Volume 21
Number 21
7 June 2025
Pages 4121–4308

Soft Matter

rsc.li/soft-matter-journal

ISSN 1744-6848

ROYAL SOCIETY
OF **CHEMISTRY**

PAPER
Piero Baglioni *et al.*
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20 YEARS
ANNIVERSARY

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Cite this: *Soft Matter*, 2025, **21**, 4165

New perspectives on green and sustainable wet cleaning systems for art conservation

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Received 7th January 2025,
Accepted 11th March 2025

DOI: 10.1039/d5sm00017c

rsc.li/soft-matter-journal

The field of cultural heritage conservation science has seen significant advancements over recent decades, particularly through the application of soft matter and colloid science. Gels, nanostructured fluids, nanoparticles, and other advanced functional materials have been developed to address challenges in cleaning, consolidation, and protection of art. More recently, the focus has shifted toward "green" materials and sustainable practices, aligning with broader trends in science and technology. This emphasis on sustainability has revealed the immense potential for cross-disciplinary exchange between conservation science and fields like drug delivery, the food industry, tissue engineering, and more. A clear example of this synergy is seen in the cleaning of artworks, where bio-derived surfactants and biomaterials are increasingly incorporated into microemulsions and gels. These innovations not only enhance cleaning efficacy but also align conservation practices with sustainable principles, drawing parallels to research in cosmetics, pharmaceuticals, and detergents. The examples and materials discussed in this contribution illustrate how advancements in art conservation science can foster mutual technological transfer with other industries. By leveraging the central role of soft matter and colloids, these collaborations produce sustainable solutions that can address critical societal, environmental, and economic challenges.

Introduction

In an era where economic re-growth and resilience are central tasks to be pursued, Cultural Heritage (CH) represents a crucial socioeconomic resource that needs to be preserved and transferred to future generations.[1] However, this is a challenging

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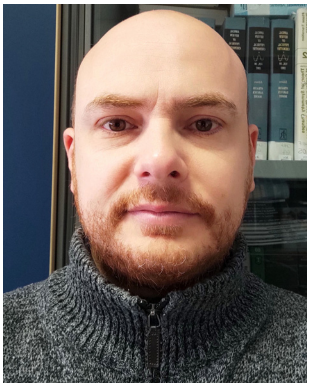

David Chelazzi

David Chelazzi received his Master's Degree in Chemistry from the University of Florence (Italy) in 2003 and his PhD degree in Science for Cultural Heritage Conservation in 2007. He is Associate Professor in Physical Chemistry at the University of Florence (Department of Chemistry and CSGI). His main research involves advanced and nanomaterials for art conservation and the industry. He is involved in European and national projects on such topics (FP7, H2020, HORIZON EUROPE). He is author and co-author of more than 100 papers in the field of physical-chemistry, conservation science, and environmental science.

Romain Bordes

Romain Bordes The research of Romain Bordes at the Division of Applied Chemistry, Chalmers University of Technology, Gothenburg, Sweden, covers surface-active materials, nanocellulose, advanced colloidal systems, acoustic levitation, and cultural heritage preservation, among other areas. His work integrates fundamental research with practical applications in surface chemistry, materials science, and environmental technologies. In 2012, he began exploring the conservation of cultural heritage, focusing on the development of novel surfactant systems and the application of colloidal science in this field.

task owing to the numerous degradation processes that affect works of art and monuments, exacerbated by climate changes and even by detrimental, serendipitous restoration approaches. In addition to the social and economic advantages provided by well maintained and accessible CH, art conservation science has large potential since it can also link to other scientific and technological sectors by addressing two fundamental issues: (1) the development of functional, advanced materials with enhanced performance as cleaning, consolidation, protection, and sensing systems;[2–7] (2) the use and support of a Safe and Sustainable by Design approach (SSbD) to devise the new materials.[8,9] The potential impact of colloids for conservation of CH was already highlighted about 20 years ago in a review article on ''Soft and hard nanomaterials for restoration and conservation of cultural heritage'' published on Soft Matter.[10]

Materials like gels, microemulsions, nanoparticles, coatings and composites, are not only beneficial to art conservation, but can also be potentially transferred to fields like detergency, cosmetics, the food industry, agriculture, tissue engineering, coatings/adhesives, textiles, and others. Regarding SSbD, CH conservation science offers a hub where this approach can be efficiently developed, put to test, implemented, and then transferred to other applications.

The scope of this article is indeed to illustrate a representative example of how soft matter and material science are contributing to develop sustainable materials for art conservation, focusing on systems for the wet cleaning

Andrea Casini

Andrea Casini earned his PhD in Chemistry (Science for Cultural Heritage Conservation) from the University of Florence in 2022 and is currently a postdoctoral researcher at CSGI@Unifi. Since 2018, his research has focused on biopolymer-based nanoconsolidants, nanostructured fluids for the removal of unwanted layers from artistic surfaces, and advanced gel systems for cleaning modern and contemporary paintings. He is part of the research team for the European project GREENART, which explores sustainable materials for cultural heritage preservation. Additionally, he contributes to CSGI-Solution for Conservation of Cultural Heritage, an initiative focused on conservation formulations developed within European projects led by CSGI.

Rosangela Mastrangelo

Rosangela Mastrangelo received her Master's Degree at the University of Florence, Italy, in 2016 and pursued a PhD in Chemistry – Science for Cultural Heritage Conservation in 2021. She is currently a guest researcher at the Health and Medical Research Institute (National Institute of Advanced Industrial Science and Technology, Tsukuba, Japan). She joined National and International Projects, involving collaborations with international companies and research centres for the formulation of innovative materials, in Cultural Heritage conservation and cosmetics. Her research is mainly focused on gels for the cleaning of painted surfaces and the relevant physico-chemical aspects involved in the cleaning mechanism.

Krister Holmberg

Krister Holmberg is Emeritus Professor in Surface Chemistry at Chalmers University of Technology. His research interest covers surfactant chemistry, reactions in microemulsions, enhanced oil recovery, nanomaterials and biotechnological surface chemistry. During the last eight years he has been heavily involved in large European projects dealing with restauration of the European cultural heritage. Since 2024 Dr Holmberg is also active in a European project on green surfactants, a project with 12 partners from academia and industry. He has written over 230 research papers and published seven books. A new book titled Natural Surfactants will be published during 2025.

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Piero Baglioni is Emeritus Professor of Physical Chemistry at the Department of Chemistry, University of Florence. He is on the editorial/advisory boards of several international journals and a member of the scientific board of several national and international Academies and Societies. He is the author of more than 550 publications and 27 patents in the field of colloids and interfaces, and a pioneer in the application of soft matter to the conservation of Cultural Heritage.

of works of art, and how this effort links with the industry.

Cleaning, *i.e.* the removal of undesired layers (soil, aged coatings, grime, vandalism) from the surface of artworks, is a representative and fundamental case in the conservation practice, and a challenging task owing to the interplay between intermolecular forces, *e.g.*, hydrogen bonding, polar and van der Waals forces, within a substance in the artwork (cohesive forces), and between the undesired layers and the underlying original artwork's components (adhesive forces). With most artistic surfaces being sensitive to aqueous solutions and organic solvents, the need to devise selective cleaning systems has driven research over the last decades, leading to the development of soft matter systems like hydrogels, organogels, and different kinds of nanostructured cleaning fluids.[11,12] While several systems have proven highly effective in the restoration of iconic masterpieces from the classic and modern/contemporary artistic production (*e.g.*, mural and easel paintings),[13,14] research is far from concluded. A ''green'' transition has only recently been initiated,[12,15] aimed at re-writing the most effective systems using non-toxic bio-derived or synthetic components, or developing completely new formulations for remedial conservation.

In this framework, surfactants play a key role. The use of surface-active compounds in restoration, in particular in cleaning operations,[16] tracks back to ancient practices, when conservators employed soaps and even different natural materials like food (wine, garlic, bread, oil) and biological fluids (saliva, bile, and urine). However, a systematic classification of useful surfactants for cleaning of works of art originates from the 1980s, with guidelines on the formulation of micellar solutions, regular emulsions and ''solvent-gels'' (polymer-thickened solvents and surfactants blends),[17,18] or with pioneering works on the use of oil-in-water (o/w) microemulsions.[6] As a matter of fact, o/w nanostructured fluids, either non-confined or uploaded in gels, still represent the most sophisticated approach to selective cleaning of art objects.[12] However, research is now addressing the formulation of fluids using ''green'' solvents and bio-based surfactants.

Our aim with this contribution is to highlight new possibilities and transversal ideas that can link the design of new sustainable art cleaning formulations with research in large industries like cosmetics, food and pharmaceutics, in an ''outside the box'', non-limited approach, rather than exclusively review past and current art restoration solutions.

First, an overview will be given on bio-based surfactants, an area subject to considerable efforts in the surfactant industry and of potential use also in CH conservation. Metrics and regulations to classify ''green'' surfactants will then be illustrated, including those currently used in art cleaning formulations. Then, the advantages and limitations of some novel ''green'' surfactants will be discussed, as potential candidates for industrial use and CH restoration. Finally, systems for the wet cleaning of art will be discussed, from the traditional practice to current sophisticated systems and future perspectives.

Bio-based surfactants: an overview

As the single largest class of specialty chemicals, surfactants are consumed in very large quantities in our daily life and in many industrial areas, in addition to their use in art cleaning formulations.

The world-wide annual production is around 30 million metric tons, and the market value of surfactants is around 50 billion US dollars. In the past, the attention was focused entirely on technical performance. However, starting from the 1970's and 80's, surfactant related environmental concerns have become the main driving force to upgrade surfactant production technology to make more benign or ''greener'' products. More recently the origin of the raw materials that are used for the synthesis of surfactants has also become very important. Particularly in the personal care sector and other consumer markets, the customers prefer surfactants made from renewable raw materials.

In principle, surfactants can be synthesized entirely from natural raw materials. Such surfactants are referred to as bio-based (or oleochemically based) and sugar esters of fatty acid are well-known examples. Surfactants can also be made entirely from petrochemical starting materials. Alkylbenzene sulfonates, the largest single type of surfactant, is one example out of many. However, many surfactants are neither fully bio-based or fully petrochemically based; instead, they are hybrids, made from one natural and one petrochemical raw material. Normal nonionic surfactants made by ethoxylation of a natural fatty alcohol are typical examples. If the ethylene oxide originates from bioethylene, which in turn comes from bioethanol, then the surfactant is fully bio-based. However, that is still rare. This has triggered some confusion in the classification of surfactants, and in order to formalize the classification the European Commission for Standardization has defined a bio-based surfactant as follows:[19]

– Wholly bio-based: $>95\%$ bio-based carbon; surfactants where all raw materials can be considered as bio-based.

– Majority bio-based: 95–50% bio-based carbon; surfactants where the majority of the raw material is bio-based.

– Minority bio-based: 50–5% bio-based carbon; surfactants where a minor part of the raw material is bio-based.

– Non bio-based: $<5\%$ bio-based carbon; surfactants where no raw material is bio-based.

The percentage of bio-based carbon is usually calculated based on data from the surfactant supplier but can also be determined experimentally by isotope analysis. The isotope composition of carbon in nature is 99% ^{12}C, 1% ^{13}C, and a tiny amount (1 per 10^{12} carbon atoms) of ^{14}C. The ^{14}C isotope is radioactive with a half-life of 5730 years. This means that in fossil petroleum there is virtually no radioactivity. Thus, an isotope analysis of the carbon in a linear alcohol made by oligomerization of ethylene will show negligible amount of ^{14}C while the same alcohol obtained from a triglyceride by methanolysis followed by hydrogenation of the methyl ester will give an abundance of ^{14}C of 1 per 10^{12} carbon atoms. In archaeology this method of dating organic artefacts is referred to as radiocarbon dating or carbon-14 dating.

During the last decades there has been a steady increase in the relative amount of bio-based raw materials in surfactants for consumer products such as personal care, food, and household cleaning. The trend is less clear for surfactants for industrial applications. That segment is still very much dominated by raw material prices and the relative volumes of bio-based and petrochemically based raw materials tend to follow the price fluctuations of the oleochemical and petrochemical feedstock.

A fully bio-based surfactant is likely to be more environmentally benign and have a lower carbon footprint than a petrochemically based amphiphile used for the same purpose. However, also surfactants made from natural starting materials, such as fatty alcohols or fatty acids as hydrophobe and a sugar or oligomerized ethylene oxide from bioethylene as polar headgroup, are not natural compounds. Their synthesis requires many steps. Take fatty alcohol ethoxylates made from bio-ethylene oxide as an example. The fatty alcohol is normally made by catalytic hydrogenation of a fatty acid methyl ester, which in turn is made by methanolysis of a triglyceride. The bio-ethylene oxide is made by oxidation of bioethylene using a silver catalyst and the bioethylene is obtained by dehydration of ethanol obtained by sugar fermentation. Taken together, four organic chemical reactions and one fermentation is required to produce the two starting materials, which are combined in a fifth reaction, the ethoxylation, to give the nonionic surfactant. Fig. 1 shows the reaction sequence. Whether such a surfactant is really "green" may be a matter of debate.

Biosurfactants, also called natural surfactants, may be the ultimate solution. These are amphiphiles produced by macro- or microorganisms without any synthetic chemistry involved. Examples of natural surfactants produced by macroorganisms are saponins and phospholipids such as lecithin. Examples of such products produced by microorganisms include rhamnolipids, sophorolipids, and mannosylerythritol lipids. Such natural surfactants are highly surface active with values of critical micelle concentration (CMC) and surface tension at the CMC that match the values of synthetic surfactants. These natural surfactants are commercially available, but the volumes produced today are relatively small and the price level is much higher than that of surfactants produced by organic synthesis from petrochemically or oleochemically based starting materials.[20,21] Fig. 2 shows structures of important natural surfactants.

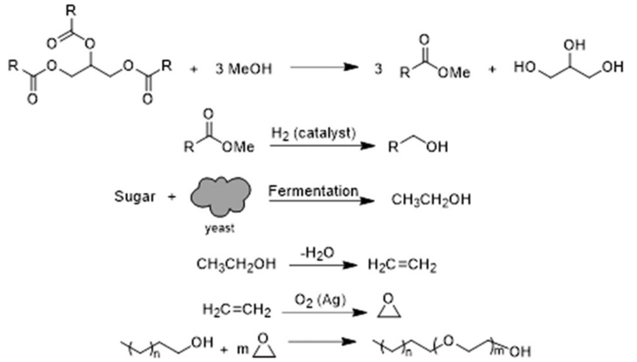

Fig. 1 Synthesis of fatty alcohol ethoxylate based on a natural fatty alcohol and bio-ethylene oxide. The fatty alcohol is produced in two steps from a triglyceride (where R is a hydrocarbon group of variable length and degree of unsaturation) and the bio-ethylene oxide is also made in two steps from bioethanol, which is produced by fermentation of sugar.

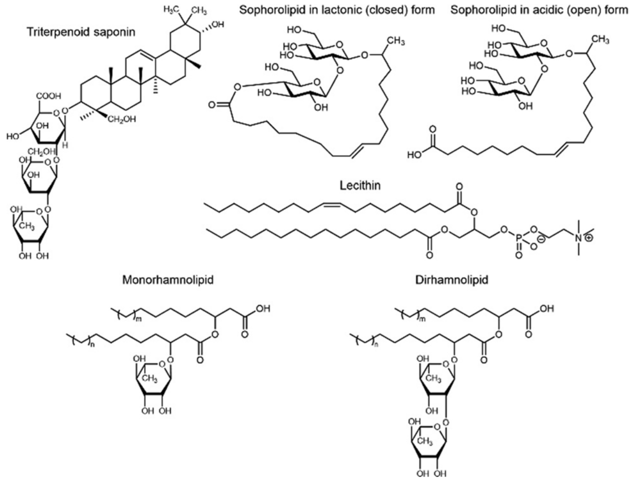

Fig. 2 Structure of representative biosurfactants.

Metrics and regulations to classify "green" surfactants

The environmental impact of surfactants has gained significant attention due to their widespread use in industrial and domestic applications. Assessing their sustainability demands a multidisciplinary approach that encompasses their entire lifecycle, ecological interactions, and chemical properties.[22] In particular, life cycle assessment (LCA) provides a robust framework for analysing the environmental impact of surfactants from production to disposal. By quantifying key metrics such as energy consumption, greenhouse gas emissions, and water usage, LCA identifies environmental hotspots and supports the development of sustainable alternatives.[23] Standardized under ISO 14040:2006, this approach has proven particularly effective in comparing petroleum-based surfactants with bio-based counterparts derived from renewable resources like vegetable oils, which generally exhibit lower environmental impacts.[23,24] The cradle-to-grave perspective of LCA ensures that all stages of a surfactant's lifecycle are considered, revealing opportunities for optimization in production processes and end-of-life strategies.[25]

Ecotoxicity assessments are another critical component of environmental evaluation, focusing on the potential harm surfactants can inflict on aquatic life, soil organisms, and microbial communities. Standardized testing protocols, such as those in the OECD Guidelines for Testing of Chemicals, assess both acute and chronic toxicity, providing essential data for regulatory decision-making and risk management. These evaluations are instrumental in identifying high-risk surfactants and informing about the development of less toxic formulations.[26–28] Advances in high-throughput ecotoxicity testing have significantly improved the understanding of surfactants' long-term effects on biodiversity and ecosystem health, particularly in sensitive environments prone to bioaccumulation.[29] Complementing ecotoxicity studies, biodegradability testing determines the rate at which surfactants break down in natural environments. Tests like OECD 301 offer critical insights into persistence and bioaccumulation potential, particularly within aquatic and terrestrial ecosystems.[27] Accordingly, surfactants with biodegradable headgroups or hydrophobic chains derived from natural sources have demonstrated promise in minimizing environmental persistence, aligning closely with green chemistry principles.[28,30,31]

Quantitative structure–activity relationship modelling (QSAR) represents a predictive tool for assessing surfactants' environmental behaviour, toxicity, and biodegradability based on their molecular structure.[32,33] By leveraging molecular data, QSAR models enable early-stage identification of hazardous properties, thereby reducing dependence on extensive experimental testing. Incorporating machine learning algorithms has further enhanced QSAR systems' predictive accuracy, facilitating the design of environmentally benign surfactants that balance efficacy and safety.[34–36]

The application of advanced analytical techniques, such as mass spectrometry and nuclear magnetic resonance spectroscopy, represents an interesting alternative for the detailed characterization of surfactants and their degradation byproducts.[37] These tools can elucidate degradation pathways and assess risks associated with stable byproducts, which are frequently observed in wastewater. High-resolution mass spectrometry has revealed the formation of persistent byproducts, underscoring the necessity for improved surfactant design and wastewater treatment technologies.[38,39]

Finally, computational chemistry tools, including molecular dynamics simulations and density functional theory calculations, offer powerful methods for predicting the environmental fate of surfactants. These simulations provide detailed insights into molecular interactions with soil, water, and organic matter, guiding the rational design of surfactants with minimal environmental footprints.[40,41] Recent advancements have successfully employed computational models to optimize amphiphilic structures for enhanced performance and sustainability, demonstrating their potential in green surfactant innovation.[42,43] These diverse methodologies tackle various aspects of surfactants' environmental sustainability, encompassing lifecycle impacts, toxicity, and molecular design. However, despite their individual strengths, these approaches often operate in isolation, lacking integration or interoperability. This fragmentation can limit their effectiveness, as the insights gained from one method may not fully inform or complement those obtained from another. For instance, while LCA excels at providing a comprehensive overview of environmental impacts, it may not delve deeply into molecular-level toxicity. Conversely, advanced molecular modelling tools, although predictive and precise, may overlook broader ecological interactions or lifecycle considerations. The absence of a unified and holistic framework that bridges these methodologies creates a significant gap in the understanding of surfactants' full environmental and health implications. Such a framework is crucial to facilitate innovation in the design of sustainable chemical solutions, as it would integrate diverse data streams and provide a coherent perspective on surfactant performance and risks. Moreover, a standardized and comprehensive approach would align with global efforts to mitigate ecological impacts, ensuring compliance with increasingly stringent regulatory standards. It would also provide the scientific foundation needed to support a transition toward greener and more sustainable chemical practices, fostering collaboration across disciplines and driving advancements in surfactant technology that meet both environmental and societal needs.

In this framework, we recently proposed a comprehensive system to evaluate and categorize eco-friendly surfactants for the conservation of CH, addressing the pressing need for safer alternatives to traditional cleaning agents, which often pose significant environmental and health risks. This system leverages a detailed, multi-criteria assessment framework to identify sustainable materials that adhere to green chemistry principles.[12] The classification uses safety, health, and environmental (SH&E) metrics to assess cleaning agents, drawing on established standards such as REACH (registration, evaluation, authorization, and restriction of chemicals) and the innovative medicines initiative (IMI)-CHEM21 public–private partnership European consortium.[44] The evaluation considers several essential properties (taken from the records of the European Chemical Agency, ECHA, and safety data sheets available from producers), including biodegradability, aquatic toxicity, human toxicity, and flammability, while excluding boiling point assessment, which was deemed not relevant for surfactants.

A ''green'' score is thus calculated for each surfactant balancing all the available metrics from research and industry, and each entry receives a color-coded rating for ease of interpretation: green (recommended, minimal concerns), yellow (acceptable with controlled conditions, moderate issues), and red (hazardous, significant risks).

Fig. 3 depicts a comprehensive evaluation conducted on surfactants traditionally used in conservation practices and on those employed in the current state-of-the-art methodologies

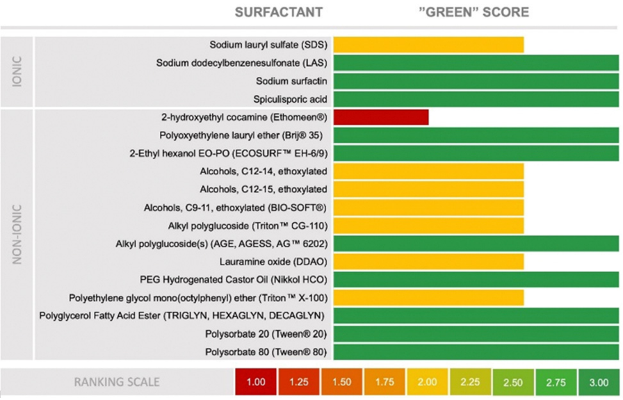

Fig. 3 Visual comparison of "green" scores assigned to traditional conservation surfactants and to those used in current advanced cleaning techniques for artworks.[12] The CHEM21 "green" score metrics were adapted and applied to evaluate the environmental and health impacts of these surfactants.

for cleaning works of art. The CHEM21 green score metrics were adapted applied to assess these surfactants. The varying green scores highlight differences in their environmental and health impacts.

Among ionic surfactants, sodium dodecyl sulfate (SDS) achieves a moderate score but requires cautious use due to its irritant properties and aquatic toxicity. Conversely, sodium dodecylbenzenesulfonate (LAS), widely used in cleaning applications,[16] has higher green scores. Bioderived surfactants like saponins or rhamnolipids have high scores, as well as spiculisporic acid and sodium surfactin, which can be of interest to cleaning formulations owing to their very efficient surface activity.

Nonionic surfactants, some of which are included in traditional cleaning formulations,[17,45] generally pose lower safety risks while still raising some environmental concern. Ethoxylated fatty alcohols, including those based on C_{9-11}, C_{12-14}, and C_{12-15} as hydrophobes, can have excellent cleaning efficacy depending on their structure and hydrophilic/lipophilic balance,[46,47] particularly for removing hydrophobic residues. According to the REACH classification, surfactants based on C_{12-14} are considered toxic to aquatic life, while currently C_{9-11} are not, but since evaluations are continuously improving, they were given the same score in Fig. 3 on a precautionary basis. The anaerobic degradability of fatty alcohol ethoxylates can vary depending on their structure (hydrocarbon/oxyethylene chain length, linearity vs branching).[48,49] Surfactants based on linear C_{12-15} were found to be biodegradable during aerobic sewage treatments. In addition, *ortho* ester-based, carbonate-based and certain gemini surfactants are of interest to art cleaning formulations, since they are cleavable, potentially avoiding the need of rinsing steps after interventions to remove non-volatile residues from the cleaning system.[16,50,51]

Surfactants with more favourable environmental profiles include alkyl polyglucosides (*e.g.*, AGE, AGES, AGTM 6202), ethoxylated hydrogenated castor oil (Nikkol HCO), and polyglycerol fatty acid esters (*e.g.*, TRIGLYN, HEXAGLYN, DECAGLYN), which tend to achieve higher green scores overall.

Nevertheless, it is essential to recognize that the green score alone cannot determine with certainty the suitability of a surfactant for CH cleaning. Factors such as cleaning efficacy, compatibility to the artworks, the specific characteristics of the artifact and soiling, availability, cost, and time-effective performance in specific cleaning scenarios, must be meticulously considered alongside the surfactants' green score.[15,52] Furthermore, ongoing research is crucial to better evaluate the environmental and health impacts of these surfactants and to develop more sustainable and effective cleaning strategies for CH objects.

Novel "green" surfactants: advantages and limitations

Formulations for cleaning usually contain both an anionic and a nonionic surfactant. A typical combination is an alkyl ether sulfate and a fatty alcohol ethoxylate. Both these surfactants belong to the intermediate segments in the classification of bio-based surfactants mentioned in the Introduction. The fatty alcohol is normally oleochemically derived while the ethylene oxide has a petrochemical origin.

Besides the issue of ethylene oxide being a petrochemical, there is the problem of small amounts of toxic substances in the products. Ethylene oxide, the starting material for all ethoxylation processes, is a reactive molecule, which is now classified as carcinogenic and mutagenic. The surfactant producers have developed a technology to eliminate unreacted ethylene oxide from their products and the remaining amounts are very small today. Low values of residual ethylene oxide are particularly important for ethoxylated surfactants intended for the food, feed, pharma, and personal care sectors. The threshold value of ethylene oxide in such products is very low and has been reduced as the analytical methods to quantify ethylene oxide have become more sophisticated. The detection limits for ethylene oxide in surfactants is in the range 0.01 to 1 ppm, depending on the type of surfactant and the analytical equipment used. However, the risk of having even traces of a toxic compound remaining in a surfactant that may be a food component or put on the skin in a personal care product is problematic, and obviously even in art cleaning there is the need to produce formulations that are non-toxic and safe to the conservators.

Another issue that the producers of ethoxylated products must deal with is that during the ethoxylation the toxic product 1,4-dioxane is formed in small amounts. 1,4-Dioxane is classified as "possibly carcinogenic to humans" and is also carefully removed after the ethoxylation step but, like the situation with ethylene oxide, the risk of having traces of 1,4-dioxane in a surfactant formulation that may be applied on the skin, is a serious concern for the cosmetics industry.

Taken together, the risk of having traces of ethylene oxide and 1,4-dioxane in products prepared *via* an ethoxylation step has triggered the surfactant producers to look for alternatives. Taurates and isethionates are examples of sulfonate surfactants that have become popular in formulations for personal care and household cleaning. They are both mild to the skin and environmentally benign. Typical structures are shown in Fig. 4. The fatty acid used as raw material is often the coconut fatty acid fraction, *i.e.* a natural product.

Sugar and sugar derivatives are the natural choice as replacement of the oxyethylene chain in nonionic surfactants. Both alkyl polyglucosides and sucrose esters of fatty acids have been around for a long time and their physical chemical properties are well documented. "Alkyl polyglycosides" is actually a misnomer. The product is a mixture of alkyl glucosides where the sugar moiety consists of glucose only slightly oligomerized *via* acetal linkages; the degree of oligomerization is typically between 1 and 2. Both are environmentally benign, and both

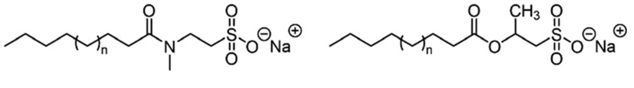

Fig. 4 Left: Sodium methyl taurate; right: sodium methyl isethionate.

are based on entirely natural raw materials. However, sucrose esters are produced by a synthesis route that involves harmful organic solvents, such as DMF, a fact that makes this surfactant class problematic from a life cycle analysis (LCA) point of view. Work is today underway to develop more environmentally friendly synthesis procedures.[53,54]

Oligomeric glycerol is another candidate to replace the oxyethylene chain in nonionic surfactants. Oligomeric glycerol with a broad homologue distribution and possibly also as a mixture of straight and branched chains can be esterified with a fatty acid to generate a surfactant entirely based on natural raw materials.[55] Organic solvents are not needed for the synthesis, which makes the product attractive from a LCA perspective. Alternatively, the fatty acid oligoglycerol ester may be produced by transesterification of the fatty acid methyl ester. Fatty acid esters of short oligoglycerol chains, typically with three glycerol units, have an established use as emulsifier in the food industry but there is now a growing interest for fatty acid esters of longer glycerol oligomers for use also in other applications.[56] Fig. 5 shows the structure of a typical oligoglycerol surfactant.

As mentioned in the previous section, natural surfactants, *i.e.* surfactants produced by macro- and microorganisms, would be the ultimate ''green surfactant''. Saponins, lecithin, rhamnolipids, and sophorolipids are examples of such amphiphiles that are commercially available. They are still produced in relatively small volumes and at much higher prices than the synthetic surfactants, but the volumes are growing. They are today mainly used for personal care and medical applications, but they are started to be used also in other areas. Household cleaning products based on soapwort saponins are available, rhamnolipids and sophorolipids are used in hand dishwashing and household detergents, and soybean lecithin has an established use in the paint and coatings industry as a wetting, grinding, and dispersion agent for pigments.[21] These examples show that there is vast potential for interactive technology exchange loops between industry and art conservation, with art cleaning formulations adopting or assessing sustainable surfactants derived from the industry, and then re-transferring effective and ''green'' formulations for adaptation in cosmetics or other sectors.

The main advantage of naturally occurring surfactants is the sustainability, in the sense that they are the result of the natural transformation of renewable substrates. There is the widespread perception that since they are a product of nature, they must be good, overlooking that some of the most potent poisons, such as curare and strychnine, are naturally occurring, not to mention the taxine alkaloids, that can be found in garden's hayes. It is generally believed that natural surfactants must be readily biodegradable and safe to human and the environment. This is usually but not always the case. A problem with some biosurfactants is that they are produced by a pathogenic species, the most well-known example being rhamnolipids produced by *Pseudomonas aeruginosa*. The biodegradability of the natural surfactants is generally excellent, however.

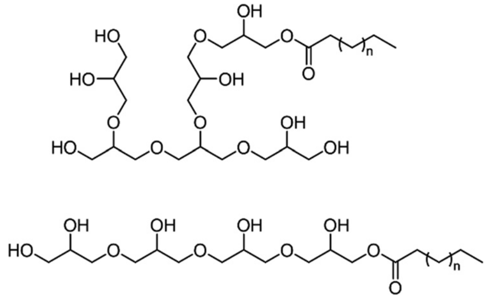

Fig. 5 Fatty acid ester of oligomeric glycerol. For the surfactant used in the food industry the value of *n* is typically around 3 but the oligoglycerol chain has a broad homologue distribution. The polyglycerol moiety can exhibit different degrees of branching.

From a carbon footprint and an LCA point of view, natural surfactants are generally superior to synthetic surfactants, also the bio-based amphiphiles. As discussed above, also bio-based surfactants are made by organic synthesis, usually by several steps, which may involve unpleasant reactants and byproducts, as well as the use of organic solvents. Biotechnological production of surfactants, including the work-up procedure, takes relatively long time and often gives low yields but the environmental impact is small. It is likely that with the growing concern about the environmental impact of chemicals and the improvements in biotechnological production, not least through the development of engineered species that are non-pathogenic and give higher productivity, natural surfactants will increase its market share in the years to come.[57] However, one should realize that the volumes of surfactant used for cleaning of artefacts is small. The driving force for a transition from conventional to natural surfactants is therefore small in that segment compared to other applications of surfactants. In these other sectors, efforts combining the development of new biobased surfactants combined with work on formulation aim at achieving similar performances, yet with a reduced environmental impact.

Systems for the wet cleaning of art

Early approaches and formulations

As mentioned in the previous sections, cleaning works of art is an old practice that relied for long time on serendipitous approaches and trial-and-error. While soaps and natural biomaterials, like wine, saliva and other biological fluids, were employed to clean artworks since ancient times, it was only in the late 1980s that a systematic classification of solvents, polymers and surfactants for use in the removal of soil and varnishes was given, in the works of Wolbers and Stavroudis.[17] Nonionic surfactants with hydrophilic/lipophilic balance (HLB) between 12 and 17, were selected to avoid swelling and damage to painted layers through the formation of oil-in-water emulsions during cleaning. Beside nonionics, also ethoxylated cocoamines, such as Ethomeen® C12 and C25, have been largely used in the ''solvent gels'' introduced by Wolbers in the late 1980s, to thicken polar and nonpolar solvents. Solvent gels have been largely employed, despite the poor health and environmental profile of these cocoamine surfactants. Wolbers and Stavroudis also illustrated regular o/w emulsions with adjustable factors like pH, ionic strength, and solubility, for optimized cleaning action.[17,45]

An alternative approach was developed and proposed by Ferroni and Baglioni in the 1980s,[6] in the framework of soft matter and nanoscience. Taking inspiration from an article by De Gennes and Taupin on the stability of o/w and w/o microemulsions or bicontinuous phases,[58] they developed and applied for the first time an o/w (dodecane-in-water) microemulsion to remove wax spots from Renaissance wall paintings in florence (Italy), using SDS as surfactant and 1-pentanol as co-surfactant. This pioneering work started a prolific research line that, over the last decades, led to the application of o/w nanostructured fluids to clean wall paintings ranging from the European Renaissance to Mesoamerican pre-Columbian art, and even modern graffiti[6] (see Fig. 6), with progressively more complex formulations,[12,46] and different surfactants, as ionic/nonionic alkyl polyglycosides (APGs), *N*,*N*-dimethyldodecylamine (DDAO), and broad-range (BR) or narrow-range (NR) fatty alcohol ethoxylates (C_iE_j). The target of these o/w fluids varied from low-molecular weight compounds found in resin varnishes or grime (terpenes, fatty acids, triglycerides) to aged polymeric coatings (acrylates, vinyl acetates, epoxy, silicone). In particular, it was found that the removal of these coatings by the fluids works through non-classic mechanisms favoured by the surfactants, such as dewetting, swelling and detachment.[59]

W/o microemulsions have also gained attention as cleaning systems, particularly for use on water-sensitive materials like latex acrylic paints or modern oils.[61] Amphiphilic agents used in these formulations included linear alkylbenzene sulfonate (LAS) or the nonionic surfactant ECOSURF® EH6 (ethoxylated/propoxylated 2-ethyl hexanol).

Fig. 6 Cleaning of wall paintings using o/w nanostructured cleaning fluids. (left) Removal of aged synthetic polymer coatings from wall paintings in the Annunciation Basilica in Nazareth (Israel), using a fluid containing SDS as surfactant: (top) before cleaning and (bottom) after cleaning. In the dashed box, an area is highlighted where the polymer coating was temporarily left untreated as a visual reference for the evaluation of the cleaning result. Reproduced with permission from Baglioni *et al.* (2012).[60] Copyright 2012 American Chemical Society. (right) Detached fresco from the S. Cristoforo church in Milan before (left panel) and after (right panel) cleaning and restoration using a fluid containing an alcohol ethoxylate surfactant. Reproduced from Baglioni *et al.* (2014)[46] with permission from the Royal Society of Chemistry.

With the wide range of solvents and surfactants that can be employed in nanostructured fluids, research on the cleaning mechanisms is still an open, challenging field, with clear connections to industrial detergency, textiles, house cleaning, *etc.*

Confinement of cleaning fluids in gels

The ability of confining aqueous solutions or organic solvents, releasing them with time- and spatial control, has progressively made gelled systems ideal tools in art cleaning interventions.[12] Over the last decades, several gel formulations have been proposed and assessed, improving over traditional polymer thickeners which can show poorer retentiveness or leave residues on the treated surfaces.[16] Formulations have so far included synthetic polymeric networks, such as polyacrylamide, networks of poly(2-hydroxyethyl methacrylate) semi-interpenetrated with polyvinylpyrrolidone (pHEMA/PVP SIPNs), and polyvinyl alcohol (PVA), or bio-derived materials like castor oil or polyhydroxybutyrate organogels.[6]

While extensive reviews can be found in the literature on the performance of these systems in cleaning artworks,[6,12,62] it is worth recalling here the possibility of uploading nanostructured cleaning fluids into hydrogels. This allows targeting soil or aged coatings through dewetting and detachment (Fig. 7), while granting controlled action on water-sensitive surfaces. In addition, the dynamics of surfactants' micelles and of water in the gels' porous networks can be combined to produce enhanced cleaning results.[63]

A first representative example is the confinement of o/w fluids into the pHEMA/PVP SIPNs.[64] Uploading the fluids in the

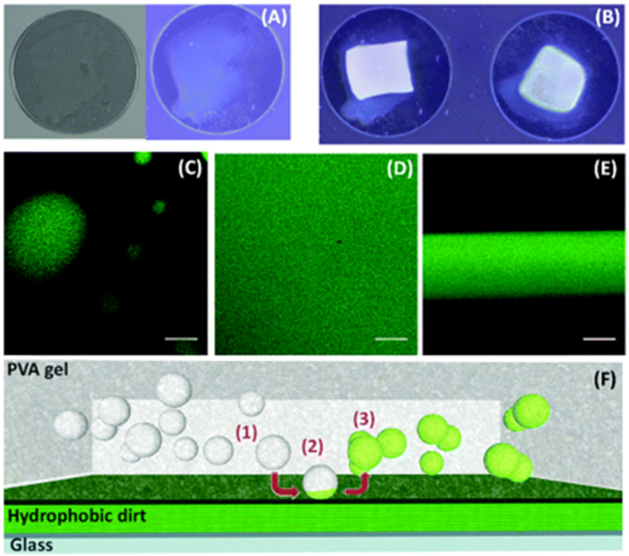

Fig. 7 Interaction of a nanostructured fluid-loaded PVA gel with a model surface (glass), covered with hydrophobic grime. (A) coverglass covered with a fluorescent dye-labelled grime under white (left) and UV (right) light; (B) the same coverglass with two PVA gels on top; (C)–(E) representative CLSM images of the grime layer, as horizontal (C) and (D) and vertical (E) sections; (F) scheme of the interaction of the loaded PVA gel with the hydrophobic dirt: the latter is partially captured in the hydrophobic core and detached from the surface. Adapted from Mastrangelo *et al.* (2017)[63] with permission from the PCCP Owner Societies.

SIPNs produced slight changes in the dimensions of the micelles, and in the nanoscale structure of the gel. In the case of a DDAO-containing fluid, the solvents in the micelles promoted some disentanglement of polymer inhomogeneities. These changes did not affect the cleaning capability of the system, which was used to efficiently and safely remove old varnishes from sensitive artworks (a painted wooden icon, Fig. 8(A)–(C), and a watercolor on paper, Fig. 8(A′)–(C′)).

The second example involves the PVA "Twin-Chain Networks" (TCNs), a novel class of hydrogels produced by freeze-thawing solutions of two PVAs with different hydrolysis degree and molecular weight.[65,66] Recently, the PVA TCNs were uploaded with an o/w fluid containing MEK, 2-butanol and a C_{9-11} alcohol ethoxylate surfactant, to remove aged polyvinyl acetate varnish and wax layers that were altering the surface of Pablo Picasso's masterpiece "The Studio".[13] X-ray scattering, Confocal Laser Scanning Microscopy (CLSM), and Fluorescence Correlation Spectroscopy (FCS) demonstrated that the fluid diffuses through the gel and also interacts with its walls without affecting small ($<$100 nm) inhomogeneities.[67] Osmotic balance among the interconnected pores controls the dynamics of the fluid at the gel–target interface, producing effective and controlled cleaning. The PVA TCNs proved crucial also in the restoration of Jackson Pollock's and Roy Liechtenstein's works.[65,68,69]

Perspectives on new "green" formulations

The previous sections have shown that there is solid ground for mutual technological transfer from CH conservation science and multiple sectors in the framework of soft matter and colloids. Novel "green" nanostructured fluids for cleaning art are expected to contain bio-based surfactants, with candidates ranging from bio-derived nonionic to glycerol-based amphiphiles, as well as biosurfactants from lecithin or from microorganisms. These surfactants can be combined with "green" solvents, such as those mentioned in this contribution and others recently reviewed[12] for art cleaning applications, to produce o/w microemulsions and nanostructured fluids with a wide range of targets (soil, coatings, over-painting) for application on diverse works of art (murals, paintings, paper, plastic, metal, *etc.*). For instance, recent applications involved the use of APGs, amino acid-type surfactants and biosolvents in stabilizing new nanostructured fluids, such as w/o nanoemulsions. Such systems (so-called "eco-removers") are intended to remove various graffiti coatings from sensitive surfaces without causing damage to the underlying layers, considering the complex characteristics and the surface properties of the substrate and paints (*i.e.*, wetting, surface free energy, surface topography and porosity).[70–72]

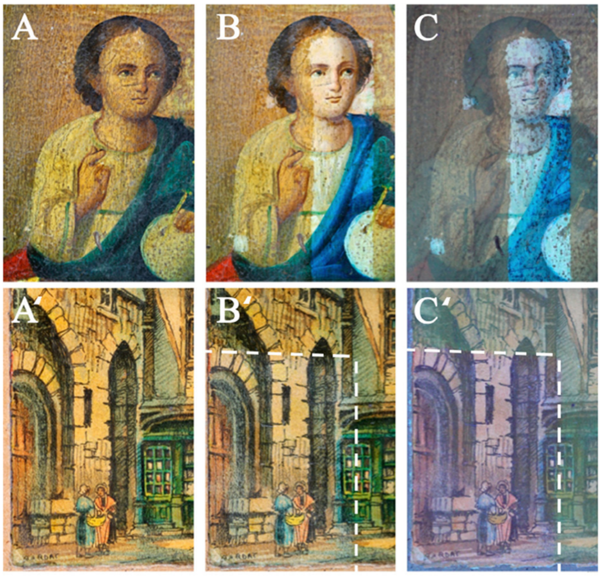

Fig. 8 Visible light (left, centre) and UV fluorescence (right) images of a painted Icon on wood (A)–(C) and a watercolor on paper (A′)–(C′), before (A), (A′) and after ((B), (B′): visible light; (C), (C′): UV light) the removal of aged, yellowed varnishes using SIPNs hydrogels loaded with nanostructured fluids. Reprinted with permission from Baglioni *et al.* (2018)[64] Copyright 2018 American Chemical Society.

Another promising class of surfactants for art cleaning, is represented by amphoteric amphiphiles that can be obtained from renewable resources, including fermentation processes. For instance, bio-based N-oxide surfactants have been obtained from monosaccharides as sustainable alternatives to traditional amphoteric surfactants.[73–75] Since amine oxide surfactants have already proven useful in art cleaning formulations,[47,64] this possibility fits in the overall effort to formulate surfactants from renewable sources, with potential transfer also to cosmetics, textiles, oil recovery, waster water treatment, and biochemistry, where amphoteric surfactants are providing important applications.[76–82]

Given the highly different surface activity, hydrophilicity/hydrophobicity, and combined physico-chemical interactions among these components, a wide range of behaviours is expected in dewetting, detergency and swelling processes induced on coatings and other undesired layers. With current possibilities offered by coupling microscopy (*e.g.*, CLSM, FCS) and scattering techniques (X-ray, neutron, or light scattering), the potential for developing and characterizing novel "green" and sustainable materials is vast, and still largely unexplored. It must be noticed that, while sustainability is fundamental, a crucial concern in art conservation regards also the efficacy of the new green cleaning systems, given the irreplaceable nature of artworks. Currently, several biosurfactants have been selected for possible formulations of nanostructured fluids.[12] The performance of these new systems is the object of current studies, which are expected to be reported in the literature over the very next years. In particular, it is important to monitor that the novel green systems compare to their synthetic counterparts in terms of effective cleaning, while showing improved sustainability.

The use of bio-derived materials is also progressing in gelled cleaning systems. Recent studies have demonstrated how biopolymers (starch, cellulose derivatives) or bio-derived molecules can be employed to tune the porosity, hydrophobicity, surface roughness and tortuosity of gel networks.[83] For instance, bio-derived diacids with different spacing lengths can be used to decorate the PVA TCNs, affecting the polymer–polymer phase-separation in the pre-gel PVA solutions.[84,85] This, in turn, modulates the porosity and nanoscale tortuosity of the gels to produce a counter-intuitive result: higher tortuosity yields higher cleaning capability, since it increases the residence time of cleaning fluids at the gel–target interface, allowing for more effective cleaning action.[7,85] Complementary to hydrogels, organogels based on bio-derived materials allow the use of organic solvents on highly-water sensitive artistic surfaces, like modern oil paintings. Examples include castor-oil based polyurethane networks,[86] whose properties can be tuned by adding "green" oligoesters with varying Hydrophilic–Lipophilic Balance,[83] or polyhydroxybutyrate gels.[87]

It is thus evident that there is virtually infinite room for scientific development and mutual technological exchange among art conservation science and all sectors where soft matter and colloids are central, opening for sustainable solutions that are much needed to face current pressing societal, environmental and economic issues.

Conclusions

Cultural heritage conservation science has deeply evolved and progressed over the last decades, with soft matter and colloids providing valuable contributions through the development of gels, nanostructured fluids, nanoparticles, and other advanced functional materials to target cleaning, consolidation, protection and sensing. Recently, conservation science has been focusing on "green" materials and sustainable solutions, an effort common to other scientific and technological fields. This trend has highlighted the vast potential conservation science holds to mutual exchange with sectors like drug-delivery, the food industry, tissue-engineering, and others, based on a common framework in soft matter, colloids and materials science. In this sense, the cleaning of artworks is a representative case, where bio-derived surfactants and biomaterials are progressively being included in microemulsions and gels to yield sustainable solutions with high efficacy. This clearly links with research efforts in cosmetics, pharmaceutics, and detergency. The possibilities and materials illustrated in this contribution constitute a representative example of how scientific development and mutual technological transfer can occur among art conservation science and the numerous sectors where soft matter and colloids are central, producing sustainable solutions that are fundamental to address societal, environmental and economic challenges.

Author contributions

David Chelazzi: writing – original draft, writing – review & editing, supervision, funding acquisition. Romain Bordes: writing – original draft, writing – review & editing. Andrea Casini: writing – original draft, formal analysis, investigation, data curation, writing – review & editing. Rosangela Mastrangelo: writing – original draft, data curation, writing – review & editing. Krister Holmberg: validation, writing – review & editing, supervision. Piero Baglioni: validation, resources, writing – review & editing, supervision, funding acquisition.

Data availability

The data supporting this article have been included in the main text. Raw data are available upon request to the authors.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

CSGI and the European Union (GREENART project, Horizon Europe research and innovation program under grant agreement no. 101060941) are gratefully acknowledged for financial support. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or the European Research Executive Agency (REA). Neither the European Union nor the granting authority can be held responsible for them. The publication was made by a researcher (RM) with a research contract co-funded by the European Union – PON Research and Innovation 2014–2020 in accordance with Article 24, paragraph 3a of Law No. 240 of December 30, 2010, as amended and Ministerial Decree No. 1062 of August 10, 2021.

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