SUMMERY

of the doctoral thesis entitled:

CONTRIBUTIONS TO THE SUPERIOR VALORIZATION OF WASTE FROM HORTI-VITICULTURAL SPECIES IN ORDER TO OBTAIN NEW COSMETIC FORMULATIONS THROUGH BIO AND NANOTECHNOLOGIES

Ph.D-student: BAROI Anda Maria

Scientific coordinator: *CS I Dr. Habil.* FIERĂSCU Irina

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The viticultural sector, an integral part of the food industry, is one of the most extensive and complex industries globally. It is well-known that waste disposal can generate significant environmental problems and related difficulties. Global demand for sustainable resources has seen a significant increase in recent years, highlighting the need to valorize vegetable waste to obtain value-added products in various industries.

Compared to other agro-food residues, viticultural waste has a low economic value and limited uses. However, existing scientific research reveals that these waste products contain significant amounts of bioactive compounds, highlighting their potential for integration in various fields. Furthermore, the use of viticultural waste in nanotechnological processes offers opportunities for the development of new, sustainable, and efficient technologies.

In the context of this, the PhD thesis titled " ***Contributions to the superior valorization of waste from horti-viticultural species in order to obtain new cosmetic formulations through bio and nanotechnologies***" had the main goal of developing topical cosmetic formulations with sun protection factor using viticultural waste. The topic is particularly relevant and important, considering the current orientation towards value-added products that contribute positively to health and quality of life. The thesis presents a methodology for creating topical formulations (gels and lip balms) with sun protection factor, based on biodegradable raw materials and synthetic nanomaterials synthesized through *green* chemistry.

The study contributes to the solution of two major problems: the valorization of viticultural waste and the development of efficient sun protection products that can absorb UV radiation.

CHAPTERS I-III constitute a thorough bibliographic study of all the concepts considered necessary to achieve the proposed thesis objective.

CHAPTER I presents a detailed overview of how the agro-food industry, along with the wine sector, contributes to the global accumulation of waste. The chapter also discusses the consequences that residues have on the environment and human well-being, as well as viable methods for exploiting them.

CHAPTER II provides a detailed study of the phytochemical composition present in plant residues. The classes of compounds identified in both fruit and vegetable residues and grape waste are presented in detail. A comparison is made between classical and modern methods used currently for extracting polyphenolic compounds from different plant matrices, highlighting the advantages and disadvantages of implementing each situation.

CHAPTER III describes general applications for using phytochemical compounds recovered from grape waste as value-added ingredients for various industries. In this chapter, priority is given to the use of natural sunscreen products, emphasizing the connection between these products and the antioxidant properties offered by bioactive compounds. The concept of plant-mediated synthesis of metal nanoparticles is also discussed, as well as their applications.

A comprehensive review of scientific literature and academic databases led to the formulation of the thesis idea, namely, that while there is intense interest in the benefits of metallic nanoparticles in various fields, no study has been conducted to develop lip balms and gels that incorporate these nanostructures, synthesized from grape waste.

CHAPTERS IV-VIII represent the original research carried out to achieve the proposed thesis objective. Most existing studies on lip balms and gels have focused on the use of traditional ingredients and formulas, with limited attention given to innovative approaches that include nanostructures synthesized through green chemistry. In this context, the element of originality lies in the development of lip balms and gels (with significant solar protection factor) that incorporate these nanomaterials, synthesized from viticultural waste.

In **CHAPTER IV**, methods for obtaining extracts from grape vine and tescovină are developed. The compositional analysis of these extracts, carried out through spectrophotometric tests and high-performance liquid chromatography (HPLC), showed a significantly increased total phenolic content in extracts obtained by microwave-assisted method: T-Mw (31,65 GAE mg/g dry substance) and C-Mw (18,34 GAE mg/g dry substance). Through HPLC analysis, 20 compounds were identified in the shoots extracts and 14 phenolic compounds in the pomace extracts. Additionally,

the diversity of composition of the four analyzed extracts played a crucial role in the plant-mediated synthesis of metal nanoparticles.

In **CHAPTER V**, experimental studies revealed the potential of grape waste from Romanian native *Fetească Neagră 6 Șt* (grape vine and tescovină) to synthesize monometallic and bimetallic nanoparticles through green chemistry. UV-Vis analysis confirmed the presence and maximum absorption specific to silver and gold. X-ray diffraction and electron microscopy validated the development of both types of nanostructures, highlighting the existence of a core-shell structure in bimetallic nanoparticles, where the core is formed by silver nanoparticles and the outer shell is composed of gold nanoparticles. Through XRF and EDX analysis, peaks associated with Ag and Au were identified, obtaining concentrations similar in monometallic Ag nanoparticles but high concentrations in bimetallic samples D_C, D_T, and C_T. Through microscopic techniques, a more uniform distribution was observed in solution for bimetallic nanoparticles, and a smaller size (3,7 nm) was found for structures synthesized with tescovină extract obtained by modern method.

In **CHAPTER VI**, the bioactive properties of both parent extracts and nanoparticles obtained are presented. In terms of antioxidant activity, a collective inhibition of the DPPH radical was observed, namely: extracts exhibited a reduced antioxidant activity compared to monometallic nanoparticles, which, in turn, had a lower antioxidant capacity compared to bimetallic nanoparticles. Additionally, the antioxidant activity of parent extracts varied, with modern method extracts (30,11% for C-Mw and 69,89% for T-Mw) showing a higher inhibition rate compared to classical method extracts (27,96% for C-Etv and 65,05% for T-Etv) associated with total phenolic content. The qualitative tests revealed exclusive antimicrobial activity against *Staphylococcus aureus*, *Bacillus subtilis*, *Pseudomonas aeruginosa*, and *Escherichia coli*, while quantitative tests showed antimicrobial activity against all tested strains except *Candida krusei*. Among all samples, the most efficient antimicrobial effect was observed in qualitative and quantitative tests: monometallic nanoparticles (A_C and B_T) and bimetallic nanoparticles (D_C, C_T, D_T), which were used in developing cosmetic formulations.

In **CHAPTER VII**, methods for obtaining gels using active ingredients such as shoots extracts (C-Etv, C-Mw) and pomace extracts (T-Mw, T-Etv), as well as monometallic and bimetallic nanoparticles dispersed in solution (D_T, B_T, C_T, D_C, and A_C), were developed. The optimal dosage of these ingredients in the gel formula was established at 6,5% extract (shoots/pomace) and a solution containing nanoparticle dispersion in a ratio of 6,5%. Furthermore, the polymer network was not affected by the presence of active substances, which presented uniform appearance, pseudoplastic character, and exhibited thixotropy in the range of shear rates from 10^{-2} - 10^{2} s^{-1}. Samples that achieved enhanced photoprotective efficiency (SPF=4) were F1 and F5, associated with antioxidant properties and metal concentrations in bimetallic

nanoparticles D_C and D_T, as well as the presence of certain phenolic compounds in parent extracts (ellagic acid and luteolin from T-Etv and sinapic acid from C-Etv).

In **CHAPTER VIII**, methods for obtaining lip balms with significant SPF values, formulated similar to gel samples, were developed. Five lip balms with stable organoleptic properties, with melting points and pH ranges between 70,5-71°C and 5,14-5,91, were obtained. The balms absorbed significant amounts of UV radiation, providing SPF values in the range of 34-107. Similar to gel samples, the materials that exhibited significant photoprotective efficiency were those formulated with 6,5% T-Etv extract and 6,5% D_T sample (sample B1, SPF=107) and 6,5% C-Etv extract and 6.5% D_C sample (sample B5, SPF=104).

CHAPTER IX presents the general conclusions of this doctoral thesis, accompanied by recommendations.

The thesis contains 63 figures, 37 tables, and 397 bibliographic references.

Through the research activities carried out in this thesis, **the following objectives were pursued**:

- Elaborating and adapting extraction processes to obtain high yields of bioactive compounds.
- Improving analysis procedures to obtain as complete as possible qualitative and quantitative information.
- Formulating gel and lip balm products with significant SPF values based on nanoarchitectures.

The realization of this thesis has an impact on the environment by valorizing plant waste and on the economy by obtaining high-value products through multidisciplinary and complex research activities.

The innovative elements brought to this thesis are:

- ❖ Optimization the obtaining process of bioactive compounds from grape waste from the native *Fetească Neagră 6 Șt* variety with high yields, using modern extraction methods adapted to the studied vegetal material;
- ❖ Green synthesis of stable nanostructures with significant antioxidant and antimicrobial properties;
- ❖ Development of polymer gels with the potential to protect skin through the presence of a medium-level SPF;
- ❖ Development of natural and biocompatible cosmetic products (lip balm) with significant SPF values.