

BOOK OF ABSTRACT

30 years of Science at CSGI

FRIDAY September 1		http://www.centrocongressi.unina.it/via-partenope/ via partenope, 36, Napoli
		OPENING SESSION
	14:30-15:00	BAGLIONI, PADUANO: 30 years of science at CSGI
SESSION 1	CHAIR: M. Monduzzi	Soft Matter 1
	15:00-15:30	LINDMAN: Hydrophobic interactions control the self-assembly of surfactants, DNA and cellulose
	15:30-15:45	RUSSO KRAUSS: Beyond canonical surfactants: chemico-physical characterization of glycolipid biosurfactants
	15:45-16:00	CANGIANO: Lipopolysaccharide biorecognition by means of aptamers: a Neutron Reflectometry study on the biorecognition interaction
	16:00-16:15	TOMASELLA: Tuning the stability nanoparticle layers at the air/water interface by protein-decoration
	16:15-16:45	Coffee break and POSTER SESSION
SESSION 2	CHAIR: C. Rossi	BIOTECH & ENVIRONMENT
	16:45-17:00	FROSI: Food Upcycling: evaluation of different Lombard cereal by-products as innovative antiglycative agents
	17:00-17:15	MARINO: Understanding the spatio-temporal behavior of crops using remote sensing data in an organic farming system
	17:15-17:30	BELLAZZI: Thermophilic membrane reactor for high strength wastewater treatment and biological sludge minimization
	17:30-17:45	CAMPANA: Green solvents for a sustainable chemistry
	17:45-18:00	BOLDRINI: Microplastic pollution: effects on marine dissolved organic matter dynamics
	18:00-18:15	NARDIN: Chemical methods and protocols for quality and traceability of food products in the context of the Agritech Project
	18:15-19:00	POSTER SESSION

SATURDAY http://www.centrocongressi.unina.it/via-parter September 2 via partenope, 36, Napoli SESSION 3 CHAIR: Soft Matter 2	
Cuarte	
P. BAGLIONI	
9:00-9:30 AMBROSIO: Tailoring the functionality of polymer based biomate interfaces	erials and their
9:30-9:45 DI FRANCO: Kelvin Probe Force Microscopy-based analysis of few ant bindings at a large-area bio-functionalized surface	tigen-antibody
9:45-10:00 CAMBIOTTI: Destruction of mature insulin amyloid fibrils through pla excitation	asmonic
10:00–10:15 CAMPIONE: Polymeric electroactive P3HT-MWCNT composites for bi applications	ioelectronic
10:15-10:30 SACCO: Advanced extracellular matrix mimics with controlled mechan of cell mechanosensing	iics for the study
10:30-11:00Coffee break and POSTER SESSION	
SESSION 4 CHAIR: ART RESTORATION, HARD MATTER, THEORY & MODE	ELLING
11:00-11:15 CASINI: Tailoring the structural properties of Jin Shofu starch nanopar precipitation: Towards sustainable nano-consolidants for art conservation	
11:15–11:30 COFFETTI: Lime-based binders for the conservation of ancient mosaic	Ś
11:30–11:45 CARTA: The generation of new interfaces as a primary process leading mechanochemical	the solid-state
11:45-12:00 GALLUCCI: Hierarchical 3D self-assembly of coated metal oxide nanop	particles
12:00–12:15 BRANCATO: Simulating the chemical equilibria of metal complexes: In ligand exchange mechanism	isights into the
12:15–12:30 SAGRESTI: Expanding the Chemical Space of Tetracyanobuta-1,3diene through a Cyano-Diels-Alder Reaction	e (TCBD)
13:00–14:15 Light Lunch	
SESSION 5 CHAIR: SOFT MATTER 3	
14:15-14:30 KRAUTFORST: Photoactive pigments from Ulva Rigida encapsulated i anti-cancer treatment in Photodynamic Therapy	in cubosomes for
14:30-14:45 BALESTRI: Hybrid lipid-copolymer assemblies as multidomain functio	nal materials
14:45-15:00 PEPI: Sodium hyaluronate derivative with enhanced affinity towards M domain to be used as viscosupplement	(MP12 catalytic
15:00–15:15 MUGNAINI: Photocross-linked gelatin methacryloyl microparticles pre emulsion method for drug delivery	pared by double
15:15–15:30 MATEOS: Surfactant effect on feline coronavirus	
15:30–15:45 LAURATI: Transition from active motion to anomalous diffusion of <i>Bac</i> confined in hydrogel matrices	cillus subtilis
16:00-17:00Beverages and POSTER SESSION	
SESSION 6 CSGI HERITAGE	
17:00–17:50 ROUND TABLE	
17:50–18:00 CONCLUDING REMARKS	
19:45- SOCIAL DINNER	

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BOOK OF ABSTRACTS:

ORALS

Hydrophobic interactions control the self-assembly of surfactants, DNA and cellulose

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It is hundred years since the concept of critical micelle concentration of surfactants was introduced and also since hydrogen-bonding emerged as an important interaction. The balance between hydrophobic interactions and hydrogen bonding is, together with ionic interactions, behind organization of biological systems and a key to industrial formulations. This talk will mainly cover interactions in DNA and cellulose, where the role of different interactions has been highly controversial. With a learning from surfactant systems, we can understand that hydrophobic interactions are crucial, for example in double helix formation of DNA and in the dissolution and self-assembly of cellulose.

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Beyond canonical surfactants: chemico-physical characterization of glycolipid biosurfactants

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The recent sensitivity towards environmental issues as well as the need to reduce the current widespread use of substances obtained from nonrenewable sources is steering research toward the discovery and development of new "green" molecules characterized by high biocompatibility and biodegradability and a low impact on human and Earth health. Due to their very large use in a plethora of different fields, a class of substances for which this need is particularly urgent is that of surfactants. In this respect, attractive and promising alternatives to commonly used synthetic surfactants are the so-called biosurfactants, amphiphiles naturally derived from microorganisms, and bioderived or bioinspired surfactants, which are chemically synthesized from biomass.

The numerous reports on the chemico-physical characterization of these molecules is highlighting on one side the need to rethink some basic concepts used to rationalize and predict biosurfactant behaviour, on the other one is unveiling peculiar features of these molecules that may be exploited for highly specialized applications.

In this respect, we will present potentialities and challenges offered by different classes of glycolipids.

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Lipopolysaccharide biorecognition by means of aptamers: a Neutron Reflectometry study on the biorecognition interaction.

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Gram(-) bacteria are pathogenic microorganisms whose outer membrane of the external envelope is composed of complex molecules, such as lipopolysaccharides (LPS), consisting of three structural domains: lipid A, the core oligosaccharide and the O antigen. They are endotoxins responsible of many infections induced by bacterial pathogens, so representing a suitable target for a selective detection of their presence in aqueous environment. [1]

Selective detection of this analyte can be achieved through specifically designed biosensors, exploiting the biological response deriving from the biorecognition molecule and the analyte into a measurable signal. Among biorecognition molecules, aptamers are very appealing. They are single-stranded DNA or RNA with high affinity and specificity towards specific analytes. Recently, a small aptamer, named LA27, has been identified for a selective recognition of LPS. [2] Actually, the LPS portion interacting with LA27 is not well-understood yet, although preliminary studies suggest a direct affinity with lipid A as well as a capability of this aptamer to interact with LPS deriving from different strains of Gram(-) bacteria.

In this context, we performed a biophysical investigation on the interaction of LA27 biorecognition molecule with asymmetric Supported Lipid Bilayers (SLBs) prepared by the Langmuir-Blodgett method: the outer leaflet was composed by the deuterated di-palmitoyl-phosphocholine (d-DPPC), while three LPS extracted from three different Gram(-) strains, such as *Akkermansia, Flavobacterium* and *Paenalcaligenes hominis* respectively, were alternatively used to form the outer leaflet of the biomimicking bacterial membranes. For each of these samples, the interaction study was carried out at 25 °C and 38 °C in the presence of various solvent contrasts by performing Neutron Reflectometry experiments. [3] This analysis gave us information about the aptamer positioning within the bilayer regions.

References.

[1] D. Koulenti et al., International Journal of Antimicrobial Agents (2019), 211-224

[2] H. Ye et al., International Journal of Biological Macromolecules, 2020, 308-313

[3] A. Vanacore et al., Carbohydrate Polymers, 2022, 11839.

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Tuning the stability nanoparticle layers at the air/water interface by protein-decoration

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Due to their unique features as intrinsic bio-compatibility, low environmental impact and specific molecular structure consisting of the balance of hydrophilic and hydrophobic moieties, proteins spontaneous assembly at fluid interfaces is a well-established tool for the fabrication of functional thin-films, yielding the stabilization of various kind of dispersed systems such as foams and emulsions [1]. In this framework, the use of proteins as amphiphilic agents, able to drive and modulate the assembly of nano-colloidal particles at the vapor/water interface, can be an outstanding tool for the fabrication of novel systems characterized by higher stability against change in the subphase composition, owing to the prompting of nanoparticle (NP) irreversible adsorption at the interfaces [2]. In this perspective, the investigation of surface adsorption capabilities of Bovine Serum Albumin (BSA), a widely used model anionic protein, have gained a particular significance in order to tune the structure and properties of protein-stabilized films under various environmental conditions [3].

Accordingly, in this communication we report the results of the study of the dynamic surface activity of BSA and its role in driving the irreversible adsorption of anionic silica nanoparticles (NPs, with a diameter of 24.6 ± 3.9 nm) under variable conditions.

By employing a combination of experimental techniques including Dynamic Surface Tension measurements, performed by the Wilhelmy plate method, and compression isotherms, we studied the effect of pH, ionic strength and protein bulk concentration on the adsorption and the stability, at the air/water interfaces, of films of pure BSA vs. BSA-decorated nanoparticles. It is shown that the protein-NP interactions significantly affect the structure of the resulting films and substantially increase their stability against external mechanical deformation. In particular, protein-decorated NP interfacial layers show, when compressed, a rather complex phase behavior which, if compared to bare protein interfacial layers, suggests that the NP presence influences the interfacial protein conformation.

References.

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[3] Abigail A. Enders et al., Langmuir 39 (2023) 5505

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Food Upcycling: evaluation of different Lombard cereal by-products as innovative antiglycative agents

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Food upcycling is currently a relevant topic as food waste still represents a good source of bioactive compounds and could be used as new feedstock [1]. In this work (supported by Cariplo foundation), we focused our attention on the valorization of different Lombard cereals processing by-products to support local waste management. In particular, considering that several epidemiological studies have shown the correlation between advanced glycation end products (AGEs) and the development of chronic disorders [2], our aim was to evaluate the potential antiglycative capacity of corn cob, rice husk, and wheat processing by-product extracts obtained by microwave assisted extraction coupled with hydroalcoholic mixture (MAE-HA). Different parameters affecting MAE-HA process were initially investigated and optimized using design of experiments (DOE) approach. For each cereal species, the obtained richest extract in polyphenols was tested for the antiglycative activity using different in vitro systems to monitor different stages of the glycation reaction. In particular, the inhibition of Amadori products and of advanced glycation end products (AGEs) formation was evaluated by NBT assay and bovine serum albumin (BSA)-glucose (GLU) or -methylglyoxal (MGO) based systems, respectively [3]. Results indicated that the optimal extraction conditions were 88 °C, 1:42.8 g/mL, 62.6% ethanol, 5 min for corn cob (CBE); 90 °C, 1:35 g/mL, 80% ethanol, 5 min for rice husk (RHE); 40 °C, 1:24.5 g/mL, 23.8% ethanol, 5 min for wheat waste (WWE) respectively. Both CBE and RHE were able to inhibit 70-90% of AGEs generated in our in vitro systems with their activity always higher than that of aminoguanidine (used as reference standard). Conversely, WWE had lower antiglycative activity in all the tested systems. In addition, a good capacity to directly trap glyoxal and methylglyoxal, well known AGEs precursors, was registered for all the cereals' extracts. RHE was the most promising and the research is currently going on to investigate its bioaccessibility and bioavailability before performing stability investigation in order to reach the final goal consisting in a suitable ingredient for food supplement.

References.

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Understanding the spatio-temporal behavior of crops using remote sensing data in an organic farming system

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Organic farming has begun to represent a practical alternative for reducing the environmental impact of crop production and increasing biodiversity. In agricultural systems, the growing demand for stable crop production requires the adoption of useful tools for the sustainable intensification of agriculture. While organic farming systems face various drawbacks, which affect crop yield. Among the limiting factors, weed management is one of the most difficult aspects of organic farming. Monitoring the spatial and temporal variability of yield crop traits using remote sensing techniques is the basis for the correct adoption of precision farming (Marino and Alvino, 2021). Remote sensing methods, which use multispectral satellite images and suitable spectral indices are part of the modern tools for crop monitoring and farm management and environmental assessment of different crops (Atanasova et al., 2021). The knowledge gap this manuscript aims to fill is to detect homogeneous subareas with different yield, yield components by NDVI data Sentinel-2 derived and cluster analysis at the different crop growth stages. The cluster analysis of NDVI data from Sentinel-2 collected at eight different stages (freom November 2020 to June 2021) detected the crop spatial and temporal variability at an early stage. In an open field of 24 ha, an area of about 9 ha, showed a high weed level with a yield average value 78 % lower than the most productive cluster area. An area of 7.3 ha showed the highest yield at harvest with a yield value 45 % higher than the mean harvest data. Sentinel-2 data and cluster analysis can improve an efficient assessment and management strategies in an organic farming agricultural system. Furthermore, the use of precision agriculture tools in organic farming can lead to a site-specific management at the farm level and therefore a sustainable intensification of agriculture systems.

References.

[1] Marino, S., Alvino, A., 2021. Vegetation indices data clustering for dynamic monitoring and classification of wheat yield crop traits. Remote Sens. 13, 541. https://doi.org/10.3390/rs13040541

[2] Atanasova, D., Bozhanova, V., Biserkov, V., Maneva, V., 2021. Distinguishing areas of organic, biodynamic and conventional farming by means of multispectral images. A pilot study. Biotechnol. Biotechnol. Equip. 35 (1), 977–993. https://doi.org/ 10.1080/13102818.2021.1938675.

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Thermophilic membrane reactor for high strength wastewater treatment and biological sludge minimization

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Abstract: TAMR (Thermophilic aerobic/anaerobic membrane reactor) is a membrane bioreactor process that works in thermophilic conditions and with pure oxygen. The biological reactor is combined with an ultrafiltration system. The filed applications of TAMR are the treatment of high strength wastewater (in fully aerated conditions) and the minimization of biological sludge (in intermitted aerated conditions). In this work the potential advantages of TAMR to treat high strength wastewater were analyzed. The results were obtained from the monitoring of a full- and a pilot-scale plant. The average chemical oxygen demand (COD) removal yield was equal to 78% with an organic loading rate (OLR) up to 8–10 kgCOD m⁻³ d⁻¹ despite significant scattering of the influent wastewater composition such as the high concentration of chlorides. Total phosphorus (TP) was removed with a rate of 90%: the most important removal mechanism being chemical precipitation (as hydroxyapatite, especially), which is improved by the continuous aeration that promotes phosphorus crystallization. Moreover, surfactants were removed with efficiency between 93% and 97%. TAMR can also be applied for the treatment of **biological sludge** derived from a municipal WWTP (wastewater treatment plant), to obtain its drastic reduction. The difference from the application to high strength wastewater is based on the system operating in alternate aeration cycles. The alternate aeration cycles were optimized to obtain the higher VS (volatile solids) removal yields and to reduce the foaming issue mainly produced in the nonaerated phase. The treatment is effective in the reduction VS content in biological sludge. A combination of TAMR and conventional activated sludge (CAS) was studied by means of two pilot plants at semi-industrial scale to simulate the new configuration adopted in a full-scale facility for the treatment of high strength wastewater or biological sludge. Wastewater with high contents of organic pollutants were treated by means of TAMR. A mixture of municipal wastewater and thermophilic permeate was fed to the CAS plant. The main results are: high COD removal yield by both TAMR (78%) and CAS (85%); ammonification of the organic nitrogen under thermophilic conditions and subsequent nitrification in mesophilic conditions in the CAS process; capacity of CAS to complete the degradation of the organic matter partially obtained by TAMR; precipitation of phosphorus as vivianite and carbonatehy-droxylapatite in TAMR plant.

The possible recovery of the permeate aqueous residue deriving from TAMR was investigated. The permeate, owing to (i) its constant qualitative and quantitative characteristics, (ii) its excellent biological treatability in the mesophilic field, and (iii) denitrification kinetics comparable to those obtained using methanol can be advantageously reused as an alternative carbon source in a post-denitrification process. Chemical and microbiological characterization of extracted thermophilic biological sludge were carried out. The aim was to evaluate a possible recovery in agriculture in compliance with the limits imposed by current legislation in Lombardy region.

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Green solvents for a sustainable chemistry

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Nowadays, most of the chemical processes used both in academia and industry require the use of different kind of solvents, usually deriving from oil feedstock and which often show a bad eco-toxicological profile.

These are widely used both as reaction media and in larger volumes, in the isolation and purification of reaction products.

Considering their usage, it becomes apparent as most of the chemical transformation associated waste derives from the large amount of solvents used.

A solution to their minimization would be to completely avoid them, by carrying out solvent free processes, a strategy which is unfortunately not always feasible. Another possible approach therefore concerns the identification of alternative media to those commonly used, which are economically sustainable and characterized by low toxicity both to human health and the environment.

In this context, our research group (Green S.O.C.) since many years has been focusing on the replacement of toxic and dangerous solvents, with green and viable alternatives, aiming at the definition of sustainable processes.

Examples of different strategies recently developed will be discussed.

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References.

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[2] N. Winterton, Clean Technologies and Environmental Policy. 23 (2021) 2499

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Microplastic pollution: effects on marine dissolved organic matter dynamics

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Plastic pollution, in particular micro and nano plastics has a range of impacts on aquatic and terrestrial environments. One area where new insights are needed is the effect of plastics on biogeochemical processes, in particular those related to the control of the carbon cycle [1]. The present study explores microplastic-related changes in organic matter in a controlled laboratory experiment with a non-axenic culture of the diatom species Chaetoceros socialis. The phytoplankton culture was grown in three different 2-L flasks. One served as a control and contained only algae, heterotrophic bacteria, and the growing medium prepared with artificial seawater. The two other flasks contained with a similar concentration of plastic and non-plastic particles (~30-µm): polystyrene microspheres in one, and SiO₂ particles in the other. The experiment was designed to compare the effects of microplastics and inorganic particles on organic matter production and degradation. Following the algal growth phase, the water from the three flasks was filtered to remove the algal cells and the particles but leave the organic matter produced and its associated bacteria. A 5-day experiment in controlled dark conditions was performed. Optical changes in CDOM (Chromophoric Dissolved Organic Matter) were monitored daily to examine changes in CDOM quality and quantity in the three systems [2]. CDOM absorbance (as a proxy for concentration) was higher in the control samples with respect to both particle-enriched systems. This suggests different rates of CDOM production and degradation in the presence of particles. CDOM indicators of microbial activity were used to examine changes in the quality of organic matter. CDOM spectral slope and slope ratio indicated that CDOM from the particle-enriched systems underwent greater microbial alteration. This confirms a higher microbial turnover of the organic matter produced in particle containing systems, especially in the presence of inorganic particles (SiO₂) [3]. These results suggest that an increased presence of particles in marine waters (eg. microplastics) can modify microbial organic matter dynamics. These results have important implications on marine surface waters, where the largest concentrations of microplastics and the largest concentrations of organic matter both occur.

References.

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Chemical methods and protocols for quality and traceability of food products in the context of the Agritech Project

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There are multiple ways in which food fraud can occur, including but not limited to mislabeling of goods, adulteration, and counterfeiting. This lead ultimately to the misleading of the consumers, who is entitled to truthful information about the food they consume [1] and a financial loss to those brands who find themselves fighting against unfair competition. Despite the present legislation body (both on the national and international level) the lack of a rigorous scientific approach to food regulation and increase in public awareness has led to numerous independent studies [2] using a number of techniques [3] for authenticity assessment.

Despite the ample literature, one clear shortcoming of the current approach is the reliance on a single technique [4,5] to investigate the authenticity and origin of food. This has proven to be successful in discrimination between different countries of origin and or sources with distances of at least 100 km, but not in separating very close origins. As the contribution of UNISI for the Agritech (Spoke 9, WP 1, Tasks 9.1.1 and 9.1.2) project, a new approach to zoning of two distinct and typical products of the Tuscany region (olive oil and red wine) is proposed.

Multiple data set for each matrix, including spectroscopic properties, trace elements contents, heavy metals isotopic ratios and stable light elements ratios will be collected in the span of multiple sampling campaigns. This, by means of polyfunctional multivariate matrix will allow to reduce furthermore the uncertainty over the production site by combining the ICP-MS, IRMS, HPLC-MS analysis of fruits (i.e., olives and grapes), leaves and end products (i.e., olive oil and wine) together with the analysis of soils collected in the same sampling campaign.

References.

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- [5] F. Gao et al., Journal of Food Composition and Analysis 105 (2022) 104248

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Tailoring the functionality of polymer based biomaterials and their interfaces

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The current challenge is to design material with specific behaviours for mimicking the natural structures and delivering appropriate signals to external interfaces defined by their specific applications.

Selection of a suitable solution is often based on material characteristics (including mechanical properties, drug release kinetics and degradation) that serve for the specific function. Micro or nano-structured materials in the form of gels, nanoparticles, nano-fibers and nano-composites have gained increasing interest in regenerative medicine because they are able to mimic the physical features of natural extracellular matrix (ECM) at the sub-micro and nano-scale levels. The same have to respond to the approach of circular economy and sustainability.

By a careful selection of materials and processing conditions it is possible to finely control characteristic shapes and sizes from micro to sub-micrometric scale and to incorporate bioactive molecules such as proteins or growth factor to develop active platforms to support the repair/regeneration of tissues as well as additives for other applications

Personalised approach is also used to design and preparation of tissue analogues by bioprinting. In this context a proper bioink is necessary to: i) confer a shear thinning behavior for the extrusion-based process and ii) improve the mechanical properties, (iii) controlling the biosensing properties.

Materials such as chitosan, gelatin, alginates are used in different applications. Among natural materials, hyaluronic acid, is widely used for numerous medical applications, such as viscosupplementation, eye surgery and drug delivery. In this study, hyaluronic acid sodium salt (HAs) was chemically modified in order to obtain a photocrosslinkable hydrogel with tailored mechanical properties for osteochondral application such as for meniscus regeneration. Within this aims natural polymer-based double network hydrogels (DNs) were developed by a two-step network-formation procedure to obtain photocrosslinkable methacrylated hyaluronic acid (HAMA) and maleated hyaluronic acid (MAHA) while controlling viability/proliferation of cells.

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Kelvin Probe Force Microscopy-based analysis of few antigen-antibody bindings at a large-area bio-functionalized surface

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Kelvin probe Force microscopy (KPFM) is a non-invasive tool to identify and quantify molecular interactions at single-molecule level, with particular reference to the antigen/antibody immune-complex formation. As a proof of concept, the changes of charge distribution of patterned high density bioreceptor layer, i.e. anti-Human-IgMs, on gold electrode have been explored, upon the highly specific binding between the bioreceptors and few molecules of the IgM cognate antigen, in a wide-field configuration [1]. The analysis has been performed always at the same scanning location, to detect changes in charging properties of the biomodified gate after the highly specific IgM binding, with micrometer-scale resolution without labeling. The formation of few immuno-complex, in a minute timescale, triggers a decrease of the capturing layer surface potential value because of the electrostatic interactions involved, at the active sites, in binding the homologous antigen. The KPFM analysis demonstrate that the surface potential shift involves the whole investigated area; this occurs despite the exiguous number of IgM ligands (10^{-19} mole·L⁻¹ $\equiv 10^2$ zM) that, by diffusion, can bind the anti-IgM dense layer [2]. This is consistent with the occurrence of an allostery phenomenon that could be driven by a long-range redistribution of charge within a dense layer of antibodies during the interaction with the binding partner, thus a small, charged ligand, i.e. IgM molecule, that binds the antibody may significantly modulate the charge re-organization effect [3].

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Destruction of mature insulin amyloid fibrils through plasmonic excitation

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Under certain conditions, native proteins can be destabilized forming highly ordered protein aggregates rich in cross β -sheet secondary structures named amyloid fibrils. These insoluble assemblies no longer have the original biological function, but they are highly toxic and cytotoxic and in some cases being involved in neurodegenerative pathologies. [1]

So far, several inhibitors such as small molecules, peptides, polymers, and hybrid materials have been discovered to block the fibrils formation restricting the aggregation pathway. [2] Recent reports have shown that nanoparticles are effective fibrils inhibitor thanks to their particles size and surface stabilizer; [3] moreover, the excitation of plasmonic resonance of nanostructures enables the activation of photothermal effect in which the absorbed light is converted into heat. It results in a significant heat release near the surface of the nanoparticles that can be exploited to alter and dissociate preformed or mature fibrils. [4,5]

The low toxicity, great stability and good biocompatibility of gold nanoparticles make them suitable for biological applications. [6] In this work, gold nanoparticles are used as photothermal agents to alter mature insulin fibrils. To this end, gold colloids bearing a negatively charged capping shell, with an average diameter of 13 nm and a plasmon resonance maximum at 520 nm are synthesized. The effects on mature insulin fibril morphology and structure upon plasmonic excitation of the nanoparticles-fibril samples have been monitored by spectroscopic and microscopic methods. The obtained data indicate that an effective destruction of the amyloid aggregates occur upon irradiation of the plasmonic nanoparticles, allowing the development of emerging strategies to alter the structure of amyloid fibrils.

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Polymeric electroactive P3HT-MWCNT composites for bioelectronic applications

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One of the main challenges in bioelectronics concerns the development of materials able to respond to external stimuli and that are compatible with neuronal tissues. In the last decades, conductive polymers (CPs) have been widely studied and developed as electroactive materials for applications in interfacing with biological systems [1]. Their conductive properties allow cells or tissues growth upon stimulation, and their "soft" nature allows to reduce the mechanical mismatch between material and cells [2]. CPs' physical and electrical properties can be optimized through the formation of composites enriched with carbon nanotubes [3] or graphene in order to improve electron transport capacity, decrease impedance and increase flexibility. Their biocompatibility can be improved using functionalization methods with biologically active molecules [4,5], even if the influence of blending agents is still under investigation. The precise control of CP films nano-topography may have interesting effects for biointerfacing in terms of protein adsorption and cell adhesion. In this work, we report on how to deposit electroactive nanocomposites using semiconducting regioregular poly(3-hexylthiophene-2,5diyl) (P3HT), with small percentages in weight of multi- walled carbon nanotubes (MWCNT). In particular, their morphology and mechanical properties (Young's Modulus) have been investigated by means of atomic force microscopy (AFM) and scanning electron microscopy (SEM), while their interaction with different extracellular matrix proteins were investigated by means of quartz crystal microbalance with dissipation monitoring (QCM-D). The biocompatibility of the systems with different cell lines has been investigated. These results pave the way to the unravelling of the role of the electrical properties of substrates on the interaction with biological moieties for future applications as platform for electrochemical devices in bioelectronics.

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Advanced extracellular matrix mimics with controlled mechanics for the study of cell mechanosensing

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Natural tissues and extracellular matrices (ECMs) are not purely elastic materials but exhibit dissipative properties. Although it has recently emerged as a novel regulator of cellular responses, the contribution of material dissipation to controlling cell fate decisions is still in its infancy. In this talk, I will present an unprecedented strategy to tune the dissipation rate of viscoplastic substrates suitable for 2D cell culture while precisely regulating linear elasticity[1,2]. In particular, I will present recent findings on viscoplastic hydrogels with varying degrees of dissipation that can modulate cellular functions. By introducing specific sugar sequences that act as stress dampers or physical entanglements, a novel approach to precisely extend the linear stress-strain range (linear elasticity) is described. Our results show a crucial link between this material property and cell response in 2D cultures. They influence the type and speed of cell migration, the geometry and size of vinculin-dependent focal adhesion, F-actin organization, force transmission and YAP nuclear translocation. I will show that cells require a common actomyosin contractility and microtubule tension to probe the substrate and decide whether to adhere or not. This reveals a clear correlation between force transmission, substrate dissipation rate and number of anchorage points. Overall, these results introduce linear elasticity as a new design parameter for the construction of tunable dissipative materials to study the mechanosensing of cells in 2D and possibly also in 3D cultures.

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Tailoring the structural properties of Jin Shofu starch nanoparticles via nano-precipitation: Towards sustainable nano-consolidants for art conservation

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In recent years, green chemistry has become essential for developing advanced materials in various scientific and technological fields, including food chemistry, cosmetics, tissue engineering, and pharmaceutics. The use of biopolymers and solvents selected according to existing standards has become an ideal starting material for processing and synthetic routes, reducing potential threats to human health and the environment [1]. Starch, being a renewable and readily available biopolymer, is a suitable candidate in the formulation of advanced colloids and soft matter for multiple applications. Specifically, Jin shofu wheat starch nanoparticles (SNPs) have been recently developed and shown to be effective consolidants for paintings, providing an alternative to traditional solutions such as natural or synthetic adhesives, which all involve aesthetic alterations or chemical degradation [2]. Here we highlight the possibility to control, during nano-precipitation, the structural order and polydispersity in the SNPs' polymer networks, along with the size distribution of the particles, playing on the mutual chemical affinity of starch with sustainable solvent and non-solvent phases. These findings can potentially affect the optical and mechanical properties of starch films/gels used in several fields, as well as their resistance to attack by microorganisms. The size distribution of the SNPs obtained with different routes was systematically characterized using various techniques, including electron microscopy, X-ray scattering, and infrared spectroscopy, which provided a basis for applicative research on SNPs. Additionally, different aqueous SNPs dispersions were tested on artificially aged painted mock-ups, assessing their consolidation effectiveness by 2D (FTIR-VIS) imaging and visible light (VIS) photography.

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Lime-based binders for the conservation of ancient mosaics

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In the field of restoration and conservation of cultural heritages, the use of binders not fully compatible with the ancient materials represents one of the main issues that could jeopardize not only the aesthetic but also the durability and structural safety of the heritage. It is well known that Portland cement-based binders cannot be used in this field due to physical, chemical and elasto-mechanical incompatibility with the materials used in the past [1]. The purpose of this work is to investigate Portland cement-free systems for the restoration and conservation of ancient mosaics laid on traditional lime-based mortars and uncommon mixtures containing boiled linseed oil, rosin (colophony) and natural sand. The experimental results evidenced that it is possible to develop a lime-based flowable paste containing acrylic latex for direct injection in cracked mosaics substrate in order to enhance the mechanical strength of the old structure. Moreover, a novel cement-free mortar for turning an ancient mosaic into a museum and to seal the gaps between the mosaic tiles was developed by using a blend of hydrated lime and a pozzolanic materials from iron production (blast furnace slag) with the addition of methylcellulose and modified starch.

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The generation of new interfaces as a primary process leading the solidstate mechanochemical transformation

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Deeply rooted in metallurgy, mechanochemistry has recently been rediscovered as a promising way for solid-state organic synthesis. The greener synthetic paths the mechanochemical methods offer make them appealing to both academia and industry [1-3]. The renewed interest in the field has emphasized further the need of giving answers to several open questions. In this respect, the relationship between the application of mechanical forces, macroscopic transformation kinetics, and microscopic mechanisms represents an outstanding subject to investigate.

Mechanochemical reactions are generally performed in ball mills where the powders undergo forging events during individual impacts. At the impact, mechanical stresses can become so intense to locally induce the forced mixing of chemical species and their chemical combination. Several lengths and time scales are involved, and any rationalization of experimental findings is definitely challenging.

We show that a discrete approach to mechanochemical kinetics can bridge the gap between macroscopic observations and microscopic processes. In particular, we relate the generation of new interfaces between different molecular crystals due to mechanical deformation to the transformation rate [4,5]. The resulting kinetic model provides equations able to satisfactorily best fit the experimental curves, paving the way to a quantitative interpretation of mechanochemical kinetics[6].

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Hierarchical 3D self-assembly of coated metal oxide nanoparticles

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The controlled clustering of inorganic nanoparticles (NPs) into ordered superstructures is scientifically interesting because of the amplified properties they exhibit with respect to individual units, enabling their potential application in the technological field. Currently, the ordered structures of 2D NPs are obtained with relative ease, while order control on a 3D scale is not yet fully optimized, although this would further improve the final properties of the aggregate [1].

Here, through the emulsion method clusters of coated cerium oxide nanoparticles (CeO₂ NPs) dispersed in water have been obtained [2]. The hydrophobic interaction between chains of the organic coating leads to the formation and the coexistence of ordered structures, such as face-centered cubic (FCC), body-centered cubic (BCC), or even hexagonal phases such as Frank-Kasper phases [3]. These structures are discussed in terms of geometric and energetic parameters with respect to the nature of the organic coating.

In particular, the contribution of the core dimensions, the ligand length, the distance between neighboring NPs, and the different colloidal forces, such as van der Waals, electrostatic, hydrophobic, and elastic will be analyzed.

Finally, to understand how the order in the superstructures can affect the properties of CeO_2 NPs, photoluminescence (PL) measurements have been performed. From which the different structured organization of NPs and probably the relative amount between them leads to different PL intensities.

The results obtained can provide a scientific platform from which to optimize the development of 3D-ordered hierarchical superstructures with original physical properties and for technological applications.

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Simulating the chemical equilibria of metal complexes: Insights into the ligand exchange mechanism

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Despite the rich history of experimental studies focusing on the thermochemistry and kinetics associated with metal-ligand complex formation and ligand exchange mechanism,[1] molecular-level computational studies on the complete chemical equilibrium and rate constants of these systems are scarce. In this presentation, we illustrate an integrated computational strategy aiming at effectively describing the structural, thermodynamic, and dynamic properties of various metal ion-amine complexes. Our innovative computational protocol is rooted into molecular dynamics simulations, enhanced sampling techniques, and a stochastic model of ligand exchange kinetics,[2] in addition to recently optimized interaction force fields.[3] Results demonstrate that an accurate description of complex chemical equilibria is computationally feasible and provide some valuable insights into the complex formation and ligand exchange mechanisms.

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Expanding the Chemical Space of Tetracyanobuta-1,3diene (TCBD) through a Cyano-Diels-Alder Reaction

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In the realm of fluorescence probes, studying the significance of tetracyanobuta-1,3-diene (TCBD) systems is crucial for future advancements.[1] TCBD serves as a versatile and potent electron-acceptor component, widely employed in the synthesis of electroactive conjugates. While its electron-accepting capabilities have been extensively explored, there remains a notable scarcity of research on its chemical modification, a crucial avenue for expanding the chemical space of this intriguing functional unit. Addressing this research gap, we present an innovative study that showcases the potential of TCBD through a high-yielding cyano-Diels-Alder (CDA) reaction.[2] This pioneering reaction involves TCBD acting as the dienophile, while an anthryl moiety acts as the diene. By leveraging this approach, we successfully generated an anthryl-fused-TCBD derivative. Through X-ray diffraction, we unequivocally determined its structure and observed its remarkable thermal stability, exceptional electronaccepting capability, and intriguing features in both the electronic ground and excited states. To gain comprehensive insights into these TCBD-based systems, we conducted a thorough investigation encompassing theoretical, electrochemical, and photophysical analyses. Additionally, we performed a detailed kinetic analysis, exploring the intramolecular CDA reaction at various temperatures. This analysis provided valuable insights into the transformation from the initial anthryl-TCBD-based reactant to the final anthryl-fused-TCBD product.

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Photoactive pigments from *Ulva Rigida* encapsulated in cubosomes for anticancer treatment in Photodynamic Therapy

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Ulva Rigida is a green marine algae that contains a wide range of bioactive compounds, including photoactive pigments such chlorophylls, potentially useful in anti-cancer Photodynamic Therapy (PDT) [1,2]. However, administration into the body of these pigments is limited by their hydrophobic nature, leading to decreased bioavailability, aggregation, and degradation [3]. One of the most common causes of cancer death in developed countries is pancreatic cancer, considered as extremally resistant to therapy because of its complex and obstructive tumor microenvironment [4]. Nanotechnology may help in bypassing this peculiar environment, offering an appropriate form of therapy for this disease.

To protect, properly deliver, and release chlorophylls in their photoactive form into the targeted pathological tissue, hydrophobic pigments obtained from the *U. Rigida* biomass using the green microwave-assisted extraction technology were here encapsulated in bicontinuous cubic lipid liquid-crystalline nanocarriers (cubosomes), originating a nanoparticles suspension with possible application in anti-cancer PDT. The physicochemical characterization of two different types of cubosomes formulations and the assessment of their biocompatibility and biological activity on pancreatic cancer cell lines (BxPC-3), will be here presented.

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Thermo-responsive lipid cubic nanoparticles as novel drug delivery nanovectors

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To date, one of the main goals of nanomedicine has been the solubilisation of therapeutic molecules and their controlled release to the target site of the disease through the formulation of drug delivery systems (DDS). Lipid assemblies are still considered the most suitable candidates for DDS due to their biocompatibility and similarity to the plasma membrane. In particular, complex lipid assemblies, denominated cubosomes, are considered one of the most promising drug delivery vectors for the in-vivo delivery of molecules of pharmaceutical and imaging interest, such as drugs, bioactives and contrast agents, for disease treatment and theragnostics. In this view, a novel class of stimuli-responsive DDS, consisting of the lipid glycerol-monooleate (GMO), has been developed using a thermo-responsive block copolymer poly(*N*,*N*-dimethylacrylamide)-*b*-poly(*N*-isopropylacrylamide) (PDMA-b-PNIPAM). Combining a series of characterization techniques, such as small-angle x-ray scattering (SAXS), quartz crystal microbalance with dissipation monitoring (QCMD), and confocal laser scanning microscopy (CLSM), we compared the thermo-responsive properties of these DDS and their affinity for lipid bilayers with those displayed by conventional Pluronic-stabilised nanoparticles and demonstrated a translation of the thermo-responsiveness of the polymer to the nanoparticles next to an increased affinity for the membranes. These findings suggest that these new cubic formulations might be promising vehicles for DDS [1].

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Sodium hyaluronate derivative with enhanced affinity towards MMP12 catalytic domain to be used as viscosupplement

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Sodium hyaluronate (NaHA) functionalization was performed with a small molecule (MMPI), having proven inhibitory activity against membrane metalloproteins (MMPs) involved in inflammatory processes, in particular the MMP12. MMPs are a family of Zn peptidases, that, if over expressed, lead to the uncontrolled degradation of specific protein substrates. Among these MMPs, MMP3, MMP12 and MMP13 attack and cleave the peptide bonds of collagen and gelatin present in the connective tissue. High concentrations of these MMPs are found even in subjects with osteoarthritis [1]. The obtained derivative (HA-MMPI) was characterized in terms of structure, thermal and rheological behavior (viscosity and viscoelastic properties in shear). Furthermore, *in vitro* cytocompatibility, sulphated glycosaminoglycans (sGAG) and hydroxyproline (HYP) content, were evaluated. The inhibition activity of MMPI and HA-MMPI versus MMP12 catalytic domain was tested to demonstrate that the MMPI grafted to NaHA maintains its function as MMP12 inhibitor. HA-MMPI demonstrated viscoelastic properties close to those of healthy human synovial fluid [2], cytocompatibility towards human chondrocytes and nanomolar affinity towards MMP12. Thus, HA-MMPI can be a good candidate as viscosupplement in the treatment of knee osteoarticular disease [3].

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Photocross-linked gelatin methacryloyl microparticles prepared by double emulsion method for drug delivery

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Gelatin microparticles, due to gelatin's excellent biocompatibility, have been extensively studied for many biomedical applications. Nevertheless, chemical cross-linkers conventionally used to stabilize gelatin systems have raised some concerns about their cytotoxicity. In this framework, photopolymerizable gelatin methacryloyl (GelMA) has been proposed as a suitable alternative material for tissue engineering and drug delivery applications [1]. Although GelMA microparticles obtained with a single emulsion method have been already proposed in the literature [2, 3], to our knowledge this is the first study where the double emulsion method [4] is combined with photocross-linking treatment.

Gelatin methacryloyl porous microparticles (GMA-MPs) were prepared using an oil-inwater-in-oil emulsion (O/W/O) and then photocross-linked under UV light. Two different degrees of substitution (DS) of GelMA were used. The size and surface porosity of GMA-MPs were assessed by optical and electron microscopy. The photocross-linking extended microparticles' stability in water at 37 °C from a few minutes up to several days. Photocrosslinked GMA-MPs displayed an inverse correlation between their swelling abilities and the DS with a difference of about two times in terms of absorbed water. The nanoscale structure of GMA-MPs was investigated with X-rays scattering, suggesting that the gel network was not dramatically affected by the cross-linking. Finally, the release properties of methylene blue loaded GMA-MPs were tested at 20 °C and 37 °C. Our results confirmed the possibility to cross-link GMA-MPs, prepared by double emulsion method, with a photo-treatment, enabling to tailor the swelling and release properties by the direct control of the DS.

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Surfactant effect on feline coronavirus

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Surfactants are low-cost chemicals whose interaction with viruses can be controlled for inhibiting the infectivity of enveloped viruses. In this work we have tried to bridge disciplines between virology and colloid science and have treated the virus as a colloidal particle. We used a feline coronavirus (FCoV) and tested the effect of surfactant type, choosing representative cationic (CPC), anionic (SDS), and nonionic (C10E8) surfactants. FCoV belongs to the same family as human SARS-CoV-2, Coronaviridae, but can be handled safely in a physical chemistry lab.

The effects of surfactant type and concentration were explored using dynamic and electrophoretic light scattering to follow possible aggregation/disruption of the virus, and fluorescence spectroscopy to probe protein denaturation. A parallel study was conducted on liposomes, probing the damage on the bilayer by following the leakage of entrapped fluorescent calcein. Finally, virucidal activity was tested on Crandell Reese Feline kidney cells.

The ionic surfactants provoke changes in dimension and protein denaturation around their CMC that coincides with viral inactivation. The kinetics around the surfactant's CMC of viral inactivation and membrane damage coincide in the case of the non-ionic surfactant, while the fluorescence of the virus is unchanged. Using SDS the kinetics of inactivation are much faster than the corresponding membrane damage and the fluorescent signal of the virus decreases, probably due to protein denaturation. We conclude the main mechanism of FCoV inactivation with the nonionic surfactant involves the disruption of the lipidic envelope, whilst the ionic surfactants also induce the denaturation of membrane proteins. We rationalise these differences in membrane damage due to the lower energy cost of a neutral surfactant to overcome a flipflop across the membrane.

The fundamental understanding and control of these interactions will aid in practical formulations for coronavirus inactivation and removal from contaminated surfaces.

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Transition from active motion to anomalous diffusion of *Bacillus subtilis* confined in hydrogel matrices

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We investigate through confocal microscopy and particle tracking the motility of *B*. *subtilis* confined into porous hydrogel matrices. The dynamical behavior of bacteria is linked to parameters describing the hydrogel porosity, extracted from the analysis of confocal stacks of fluorescently labeled hydrogels. Mean square displacements (MSDs) reveal that the run-and-tumble motility of unconfined bacteria progressively turns into sub-diffusive motion with increasing confinement. Single-trajectory analysis shows that the average MSD is the result of changes in the populations of active, diffusive, and sub-diffusive bacteria, with that of active bacteria continuously decreasing and the one of sub-diffusive bacteria increasing with increasing confinement. Interestingly, the diffusive population is maximal at intermediate confinement. We demonstrate that the observed transition can be interpreted in terms of a recently proposed hopping and trapping model for the motion of *E. coli* in confinement, that we revisit for our conditions. Finally, we extract a quantitative relation that links the median run velocity under confined and unconfined conditions through the confinement length.

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POSTERS

FROM PLANTS TO TECH: Developing 3D-Printed Biobased Composites with Micro- or Nanocrystalline Cellulose

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The usage of additive manufacturing (AM) for (bio)medical applications has been growing during the last decades as a versatile and cost-efficient method for fabricating complex and personalized (bio)medical devices.[1] In some cases, these (bio)medical devices need extremely high resolutions, to mimic the internal structure of bones or other tissues.[2] Stereolithography (SLA) is an AM technology that uses photosensitive resins and is suitable for fabricating high-resolution parts (down to 5 µm). Although the high precision of SLA makes it perfect for (bio)medical usage, the lack of biocompatible and biobased resins limits its utilization.[3] Therefore, the development of new materials is essential. Here, poly(ethylene glycol) diacrylate (PEGDA) and acrylated epoxidized soybean oil (AESO) were combined with micro- or nanocellulose crystals to create a resin suitable for 3D printing. The best AESO/PEGDA ratio was 80:20 on weight: it exhibited the highest tensile strength (4.4 ± 0.2) MPa) and elongation at break $(25\% \pm 2.3\%)$, viscosity > 1.5 Pa s, and a biobased content of 68.8%. Furthermore, when 2.4% of micro- or nanocrystalline cellulose was incorporated into this resin formulation, the tensile strength increased by 2.3 and 59.1%, respectively. Finally, the introduction of fillers did not impact the UV-light penetration, and the printed parts exhibited exceptional quality, thereby establishing the resin potential.

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Improvement of chia mucilage (*Salvia hispanica*) stability through the formation of emulsion systems dispersing lemongrass essential oil

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Chia (*Salvia hispanica*) is an annual herbaceous crop species of the *Lamiaceae* family whose seed nutritional properties and health benefits are deeply documented [1]. When soaked in water, chia seeds are able to form a hydrogel-like matrix through an extensive network of nanoscale fibers which are indicated as mucilage [2]. Thanks to its mechanical and nutritional properties, chia mucilage (CM) has been widely used in food industry [3]. Freeze-dried mucilage dispersed in solvent undergoes degradation during storage, probably because of oxidative phenomena that results in the loss of the initial mechanical characteristics. The ageing effect on CM suspensions was evaluated considering the structural changes that were investigated through scanning electron microscopy (SEM), rheology and small angle X-ray scattering (SAXS) [4].

To slow-down the auto-oxidative processes, lemongrass essential oil (LEO) was emulsified in the polymer matrix and the rheological responses of CM suspensions (without LEO) and CM emulsions (with LEO) were compared. The collected outcomes showed that both CM suspensions and CM emulsions can be classified as plastic fluids and a decrease of CM suspensions viscosity was detected during storage, while the viscosity of CM emulsions remained constant. More in detail, the short-term stability of CM suspensions was attributed to oxidation reactions, thus the presence of LEO with antioxidant properties allowed to prevent degradation phenomena in CM emulsion [5, 6].

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Nanoemulsion formulations as edible coatings for *ready-to-use* foods

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In recent years, growing attention has been paid to food packaging in order to reduce the use of non-recyclable materials and food waste. At the same time, consumer demand for ready-to-use foods such as fruits and vegetables, which are highly perishable, has increased. As a result, the food industry is looking for solutions to reduce and replace traditional petroleum-based plastic packaging and extend the shelf life of food products. Edible packaging meets the needs of the industry and is perceived positively by consumers. Among edible packaging, edible coatings applied as a thin, adherent layer to the product surface preserve food from weight loss and other spoilage phenomena.

In this study, edible coatings combining hydrophilic and hydrophobic properties were formulated, as nanoemulsions using polysaccharides and essential oil, to provide good mechanical and gas barrier properties to slow down spoilage of fresh-cut or whole fruits. The edible coating formulations were first characterized by dynamic light scattering and rheology and then applied to fruit in different ways. The effect of the nanoformulations on product quality was assessed by evaluating various parameters such as weight loss, pH and titratable acidity, total phenolic content, and fruit appearance during storage [1,2].

Overall, the results showed that the application of edible coatings helped to extend the shelf life of the studied products while maintaining their quality during storage.

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Nanoemulsion formulations as edible coatings for *ready-to-use* foods

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Antioxidant Effect of Vitamins in Olive Oil Emulsion

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In this study, water-in-oil emulsions with virgin olive oil have been fortified with vitamins. Water-in-oil emulsions are heterogeneous systems that can solubilize both hydrophilic and hydrophobic compounds. Thus, hydrophilic vitamin C and lipophilic vitamin E were added separately or together in the emulsions. A suitable emulsion composition was selected considering different surfactant (mono- and diglycerides of fatty acids, E471; sorbitan monooleate, Span 80; polyoxyethylene sorbitan monooleate, Tween 80) and water concentrations. The emulsion best suited for high stability was the one with a concentration of Span 80 (1% w/w) and water (1% w/w). The antioxidant effect of vitamins in emulsions was studied considering the variation of peroxide levels during storage. The oxidation reaction was slowed down in emulsions containing vitamin C, but was accelerated by the addition of vitamin E in high concentration. Peroxide levels were higher in emulsions containing vitamin E than in emulsions prepared without vitamins or in oil. The antioxidant activity produced by the simultaneous addition of vitamin C and E was so effective that peroxide levels did not change in the presence of high amounts of vitamin after about 40 days of storage, which was due to the regeneration of vitamin E by vitamin C.

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C-based materials for solid state hydrogen storage: a new perspective

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In the last 10 years, our research groups started a deep investigation on the possibility to use C-based materials for both energy and solid state hydrogen storage. The research started with fullerene, reported in literature to absorb interesting amount of H₂ in harsh conditions (high working temperature and pressure) and in a non-reversible way. To make the desorption reaction possible, we started to synthesize alkali cluster-intercalated fullerides (ACIF), consisting in crystalline nanostructures in which positively charged metal clusters are ionically bonded to negatively charged C₆₀ molecules, forming charge-transfer salts. We synthesized mixed Li-Na clusters intercalated fullerides belonging to the Na_xLi_{12-x}C₆₀ ($0 \le x \le 12$) and Na_xLi_{6-x}C₆₀ ($0 \le x \le 6$) families. By manometric and thermal analyses it has been proved that C₆₀ covalently binds up to 5.5 wt% H₂ at moderate temperature and pressure, thanks to the catalytic effect of the intercalated alkali clusters. Moreover, the destabilizing effect of Na in the co-intercalated Na_xLi_(6-x)C₆₀ compounds leads to an improvement of the H₂-sorption kinetics by about 70%, together with a decrease in the desorption enthalpy from 62 to 44 kJ/mol H₂. The addition of Pt and Pd nanoparticles to Li fullerides increases up to 5.9 wt% H₂ of about 35 % the absorption performance and rate respectively.

Recently our attention moved to biochar, the carbon side-product in the pyrolysis/gasification of residual waste biomasses, that started to receive a widespread attention in the field of energy-storage thanks to its inexpensiveness, porous structure (inherited from biomass precursors), and excellent chemical stability. Biochar can be converted into activated carbon (materials with specific surface area > $1000m^2/g$) through a chemical treatment with bases giving a new cost-effective and environmentally friendly carbon material. In this frame, we prepared novel super-activated carbon materials originating from biochar derived by the pyrolysis of agrifood wastes (rice bran and husk, corn bracts, melon and pumpkin peels). The materials obtained by rice bran and melon peels, having specific surface area up to $3000 \text{ m}^2/g$, show a very good H₂ storage ability, adsorbing up to 4.5 wt % H₂ in around 30 seconds at 77K. Work is in progress to optimize the pyrolysis and activation conditions and to improve the sorption performance by intercalating with alkaline metals and doping with metals oxides.

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NOVEL AND SUSTAINABLE POROUS MATERIALS FOR OFLOXACIN REMOVAL FROM POLLUTED WATERS

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Emerging contaminants (ECs) are natural or synthetic substances that enter the environment at low concentrations (ng - μ g L⁻¹) due to the anthropic impact. Antibiotics are among the most widespread ECs, found ubiquitously, especially in the aquatic environment. Their presence causes the spread of antibiotic resistance, so it is mandatory to find new ways to remove them [1]. The project aims to study novel and sustainable materials for antibiotic removal from contaminated waters. Some metal-organic frameworks [2,3] and halloysite nanotubes have been synthesized, characterized, and investigated, choosing ofloxacin (OFL) antibiotic as the model molecule. Some of them were magnetically modified [4].

Different synthetic approaches were applied to obtain the adsorbents, paying attention to choose easy, quick, sustainable and feasible processes. Both unmodified and magnetically modified materials were characterized by several techniques (XRPD, TGA, FT-IR, SEM, EDS, TEM, surface area and pore size) and the obtained morphological and structural features and composition were put into relation with the adsorption performances.

First, adsorption and kinetic experiments were performed in tap water due to its invariant composition and a more remarkable similarity to environmental waters. The adsorption capacity, mechanism of each material, and antibiotic uptake on the solid sorbents were evaluated and compared. Then, the suitability of the best porous materials as adsorbent phases for water depollution was tested on actual samples (river and wastewater effluent) spiked with a few μ g L⁻¹ of OFL. The obtained removal efficiencies, indicate that these materials are promising candidates for removing fluoroquinolone antibiotics from polluted waters. Noteworthy, the magnetically modified porous materials could be easily removed from the media after treatment and reused, as no degradation occurs.

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ZnS–GO/CNF FREE-STANDING ANODES FOR SIBs: IMPROVED ELECTROCHEMICAL PERFORMANCE AT HIGH C-RATE

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Among rechargeable batteries for energy storage, SIBs are receiving growing interest compared to LIBs, as Na is abundant and low-cost. However, its size poses concerns about the electrode materials suitable to reach adequate specific capacity, high coulombic efficiency and long life-cycle. In the present study we synthesize and characterize ZnS-graphene (ZnS-GO) composites embedded into carbon nanofibers (CNFs) as self-standing anodes for SIBs. ZnS-GO were synthesized by hydrothermal process [1] and an amount of 10 wt% (10%ZnS-GO/CNF) and 30 wt% (30%ZnS-GO/CNF) was loaded onto CNFs by electrospinning [2]. The characterization techniques (XRPD, SEM, TEM, EDS, TGA, and Raman spectroscopy) confirm that the ZnS nanocrystals of 10 nm with sphalerite structure covered by the graphene sheets were successfully synthesized. Moreover, in the case of ZnS-GO/CNF anodes, the active material is homogeneously dispersed in the CNFs' matrix and the ordered carbon source mainly resides in the graphene component. The actual active material amount was 11.3 and 24.9 wt% in the self-standing anodes 10%ZnS-GO/CNF and 30%ZnS-GO/CNF, respectively. The ZnS-GO/CNF electrodes were electrochemically tested and compared to a tape-casted ZnS–GO example prepared by conventional methods (active material amount of 70 wt%). The electrochemical results demonstrated improved specific capacity at high C-rate for the freestanding anodes compared to the tape-casted example. Indeed, the specific capacities were 69.93 and 92.59 mAh g⁻¹ at 5 C for 11.3 and 24.9 wt% free-standing anodes, respectively, vs. 50 mAh g⁻¹ for tape-casted. The 24.9 wt% ZnS-GO/CNF anode gives the best cycling performances: we obtained capacity of 255-400 mAh g⁻¹ for 200 cycles and coulombic efficiencies \geq 99% at 0.5 C, and a specific capacity of 80–90 mAh g⁻¹ for additional 50 cycles at 5 C. The results suggest that self-standing electrodes with improved electrochemical performances at high C-rates can be prepared by a feasible and simple strategy as an ex-situ synthesis of the active material and addition to the carbon nanofibers precursor by electrospinning.

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ENHANCED SOLUBILITY AND DISSOLUTION RATE OF CARVEDILOL LOADED ONTO ETCHED HALLOYSITE NANOTUBES

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It is established that the poor water solubility of drugs represents a critical issue for the pharmaceutical industry [1], as solubility is crucial to achieving proper bioavailability for orally administered drugs. Carvedilol is a poorly water-soluble drug employed to treat chronic heart failure [2,3]. One of the most promising methods for enhancing solubility and dissolution rate consists in loading the active principle onto biocompatible supports [4].

In this study [5], we used halloysite nanotubes (HNTs) as support and prepare composites through the impregnation method. Commercial HNTs were treated by acid (HCl and H₂SO₄) or alkaline (NaOH) etching. In all the systems we obtained good drug loading: 30-37 wt% against the theoretical value of 40 wt%.

Etching and loading processes do not induce structural nor morphological changes, as demonstrated by XRPD, SEM, and TEM analysis.

¹³C and ²⁷Al solid-state NMR, supported by FT-IR findings, show that the interactions between carvedilol and HNTs involve only the external siloxane surface, not the internal lumen of nanotubes.

All the carvedilol-halloysite composites display enhanced dissolution rate, wettability, and solubility, as compared to raw carvedilol. In a period of 4 hours, raw carvedilol reaches a maximum release of 80% in gastric-fed conditions (pH 4.5) and only of about 25% in intestinal conditions (pH 6.8). The best performance is obtained for the composite with HNTs treated with HCl 8M. This support displays the highest specific surface area value: $91 \text{ m}^2 \text{ g}^{-1}$ against 58.2 m² g⁻¹ for commercial HNTs. This system releases 100% of the drug in 4 hours in both gastric-fed and intestinal conditions.

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GERMANIUM FERRITES AS ANODES FOR SODIUM ION BATTERIES

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The ferrite spinels are well-known and studied materials with an impressively wide range of applications extending from millimeter wave integrated circuitry to power handling, simple permanent magnets and magnetic recording, catalysis, sensors, energy, nanomedicine and imaging in magnetic resonance [1]. ZnFe₂O₄, CoFe₂O₄, Fe₃O₄, NiFe₂O₄, MgFe₂O₄, and MnFe₂O₄, each of them having peculiar functional properties, represent some examples of the most studied and applied ferrites. Their electrochemical applications, mainly as anodes in lithium and sodium ion batteries (LIBs and SIBs), are due to the intriguing features of their cubic crystal structure. The need to speed up the transition towards post Li technologies for the well-known Li issues forced the research to search new cathode and anode materials. Ge-based ternary oxides are currently considered as promising anode candidate for both LIBs and SIBs due to their unique reaction mechanism, based on conversion and alloying. In particular, GeFe₂O₄ seems particularly promising [2, 3]. However, volume expansion and poor conductivity represent the main challenges of Ge-based ternary oxide when implemented for practical applications. The nanostructured engineering and hybrid structures have been regarded as two main strategies to relieve above issues, as well as doping.

We synthesized pure and Mg and Sn doped GeFe₂O₄ samples by means of the mechanochemical synthesis. The thorough physical- chemical characterization by using X-ray powder diffraction with Rietveld refinement and spectroscopic techniques (EPR and Mössbauer) allowed us to determine the structural features and purity degree useful to better understand the electrochemical features. The powders were then used to prepare electrodes in order to carry out preliminary electrochemical tests. Sodium charge storage of the samples was investigated through conventional cyclic voltammetry and charge and discharge measurements. The CV curves showed interesting results, with the presence of the peaks related to the conversion process of GeFe₂O₄ and the alloying reaction of Ge with Sodium. Galvanostatic charge and discharge measures at different C rate revealed a gradually reduction of the capacity and rate capability by increasing C rate for GeFe₂O₄ alone, despite its initial discharge capacity of 600 mAh.g⁻¹. However, some improvement-in electrochemical performances was observed with Sn and Mg-doped samples.

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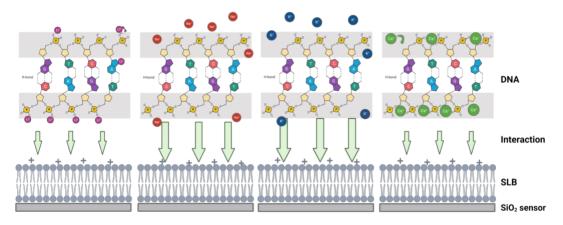
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THE INTERACTIONS BETWEEN DNA – LIPID BILAYERS ARE CATION AND BUFFER SPECIFIC

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Specific buffer effects are emerging as the new frontier of "Hofmeister phenomena" [1]. Understanding the interactions between the DNA and lipid bilayers in aqueous media is fundamental for the development of biosensors, synthetic nanopores, scaffolds and gene delivery systems [2]. Here, we studied the combined effect of monovalent cations (100 mM chloride salts) and buffers (50 mM) at pH 7.4 and 298 K on DNA-lipid interactions through quartz crystal microbalance (QCM) and ellipsometry measurements. We found that DNA layer thickness adsorbed onto DOTAP/DOPC 30:70 w/w supported lipid bilayer onto silica surface decreased in the cations order: $K^+ > Na^+ > Cs^+ \sim Li^+$ and buffer order: citrate > phosphate > Tris > HEPES. DNA adsorption is cation dependent due to specific charge screening, with a "bell-shaped" Hofmeister series as the result of two opposing mechanisms. For kosmotropes (Li⁺) the *law of matching water affinities* prevails, while for chaotropes (Cs⁺) ion dispersion forces dominate. In addition, buffers superimpose their effect by modulating the specificity of the cations [3].



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Influence of the xanthan gum on the rheological properties of alginate hydrogels

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The selection of biopolymers as constituents of hydrogels is of great importance to enable their use in various fields. Here, a mixed hydrogel of alginate and xanthan gum has been prepared by the in- situ gelation method promoted by calcium crosslinking [1,2]. The influence of xanthan gum and calcium cations on the rheological behavior of alginate hydrogels were investigated using steady shear, dynamic and transient shear rheology experiments. The results showed that the hydrogels behaved as Carreau fluids, and that the overall viscosity of the hydrogel was dependent on both Ca²⁺ and xanthan gum concentrations. The length of linear viscoelastic range was influenced by xanthan gum content only at low calcium concentration, while the storage modulus (G') was found to increase with xanthan gum and calcium content. The interpolation of mechanical spectra with a power law demonstrated that G' and G'' were slightly dependent on the frequency and that G' became less frequency dependent with the addition of xanthan gum. Even though the elastic contribution of the hydrogel increased with calcium and xanthan concentration, the hydrogels obtained were not able to fully recover their original structure after the application of a high load. The behavior at large amplitude oscillation strain, mimicking real processing conditions, showed that hydrogels crosslinked with a low calcium concentration were affected by xanthan gum even at lower concentrations than hydrogels crosslinked with high calcium content [3].

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Preparation and characterization of Persistent Phosphors in solid and gel phases.

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Persistent luminescence is a fascinating phenomenon which has been known for years. It can be defined as the long-lasting emission by a phosphor, sometimes wrongly called phosphorescence, after its excitation has stopped; this emission can last for a few seconds to days, depending on the features of the emitting material.^[1]

Starting from the discovery of SrAl₂O₄:Eu,Dy by Matsuzawa ^[2], several types of materials have been proposed up to now, ranging from inorganic ^[3] to organic ^[4] and hybrid ^[5] phosphors. These find applications in different fields, such as anti-counterfeiting, road marking, toys decoration, photocatalysis, etc. ^[1].

In this work, we focus our attention on silicate-based phosphors. We synthesized several materials, comparing different synthetic approaches. The optical, structural, and luminescent properties have been further investigated. To start, the silicate matrix is synthesized and studied in detail, then later we move to the doping process, to evaluate the effects of the dopants on the properties of the host matrix. Different types and concentrations of dopants have been considered. The purpose of this work is the development of new persistent phosphors with advanced features in terms of initial brightness and long-lasting afterglow, with the final goal to replace the widespread lanthanide-based ones. In case of promising results, the idea is the inclusion of the active material in a solid/gel phase and application of this construct as sustainable source for cultural heritage lighting.

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Modelling the Impact of Chemisorption and Steric Forces in Cyclic Voltammetry Curves

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Our study analyzes the phenomena of ion adsorption on charged surfaces immersed in an electrolyte solution. Understanding these phenomena is useful for the development of devices such as biosensors or batteries, as well as for simulating the results of electrochemical techniques such as cyclic voltammetry. In equilibrium conditions the Poisson-Boltzmann model can be used, but this fails at large voltages or ion concentrations due to the fact that some effects, i.e. steric effects due to the finite size of ions [1], are not considered. For this reason more complex theories need to be used, also to include chemisorption phenomena that are important in the context of charge regulated surfaces. We are developing a python library to solve the Poisson-Nernst-Plank model [2], the time dependent counterpart of the Poisson-Boltzmann model, numerically by finite element methods [3]. The model is being used to study the cyclic voltammetry curves of protein adsorption, supporting the development of electrochemical bionsensors.

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Eco-sustainable nanostructured formulation for applications in agrifood productions: the operative unit CSGI-University of Naples in the ProFood-IV project

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In the framework of the ProFood-IV project, the operative unit CSGI-University of Naples has focused on green alternatives to the common productive practices of IV-range fruits and vegetables, with particular emphasis on the innovative design, prototypical production and physico-chemical characterization of: i.) eco-sustainable pesticides, ii.) safe formulations for the industrial washing, iii) smart packaging.

The growing attention to the rational use of environmentally friendly compounds, such as natural metabolites deriving form plants, endowed with insecticide and antiparasitic activity, arises from the necessity of reducing the impact of conventional pesticides. We focused our attention on the development of micro-gels of hydroxypropyl cellulose (HPC) for the encapsulation and controlled release of natural biopesticides, such as Inuloxin A and Cnicin.

The washing step in IV range vegetable production is aimed at physical contaminant removal and bacterial load reduction. Till a few years ago, this was mostly accomplished by using chlorine-based agents, which could lead to the formation of carcinogenic compounds. In the ProFood project, natural metabolites derived from bacteria and plants are proposed as a possible alternative approach. Ungeremine and diacetyl lycorine, alkaloids obtained from different species of the Amaryllidaceae plant family, appear very promising from this viewpoint. In fact, their bactericidal, fungicidal and insecticidal functions justify their exploitation as bio-preservatives. After a preliminary physicochemical study focused on their solubility and protonation state in aqueous solution, their co-formulation with natural biosurfactants is currently under investigation, with the aim to enhance their solubility and spreadability.

Last, the development of smart packaging capable of detecting the deterioration of the final product gives the consumer a safe food experience. With this aim, we developed hybrid nanoparticle HPC systems able to fulfil this task. We used a natural polymer in combination with high-efficiency nanoparticles, such as gold, silver and zinc oxide, which allowed us to design high-efficiency hybrid systems.

Overall, the results obtained by the operative unit CSGI-University of Naples, which mainly focuses on relatively upstream approaches, furnish a reliable technological platform for future exploitation of very innovative bio-inspired approaches in IV-range fruit and vegetable production.

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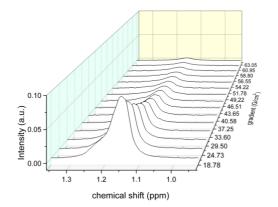
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Characterization of the Non-Ionic Surfactant TRITON™ CG-110 in water

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We analyzed a commercial nonionic surfactant (TRITONTM CG-110) from the family of alkylpolyglucosides. The critical micelle concentration (cmc) was determined through surface tension and conductivity measurements, resulting in $(4.5 \pm 0.2) \cdot 10^{-3} M$. A newtonian behavior of the solutions was observed in the entire range of concentrations investigated, from 0.01 to 90 wt%. Interestingly, two critical concentrations were identified in the viscosityconcentration curve. The first critical concentration is close to the obtained cmc, while the second critical concentration may be due to chain-chain surfactant interactions. Self-diffusion of the surfactant and water is fairly constant until the second critical concentration is exceeded. A strong decrease in the surfactant diffusion coefficient and water self-diffusion at high surfactant concentrations confirms the chain-chain interactions. Although not surprising, the three-fold increase in viscosity is interesting, as reverse micelles can be employed for the solubilization of hydrophobic substances, nanoparticle synthesis, separation of biomolecules, and the study of biomolecules.



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Biosurfactants drive the spontaneous formation of nanovesiscles in waterbased formulations

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The increasing ecological awareness has led to the preference for surfactants which present additional properties such as biodegradability and biocompatibility. The principles of Green Chemistry steer the scientists' and technologists' interest for even more-eco-compatible alternatives, which are inspired by natural substances or directly extracted from natural sources, such as the biosurfactants. Rhamnolipids (Rha), biosurfactants naturally produced by bacteria and largely available thanks to the development of industrial biotechnological production [1], are increasingly proposed as a new class of surface agents with low environmental impact, low toxicity, and high spreadability when employed in industrial formulations.

With the aim to build the scientific and technological basis for Rha co-formulation with other surfactants, here we analyse the mixtures of Rha with the conventional anionic and cationic surfactants, such as sodium lauryl ether sulfate (SLES) and cetyltrimethylammonium chloride (CTAC), in both neutral and acidic solution, in order to investigate the interfacial and bulk behavior and when Rha present negative and neutral charges, respectively [2]. The mixtures have been investigated by surface tension, DLS, SANS, EPR, conductimetry and contact angle measurements.

The results show that Rha are able to co-micellize with synthetic surfactants, driving the spontaneous formation of vesicles spreading ability. The aggregate morphology is mainly regulated by mismatch between the molecular architecture of Rha, which present a bulky headgroup and two short tails, and the conventional surfactants, which present a relatively small headgroup and a single long tail. Other factors, such as electrostatic interactions play only a minor role. This spontaneous vesicle formation pave the way to the applications of Rha mixtures as eco-friendly cargos of both hydrophilic and lipophilic actives.

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Characterization of Hydroxypropylcellulose gel containing fluorine doped zinc oxide nanoparticles

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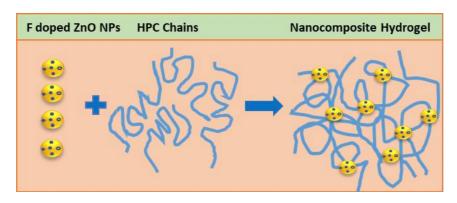
The project aims to design and characterize nanocomposite materials composed of polymeric gels (Hydroxypropyl cellulose HPC, the most well-known cellulose derivatives) and inorganic nanoparticles (Fluorine doped ZnO NPs). Nanocomposite hydrogels have been proposed for the functional implementation of conventional hydrogels. Hydroxypropylcellulose (HPC) has the most interesting property of thermoresponsivity upon temperature increase (around 42 °C, lower critical solution temperature, LCST) forms aggregates. The incorporation of suitably nanoparticles with physico-chemical properties produce a hybrid nanocomposite material with peculiar properties with potential application in several fiels such as electronic, electrochemical and biomedical devices. Here we present a structural characterization of hydroxypropyl cellulose containing fluorine-doped zinc oxide nanoparticles through DLS, Raman and small-angle x-ray scattering measurements as temperature increases. Fluorescence measurements were also collected in parallel to evaluate the effect of nanoparticle clustering during polysaccharide gel formation. The preliminary results suggest that the nanoparticles interact with the HPC chains and that play a crucial effect in ruling the structural organization of the gel.

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Effect of micro-nanoplastics from airborne pollution on *Tillandsia* usneoides as a green biosensor

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The increasing evidence of widespread plastic pollution has engendered numerous studies to shed light on the impact of micro-nano plastics (MNPs) on plants. Here the effects of airborne PC, PET, PE, and PVC particles were investigated on *Tillandsia usneoides*, that is an epiphytic species and an ideal candidate for studying airborne contaminants. To simulate MNPs diffusion in the atmosphere, an *ad hoc* designed set-up was built. Pollution tests were performed by administering pristine and artificially aged plastics in a closed box (width: 30 cm, depth: 30 cm height: 20 cm) in which the samples were folded and hung to the cover lid by means of hooks. Inside this set-up, the air was kept moving by two fans (size60×60×15mm, direct current 12 V, speed 2500-6000RPM, 13 CubicFeet per Minute CFM) directed towards the bottom, which produced a continuous but moderate motion. Results showed that exposing the plants to MNPs could significantly reduce their growth with respect to controls. In particular, we found that PVC was the most toxic material in its pristine state, while PC toxicity was the highest after aging, implying that plastic permanence in the environment can either decrease or increase the impact on plants. MNPs toxicity was not only responsible for growth reduction but also changed the micro/macro-elemental profile of plants and impaired their photosynthetic efficiency. Microscopy investigations indicated that MNP particles were localized on the leaf trichomes and preferentially on the wings [2].

In summary, our findings clearly showed that airborne plastic pollution can pose a direct threat to plants, thus raising concerns about negative consequences for the whole ecosystem. Further research will extend this study to other plant species, including crops, to evaluate the MNPs transfer into the food chain with consequent impact on food quality and human health.

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Neem oil administration by nanocapsules from plant polymers to fight phytopathogenic fungi of grapevine

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In the last decades, the misuse of conventional pesticides has led to severe consequences for the environment and human health. Therefore, natural antimicrobials have gained attention as bioactive compounds, especially when administered in the form of finely dispersed particles, the so-called nanopesticides. In this work nanocarriers built from natural polymers were chosen to deliver poorly soluble bioactive molecules in aqueous dispersant [1]. Specifically, lignin and tannins were used for preparing nanoparticles to encapsulate and transport neem oil against pathogenic fungi which attack grapevine and cause the ESCA disease [2]. This choice was motivated by the need of treating the target plants with highly compatible carriers. The new formulations were characterized in terms of dimension, shape and surface charge of the dispersed particles prior to being tested against three pathogenic fungi: Botrytis cinerea, Phaeoacremonium minimum, Phaeomoniella chlamvdospora, DLS analysis showed that all the nanocapsules had an average diameter of 250-300 nm. The polydispersity index of most samples was low, i.e. below 0.3, indicating that objects with fairly uniform size were present in solution, a finding that was also in agreement with TEM investigation. The surface charge was measured by Zeta Potential, showing that the nanocapsules surface charge was in the range -25 mV - -80 mV.

Concerning antifungal assays, the most promising results were obtained against *Phaeoacremonium minimum*. In this case, the administration of neem oil by nanocapsules allowed to boost its biocide action, reducing the effective dose by \sim 400 times.

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Edible coating solutions for fresh-cut salad

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Fresh-cut lettuce is one of the most requested commodities thanks to its ease of use and consumption, but due to process operations such as washing and cutting, it is characterized by a short shelf-life of the product. In particular, phenomena such as microbial growth, browning of tissues, and qualitative deterioration of products may occur, reducing the storage period.

The development of edible coatings for the storage of fresh-cut salads could be an effective method, applied on salad leaves immediately after processing and before the final packaging to extend the shelf-life of the product [1,2].

The presented study deals with the application of different emulsions based on different polymers to two types of salads types: iceberg and lettuce. The emulsions used were based on three different types of edible polymers; alginate, chia seed mucilage and chitosan, in the presence of lemongrass essential oil and the surfactant (Tween 80).

The selected emulsions were sprayed onto fresh-cut salad leaves and dried under forced air flow. Uncoated fresh-cut salads leaves were used as control. Parameters such as appearance, color, and weight loss were evaluated at predetermined time intervals for 14 days. Taking into account all the parameters we were able to assess that among the tested compositions, alginate-based coating could represent a good way to reduce the deterioration of salads matrices.

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Evaluation of inhibitory activity of sodium acetate in alginate edible coating model

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Enzymatic browning is one of the factors affecting the shelf life of fresh fruits and vegetables. It is caused by phenol oxidase enzymes (POs), such as polyphenoloxidase, catecholase, catecholoxidase, phenolase, monophenoloxidase, o-diphenoloxidase, tyrosinase and laccase, that, in presence of oxygen, catalyse the transformation of phenols in quinones; successively the quinones polymerize, through non-enzymatic reactions, forming coloured high molecular weight pigments. Therefore, control on POs is a constant research topic. Sodium acetate is a well-known POs inhibitory agent, already allowed in foods in Europe. With aim to improve the performance of salad protective film, in this research the inhibitory effectiveness of sodium acetate was investigated directly in an alginate edible coating model. In detail, emulsion was composed (w/w) by 1% alginate solution, 1% Tween 80, 0.1% lemongrass essential oil and variable concentration of sodium acetate (ranging from 1-5%). To complete the reaction solution, caffeic acid (at known molarity), as phenolic substrate, and laccase from *Trametes versicolor*, as enzyme, have been added; conversely, the enzyme was omitted in the control. Incubation was carried out under dark and room temperature and the reaction was stopped by adding absolute methanol. Instantaneous and residual laccase activity was evaluated after 15 minutes and 24 hours of incubation, respectively. Enzymatic activity was determined by visual observation of color change and by measuring the caffeic acid depletion by HPLC. In the experimental conditions used, sodium acetate showed highest capacity of inhibition at 4% concentration. However, despite this at this concentration a significant residual laccase activity was registered.

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ACTIVITY OF NATURAL BIOMOLECULES AGAINST THE MAIN FUNGAL PATHOGENS OF CROPS FOR 4th GAMMA PRODUCTS

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Plant-based antimicrobials represent a promising alternative to the use of synthetic fungicides in agriculture both for their lower toxicity and low environmental impact [1]. In this study, we tested the antifungal activity of 16 formulations based on plant-derived biomolecules (with different types of formulations) against the main fungal pathogens of fresh-cut baby leaf crops (rocket, lettuce, spinach). The method applied for in vitro screening has been based on the poisoned food method [2] modified according to the physical properties of the formulations of the biomolecules under study. Therefore, the method of applying the biomolecules to the crop in greenhouse was also performed according to the different formulations. The most promising formulations for antifungal activity against Botrytis cinerea, Fusarium solani and Rhizoctonia solani was the ones based on diacetyl lycorine, a compound derived from the alkaloid lycorine. As regards the biomolecules formulated in hydrogel beads, we detected a strong antifungal activity, especially for two products based on carboxymethylcellulose that includes sulforaphane or glucoraphanin; in particular, the formulates based on these two products showed an antifungal activity comparable with that of carboxymethylcellulose combined with the synthetic chemicals napropamide and benfluranine as main active ingredients. In conclusion, based on our results, the application of these new natural biomolecules can be useful for reducing chemical residues in 4th gamma fresh-cut products, especially in the light of a further possible new policy of restriction in the use of synthetic chemical products.

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Phytotoxicity evaluation of innovative hydrogel beads for compounds modified release in sustainable agriculture

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ProFood IV project aims to study innovative and low-environmental impact solutions to improve the safety and quality of fresh-cut products (particularly baby leaf salads) and extend their shelf-life. The main objective is to apply innovative and sustainable systems for improving efficiency by eliminating using soil fumigants Metam-sodium. Using absorbent polymers, e.g. hydrogels would replace conventional formulations in an environmentally friendly view for obtaining healthy foods containing no residues of pesticides. 16 biomolecules absorbed on alginate and carboxymethylcellulose beads containing different organic bio compounds (produced by the University of Siena) were investigated by Vis-NIR spectroscopy and Scanning electron microscopy (SEM) by the University of Molise to support the germination and phytotoxicity tests on lettuce seeds (Lactuca sativa L.). Root elongation, Germination and Seed germination index (%) at 72 hours $(T_0 - T_{72})$, 144 hours $(T_0 - T_{144})$ and 216 hours $(T_0 - T_{216})$ after sowing were monitored. Germination index at T_{72} , 4 biomolecules showed high phytotoxicity values (GI% < 50); 11 biomolecules were found to be low or moderately phytotoxic (50 < GI% < 100), 1 biomolecule exhibit a possible biostimulator effect (GI% > 100). At T_{144} , 14 biomolecules obtained low or moderate values of phytotoxicity (50 < GI% < 100), 2 biomolecules exhibited a possible biostimulator effect (GI% > 100). At T₂₁₆, GI% values showed that 15 biomolecules were found to be low or moderately phytotoxic (50 < GI% < 100), and only 1 showed a biostimulator effect (GI% >100%). SEM and NIR spectroscopy indicate important changes in alginate and carboxymethylcellulose beads over time. These preliminary results showed that some biomolecules were found to be highly phytotoxic, according to the type of hydrogels, in the first hours of germination for lettuce seeds.

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PRO-FOOD-IV PROJECT AND SUSTAINABILITY IN FOOD INDUSTRY: LIFE CYCLE ASSESSMENT OF INNOVATIVE SOLUTIONS FOR FRESH-CUT PRODUCTION SYSTEMS

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Fresh-cut sector undergoes important changes in order to enhance product quality, food safety and environmental performances. Life Cycle Assessment (LCA) is the most suitable method to assess sustainability of fresh-cut production systems [1], allowing the estimation of environmental impacts of a product along its whole life cycle [2]. Within this framework, ProFood-IV project aims at the development of innovative and low environmental impact solutions to improve safety and quality of fresh-cut products. Present work focuses on the assessment of the environmental performances of innovative solutions developed in ProFood-IV project in accordance with the standards of ISO 14040 series. Specifically, environmental impacts of a conventional and an innovative production system were compared through an LCA method. Main differences between the two compared systems regard soil disinfestation with Metam-Na that is replaced by solarization before sowing in the innovative system. The conventional sanitization through oxidizing role of chlorine is replaced by ozone in the innovative system. Finally, traditional packaging is replaced by a biopolymer packaging combined with a functional film based on Na-Acetate, in order to decelerate product deterioration. Comparative LCA is carried out using SimaPro software 8.5.2.0. Results show that innovative system reduces the overall impacts by 43% respect to the conventional one. In particular, soil disinfestation impacts by solarization decrease by 97% compared to Metam-Na use. The use of ozone reduces impact by 54% compared to chlorine sanitization. Moreover, innovative sanitization regulates water consumption/contamination, reducing impacts on climate change and resource depletion. Finally, innovative packaging reduces overall impacts by 14% respect to conventional one. We highlight the importance of impact reduction by solarisation. Although sanitization and packaging are not equally influential on the whole production system, innovative processes lead to an increase in product shelf-life, implying a substantial reduction in overall impacts. Our findings could support decision-making, evaluating the introduction of innovative products and techniques in fresh-cut production systems.

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Characterization of extracts of coffee leaves (*Coffea arabica L.*) by spectroscopic and chromatographic/spectrometric techniques

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Coffea arabica L. leaves represent a viable alternative to the canonical matrices used for preparation of beverages, such as tea leaves and grounded coffee beans [1]. Coffee leaves infusions are rich in antioxidant phenolic compounds and have a lower concentration of caffeine [2]. Due to increasing interest in this field, a complete study of the bioactive compounds as chlorogenic acids, xanthones and alkaloids is noteworthy [3]. C. arabica leaves were subjected to ultrasound-assisted extraction, and the extracts were studied via nuclear magnetic resonance spectroscopy (NMR) and chromatographic techniques coupled with mass spectrometry (HPLC-MSⁿ) to identify and quantify the secondary metabolites profile through an untargeted data dependent approach [4,5]. A quantitative analysis was performed for the major components—chlorogenic acids, mangiferin, caffeine and trigonelline—via HPLC-MS in Single Ion Monitoring (SIM) mode. In total, 39 compounds were identified. The presence of these bioactive compounds proved the strong potential of C. arabica leaves as functional food and as an alternative to classic infused beverages.

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Comparison of analytical methods to determine phthalates release from macroplastics

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Plastic pollution is a global issue of growing concern because of the large amount of waste ending up into terrestrial and aquatic ecosystems. Biodegradable plastics, capable of being decomposed into harmless compounds by microorganisms, are promoted as an ecofriendly alternative to fossil-based polymers. However, environmental impact of these materials is a matter of intense debate, there is limited knowledge of the release and decomposition of the chemicals they contain and how living species are affected by biodegradable plastic waste [1]. In this regard, the present study focused on biodegradable plastic films (biobags) made up of poly(lactic acid) (PLA) and poly(butylene adipate-coterephthalate) (PBAT). The biobag samples were found to contain phthalic acid esters as additives, whether low molecular weight as dimethyl phthalate (DMP), diethyl phthalate (DEP), benzyl butyl phthalate (BzBP9 and dibutyl phthalate (DBP), or high molecular weight including di-2-ethylhexyl phthalate (DEHP) and di-n-octyl phthalate (DnOP). Phthalates are considered as hazardous endocrine disrupting compounds, that are able to induce toxic effects in humans and aquatic animals [2]. Quantification of these chemicals in examined biobags was performed by means of HPLC-DAD. A degradation experiment under natural environmental conditions was set up to evaluate if such species could be released in natural seawater, since phthalates and other additives are generally not chemically bound to the polymers. Duplicate samples were immersed in marine water for 120 days, one exposed to heat and sunlight (LIGHT), the other one shielded from UV light (DARK). Results of NMR analysis of seawater samples [3] after the experiment showed that phthalates leaching occurred in one of the DARK samples; however, quantification through HPLC was not achieved due to the low concentration or modification of chemical structure of phthalate esters through photo- or thermal degradation. Diverse factors can affect phthalate structure in aquatic environments, such as hydrolysis, photolysis and biodegradation, therefore a comprehensive analysis of which degradation mechanisms are involved in biodegradable plastic decomposition is crucial to assess how and at which concentration additives and breakdown products can harm living species.

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Physicochemical Characterization of Hyaluronic Acid and Chitosan Liposome Coatings

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Hyaluronic acid (HA) and chitosan (CH) are biopolymers that are widely used in many biomedical applications and for cosmetic purposes. Their chemical properties are fundamental to them working as drug delivery systems and improving their synergistic effects [1]. In this work, two different protocols were used to obtain zwitterionic liposomes coated with either hyaluronic acid or chitosan. Specifically, the methodologies used to perform vesicle preparation were chosen by taking into account the specific chemical properties of these two polysaccharides [2]. In the case of chitosan, liposomes were first synthesized and then coated, whereas the coating of hyaluronic acid was achieved through lipidic film hydration in an HA aqueous solution. The size and the zeta potential of the polysaccharide-coated liposomes were determined by dynamic light scattering (DLS).

This approach allowed coated liposomes to be obtained with hydrodynamic diameters of 264.4 ± 12.5 and 450.3 ± 16.7 nm for HA- and CH-coated liposomes, respectively. The chemical characterization of the coated liposomal systems was obtained by surface infrared (ATR-FTIR) and nuclear magnetic resonance (NMR) spectroscopies. In particular, the presence of polysaccharides was confirmed by the bands assigned to amides and saccharides being in the 1500-1700 cm⁻¹ and 800-1100 cm⁻¹ regions, respectively. This approach allowed confirmation of the efficiency of the coating processes, evidencing the presence of HA or CH at the liposomal surface. These data were also supported by time-of-flight secondary ion mass spectrometry (ToF-SIMS), which provided specific assessments of surface (3–5 nm deep) composition and structure of the polysaccharide-coated liposomes. In this work, the synthesis and the physical chemistry characterization of coated liposomes with HA or CH represent an important step in improving the pharmacological properties of drug delivery systems.

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Click-Chemistry Cross-Linking of Hyaluronan Graft Copolymers

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A click-chemistry crosslinking (click-crosslinking) procedure was developed to obtain cross-linked HA derivatives to be used in the formation of hydrogels. In particular, the clickable propargyl groups of HA-FA-Pg graft copolymers showing low and medium molecular weight values were employed in crosslinking by click-chemistry through a biocompatible hexa(ethylene glycol) spacer as an example of another possible application of our technology platform based on HA-FA-Pg graft copolymers [1]. A short series of medium weight HA-FA-Pg graft copolymers was synthesized, characterized, and used in a CuAAC dimerization reaction under very mild conditions in the presence of very low amounts of copper(I) catalyst. The dimerization reaction was also applied to the HA-FA-Pg-3F graft copolymer showing a low molar mass value, and hydrolysis studies confirmed the importance of the dimerization reaction in the formation of cross-linked HA-FA-HEG-CL materials. The interaction of the resulting HA-FA-HEG-CL materials with water led to the formation of hydrogels showing a wide range of gelation features thanks to the possibility of tuning the crosslinking degree. As a consequence of that, different rheological behaviours have been observed. The tuneable rheological behaviour of HA-FA-HEG-CL materials led to their applicability in different biomedical fields. In particular, HA(270)-FA-HEG-CL-10 seems to be a good candidate for potential application in the treatment of osteoarticular diseases.

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LIPID-BASED NANOPARTICLES AS CARRIERS FOR TREATMENT OF INFECTIOUS AND DEGENERATIVE EYE PATHOLOGIES

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Among the leading causes of blindness worldwide both infectious and degenerative eye diseases play a major role. Due to its anatomy and the direct exposure to the environment, the human eye is particularly vulnerable to fungal and parasitic infections, caused e.g. by trauma from penetrating objects, carriage of microorganisms from adjacent structures, use of contact lenses. Negligence in timely treatment often results in vision impairment [1]. Fungal keratitis is a major cause of blindness in corneal diseases and its topical treatment is complex and may require additional injections or surgery. Natamycin, a tetraene polyene which acts by binding to the main component of fungal walls ergosterol, thus blocking fungal growth, is the main antifungal drug for topical treatments. However, its low retention at the ocular surface and scarce penetration across inner ocular tissues pose significant challenges [1]. Among degenerative pathologies, Age-Related Macular Degeneration (AMD) is the leading cause of irreversible vision loss in people over 60 years, affecting 67 millions of people in the European Union. The wet AMD form that is the most severe is characterized by massive production of vascular endothelial growth factor (VEGF), which leads to excessive choroidal neovascularization, accumulation of subretinal fluids and haemorrhage, that eventually result in acute vision impairment. Common therapies involve repeated intravitreal injections of anti-VEGF drugs, however such procedures are invasive and might cause collateral damages [2]. Thus, the topical use of corticosteroids as anti-inflammatory agents has proven effective in decreasing permeability of choroidal endothelial cells and VEGF expression. Triamcinolone acetonide is an angiostatic steroid that showed efficacy against neovascularization in various eye segments, yet its poor water solubility and consequent low bioavailability limit its administration [2]. In this work, lipid nanoparticles (LNPs) with varied composition are proposed as carriers for topical administration of natamycin and triamcinolone acetonide to enhance delivery and permeation as eye drop formulations. Size and stability of the nanosystems were characterized by DLS and Zeta potential, supramolecular structure was investigated by Small Angle X-ray Scattering, whereas encapsulation efficiency was assessed by HPLC-DAD.

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A SAXS-USAXS STUDY ON PVA-BASED CRYOGELS LOADED WITH NANOSTRUCTURED FLUIDS FOR THE CLEANING OF CULTURAL HERITAGE

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The combination of nanostructured fluids (NSFs) and highly-retentive hydrogels, such as PVA-based cryogels, represents nowadays one of the most promising and innovative approach in the field of conservation of cultural heritage, as it enables the highest control available during cleaning interventions. However, at present, little is known about the confinement of NSFs into PVA-based cryogels. In the present work, small-angle X-ray scattering (SAXS) and ultra-small-angle X-ray scattering (USAXS), combined with fluorescence correlation spectroscopy (FCS), were used to address this issue. Two different NSFs were selected for this purpose, based respectively on anionic or nonionic surfactants, and they were confined into four different gels: two single PVA and two semi-interpenetrated PVA/PVA "twin-chain polymer networks" (TC-PNs). The analysis of the experimental results shows that surfactant nature is crucial in determining i) the interaction of NSFs, i.e. the cleaning fluid, with the gels' polymer network [1], i.e. the vehicle for the cleaning fluid; and ii) the interaction of NSFs with the target material to be removed from works of art [2,3] (which can range from small oily compounds to hydrophobic polymeric coatings). This study highlights that loading NSFs on PVA-based cryogels does not significantly affect the nanostructure of neither the NSFs nor the gels, and this is the physico-chemical reason behind the excellent cleaning performances of this combined system, which is being growingly considered as one of the most promising and innovative cleaning tools in art conservation.

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ISOTHIOCYANATE-BASED MICROEMULSIONS LOADED IN GREEN HYDROGELS FOR THE DISINFECTION OF AGRICULTURAL SOILS

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Synthetic pesticides have been intensively used in agriculture since the second half of XX century, and during last decades the issues connected to environmental and health impact of such practice have been considered in order to find more sustainable and eco-compatible alternatives. The biofumigation technique [1-3] was developed in this context, i.e. an approach that involves the use of plants belonging to the *Brassicaceae* family as green-manure crops. These plants, once pulverized, release glucosinolates, which in turn are hydrolyzed into other chemical species such as isothiocyanates. The latter have a proven biocidal activity against soil nematodes, fungi and bacteria. The present study focuses on the development of biocompatible polymeric systems, which allow the direct and controlled release into the soil of isothiocvanates, i.e. those same molecules that represent the arrival point of the degradation processes of glucosinolates contained in the Brassicaceae species. In particular, hydrogels based on natural and biocompatible polymers, such as alginate and carboxymethylcellulose (CMC), have been synthesized. These gels were loaded with o/w microemulsions based on water, surfactant and either ethyl isothiocyanate, phenyl isothiocyanate, or allil isothiocyanate. Several surfactants were considered, namely SDS, Tween 80 and Brij 30, and their ternary phase diagram was explored. The most promising formulations were characterized by means of DLS measurements, and loaded into alginate and CMC preformed hydrogel beads. The gels were characterized by means of ATR-FTIR and DSC measurements, while the loading efficiency and release profile of isothiocyanate-based microemulsions were investigated by means of UV-Vis spectrophotometry. The obtained results show that these systems represent a versatile, ecofriendly and non-expensive alternative to biofumigation processes currently employed in agriculture.

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BIODEGRADABLE AND HOME-COMPOSTABLE ACTIVE PACKAGING MATERIAL FROM CHITINOLYTIC AND LIGNIN WASTES*

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An innovative active and sustainable packaging material based on chitinolytic derivatives, using marine biomass wastes, has been produced. Such biodegradable and home compostable packaging biocomposite is able to tackle microbial spoilage, enhancing fish shelf life. Chitin obtained from marine biowastes has been treated to obtain chitosan and chito-oligomers [1]. Lignin nanoparticles, functionalized with chito-oligosaccharides confer antioxidant, antimicrobial, UV-shielding and improved mechanical properties [2].

Tray and film prototypes have been obtained and tested in presence of fresh fish. The packaging material presents the following properties:

- high content of renewable raw material (80%)
- the fish shelf-life is prolonged due to the antimicrobial and UV- shielding properties of the biocomposite components
- no release of allergens or toxic compounds
- the material is fully biodegradable and home-compostable with fertilizing activity.

A Life Cycle Sustainability Assessment study (LCA, LCC and social LCA) has been performed to assess the sustainability of the whole process and products.

The production of this biocomposite represents an example of circular bio based economy where renewable resources are exploited in a sustainable manner, promoting biobased, environmentally friendly and beneficial technologies, and create high-performing materials for a wide range of applications.

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THE USE OF THE EPR TECHNIQUE FOR THE STUDY OF COMPLEX MATRICES IN AGRICULTURE

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The Electron Paramagnetic Resonance (EPR) spectroscopy is recognized at European level as an accepted technique for the traceability of different type of edible foods. This technique is used in various fields for the detection and identification of organic free radicals and paramagnetic transition metal ions. Furthermore, it is widely used as a powerful, non-destructive and very sensitive technique for the study of oxidative processes and detection of free radicals in food systems [1]. Recently we have used the EPR technique for the analysis of soil composition from vineyards and olive groves.

The first screening was based on measurements performed at room temperature and at low temperature with liquid nitrogen (120 K), to better analyze the presence of transition metal ions. From this analysis, the different composition of soils was highlighted. The soil samples were characterized by the presence of transition metal complexes signals such as high and low spin Fe³⁺ and Mn²⁺ with the relative forbidden transitions. The signal of organic free radical was attributed to the carbonate present in the mineral structure. The EPR signal of Manganese complexes was a common characteristic in many of the analyzed soils, consequently the attention was focused on the study of this metal. For each soil, the Manganese concentration was determined by the use of a manganese calibration curve. At the end, to confirm the attribution of the free radical signal to the carbonate, present in the mineral structure of the soils, an extraction in acid and basic condition of soil was carried out [2].

Furthermore, for traceability purposes, the vineyards and olive groves were collected into different clusters on the basis of the EPR data.

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CS4River: new monitoring approaches in the freshwater quality assessment.

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In the last decades, most of the world's freshwater ecosystems have suffered dramatic changes mainly due to global warming and anthropological activities. A crucial step in river ecosystem preservation and restoration projects is the assessment of river-based habitat quality. Citizen Science (CS) is increasingly being used, among the several approaches used, in these kind of works [1]. Although the reliability of data obtained by CS measurements is still matter of debate, the possibility of collecting data at wider spatial and temporal scales is one of the main reasons why volunteers from the general public are involved in these projects [2], with respect to the traditional monitoring methods. In this context, a new CS-based research project called "CS4River" has been created by the University of Siena and developed within the National Biodiversity Future Centre (NBFC). "CS4River" aims to monitor the biodiversity and the river ecosystem quality by using trans-disciplinary approaches. Initially, the monitoring will be performed on the Idice (Emilia-Romagna) and Ombrone (Tuscany) rivers, including their tributaries. The assessment of river ecosystems quality will consist in a periodic monitoring of the main parameters for the freshwater quality (monthly; phosphates, nitrates and turbidity), macroinvertebrates (every six months), riparian vegetation (annually) and the fundamental target species for the biodiversity on the waterway river corridor. Freshwater quality monitoring could be enriched by measures of the fDOM (fluorescent Dissolved Organic Matter, a fraction of the Chromophoric Dissolved Organic Matter CDOM), closely related to the freshwater quality. Part of this project will be related to the development of a low-cost and easy-to-use fluorescence-based sensor potentially exploitable in CS freshwater monitoring projects. In this regard, tryptophan-like compounds, which belongs to the fDOM compounds, could be measured with these sensors. Tryptophan-like Fluorescence (TLF) includes a range of compounds which possess excitation-emission wavelengths associated to the fluorescence peaks of tryptophan. TLF is employed in the detection of microbial contamination in water.

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Design and Optimization of Solid Lipid Nanoparticles loaded with Triamcinolone Acetonide

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Principles of Quality by Design and Design of experiment are acquiring more importance in the discovery and application of new carriers, such as Solid Lipid Nanoparticles. In this work, an optimized synthesis of Solid Lipid Nanoparticles loaded with Triamcinolone Acetonide is presented as a potential formulation for the development of new topical ophthalmological solution for the treatment of wet AMD. The constructed Central Composite Design considers the lipid and nonionic surfactant quantities, and the sonication amplitude to optimize Particle size and Zeta Potential both measured by means of Dynamic Light Scattering, while the separation of unentrapped drug from the optimized Triamcinolone Acetonide-loaded Solid Lipid Nanoparticles is performed by Gel Permeation Chromatography and subsequently the Entrapment Efficiency determined by HPLC-DAD. As current treatment for Age-Related Macular Degeneration re-quires intravitreal injections of various kinds of drugs. Among them, Triamcinolone Acetonide and other corticosteroids are used as anti-inflammatory for treating the inflammatory process that accompanies the typical neovascularization caused by AMD. As the incidence of Age-Related Macular Degeneration is expected to increase in the immediate future, new delivery systems to enhance the formulation of drugs and more patient-oriented administration routes are needed.

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GREEN HYDROGELS LOADED WITH EXTRACTS FROM SOLANACEAE FOR THE CONTROLLED DISINFECTION OF AGRICULTURAL SOILS

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The massive use of synthetic pesticides and fertilizers in agriculture since the 1950s, though granting crops protection and boosting production, generated negative consequences on the environment and risks for the health of living organisms. Therefore, the UN 2030 Agenda for Sustainable Development established the goal to cut the use of synthetic pesticides in the EU by 50% within 2030. However, since the world human population is still rapidly growing, a ban on pesticides could seriously affect the productivity of agriculture, resulting in severe issues due to global hunger and food deficiency [1]. Thus, some effective alternatives to the current use of pesticides should be carefully and promptly evaluated. Controlled release (CR, hereinafter) of bioactive chemicals could play a major role in this context [1,2]. To this aim, in this work, two biocompatible and biodegradable polymers, namely sodium alginate and sodium carboxymethylcellulose (CMC), were employed to obtain crosslinked hydrogel beads for the encapsulation and CR of glycoalkaloids extracted from tomato and potato leaves, to be used as a biocompatible disinfectant for agricultural soils. The physico-chemical characterization of the controlled-release systems was carried out by means of Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy, thermogravimetry (TGA), Differential Scanning Calorimetry (DSC) and deswelling kinetics. The plant extracts and the encapsulation efficiency were respectively characterized and evaluated by HPLC-MS. Finally, preliminary microbiological tests were conducted to test the efficacy of the most promising systems as biocidal formulations both in the lab and on a model soils, and promising results were obtained in the reduction of bacterial and fungal load, which open to interesting and sustainable perspectives in the field.

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EFFECT OF PROTEINS AND STABILIZERS ON THE STRUCTURE AND STABILITY OF CALCIPROTEIN-LIKE PARTICLES

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Calciprotein particles (CPPs) are hybrid protein-mineral nanoparticles made of calcium phosphate stabilized by a glycoprotein called Fetuin-A (Fet-A). CPPs circulate in our serum and contribute to preserve calcium and phosphate homeostasis and prevent the formation of undesired calcium phosphate deposits in soft tissues [1]. In the early stages, CPPs consist of spherical amorphous calcium phosphate nanoparticles (CPP1-primary CPPs). In pathological situations, CPP1 may mature into needle-like crystalline hydroxyapatite particles (CPP2-secondary CPPs), eventually resulting in ectopic calcifications and inflammatory conditions. This biological pathway is particularly relevant for patients suffering from chronic kidney diseases and vascular calcifications. In this context, the role of albumin is also important, given the abundance of this protein in serum and its ability to complex Ca²⁺ ions. Understanding from a physico-chemical perspective the ripening from CPP1 to CPP2 and the factors affecting the process is fundamental to prevent the surge of ectopic calcifications by developing strategies to delay the crystallization and precipitation of CaP in serum.

In this contribution we present the effect of proteins (Fet-A and Albumin) and ions (Mg^{2+} , pyrophosphate and citrate) on the formation and crystallization of CPPs [2-3]. Synthetic CPPs were prepared using different concentrations of Fet-A and their formation, colloidal stability and ripening were followed *in situ* by means of turbidimetry and scattering techniques. The morphology of the nanoparticles was analyzed with scanning and cryo-transmission electron microscopy whereas FT-IR spectroscopy and X-Rays diffraction allowed for the study of their crystallinity. Experiments were also conducted with different concentrations of albumin and Mg^{2+} , pyrophosphate and citrate. This multi-technique approach allowed us to identify the most effective conditions for preventing the crystallization of CPP1, suggesting novel strategies to inhibit and treat cardiovascular calcifications.

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pH responsive pHEMA/PAA hydrogel for the capture of Copper Ions and Corrosion Removal: implication in Cultural Heritage Fields

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In case of metallic objects, cleaning requires a deep knowledge of the alteration processes, especially in case of outdoor monuments, buried or underwater artefacts. The alteration products of Cu-based allovs cause the formation of overlapping structures. characterized by the presence of cuprite at the interface with the metal, and by an external layer of Cu(II) salts. Cuprite represents a protective layer against further corrosion; on the other hand, the presence of Cu(II) salts is usually considered as a symptom of the so called "bronze disease", a particularly dangerous phenomenon induced by the presence of copper oxychlorides (atacamite and paratacamite) [1]. For this reason, an adequate cleaning procedure should aim at the complete removal of the corrosion products while preserving the protective cuprite layer. We propose the formulation and application of novel poly(2-hydroxyethyl methacrylate) (pHEMA) networks semi-interpenetrated (SIPN) with poly(acrylic acid) (PAA) to achieve enhanced capture of copper ions and removal of corrosion products. The pHEMA/PAA SIPNs were designed to improve previous pHEMA/poly(vinylpyrrolidone) (PVP) networks [2], taking advantage of the chelating ability of pH-responsive carboxylic groups in PAA. Upon application of the SIPNs loaded with tetraethylenpentamine (TEPA) onto corroded bronze, copper oxychlorides dissolve and migrate inside the gels, where Cu(II) ions form ternary complexes with TEPA [3] and carboxylates in The removal of oxychlorides is more effective and faster for pHEMA/PAA than its /PVP counterpart. The selective action of the gels preserved the cuprite layers that are needed to passivate bronze against corrosion, and the pHresponsive behavior of pHEMA/PAA allows full control of the uptake and release of the Cu(II)-TEPA complex, making these systems appealing in several fields even beyond Cultural Heritage conservation (e.g., drug delivery, wastewater treatment, agricultural industry, and food chemistry).

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Alkaline activation of blast furnace slag using calcium hydroxide nanoparticles for stone consolidation

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Ground Granulated Blast-furnace Slag (GGBS) is an abundant and green material obtained by quenching molten iron slag to a glassy and granular product, which is then grounded into a fine powder with latent hydraulic properties. The presence of strong alkali favors the dissolution in water of GGBS, thus fostering the slag hydration rate and yielding more abundant calcium silicate hydrate (CSH) binding phases [1, 2]. Specifically, the use of Ca(OH)₂ as alkaline activator has gained attention as it promotes water absorption and increases the alkalinity of the pore solution, providing cementitious material with enhanced durability [3].

Here we propose the use of Ca(OH)₂ nanoparticles to burst the alkaline activation of GGBS, exploiting their major reactivity arising from their high specific surface area: Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), and Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) were used to follow the hydration kinetics, evaluating the influence on the process of the precursors' particle size and of the presence of alcohols into the system.

We then developed an aqueous formulation containing Ca(OH)₂ nanoparticles and GGBS for consolidating treatments on stone materials of artistic and architectural interest: after preliminary application trials, the in situ formation of CSH phases among the substrate porosities was assessed by means of Confocal Raman microscopy [4, 5], and surface mechanical tests were performed on treated and not treated stone mock-ups (peeling test and abrasion test) to evaluate the treatment efficacy.

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The GREENART project: environmentally friendly and low impact materials for cultural heritage conservation

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European Cultural Heritage (CH) is a crucial resource that must be maintained, preserved and made accessible, to counteract degradation enhanced by unfavorable environmental conditions and climate changes. Some of the conservation methodologies nowadays available lack sustainability and cost-effectiveness, and are typically based on energy-consuming processes or non-environmentally friendly materials. This contribution will report on the main results so-far achieved in the EU-funded project GREen ENdeavor in Art ResToration (GREENART), coordinated by the Center for Colloid and Surface Science of the University of Florence (CSGI). Coping with the imperatives of EU Green Deal, the project proposes new solutions based on green and sustainable materials and methods, to preserve, conserve and restore CH. In particular, several innovative materials have been developed and tested: 1) Protective coatings based on green materials from waste and plant proteins, with self-healing and reversibility character, possibly functionalized with organic/inorganic nanoparticles to impart VOC capture, anti-corrosion and barrier behaviors. 2) Foams and packaging materials made by biodegradable/compostable polymers from renewable sources (polyurethanes and natural fibers) to control temperature and relative humidity. 3) Consolidants based on natural polymers from renewable sources, to mechanically strengthen weak artifacts. 4) Gels and cleaning fluids inspired by the most advanced systems currently available to conservators, which will be improved according to green metrics and circular economy requirements. 5) Green tech solutions for monitoring CH assets non-invasively against pollutants and environmental oscillations. Life Cycle Assessment and modeling favor the "safe-by-design" creation of affordable solutions safe to craftspeople, operators and the environment, and minimize energy-consumption in monitoring museum environments. Such holistic approach is granted in GREENART by a multidisciplinary partnership that gathers hard and soft sciences and engineering, including academic centers, innovative industries and SMEs, conservation institutions and professionals, museums whose collections hold absolute masterpieces in need of conservation, public entities and policy makers. Innovative materials and products have been assessed at the lab scale on representative mock-ups of works of art (remedial conservation), or in simulated museum/archive environments (preventive conservation). The project intends to transfer the most promising systems to field assessment on actual artefacts and museums/archives, in cooperation with conservator partners. The best products are also fed into a GREENART open repository and an App to illustrate the new solutions and involve citizens in good preservation practices. Constant feedback from conservators (internal or external to the partnership) can stimulate iterative refinement of the products, triggering a positive loop in this methodological approach. Covering these topics, we provide here an overview of the most advanced green materials for art conservation that can be useful to endusers in this field.

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Toward the design of anisotropic composites: alginate wires with aligned halloysite nanotubes

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The design of hybrid organic-inorganic systems with anisotropic properties is gaining more and more attention for the development of various systems, combining the advantages of natural polymers with those of functional inorganic fillers, potentially useful in different fields, including agriculture, biomedical applications, and multifunctional design.[1-2] Alginate is a polysaccharide derived from marine brown algae, whose well-established applications are based on its ability to coordinate divalent cations (*e.g.* Ca^{2+}) resulting in physically cross-linked hydrogels.[3] Halloysite nanotubes (HNTs) are naturally occurring biocompatible and economic aluminosilicate clays with a multi-walled tubular structure, allowing for the entrapment and slow release of various active molecules, and were already proven to be effective in different fields of applications.[4] To fully exploit their anisotropic nature, the control of preferential particle alignment is essential, but it can be trivial to achieve their orientation in organic matrixes.

Here we developed a method for the preparation of alginate wires containing aligned HNTs. The nanotubes were dispersed in water and various mixing procedures were evaluated, also in presence of a dispersant. As a matter of fact, to improve the dispersion stability of HNTs in water, it was already demonstrated that it can be effective to use sodium hexametaphosphate (HMP).[1,5] The efficacy of the mixing methods and the proper amount of HMP to be used were evaluated by means of zeta potential experiments, particle size analysis and scanning electron microscopy. HNTs were then dispersed with alginate, to obtain a homogenous formulation enriched with different concentration of nanotubes. Finally, the organic-inorganic mixtures were extruded into a CaCl₂ solution, and the injection parameters were adjusted, being of paramount importance for the development of the desired architecture.[2] Preliminary electron microscopy investigations showed that this processing technique can induce an alignment of HNTs in some selected conditions, and tensile tests suggest that the composites differ also in terms of breaking strength and maximum elongation.

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HOW TO EVALUATE THE DISPERSION DEGREE FROM AN OPTICAL MICROGRAPH: THE USE OF LACUNARITY AS IMAGE DESCRIPTOR

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The formation of carbonaceous deposits is one of the main problems related to the aging of engine lubricants. Indeed, engine oil plays an important role not only in maintaining engine cleanliness but also in controlling the friction during engine operation that influences fuel economy. Therefore, the development of additives for the inhibition and control of this process is mandatory to improve the performances of lubricants [1-2].

Usually, the oil dispersing capacity is evaluated through expensive and qualitative engine tests; a novel lab-scale approach based on optical microscopy is proposed for the direct ranking of the dispersant ability of a series of amphiphilic active molecules with different structure [3]. It was demonstrated that the dispersant ability well correlates with the amount of polar fraction in the molecule acting as anchoring point on the polar surface of the carbonaceous substrate.

This study represents a step forward in the comprehension of the stabilization mechanism against carbonaceous deposits and can help to develop the next generation of lubricant formulations. In addition, the proposed "simple" lab-scale optical microscopy approach combined with the "sophisticated" image analysis via the lacunarity descriptor can find application in other fields where the classification and quantification of patterns with different morphologies is necessary to access the effect of additives or active molecules in the dispersion of different phases.

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SODIUM ALGINATE BASED ACTIVE EDIBLE COATINGS FOR FOOD PACKAGING APPLICATIONS

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Alginate is a naturally occurring polysaccharide used in the bio-industry. It is mainly derived from brown algae species. Alginate-based edible coatings and films have attracted increasing interest for improving/maintaining quality and extending the shelf-life of fruits, vegetables, and other products, by reducing dehydration, enhancing product appearance, preventing rotting, etc. [1].

A wide variety of antimicrobial agents has been described for its use in coating/packaging solutions for fresh foods relying on sodium alginate (SA): sources of antimicrobial metal ions, from food additives awarded with the "Generally Recognized as Safe" (GRAS) label, are widely preferred [2].

To this aim, in the present research, various GRAS-labelled inorganic salts have been used to modify the polysaccharidic matrix directly or as cross-linking coadjutants. Zinc chlorides were exploited, along with CaCl₂. Metal-containing coatings were fully characterized, from both the analytical and the physicochemical point of view.

SA-based coatings were used to cover fresh strawberries and cherry tomatoes from biological culture, following a simple deep coating procedure [3]. An aqueous solution of SA, at a concentration of 1.5%_{w/v}, was used in all the coating experiments. Different concentrations of metal salts were tested, to correlate the anti-spoilage efficacy of the coating with its possible phytotoxic effect on the coated fruit/vegetable. Shelf-life experiments were conducted, storing treated foods at normal conservation temperatures (4°C for strawberries, 10°C for tomatoes), and observing them periodically to check for rotting symptoms.

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ANALYTICAL SPECTROSCOPIC CHARACTERIZATION OF COPPER NANOPARTICLES AND THEIR COMPOSITES FOR ANTIMICROBIAL APPLICATIONS

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Cu is an essential component of many enzymes involved in chemical reactions and possesses good antimicrobial activity. This study demonstrate a simple approach to synthesize green core-shell CuNPs stabilized by poly(n-vinyl)pyrrolidone (PVP) [1]. PVP can act as stabilizer, dispersant and reducing agent; its presence in synthetic medium also eliminates the need for an

dispersant and reducing agent; its presence in synthetic medium also eliminates the need for an inert atmosphere during the process. CuNPs were prepared using copper sulfate as precursor and glucose as reducing agent. Synthetic parameters were properly tuned to obtain NPs with diameters above 100 nm to be human-safe and prevent dangerous nano-cytotoxicity [2]. The glucose concentration was here varied to investigate its effect on colloidal stability, kinetics and NP average size. Spectroscopic characterization of CuNPs was performed by infrared, UV-Vis and X-ray photoelectron spectroscopies, demonstrating the formation of PVP layer around a Cu core with oxidation states from Cu(0) to Cu(II), depending on the glucose concentration. CuNP size distribution was obtained by statistical analysis on transmission electron microscopy micrographs. Cu@PVP particles were first washed, to remove unbound PVP and reactions byproducts, and then dispersed in EtOH, to be embedded in biodegradable/recyclable chitosan (CS) polymer matrix, to prepare coatings for food packaging applications. CS was dissolved in 1%v/v acetic acid solution with the addition of crosslinking agents, such as glutaraldehyde and tannic acid. Self-standing membranes were easily prepared by solution evaporation [3]. Obtained films were characterized by attenuated total reflection infrared spectroscopy and tested against three different model fungi responsible for food spoilage.

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BIOCOMPATIBLE ZEIN-BASED COATINGS FOR FOOD PRESERVATION

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According to the Food and Agriculture Organization (FAO) of the United Nations in 2021, about one-third of food is wasted every year because of shelf-life expiration, as well as the spoilage caused by microbial activities [1]. Furthermore, the growth of potential pathogenic microorganisms is cause of possible infection spreading and public health concerns. Antimicrobial coatings are promising active packaging that could be applied to improve product shelf-life and increase the safety of goods, being able to reduce food oxidation, prevent microbial contamination, and maintain the sensory quality and nutritional value of food [2]. Here we report the preparation and characterization of silver nanoparticles (AgNPs) embedded in zein films for potential food packaging applications. Zein, a protein obtained from corn, is biodegradable, biocompatible and non-toxic, with good hydrophobicity, and excellent barrier properties against humidity and gases [3]. Considering the well-known antimicrobial properties of AgNPs and excellent film-forming properties of zein, new coatings combining both components are proposed for the development of bioactive and sustainable food packaging. AgNPs were prepared through a reduction process using AgNO₃ as precursor, in the presence of zein, sodium dodecyl sulphate and ascorbic acid. A suitable protocol was developed for fabricating self-standing AgNPs/zein films. Morphological and spectroscopic characterizations were performed to investigate NPs and nanocomposites.

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