A step towards Green Nanotechnology: biomass-NADES extracts for the development of nanocomposite alginate-silver nanoparticles hydrogels

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Introduction:

Silver nanoparticles (AgNPs) have gained significant attention in the field of biomedicine due to their remarkable antibacterial and antimicrobial properties. To synthesize AgNPs, a plant extract-mediated method is frequently utilized. This method is considered to be environmentally friendly, effective, non-toxic, and sustainable. By using plant extracts, the need for harsh chemicals and toxic solvents is eliminated, making this approach ideal for the production of AgNPs for biomedical applications.

Natural Deep Eutectic Solvents (NADES) are mixtures of two or more naturally occurring components that have a low-temperature eutectic point. Researchers have been using NADES to develop environmentally friendly processes that have a wide range of applications. Due to their unique properties, NADES are used as an alternative to conventional solvents, which are often hazardous to human health and the environment. The use of NADES in the synthesis of AgNPs is advantageous due to their biocompatibility and potential for improving the physiochemical properties of the nanoparticles [1-3].

In conclusion, the plant extract-mediated synthetic method in combination with NADES offer green, clean, and effective approaches for the synthesis of AgNPs. These methods have the potential to revolutionize the production of nanoparticles for biomedical applications, as they are non-toxic, nature-friendly, and sustainable. With further research and development, these approaches may become the preferred methods for the synthesis of nanoparticles in the future.

Material and methods:

In the present work, a method for the preparation of alginate hydrogel impregnated with AgNPs is developed. A NADES consisting of glucose and lactic acid, was used as extraction solvent in order to obtain an extract with high antioxidant (thus reducing) activity from olive leaves. The ‘as-obtained’ NADES extract efficiently acted as the reducing agent for the formation of AgNPs inside the polymer network in the presence of sunlight.

Results and discussion:

Swelling ratio and water retention ratio were measured by soaking the hydrogel in a phosphate buffer (pH=5.5). The alginate nanocomposite hydrogel reached a swelling ratio of 1220% after 50 min. The water retention remained over 60% after keeping the swollen sample in the buffer for 2 h, showing the maximum value at 3 h. The size of AgNPs was found to be 103.2±5.6 nm while the high zeta potential values (-36 mV) indicate the increased stability of AgNPs in the hydrogel matrix.

Antimicrobial activity was tested against the gram-negative *Escherichia coli* ATCC 25922 and *Salmonella* Typhimurium ATCC 14028 and the gram-positive *Listeria monocytogenes* ATCC 35152, *Staphylococcus aureus* ATCC 6538 and *Bacillus cereus* NCTC 10320/ATCC 9634 by automatic turbidometry with Bioscreen C. Data were processed with the ComBase tool DMFit for Excel to estimate microbial kinetic parameters, such as the specific growth rate (μ) and lag time of the growth curve of microorganisms.

Hydrogels with NADES-olive leaf extract and AgNPs showed the highest antimicrobial activity against all tested bacteria, followed by hydrogels with NADES-olive leaf extract. *S.aureus* was the most sensitive to hydrogels, showing 79.1% inhibition of growth rate, as well as *E.coli* and *Y.enterocolitica* (64.9% and 60.6% respectively). *Bacillus cereus* was inhibited by 51.8% by the AgNPs hydrogel, whereas the least sensitive was *L.monocytogenes* (25.5%).

The developed *in situ* synthesis of AgNPs within a hydrogel is a highly promising, economical and environmentally friendly method for the preparation of multifunctional materials.

Conclusions:

- Olive leaf biowaste was extracted using a NADES consisting of glucose and lactic acid
- The extract efficiently acted as the reducing agent for the formation of silver nanoparticles in alginate hydrogels in the presence of visible light
- This approach does not require the addition of a crosslinking agent for the formation of the hydrogel because this role is played by the NADES
- The formation of silver nanoparticles (AgNPs) is monitored by recording the UV–Vis absorption spectra for surface plasmon resonance (SPR) peak at 440 nm
- The zeta potential and PDI values of AgNPs indicate increased stability of the AgNPs in the hydrogel matrix
- The photo-induced phytomediated *in situ* synthesis of AgNPs within a hydrogel is a highly promising, economical and environmentally friendly method for the preparation of multifunctional materials

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References:

1. Tzani, A., Kalafateli, S., Tatsis, G., Bairaktari, M., Kostopoulou, I., Pontillo, A.R.N., Detsi, A., Sustain. Chem, **2** 576-599 (2021).
2. Pontillo, A. R. N., Koutsoukos, S., Welton, T., Detsi, A., Materials Advances, **2** 3954-3964 (2021).
3. Tzani, A; Karadendrou, M.A.; Tsiaka, T.; Kritsi, E.; Zoumpoulakis P.; Detsi A. "Deep Eutectic Solvents: Properties, Applications and Toxicity", Chapter 2: Exploring the Role of Natural Deep Eutectic Solvents (NADES) Towards the Valorization of Food Processing Industry Waste. Nova Science Publishers, 19-51 (2022).