

Nanocellulose-Stabilized Oil-in-Water Pickering Emulsions for Removing Natural Resin Varnishes From Canvas Paintings

Maria Rita Caruso¹, Olivia Gómez Laserna², Giuseppe Cavallaro¹, Francesco Caruso³,
Giuseppe Lazzara¹, Maite Maguregui³

¹Department of Physics and Chemistry "Emilio Segrè", University of Palermo, Viale delle Scienze, Ed. 17
Stanislao Cannizzaro, 90128 Palermo, Italy. mariarita.caruso02@unipa.it, giuseppe.lazzara@unipa.it.

²Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque
Country UPV/EHU, Barrio Sarriena s/n, 48940 Leioa, Spain, olivia.gomez@ehu.eus.

³Department of Analytical Chemistry, Faculty of Pharmacy, University of the Basque Country UPV/EHU,
Paseo de la Universidad 7, 01006 Vitoria-Gasteiz, Spain, francesco.caruso@ehu.eus
maite.maguregui@ehu.eus.

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The removal of the yellowing varnish layer is considered as one of the most complex steps in conservation. Key requirements are homogeneous treatment, absence of residues, and minimal (if any) alterations to pictorial layers. Therefore, the development of advanced solutions to remove varnish should not only demonstrate effectiveness but also include a testing phase that ensures the artwork preservation, as well as address concerns related to human health and the environment [1].

In various fields such as food industry, cosmetics, pharmaceuticals, and medicine, Pickering Emulsions (PE) have gained widespread use due to their stability and formulation versatility [2]. Recently, PEs have also emerged in the field of art conservation as a safe alternative to conventional surfactant-based emulsions to provide a controlled and effective cleaning of artworks [3-5]. PEs demonstrate the ability to encapsulate cleaning agents, which can be then applied in a controlled way onto the painting layer to softly remove soiling or varnish release residues.

Cellulose, the most abundant biopolymer on earth, is renewable, nontoxic, and biodegradable. It can be employed for the stabilization of PEs, ensuring safety for both the operators and the environment. Among others, cellulose nanocrystals (CNC) are the main stabiliser used for oil-in-water (o/w) PE [6].

This work presents the use of CNCs to create PEs for the removal of yellowed natural resin varnishes on canvas paintings. For the o/w PEs, green solvents (such as ethyl acetate) have been integrated as an alternative to traditional petroleum-based solvents.

The influence of various CNC concentrations and ratios between oil and water phases on the formation, stability, dimensions, and viscosity of PEs were investigated by optical microscope microscopy and Confocal Laser Scanning Microscopy. Rheological, zeta Potential and Dynamic Light Scattering measurements complement this study. The effectiveness of the most promising formulations was tested on canvas paintings using a non-invasive analytical approach to monitor the cleaning. Initially, observations under the stereo-microscope and colorimetric analyses were carried out. Eventually, the use of more advanced techniques, like Fiber Optics Reflectance Spectroscopy and

Hyperspectral Imaging in the Vis-NIR-SWIR range (400-2500 nm), among others has been implemented.

The results demonstrate the capability of CNCs as stabilizers in the formation of new ethyl acetate o/w PEs. The concentration of CNC plays a crucial role in particle aggregation or repulsion at the o/w interface, due to its electric charge, thereby influencing the hydrodynamic radius of nanoparticles and the formation of PEs. Additionally, the addition of NaCl reduces the electrostatic forces that contribute to the PE formation. The testing phase of stable formulations revealed the potential of ethyl acetate within the PE system, with the best-admitted ratio between oil-in-water phase, for removing the aged varnish layer.

Based on the positive results obtained from this initial study, we aim to provide a range of tailored alternatives for different types of varnishes and painting supports.

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References

- [1] Casini A., Chelazzi D., Baglioni P., Advanced methodologies for the cleaning of works of art. *Sci China Tech Sci*, 2023, <https://doi.org/10.1007/s11431-022-2348-7>.
- [2] Ming, L., Wu, H., Liu, A., Naeem, A., et al., Evolution and critical roles of particle properties in Pickering emulsion: A review, *Journal of Molecular Liquids*, 2023, <https://doi.org/10.1016/j.molliq.2023.122775>.
- [3] Myers, J.M., Matthew Cushman, M., Analysis of Cleaning Efficacy and Clearance of Silicone-Based Pickering-Type Emulsions Used in the Cleaning of Water-Miscible Oil Paints, *Conservation of Modern Oil Paintings*, 2019
- [4] Cavallaro, G., Milioto, S., Nigamatzyanova, L., Akhatova, F., Fakhrullin, R., and Lazzara, G., Pickering Emulsion Gels Based on Halloysite Nanotubes and Ionic Biopolymers: Properties and Cleaning Action on Marble Surface, *ACS Applied Nano Materials*, 2019, DOI: 10.1021/acsanm.9b00487.
- [5] Caruso, M.R., Megna, B., Lisuzzo, L. et al., Halloysite nanotubes-based nanocomposites for the hydrophobization of hydraulic mortar. *J Coat Technol*, 2021, <https://doi.org/10.1007/s11998-021-00522-9>.
- [6] Chuye Ji, Yixiang Wang, Nanocellulose-stabilized Pickering emulsions: Fabrication, stabilization, and food applications, *Advances in Colloid and Interface Science*, Volume 318, 2023, <https://doi.org/10.1016/j.cis.2023.102970>.