICATIONS: A SYSTEMATIC REVIEW

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SUMMARY:

This systematic review explored the green synthesis of metallic nanoparticles using plant extracts and their application in the modification of electrodes for electrochemical sensors. The use of the PRISMA method served as a guide for the selection of articles to be analyzed, which revealed the versatility of green synthesis and the potential of nanoparticles as electrode modifiers, improving the sensitivity and selectivity of sensors. The use of plants as reducing and stabilizing agents offers a more sustainable and economical alternative to traditional methods. Electrodes modified with nanoparticles have promising applications in several areas, such as environmental monitoring and medical diagnosis. The review highlights the importance of continued research in this field for the development of more efficient and sustainable technologies.

Keywords: Green synthesis. Metallic nanoparticles. Electrochemical sensors. Modified electrodes. PRISMA.

ABSTRACT:

This systematic review investigated the green synthesis of metallic nanoparticles using plant extracts and their application in modifying electrodes for electrochemical sensing. Employing the PRISMA methodology, the study revealed the versatility of green synthesis and the potential of nanoparticles to enhance the sensitivity and selectivity of electrochemical sensors. By utilizing plant-based reducing and stabilizing agents, this approach offers a sustainable and economical alternative to traditional methods. Modified electrodes with nanoparticles demonstrate promising applications in diverse fields, including environmental monitoring and medical diagnostics. The review underscores the significance of continued research in this domain for advancing more efficient and sustainable technologies.

Keywords: Green synthesis. Metallic nanoparticles. Electrochemical sensors. Modified electrodes. PRISM.

1. INTRODUCTION

Metallic nanoparticles (MPPs) are materials considered to be between 1 and 100 nm in size. The study of nanotechnology has advanced through the process of individually controlling atoms and molecules on a nanometric scale. There has been a great deal of attention to nanoparticles due to the fact that this knowledge can be combined with several areas, such as physics, chemistry, biology, health and materials sciences (JAMKHANDE et al., 2019). There are numerous advantages of NPMs, such as reducing the size of the particles to generate physical, chemical, optical and electronic advantages, as well as increasing the contact surface (MOMENI; NABIPOUR, 2015). Metallic nanoparticles such as copper, gold, silver, iron, platinum and nickel can acquire multifunctional properties that can generate their use as catalysts (BHAVANI; ANUSHA; BRAHMAN, 2019), electrical conductors (SULTAN; MOHAMMAD, 2017), sensors (LI et al., 2019) and antioxidants and antibacterial agents (IKHSAN et al., 2015).

There is more than one way to synthesize NPMs, however, physical or chemical methods are generally used. The physical method requires the use of energy, pressure and temperature, while the chemical reduction method uses compounds that are toxic to humans and marine life (such as Hydrazine and Dimethylformamide) (AHMED et al., 2016). Due to all these factors, the synthesis of NPMs by these means has been restrictive, and a new method has become necessary to avoid and overcome possible environmental and toxicological problems, since advances in studies have allowed the synthesis with bacteria, fungi, essential oils, proteins and enzymes. In this sense, the synthesis of nanoparticles with plant extract has been the stage for much research (TURUNC; KAHRAMAN; BINZET, 2021), since this synthesis provides safety, attractive cost, and is*eco-friendly* and can also ensure particle size control (MASHWANI et al., 2016). Because of these advantages, many plants have been used in the synthesis of metal nanoparticles

(KAHRAMAN et al., 2018; WANG et al., 2009). In this sense, one of the main applications of NPMs is in the field of electrochemistry, especially in the modification of electrodes.

Electrodes are mostly made of metallic materials, such as gold and silver, due to their high electrical conductivity, biocompatibility, and stability in solutions (VAFAIEE et al., 2024). In order to improve their capabilities and alter the surface of the electrodes, by reducing the impedance, it is possible to increase the contact surface without altering their geometric shape (CHOI et al., 2021). Carbon paste electrodes (CPEs) have stood out as valuable tools in several areas of electrochemistry due to their easy preparation, low cost, and versatility. The possibility of modifying the composition of the paste, incorporating different materials, gives CPEs a wide range of applications, from the electroanalysis of organic and inorganic compounds to the development of electrochemical sensors. In addition, the renewal of the surface of CPEs is simple and fast, allowing multiple measurements to be performed on the same electrode.

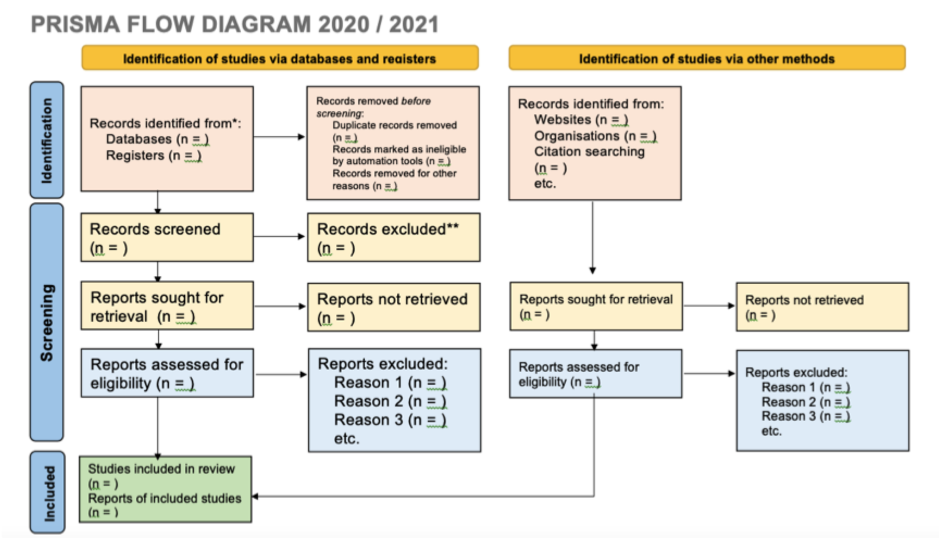
In this context, this literature review aims to provide an overview of the production of metallic nanoparticles through the green route and potential applications in the modification of electrodes. Thus, a brief introduction on the subject was made and, then, the methodology that guided the development of this review was described. Finally, the results and discussion of the bibliographic survey will be presented.

2. MATERIAL AND METHOD

This study is a descriptive research with qualitative analysis, focused on deepening knowledge about the green synthesis of NPMs and their application in the modification of electrodes. To this end, a bibliographic review was carried out on the digital platform*ScienceDirect*, using as search keywords "*Carbon paste electrode modification*", "*silver nanoparticles*", "*biosynthesis*", "*green synthesis* " and "*plants*". For this study, only articles published in scientific journals between January 2015 and December 2023 were considered, where the PRISMA method was considered (*Preferred Reporting Items for Systematic Reviews and Meta-Analysis*).

This method, used to carry out the review, is an updated version of the QUORUM recommendations (*Quality of Reporting of Meta-Analyses*). The PRISMA recommendations include a checklist with 27 detailed and exemplified items, as well as a flow diagram divided into four phases (PAGE et al., 2021). Following these guidelines, the research was structured in four stages: identification, screening, eligibility and inclusion, as illustrated in the flowchart presented in figure 01.

Figure 01: PRISMA Flowchart



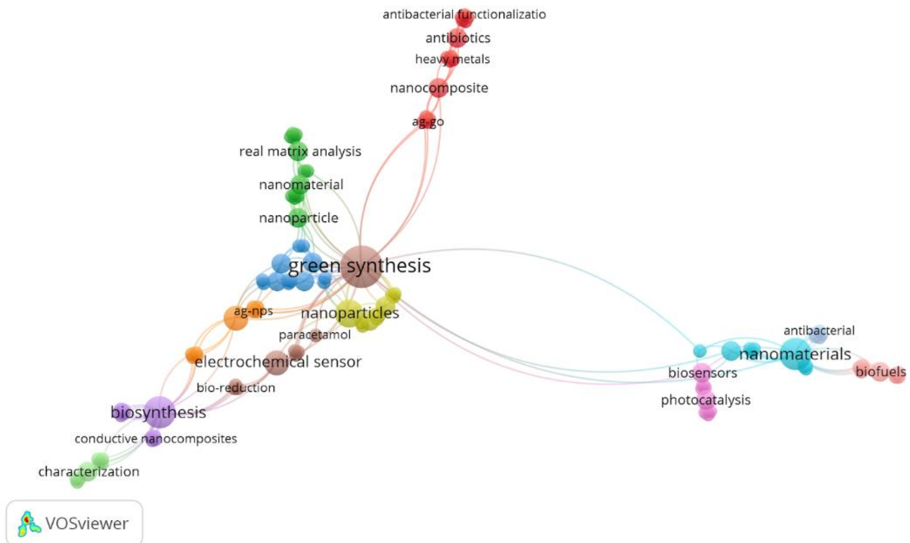
Source:https://www.htanalyze.com/wp-content/uploads/2021/04/Untitled.png

The titles of all these articles were reviewed, resulting in the selection of 55 articles for reading of the abstracts. The collected bibliometric data were exported to the software *VOSviewer*, where, through this environment, bibliometric networks were built that allowed the identification of the main words present in the titles and abstracts, in addition to mapping the authors, their connections with other researchers and the number of citations each one has. After this phase, 23 articles were chosen for full reading. The eligibility criteria considered articles in Portuguese and English that offered a comprehensive view on the green production of nanoparticles and also electrode modification.

3. RESULTS AND DISCUSSION

For the initial analysis of the most frequent words, a competition network was used in the software *VOSviewer*. A grouping of words is carried out, and it is possible to observe the formation of groups from 227 words identified algorithmically by the software. It is also possible to verify that the words presented in each group are related to different areas of research and have a strong connection between them, with a strong focus on green synthesis, electrochemical sensors and nanoparticles.

Figure 02: Keyword Competition Network

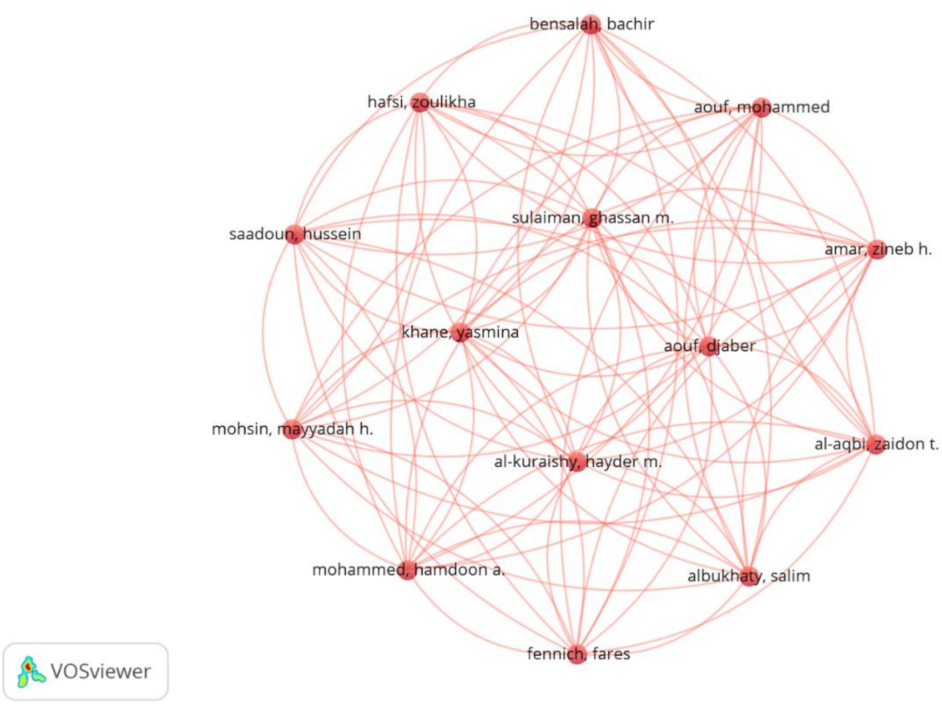


Source: Author, 2024.

Figure 02 shows the groups of words with random colors, just for distinction. Each circle represents a term, and the size represents the frequency of the words used, however, some of them have their names displayed to avoid overlaps, as identified by the software. The words in the groups have a direct relationship with each other, defining the separation factor of these groups. Thus, it can be observed that the words with the greatest importance are "*green synthesis*", "*biosynthesis*", and "*nanomaterials*". As words of lesser importance, we can observe "*electrochemical sensor*", "ag-nps" and "*nanomaterial*".

The software also identified 317 authors, linked by 14 key authors. The size of the author's name in the group is related to the number of published works, the number of citations these works have and the strength of the connection between the authors, which can be seen in Figure 03.

Figure 03: Authors' relevance network



Source: Author, 2024.

During the advanced database search, the most relevant items were in the title, abstract, and keywords of the articles. Using the selection method employed in this study, 49 articles were found, which underwent the following filtering and elimination procedures: removal of duplicates; exclusion of articles whose title, abstract, or keywords were not aligned with the research topic; and exclusion of articles whose content was not aligned with the research objectives, following the PRISMA Protocol. At the end of this process, 23 articles remained that were studied in full. Of these, 13 were included in this systematic review because they were within the scope of the research. The systematic analysis of the data from this review revealed valuable insights into the green synthesis of nanoparticles and their use in altering electrodes was also considered. The summary of the studies can be seen in Table 01.

Table 01: Synthesis of nanoparticles through different matrices for altering electrodes.

Reference	Year	Headquarters	Metal	Electrode	Analyte identified
(TURUNC; KAHRAMAN; BINZET, 2021)	2021	Extract from pollen *Cupressus sempervirens L.*	Silver	Electrode of glassy carbon	Hydrogen Peroxide
(JEBRIL et al., 2021)	2021	Leaves of olive tree	Gold	Sonogel electrode carbon	Bisphenol A
(DAVARNIA et al., 2020)	2020	Extract from *Peganum harmala*	Silver	Paste electrode carbon	Quercetin
(ZAMARCHI; VIEIRA, 2021)	2021	Araucaria *angustifolia*	Silver	Electrode of glassy carbon	Paracetamol (N-acetyl-p-aminophenol)(ZHOU, 2024)
(ZHOU et al., 2024)	2024	Leaf extract of parsley	Silver	Electrode silkscreened	Bisphenol
(KARTHIK et al., 2016)	2016	*Cerasus serrulata*	Silver	Electrode of glassy carbon	4-Nitrophenol
(GULER; MEYDAN; SECKIN, 2023)	2023	*Arum italicum*	Silver	Electrode of glassy carbon	Vitamin B2
(TURUNC et al., 2017)	2017	*Lithodora hispidula*((Sm.) *Griseb*.	Silver and Palladium	Electrode of glassy carbon	Hydrogen Peroxide
(KHALILZADEH ; BORZOO, 2016)	2016	Onion (*Allium strain L.*)	Silver	Paste electrode carbon	Ascorbic acid
(PATEL et al., 2023)	2023	Neem (*Azadirachta indicates*)	Silver	Gold electrode interdigitated	*Escherichia coli*
(LALMALSAWMI et al., 2021)	2021	Leaves of avocado	Gold	Electrode of glassy carbon	Lead ions (Pb^{2+})
(LIKASARI et al., 2021)	2021	*Marigold erecta L.*	Oxide of nickel (NiO)	Paste electrode carbon	Glucose
(BATISH; RAJPUT, 2023)	2023	Quercetin (bioflavonoid)	Silver	Quercetin covered with nanoparticles of silver	Chloramphenicol

Source: Author, 2024

The studies presented have proven the efficiency of using the green method for the synthesis of nanoparticles. Using biological organisms such as bacteria, fungi, algae and plants, biosynthesis allows the production of nanoparticles with less environmental impact compared to traditional chemical and physical methods, which often involve toxic substances and extreme conditions. In environmental issues, AgNPs also have advantages, as they are not toxic to humans and animals. It is also possible to observe an economic benefit, since many of the materials used come from discarded or reused resources. Regarding their application as electrode modifiers, these also presented, for the most part, good results since AgNPs increase the surface area, allowing a greater quantity of analyte to interact with the electrode surface, increasing the sensitivity of the measurements. This allows the detection of substances in very low concentrations and improves resistance to interference from other species present in the sample. This technology is crucial for environmental monitoring and control of industrial processes, providing faster, more reliable and specific results.

Silver has excellent catalytic properties and is an excellent conductor of electricity. Thus, electrochemical reactions can be accelerated, the oxidation potential of analytes can be reduced, improving signal resolution and sensitivity, in addition to facilitating electron transfer between the electrode and the solution, reducing resistance and increasing measurement efficiency. This modification expands the possibilities for applying electrochemical techniques in areas critical to health, safety and sustainability. Electrodes modified with nanoparticles represent a significant advance in the identification of specific analytes, due to the unique properties of nanoparticles, such as high surface-to-volume ratio, improved electrical conductivity and functionalization capacity. The incorporation of nanoparticles on the surface of the electrodes increases the active area available for interaction with the analytes, improving sensitivity and allowing the detection of extremely low concentrations of substances. In addition, nanoparticles can be chemically modified to confer specific selectivity to the electrodes, making them capable of recognizing and quantifying accurately a wide range of analytes, from metal ions to complex biomolecules.

In the environmental field, electrodes modified with nanoparticles facilitate the monitoring of pollutants, contributing to the preservation of water and air quality. Thus, the use of nanoparticles in the modification of electrodes enhances the detection capacity and applicability of electrochemical techniques, promoting advances in several scientific and technological areas.

FINAL CONSIDERATIONS

This review sought to analyze the available literature regarding the use of green techniques for the production of nanoparticles and their use for altering electrodes. The PRISMA method (*Preferred Reporting Items for Systematic Reviews and Meta-Analyses*) was used in order to minimize interpretation bias and to ensure a more defined and reliable research and systematic review methodology. The software *VOSviewer*.

The identification of specific analytes by means of electrodes is vital importance in several areas, including chemistry, biology, medicine and the environment. This technique allows the precise detection and quantification of substances in solutions, enabling the monitoring of crucial parameters such as pH, ion concentrations, among others. The electrodes, often configured as electrochemical sensors, offer high sensitivity and selectivity, allowing real-time analysis and *in situ*. This is particularly essential in industrial processes, where strict control of chemical conditions is required to ensure product quality and operational safety. Identifying specific analytes not only improves the accuracy of analyses, but also contributes significantly to technological advances and improvements in quality of life.

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ACKNOWLEDGMENTS

This work was carried out with the support of the Coordination for the Improvement of Higher Education Personnel – Brazil (CAPES) – Financing Code 001.