

REVIEW

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# Leaching of nanoparticles from nano-enabled products for the protection of cultural heritage surfaces: a review

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## Abstract

The development of highly innovative techniques and technologies to enhance performance and technical sustainability of materials used in the field of cultural heritage conservation is providing conservators with innovative nanocomposites materials, including protective coatings, by merging the performances of engineered nanoparticles (NPs) with conventional chemicals. However, the human health and environmental risks that may potentially arise from these new materials are still largely unknown, requiring an adequate assessment and management along their entire life cycle. Concerns could emerge due to the leaching of the material containing NPs or of the NPs alone, especially during their use (exposure of the treated object to, e.g., heavy or acid rain) and disposal (when the wasted product is processed in, e.g., waste water treatment plants). To date, no standard leaching test methods have been specifically developed for nano-enabled products, with the consequent lack of data on the NPs potential exposure also in the field of cultural heritage. Therefore, an extensive review over the last 10 years by querying to the Scopus database “nanoparticles”, “leaching” and “coatings” has been herein reported to clearly highlight (i) the standard test methods used or adapted to estimate the NPs leaching from nano-based coatings; (ii) the available studies in which the NPs leaching from nano-based coatings was estimated without following any specific standard test method; (iii) the works focusing on other nanocomposite materials performances than leaching, in which standard test methods were applied, potentially useful to indirectly estimate NPs leaching. All the information gathered by this bibliographic search have been used to identify the most promising leaching tests for NPs estimation to be applied in the field of cultural heritage, especially for both large, e.g., building façades, and small, e.g., bronze works of art, surface areas from which the leaching of nano-based materials could be significant in terms of human health and ecological risks, based also on the (eco)toxicity of the leachate. The derived information can thus ultimately support effective risk management of innovative nano-enabled products, including the implementation of Safe by Design approaches.

**Keywords:** Leaching test, Engineered nanoparticles, Coatings, Environmental exposure assessment, Cultural heritage

## Background

Regardless of their nature, movable and immovable cultural heritage assets, especially those located outdoors, are irremediably exposed to several degradation agents

such as temperature, humidity, light, microorganisms and air pollutants, all accounting for the natural aging of art materials [1, 2]. In recent years, engineered nanoparticles (NPs), consisting of particles deliberately designed with all the three dimensions in size between 1 and 100 nm, are emerging as a successful solution for the preservation of cultural heritage because of their capability in enhancing performances, e.g., by improving transparency, resistance, cleaning and anti-microbial properties, ensuring

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greater durability of art materials [3]. Because of the variety and complexity of artistic and historical substrates, conservation science has explored different routes, developing several technical approaches for solving conservation issues. In the field of stone conservation, colloidal  $\text{Ca}(\text{OH})_2$  is one of the most promising products for stone's consolidation because it is easily converted into calcium carbonate ( $\text{CaCO}_3$ ) as result of carbonation when exposed to atmospheric  $\text{CO}_2$  under moist conditions [4]. Another example is provided by coatings incorporating  $\text{SiO}_2$  NPs for improving abrasion resistance and for adding hydrophobic properties to the stone surface [5, 6]. Both hydrophilic and hydrophobic silica are used in solvent-borne coatings to enhance the anti-settling additives for pigments [7]. The addition of Ag NPs to paints for outdoor applications on building façades, instead, determines an antimicrobial effect derived from the activity of silver [8], while photoactive  $\text{TiO}_2$  NPs are used to optimize the mechanical properties of the products and to give the paint self-cleaning properties through photocatalytic and hydrophilic properties [9]. The addition of zirconia NPs to coatings for metal substrates showed to remarkably improve their properties, such as strength and fracture toughness, wear resistance, hardness, chemical and corrosion resistance [10]. Recently, further innovative nano-based products for the conservation of movable and immovable property have been developed within H2020 projects such as NANORESTART (Grant agreement no: 646063) and NanoCathedral (Grant agreement no: 646178). Some examples from the NANORESTART project are nano-based fluids for undesired graffiti removal [11, 12], alkaline NP dispersions for restoration of alum-treated archaeological wood [13], layered double hydroxide nanocarriers in protecting bronze artworks [14] or nanocellulose-based materials for canvas consolidation [15, 16]. In addition, nanocomposite materials have been specifically developed in the field of stone protection within the NanoCathedral project [17, 18].

However, similarly to other market sectors benefiting from nanotechnology innovation, the design and use of nano-enabled products in the conservation field raise issues concerning human health and environmental risks that could emerge from exposure to NPs embedded in conservation products and into innovative materials used in the construction field and that need to be carefully assessed to satisfy current European regulatory provisions. According to the revision of Annexes of the EU REACH regulation with regards to nanomaterials, effective from the 1st of January 2020 [19], manufacturers and importers must register a nanomaterial if the total amount per year (including both nanoforms and potential bulk form) is above one tonne and submit

a complete Chemical Safety Assessment (CSA) report if this quantity exceeds 10 tonnes. The CSA shall identify and describe the risks associated with the bulk form and the nanoform(s) along the life cycle of the substance and document that these risks are adequately controlled. Therefore, human and ecological exposure assessment requires the investigation of possible release scenarios of NPs along the life cycle of nano-enabled products, including: (1) release during NPs production; (2) release from the manufacturing processes of products containing NPs; (3) release into the environment during use (including release from the objects treated with such products), re-use and recycling of nano-enabled products, and (4) indirect release at the end-of-life stage as consequence of processes within wastewater treatment plants or waste incineration plants, to different environmental compartments (i.e. surface water, soil, air, and groundwater) [20]. In parallel, (eco)toxicological testing should also be carried out at each of the different stages of the life cycle, to provide information useful of real exposure scenarios.

On this regard, a recent review by Reyes-Estebanez et al. [21] collected numerous studies dealing with the impacts of the most used and widespread NPs in cultural heritage on biota at both the biochemical and organism levels for different environmental compartments.

Such data and information would also support the development of "green" or "Safe by Design" approaches, which are still in their infancy in the field of cultural heritage conservation [22, 23]. In particular, Semenzin et al. [23] recently proposed a sustainability framework implementing the Safe by Design concept to support product's developers in the early steps of product development, with the aim to provide safer nano-formulations for conservation, while retaining their functionality. Such framework takes into account the current EU legislative context (i.e. CLP and REACH regulations) as well as the specific features of the innovation process in the cultural heritage conservation field, which demands a high interaction between the product developers and the restorers [24]. In detail, starting from the development of a nano-based formulation (step 1), the following main steps of the framework are the: screening hazard assessment (step 2); advanced hazard assessment (step 3); safety assessment (step 4) and, finally, sustainability assessment (step 5). While the hazard assessment in step 1 is mainly based on the EU CLP self-classification approach for health and environmental hazards of the mixture, step 2 can include computational (e.g., *in silico* models) as well as experimental [e.g., *in vitro* and *in vivo* (eco)toxicological tests] approaches according to an Integrated Testing Strategy (ITS), where information about relevant exposure scenarios for both human health (i.e. occupational and public health) and the environment (i.e. technical

compartments such as waste systems and environmental compartments such as soil and water systems) along the life cycle of the innovative products should also be collected or generated. More specifically, in order to allow safety assessment (i.e. integration of risk assessment and risk control as required by the EU REACH regulation; (step 3), data/information on product degradation and/or release throughout their life cycle should be collected, to evaluate medium and long-term behaviour of nano-based products [9].

Indeed, NPs that reach the environment may be completely different from the materials originally produced by industry because of aging processes that may cause transformations [25, 26], making the monitoring and quantification of the NPs release highly challenging, especially when they are present at trace levels in environmental compartments (e.g., freshwater, soil) [27]. In this context, leaching tests could provide a valuable support to exposure assessment, particularly in the post-application phase of nano-enabled products, i.e. when the treated work of art is exposed to outdoor conditions (e.g., heavy rain) or the wasted product is processed in waste systems, and therefore NPs can reach the surrounding environment.

To the best of our knowledge, only recently the release of hazardous substances from nano-based products has been studied in depth. Froggett et al. [28] reviewed the literature on releases from solid, non-food commercial nanocomposites during use, disposal, or recycling, claiming that there is a paucity of data on release of NPs from solid nanocomposites under the five scenarios considered: machining, weathering, washing, contact and incineration. Among the 54 nanorelease studies identified, most of them detected only the particles from the matrix alone, followed by matrix debris embedding NPs. Far less frequently the added NPs entirely dissociated from the matrix were determined, and even more rarely dissolved ionic forms of the added NPs. Besides this review, Koivisto et al. [29] provided a library for nano-based products, calculating the quantitative NPs release from the literature. Following the approach suggested by Froggett et al. [28], the 96 peer-reviewed scientific publications identified by Koivisto and et al. [29] were divided into six groups: (1) thermosets; (2) thermoplastics; (3) coated surfaces; (4) sprays; (5) textiles; (6) other articles. The quantitative release was defined as “the amount of mass released from a nano-application under experimental setups (scenarios) that intend to simulate situations that result in the liberation of material, calculating it from the measured average concentration levels and volumes of immersion fluid or dilution air”. The authors underlined the lack of general available guidance to measure

quantitative release under various release scenarios and called for developing systematic experimental methods to support hazard and exposure assessment of nano-based products.

In this context, the overarching objective of this review was to provide an analysis of the available leaching standard test methods already used for different nano-enabled products to support the environmental exposure assessment of NPs from innovative products employed for surface protection in cultural heritage conservation. In addition to standardized leaching test, non-standardized leaching procedures, as well as standard tests used to evaluate technical performances of nano-enabled products, have been collected and investigated, with the aim to provide all the procedures that can be suitable in the field of cultural heritage, where more sensitive substrates could require less invasive testing. This work can therefore contribute to the assessment of human health and ecological risks as well as to the implementation of Safe by Design approaches for effective risk management of innovative nano-enabled products, especially taking into account their use (application and post-application phases, including exposure of the treated object to heavy or acid rain or other weather conditions) and disposal (when the wasted product is processed, e.g., in waste water treatment plants).

### Materials and methods—literature search approach

The leaching of hazardous substances from a material is often investigated under the broader topic of materials' performances (e.g., assessment of hardness/flexibility, resistance to abrasion, resistance to a falling weight, adhesion, artificial weathering, release). The systematic search herein reported was performed by querying the Scopus database, from 2010 to present, using three broad search terms: nanoparticles, leaching, and coatings.

This analysis identified 930 documents, among which 53 relevant studies focus on NPs leaching from different nanocomposite materials, including nano-based paints and preservatives materials, nanoscale fillers as well as photocatalytic coatings, nanopigments and antibacterial nano-based products. The studies selected were divided into: (i) leaching tests of nano-enabled products in which standard methods (e.g., ISO and ASTM standards) have been applied or adapted; (ii) leaching tests from nano-enabled products without any standardized test methods; (iii) assessment of performances other than the direct assessment of leaching, useful to indirectly estimate the NPs leaching from nano-enabled products.

## Results and discussion

The bibliographic search performed highlighted that no specific standard leaching test methods properly designed to estimate the NPs leaching from nano-enabled products are present in the literature. Nevertheless, all the outcomes potentially linked to this aim have been considered and discussed. The results of this literature analysis were divided into three tables: Table 1 includes seven studies in which four different standard leaching test methods were used, i.e. two for nano-based paints and coatings and two for nano-based wood preservatives; Table 2 lists 35 studies for evaluating leaching of NPs from products by using only standard preparation test methods but without any specific standard leaching test; Table 3 summarizes additional ten works, in which eight more standards for evaluating other nano-based materials' performances than leaching have been applied and could be adapted for developing useful leaching tests in the field of cultural heritage. A schematic representation of the available methods is reported in Fig. 1.

Besides the standards already mentioned, other two standard leaching test methods for the determination of the release of dangerous substances from non-nano coatings and construction products have been considered and discussed.

Lastly, specific information from the studies listed in Table 1 on the estimated amount of species detected in the leachate has been collected in Additional file 1: Table S1.

### Standardized testing to estimate NPs leaching from nanocomposite materials

#### *Nano-based paints*

The leaching of NPs from nano-based paints was assessed by following two standard tests, i.e. ISO 2812-2:2007 [30] on paints and varnishes, focusing on the determination of resistance to liquids by water immersion method and 12457-3:2002 [31], related to leaching of granular waste materials and sludges. The first standard leaching test was employed by Zuin et al. [9], Zhang et al. [26] and Lopez-Ortega et al. [32] while Zuin et al. [7] estimated the nano-based paint debris leaching according to the second one. In detail, both Zuin et al. [9] and Zhang et al. [26] investigated the leaching of TiO<sub>2</sub>, SiO<sub>2</sub> and Ag NPs embedded in paints applied on fibre cement panels. Zuin et al. [9] adapted this standard method, collecting leachates after UV exposure (according to ISO 11507:2007 [33], currently revised by ISO 16474-1:2013 [34]) and Taber Abraser test (using ISO 7784-2:2006 [35]), by immersing ¼ of the length of the panels and with a surface/volume ratio equal to 2. Leachates were collected after 4, 8, 24, 120 h and analysed by inductively coupled plasma-optical

emission spectroscopy (ICP-OES). After the water immersion test, a small amount of acetic acid was added to the leaching solution to simulate acid rain effect on coated panels. Surface degradation was investigated by transmission electron microscopy (TEM), energy dispersive X-ray analysis (EDX) and X-ray fluorescence (XRF). The results highlighted that only very little Si migration from SiO<sub>2</sub> NPs-based paints occurred in these accelerated tests. With regard to TiO<sub>2</sub> NPs-based paint and its reference based on bulk TiO<sub>2</sub> pigment, it was observed that both paints released only very low amounts of Ti into the leachates during the immersion test, without any increase of Ti concentration over time and no TiO<sub>2</sub> particles were identified in the leachate by TEM. As far as the Ag NPs-based paint, the Ag concentration from Ag NPs-based paint in leachates was below the detection limit of the ICP-OES (0.1 µg/l).

Zhang et al. [26] also applied ISO 2812-2:2007 standard [30] for determining the resistance of single-layer or multi-layer systems of coating materials to the effects of water by partial or full immersion, analysing the leachates after 100, 150, 200, 250, 300, 350, 400 and 500 h of weathering chamber. The role of pH on the releases was also investigated by varying the pH from 3 to 10. As far as weathering before obtaining leachates, EN 1062-11:2002 standard [36] was used for conditioning the samples before testing and ISO 11507:2007 standard [33] was followed for UV weathering. Particles size distribution of the leached NPs was evaluated by means of Dynamic Light Scattering (DLS) technique, the NPs' release by inductively coupled plasma-mass spectrometry (ICP-MS), while scanning electron microscopy (SEM) and TEM were employed to identify size and shape of NPs in the matrix before and after leaching. The results obtained showed that the duration of weathering test and rainfall are more important in controlling the NPs' release than the variation of pH.

The evaluation of SiO<sub>2</sub> NPs leaching from paint debris was carried out by Zuin et al. [7], following 12457-3:2002 [31]. Polyvinyl chloride panels were coated with different paints containing the same amount of SiO<sub>2</sub> NPs, but different pigment volume concentrations and different amount and type of binder and pigment. After 24 h of drying in indoor environment, paints were taken off from panels and mechanically milled until a fine powder in the range of approx. 100 µm to a few mm was obtained. The leaching test involved approx. 300 g d.w. of paint debris added into a high-density polyethylene bottle. Deionized water (DW) was used to obtain a liquid-to-solid (L/S) ratio of 2:1 and of 8:1 (cumulative L/S of 10:1). The mixture at L/S of 2:1 was shaken by end-over-end rotation at 10 rotation per minute (rpm) for 6 h, while the mixture at L/S of 8:1 was agitated for 18 h. The supernatant

**Table 1** Studies including standard leaching testing methods for NPs estimation from nano-enabled products

Nano-enabled product	Substrate	Tested media	Standard leaching test method	Elements/NPs detection and analytical techniques	Species detected in the leachate (ionic form, free NPs, embedded in the matrix)	Literature source
Nano-based paints	Fibre cement panels	Rain water	ISO 2812-2:2007	Ti, Ag and Si from TiO <sub>2</sub> , Ag and SiO <sub>2</sub> NPs in paints by XRF and ICP-OES	Ionic form: Ti, Si	Zuin et al. [9]
	Fibre cement panels	Rain water Acid rain water	ISO 2812-2:2007	TiO <sub>2</sub> , SiO <sub>2</sub> and Ag NPs detection by TEM-EDX	Free NPs: SiO <sub>2</sub>	
	Fibre cement panels	Rain water	ISO 2812-2:2007	Si, Ti and Ag by ICP-MS	Ionic form: Ti, Si, Ag	Zhang et al. [26]
	Aluminium layer	Synthetic seawater (according to ASTM D1141)	ISO 2812-2:2007	SiO <sub>2</sub> NPs size by DLS (Ag and TiO <sub>2</sub> NPs were not detected by DLS due to low concentration)	Free NPs: SiO <sub>2</sub>	
	Polyvinyl chloride panels	DW	EN 12457-3:2002	SiO <sub>2</sub> NPs by TEM		
Wood preservatives	Treated lumber	Ammoniacal copper solution	AWPA E11-97	Si and Cu from SiO <sub>2</sub> and Cu <sub>2</sub> O NPs by ICP-OES	Ionic form: Cu	Lopez-Ortega et al. [32]
	Treated wood	Rain water	EN 84:1997	Si from SiO <sub>2</sub> NPs in paints by ICP-MS	Ionic form: Si	Zuin et al. [7]
	Treated wood	Water-based suspensions	EN 84:1997	SiO <sub>2</sub> NPs by TEM-EDX	Free NPs: SiO <sub>2</sub>	
	Beech and pine planks	Distilled water	EN 84:1997	Cu <sup>2+</sup> by AAS	Ionic form: Cu	Ding et al. [44]
	Treated wood	Rain water	EN 84:1997	CuO NPs (10 and 50 nm), PVP-CuO-10 NPs, water soluble modified chitosan HTCC-CuO-10 and HTCC-CuO-50 NPs by TEM-EDS	Free NPs: all the Cu-based NPs	
	Treated wood	Rain water	EN 84:1997	Total copper content determination by ICP-MS	Ionic form: Cu	Pantano et al. [46]
	Beech and pine planks	Distilled water	EN 84:1997	CuO NPs in an acrylic paint by spICP-MS and TEM-EDX	Free NPs: CuO	
	Beech and pine planks	Distilled water	EN 84:1997	Percentage weight loss of samples before and after the addition of 5 different NPs (ZnO, zinc borate, Ag, Cu and copper borate) suspensions. Only indirectly NPs leaching estimation	Not determined	Bak and Németh [47]

A4F Asymmetric flow field fractionation; AAS Atomic absorption spectroscopy; AUC Analytical ultracentrifugation; DLS Dynamic light scattering; EDX Energy dispersive X-ray; ICP-MS Inductively coupled plasma-mass spectrometry; ICP-OES Inductively coupled plasma-optical emission spectrometry; TEM Transmission electron microscopy; XRF X-ray fluorescence



**Table 2** Studies with non-standardized procedures to estimate NPs leaching from nano-enabled products

Nano-enabled product	Substrate	Tested media	Experimental procedure	Time of leaching evaluation	Elements/NPs detection and analytical techniques	Species detected in the leachate	Literature source
<b>Immersion test procedures</b>							
Ag nanocomposite films	Stainless steel	NaCl 0.15 M solution	Immersion of 10 × 10 mm (0.9 mm thickness)	60 days	<sup>108</sup> Ag <sup>+</sup> detection by XPS and ToF-SIMS	Ionic form: Ag	Zanna et al. [83]
TiO <sub>2</sub> NPs coatings	Glass substrate	DW, DW with humic acids and NaCl	Immersion of 30 × 25 mm tiles	1–4 weeks	Total [Ti] by ICP-OES TiO <sub>2</sub> NPs by SEM-EDX	Ionic form: Ti Free NPs: TiO <sub>2</sub>	Olabarrieta et al. [50]
Ag NPs	Glass	DW, phosphate buffer (pH 7.4, 1.25 mM KH <sub>2</sub> PO <sub>4</sub> , 2.5 mM K <sub>2</sub> HPO <sub>4</sub> , 4.7 mM Na <sub>2</sub> HPO <sub>4</sub> , supplemented with 0.4% glucose)	Immersion of 1 × 1 cm <sup>2</sup> glass substrates	60 min	Total [Ag] by ICP-AES Ag NPs by FEG-TEM and FEG-SEM	Ionic form: no significant amount of Ag	Agnihotri [58]
TiO <sub>2</sub> NPs-based paints	Fibre cement panels	DW, tap water, rain water	Immersion of 10 × 10 cm	113 cycles of 6 h each (3 h of UV light, 0.5 h of irrigation and 2.5 h of drying)	Total [Ti] by ICP-OES TiO <sub>2</sub> NPs by TEM-EDX	Ionic form: very low amount of Ti	Al-Kattan et al. [51]
Ag nanocomposite	Ag–chitosan film	DW	Immersion of film	24 h	Total [Ag] by UV–Vis	Ionic form: Ag, especially with low MW chitosan	Regiel et al. [82]
Ag NPs-based antimicrobial material	Hyperbranched epoxy	Phosphate buffer saline, synthetic seawater	Immersion of 1 × 1 cm	7 days	Total [Ag] by UV–Vis	Ionic form: Ag	Barua et al. [84]
Ag NPs-based coatings	Wood panels	Rain water	Immersion of facade elements with an area of 0.75 × 1.44 m <sup>2</sup>	1 year—outdoor	Total [Ag] by ICP-MS Ag NPs detection by TEM	Ionic form: Ag	Künniger et al. [48]
Ag NPs-based coatings	Polystyrene, glass, metal binder clips	Seawater	Immersion of 20 cm diameter petri dishes	120 h	Total [Ag] by AAS	Ionic form: Ag	Ren et al. [85]
Chitosan–zinc oxide nanocomposite coatings	Glass substrate	DW	Immersion of 25 × 75 mm coated slides	0–4 weeks	Total [Zn] by ICP-OES	Ionic form: Zn	Al-Naamani et al. [86]
Diketopyrrolopyrrole, Fe <sub>2</sub> O <sub>3</sub> NPs-based pigments	Polymer matrix	Food simulants: DW, DW with 10% EtOH, DW with 3% acetic acid; environmental media: DW, moderately hard water (pH 7.6) and DW+SRNOM, pH 8)	Immersion of plates, granules and fragments	Food simulants: 10 days Environmental media: 3 months	Fe <sub>2</sub> O <sub>3</sub> NPs-based fragments detection by TEM, UV–Vis, AUC, ICP-MS, spICP-MS	Ionic form: Fe Free NPs: Fe particles	Neubauer et al. [52]

**Table 2** (continued)

Nano-enabled product	Substrate	Tested media	Experimental procedure	Time of leaching evaluation	Elements/NPs detection and analytical techniques	Species detected in the leachate	Literature source
MWCNT	Epoxy and polyamide polymers	Rain water	Immersion of MWCNT-based polymers	Toxicity characteristic leaching procedure extraction fluid #1: 24 h + 1 h	TEM to identify the form of release ICP-MS to quantify Al and Co, tracers for MWCNTs UV-Vis/turbidity to semi-quantitatively rank the release quantity AUC or AF4 to quantify the free ENMs category by size-selectivity	Ionic form: Al, Co, Fe  Free NPs: only MWC-NTs from epoxy-MWCNT  Embedded in matrix: epoxy-MWCNT and polyamide-MWCNT	Wohleben et al. [54]
TiO <sub>2</sub> NPs coatings	Silicon substrates	DW, Acid rain solution (EPA method 1320), boiling water for industrial test conditions	Immersion of 20 × 20 mm silicon substrates	7 days 1 h for boiling water	Total [Ti] by ICP-OES	Ionic form: Ti	Cedillo-González et al. [87]
CeO <sub>2</sub> NPs	Micronized copper-azole pressure treated lumber, composite decking material	Synthetic precipitation liquid procedure solution	Immersion of 4 × 4 cm coupons	72 h	Total [Ce] by ICP-OES Speciation analysis by XAFS CeO <sub>2</sub> aggregates by BSE-FESEM-EDX	Ionic form: Ce Embedded in the matrix: aggregates with also Ce signal	Clar et al. [88]
Cu NPs	Lumber treated with Cu	DW, 1, 10 and 30 ‰ seawater	Immersion of 2 × 2 × 2 cm lumber blocks	8 h, 1, 2, 7, 14, 28 and 133 days	Total [Cu] by ICP-AES	Ionic form: Cu	Parks et al. [89]
ZnO NPs	Micronized copper-azole pressure treated lumber, composite decking material	Synthetic precipitation liquid procedure solution	Immersion of 4 × 4 cm coupons	72 h	Total [Zn] by ICP-OES Speciation analysis by XAFS ZnO aggregates by BSE-FESEM-EDX	Ionic form: Zn Embedded in the matrix: aggregates with also Zn signal	Clar et al. [90]
ZnO NPs	Micronized copper-azole-treated lumber, aqueous copper-azole-treated lumber	Synthetic precipitation liquid procedure solution	Immersion of 4 × 4 cm coupons	72 h	Total [Zn] and [Cu] by ICP-OES Speciation analysis by XAFS	Ionic form: Zn	Clar et al. [91]

**Table 2** (continued)

Nano-enabled product	Substrate	Tested media	Experimental procedure	Time of leaching evaluation	Elements/NPs detection and analytical techniques	Species detected in the leachate	Literature source
Diketyropyrroliol, Cu-phthalocyanine, Fe <sub>2</sub> O <sub>3</sub> NPs pigments	Acrylic and melamine coatings	Nanopure water with sodium dodecyl sulfate	Immersion of 7 × 8 cm and 10 × 9 cm plates	1 and 12 h	Nano-based fragments by TEM-EDX, UV-Vis and AUC	Embedded in the matrix: fragments, potentially with embedded pigments	Ruggiero et al. [53]
Polystyrene-TiO <sub>2</sub> NPs coatings	Aluminium alloy	3.5 wt % NaCl aqueous solution	Immersion of Al alloy samples	6 h, 1 and 3 days	Corrosion by XRD, EDX and EIS	Not determined	Zhang and Zhang [92]
TiO <sub>2</sub> NPs	Oak slats	Indoor: DW Outdoor: Rain and snow melt waters	Immersion of 0.64 cm thick × 6.4 cm wide oak slats	2, 4, 7 and 10 weeks in winter—2 weeks in summer—outdoor	TiO <sub>2</sub> NPs by spICP-MS	Ionic form: Ti Free NPs: TiO <sub>2</sub>	Azimzada et al. [49]
PET-Ag NPs fibres	Textiles	DW	Immersion of 38 mm length PET fibres	15 min, 30 min, 2 h, 8 h, 12 h and 24 h	Total [Ag] by ICP-MS	Ionic form: Ag	Gadkari et al. [93]
Ag NPs	Cellulose membranes	Bacterial suspension	Immersion of cellulose membrane filters	24, 48, 72, 96 h	Indirect measurements by SEM, TGA and EDX	Not determined	Hanif et al. [94]
ZnO NPs	Micronized copper azole pressure treated lumber	Synthetic precipitation liquid procedure solution	Immersion of 4 × 4 cm coupons	72 h	Total [Zn] and [Cu] by ICP-OES Speciation analysis by XAFS	Ionic form: Zn	Thornton et al. [95]
Water spray or/and outdoor runoff methods	Ag NPs-based paint	Rain water	Runoff from outdoor façades	1 year under natural outdoor weather conditions	Total [Ag] and [Ti] by ICP-MS Ag NPs by TEM-EDX	Ionic form: Ag, Ti Free NPs: Ag	Kaegi et al. [8]
SiO <sub>2</sub> NPs	Epoxy-based material	DW	Water spray on amine-cured epoxy containing nanocoating (10 cm diameter)	–	Total [Si] by ICP-OES	Ionic form: Si	Sung et al. [81]
TiO <sub>2</sub> NPs	Brick, concrete panels	DW	Water spray on masonry brick (11 cm × 5 cm × 5 cm)	At selected time points of the weathering process: 2, 4, 6 and 7 months	Total [Ti] by ICP-MS TiO <sub>2</sub> NPs by TEM-EDX	Ionic form: Ti Embedded in the matrix: particle agglomerates	Shandilya et al. [55]



**Table 2** (continued)

Nano-enabled product	Substrate	Tested media	Experimental procedure	Time of leaching evaluation	Elements/NPs detection and analytical techniques	Species detected in the leachate	Literature source
TiO <sub>2</sub> NPs	Photocatalytic pavements	Rain runoff high-pressure water cleaning	Runoff on 4 × 4 m slabs	800 days	Total [Ti] by ICP-MS TiO <sub>2</sub> NPs by FE-SEM and EDX	Ionic form: Ti Embedded in the matrix: particles containing Ti	Jimenez-Relinque et al. [56]
ZnO-graphene oxide nanocomposites	ZnO, rGO and ZnO-rGO functionalized surfaces	DW	Aerosol spray on 1 × 1 cm glass substrate	20 h	[Zn <sup>2+</sup> ] in µg/cm <sup>2</sup> by TXRF	Ionic form: Zn	Valenzuela et al. [96]
Leaching from milled paint/aged particles in contact with a liquid							
TiO <sub>2</sub> NPs-based paints	Paints	DW, 10 mM NaCl, 3 mM CaCl <sub>2</sub>	Extractability of Ti from aged milled paint dispersed in waters	3 days shaken + 24 h rest to obtain supernatant	Total [Ti] by ICP-MS TiO <sub>2</sub> NPs by STEM-EDX	Ionic form: Ti Free NPs: TiO <sub>2</sub> Embedded in the matrix: TiO <sub>2</sub> NPs	Al-Kattan et al. [57]
SiO <sub>2</sub> NPs-based paints	Fibre cement panels	Tap water, DW	Water spray on treated panels (195 × 75 cm)	46 L for 89 cycles of 6 h each	Total [Si] by ICP-MS	Ionic form: Si	Al-Kattan et al. [5]
SiO <sub>2</sub> NPs	Silicate coating	DW, tap water, soap solution, 0.5 M nitric acid, artificial sea and rainwaters	Extractability of Si from aged milled paint	24 h stirring + 24 h rest to obtain supernatant	Elemental composition by XRF SiO <sub>2</sub> NPs by STEM-EDX	Free NPs: SiO <sub>2</sub> Embedded in the matrix: SiO <sub>2</sub> NPs	Jolin et al. [97]
Leaching in contact with water-based liquid							
TiO <sub>2</sub> NPs-based paints	PVC and glass substrates	Wet (2.5 g/l of dodecylbenzenesulfonate of sodium) and dry conditions	Solution spread onto the coating	37 abrasion cycles/ min	NPs by laser granulometer and SEM	Embedded in the matrix: TiO <sub>2</sub> NPs	Golanski et al. [98]
TiO <sub>2</sub> NPs and hydroxyapatite	Marble	Simulated rain	Drip DW over 30 × 30 × 20 mm samples	Simulated 6 years rain	Total [Ti] by ICP-OES TiO <sub>2</sub> NPs by EDX	Ionic form: Ti	Sassoni et al. [59]
CuO:Ag NPs	Activated carbon	DW	Flushed water	10 l of water contaminated with <i>E. coli</i> ; 600 l of uncontaminated water; 10 l of contaminated water	Total [Ag] and [Cu] by AAS	Ionic form: Ag and Cu	Arakawa et al. [99]

**Table 2** (continued)

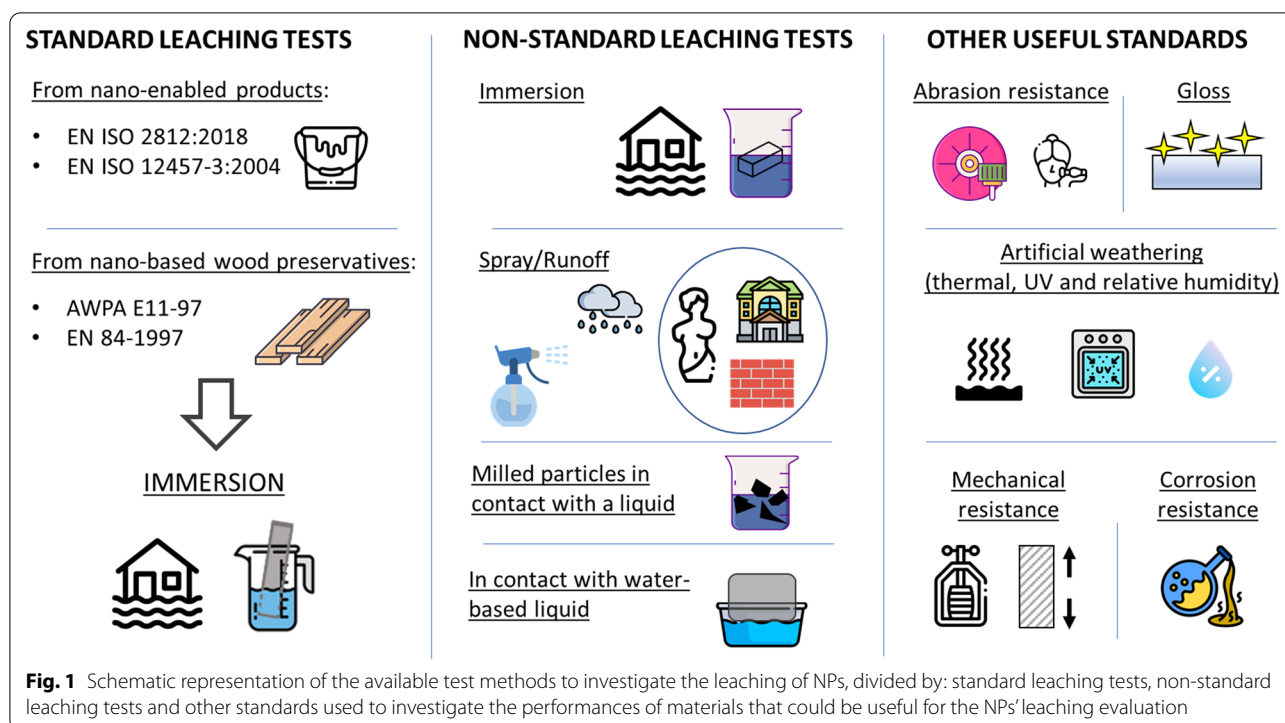
Nano-enabled product	Substrate	Tested media	Experimental procedure	Time of leaching evaluation	Elements/NPs detection and analytical techniques	Species detected in the leachate	Literature source
Cu NPs, Cu <sub>2</sub> O NPs and CuO NPs	LLDPE polymer	Saline solution and bacterial suspensions	Thickness between 0.2 and 0.5 mm of PE with NPs in contact with water	Mixing by magnetic stirrer over 1 month	Total [Cu] by ICP-AES	Ionic form: Cu	Gurianov et al. [100]
Ag NPs	Textiles	DW and detergent solution	5 x 5 cm of cotton print cloth in a PP bottle with 15 ml of DW or detergent solution	Samples in a plastic bottle with 15 ml of DW or detergent solution with glass balls to simulate frictions of home laundering	Total [Ag] by ICP-MS Ag NPs by SERS	Ionic form: Ag Embedded in the matrix: Ag NPs complexed with detergent components	Nam et al. [60]

Immersion test, water spray and/or runoff methods, leaching from milled paint/aged particles in contact with a liquid and leachate from nano-enabled products in contact with a water-based liquid were the four non-standardized procedures categories identified

AAS Atomic absorption spectroscopy; AUC Analytical ultracentrifugation; DW Deionized water; EDX Energy dispersive X-ray spectroscopy; EIS Electrochemical impedance spectroscopy; FEG-SEM Field emission scanning electron microscopy; FEG-TEM Field emission gun-transmission electron microscopy; FTIR Fourier-transform infrared spectroscopy; ICP-OES Inductively coupled plasma-optical emission spectroscopy; ICP-AES Inductively coupled plasma atomic emission spectroscopy; LLDPE Linear low-density polyethylene; s/ICP-MS Single particle inductively coupled plasma-mass spectrometry; SERS Surface enhanced Raman spectroscopy; TGA Thermogravimetric analysis; ToF-SIMS Time of flight-secondary ion mass spectrometry; TXRF Total reflection X-ray fluorescence spectroscopy; XRD X-ray diffraction; XPS X-ray photoelectron spectroscopy; XAFS X-ray absorbance fine structure

**Table 3** Studies evaluating other nano-based materials' performances than leaching by standard test methods

Nano-enabled product	Substrate	Standard tests for materials performances	Tested performance	Literature source
SiO <sub>2</sub> NPs	Steel panels	ASTM D6037, ASTM D4060, ASTM D968 (resistance to abrasion), ASTM G154, ASTM B117 (artificial weathering), ASTM D523-14 (gloss) [61–65, 101]	Abrasion resistance, artificial weathering, gloss	Scrinzi et al. [102]
ZrO <sub>2</sub> NPs, nano clay	PFTE sheets	ASTM B117 (artificial weathering), ASTM D638 (tensile and flexural properties) [61, 67]	Mechanical, thermal and corrosion resistance	Mirabedini et al. [10]
TiO <sub>2</sub> and SiO <sub>2</sub> NPs	Paperboard	ASTM D4060 (resistance to abrasion) [64]	Abrasion resistance	Stepien et al. [103]
Ytria doped zirconia, Si glass, alumina titanate, nanoclay, Si NPs	No substrate	ISO 2812-2:2007 (permeability), ISO 2409:2007 (resistance to abrasion), ASTM D3359 (adhesion), ASTM D7136 (resistance to a falling weight), ISO 14125:1998 (tensile and flexural properties) [30, 66, 68, 104, 105]	Thermal, peeling, water, impact and flexural tension resistance	Luangritratana et al. [69]
SiO <sub>2</sub> NPs	Concrete	ASTM C109/C109M (compressive strength), ASTM C1202 (rapid chloride penetrability), ASTM C1585 (rate of water absorption by hydraulic cement concrete) [106–108]	Mechanical properties and durability	Mahdikhani et al. [109]
TiO <sub>2</sub> NPs-PDMS coating	Thermally treated wood	ASTM G154 (artificial weathering) [62]	Water and UV-resistance	Shen et al. [110]
SiO <sub>2</sub> NPs	Poly(ether ketone) composites reinforced	ASTM G99-04 (wear resistance) [111]	Water-resistance, mechanical and thermal properties, tribological performances	Hou et al. [112]
SiO <sub>2</sub> NPs	Cement mortar	ASTM C230 (flow test for consistency); ASTM C191 (time of setting of hydraulic cement); ASTM C109 (compressive strength); NT BUILD 492 (chloride migration coefficient); ASTM C1585-04 (rate of water absorption by hydraulic cement concrete); ASTM C490 (length change of hardened cement paste, mortar and concrete) [106, 108, 113–116]	Mechanical properties (shrinkage measurements, compressive strength, water sorptivity, cement hydration, flow ability, setting times and rapid chloride migration coefficient)	Kooshafar and Madani [117]
SiO <sub>2</sub> NPs	Denim fabric	ASTM D1388 (stiffness of fabric); ISO 9237:1995 (determination of permeability of fabrics to air) [118, 119]	Self-cleaning features, air permeability, hydrophilicity, flame retardant, shrinkage, bending rigidity and tensile strength of the fabrics	Talebi and Montazer [120]
SiO <sub>2</sub> NPs	Glass fibre-reinforced polymer composites	ASTM D3039/D3039M (tensile properties of polymer matrix composite materials); ASTM D7264/D7264M (flexural properties of polymer matrix composite materials) [121, 122]	Permeability, tensile strength, bending resistance performance	Zhang and Mi [123]



was collected for analysis after 24 h of agitation, filtered at 0.45  $\mu\text{m}$  under vacuum on a standard cellulose nitrate filter and acidified (1% v/v) to determine the “dissolved”  $\text{SiO}_2$  by ICP-MS according to ISO 17294-2:2003 standard [37]. Total Si was also quantified via acidification with nitric acid of unfiltered samples. Following the procedure of the standards method 2540C of the American Public Health Association, both total dissolved solids and total suspended solids were also determined. The NPs detection was carried out by TEM–EDX. The main outcomes of this study were that: (i) the Si leached out was 1.8% with respect to the initial amount of Si in paint; (ii) some agglomerates of  $\text{SiO}_2$  NPs were detected in some leachates; (iii) the pigment volume concentration is a crucial factor for  $\text{SiO}_2$  NPs leaching, and (iv) by balancing the binder to pigment ratio, it would be possible to reduce the  $\text{SiO}_2$  NPs leaching.

Within the field of antifouling paints for offshore structures, Lopez-Ortega et al. [32] compared the water resistance of an aluminium layer treated with Carboguard® epoxy mastic coating with one coated with a product functionalized by NPs. The evaluation of water resistance was assessed according to several standards, such as ISO 6270-2:2018 [38] on water condensation test, ISO 9227:2017 [39] on salt-fog test and ISO 4628 1-5:2016 [40] on the evaluation of degradation of coatings, including the ISO 2812-2:2007 [30] on leaching test. In detail, an organic topcoat paint was functionalized with a  $\text{SiO}_2$

NPs dispersion to enhance hydrophobicity and with three different biocides, including  $\text{Cu}_2\text{O}$  NPs. Briefly, the panels were immersed in 1 l of synthetic seawater and stirred over 28 days. Unlike the first two studies, here the NPs leaching was assessed only indirectly by determining the release rate of copper and other main elements present in the painted samples by ICP-OES every 24 h. After this step, a set of new samples was tested under the same experimental conditions, till reaching the plateau of copper maximum release. The leaching results highlighted the presence of Si and negligible Cu release for both original and nano-based topcoat paints, with the silicon content in the modified paint decreasing with time to lower values than those of the original paint at the end of the test. Following the marine algal growth inhibition test (ISO 10253 [41]), in accordance with the OECD Guidance Document no: 23 [42], the ecotoxicity assessment with the algae *Phaeodactylum tricorutum* showed a toxicity level of the leachate which fulfilled the legislation requirements for modified nano-based paint and lower than that of the bulk material.

#### Wood preservatives

Two different standard test methods for NPs leaching investigation from wood were applied in three studies. The AWPA E11-97 standard method [43] for accelerated laboratory evaluation of the leachability of waterborne wood preservatives was employed by Ding et al.

[44]. The nano-based wood preservatives tested included (i) CuO NPs with an average particle size of 10 or 50 nm (CuO-10 and CuO-50) and (ii) CuO NPs stabilized by weakly acidic or weakly basic polymer-stabilizers, i.e. [(2-hydroxy-3-trimethylammonium)propyl] chitosan chloride (HTCC-CuO-10 and HTCC-CuO-50) and Poly(vinylpyrrolidone) (PVP-CuO-10). The description of the leaching method applied clearly states that the data collected are not intended to, nor shall it be used to predict environmental impacts of treated wood. The test involved the leachate collection over 500 h, followed on one side by TEM-EDS analysis, revealing the presence of NPs, and, on the other side, by heating at 80 °C and by acid digestion to dissolve solid NPs and determine Cu<sup>2+</sup> via Atomic Absorption Spectrophotometry (AAS). Ding et al. [44] concluded that the size was the most significant factor affecting leaching, showing the highest Cu<sup>2+</sup> concentration derived from the smallest NPs tested. Moreover, the authors found that the polymer stabilizers used enhanced leaching with respect to the unstabilized CuO NPs, hypothesizing that aggregation of bare CuO NPs prevents the leaching.

The other standard test method for the NPs leaching assessment was EN 84:1997 [45], employed in Pantano et al. [46] by comparing nano-enabled and molecular copper-based formulations for wood preservative. The test was conducted at 4 kPa vacuum-atmospheric pressure cycle in DW, by maintaining the wood blocks (DW:wood 5:1 v/v) for 14 days with nine water changes at 20 °C and 65% of relative humidity. The leachate was analysed by ICP-MS for the total copper content determination and by single particle ICP-MS (spICP-MS) to detect any NPs. The results indicated that the highest Cu leaching rate was about 3 orders of magnitude higher for molecular Cu-based formulations than for nano-based preservatives. Furthermore, NPs leaching was assessed by a combination of analytical methods, i.e. filtration-ICP-MS, TEM-EDX and spICP-MS, allowing to conclude that the nano-enabled micronized Cu formulation released only ionic Cu, with a rate nearly identical to the conventional no-nano formulation.

The same leaching test standard method used by Pantano et al. [46], was applied in Bak and Németh [47] by employing ZnO NPs, Zn-borate NPs, Ag NPs, Cu NPs and Cu-borate NPs dispersions to beech and pine planks. However, the authors investigated the NPs leaching only by indirectly measuring the weight variations before and after NPs suspensions impregnation. By comparing the weight variations, they supposed that zinc-oxide, copper and silver NPs showed much higher resistance to leaching with respect to zinc- and copper-borate dispersions.

### **NPs' leaching estimation**

For the studies listed in Table 1, information on both qualitative and quantitative estimation of NPs' leaching from nano-enabled products by applying a standard leaching test method has been included in Additional file 1: Table S1. When specified, the data provided about NPs' leaching were quite scattered in terms of the metric used for the species detected in the leachate, providing the results as mg/m<sup>2</sup> or as a percentage of a species of interest. The studies in Additional file 1: Table S1 highlighted that the experimental conditions (e.g., immersion cycles, weathering time, duration) and the matrix in which NPs were embedded are key parameters in driving the amount of NPs leaching from nano-enabled products.

### **Non-standardized procedures to estimate NPs leaching from nanocomposites materials**

Among the 34 studies listed in Table 2 in which no specific standard leaching test was used, a wide set of type and size of treated substrates have been considered, assessing NPs leaching in several aqueous-based solutions, ranging from deionized water, to simulated and natural rain, saline solutions, synthetic and natural seawater, as well as phosphate buffer saline and biological media. The only standard test methods followed by the authors mentioned in Table 2 were related to UV weathering before performing any leaching experiment. By analysing the similarities and the differences among these studies, they can be further divided into four different sub-groups. The largest group (22 studies) includes works where different sample immersion test procedures were employed, estimating the leaching of targeted compounds at different time points: most of the authors analysed the leachate after the typical exposure time points of bacterial growth (till 96 h), up to days (maximum 10) or weeks (maximum 4), while only in Künninger et al. [48] and Azimzada et al. [49] the leaching test was carried out under natural weather conditions. Within this first sub-group, besides determining the concentration of the targeted elements, only Olabarrieta et al. [50], Al-Kattan et al. [51], Künninger et al. [48], Neubauer et al. [52], Ruggiero et al. [53], Wohleben et al. [54] and Azimzada et al. [49] directly focused on the NPs detection in the leachate, by using electron microscopy techniques (SEM or TEM-EDX), spectroscopy or spectrometry techniques (UV-Vis, or spICP-MS) or centrifugation techniques (AUC). The other three sub-groups consist of: 5 studies where water spray or/and outdoor runoff methods were used, including Kaegi et al. [8], Shandyla et al. [55] and Jimenez-Relinque et al. [56] that directly assessed the amount of NPs after leaching experiments by electron microscopy techniques; 3 studies investigating leaching from milled paint/aged particles in contact with a liquid,

providing an estimation of the NPs in the leachate only in the works by Al-Kattan et al. [5, 57] again by electron microscopy techniques; other 5 studies focused on the leachate from nanocomposite materials when in contact with a water-based liquid by flushing, dripping or spreading it, investigating the presence of NPs after leaching test only in Agnihotri et al. [58], Sassoni et al. [59] and Nam et al. [60] by employing either electron microscopy or spectroscopy (surface enhanced Raman spectroscopy, SERS) techniques.

#### **Standard test methods for evaluating nanocomposite performances potentially useful for NPs leaching estimations**

The leaching of NPs from coatings and materials can be heavily influenced by their mechanical performances (e.g., permeability, wettability, durability, thermal stability, and resistance to abrasion and corrosion), thus standardized test methods investigating them can give very useful information to indirectly estimate NPs leaching under different conditions. Considering for example a nano-based material with high abrasion or corrosion resistance that is also chemically and biologically inert, good leaching resistance could also be assumed. Therefore, besides the information reported in Tables 1 and 2, 10 additional studies investigating other performances of nanocomposite materials are listed in Table 3. Among all the standard methods included within these works, the most suitable ones for obtaining indirect information on a potential NPs leaching were: (a) ASTM B117-19 [61] and ASTM G154-16 [62] for artificial weathering; (b) ASTM standards D6037 [63], D4060 [64], D968 [65] and the ISO 2409:2007 [66] for resistance to abrasion; (c) ASTM D638 [67] and ISO 14125:1998 [68] for tensile and flexural properties. Moreover, the resistance of coated materials to water by partial or full immersion test described in ISO 2812-2:2007 [30], followed by Zuin et al. [9], Zhang et al. [26] and Lopez-Ortega et al. [32] (as reported in Table 1), has also been used by Luangtriratanana et al. [69] (Table 3), but only for determining the weight loss of coated samples instead of analysing the potential presence of NPs in the leachate. Most of the studies included in Table 3 tested these performances on SiO<sub>2</sub> NPs-based materials.

#### **General remarks and conclusions**

In the field of cultural heritage conservation, nano-enabled products that are thermally stable, biologically and chemically non- or little-reactive, are effective to prevent and/or mitigate the effect of weathering (e.g., rainfall, relative humidity, temperature, wind, sunlight, micro-organisms and air pollution) [70]. However, safety and sustainability assessment of nano-enabled materials and

products have not kept pace with their rapid commercialization [71], calling for further efforts in assessing the potential release of NPs by leaching to support the comprehensive investigation of potential risks along their life cycle.

The new technical data requirements for NMs, as clarified in the revised Annexes of REACH regulation in force since 1st of January 2020 (and corresponding guidance manuals), include a comprehensive set of information on physico-chemical properties of NMs (e.g., particle size distribution, shape, crystallinity, surface area, solubility/dissolution rate), as well as knowledge on environmental fate and toxicity. In particular, 20 additional nano-specific information requirements must be satisfied in order to register substances as nanoforms in REACH [72]. If for some information requirements standard methods are available or under development (see [72] for a critical appraisal), current technical guidance entail no assistance on how to measure and report transformations that nanoforms and related nano-enabled products can experience when considering all stages of the life cycle and with regard to their environmental behaviour and fate [73]. Therefore, especially in the case when a Chemical Safety Assessment would be required, methods to identify and investigate relevant exposure scenarios (including the justification of “no exposure” or “low exposure” evaluations) are needed. In this context, this review covers experimental methods that can effectively support the overall exposure assessment by identifying and, where possible, quantifying the releases from nano-enabled products especially during the use and end-of-life stages. Moreover, the identification of a variety of approaches and some difficulties in comparing the results revealed the need to move towards agreed and standardized methodologies to provide risk assessors with quantitative, comparable results, easy to interpret and to be integrated with hazard data.

Summarizing all the information gathered throughout the studies reviewed, to date, the standard leaching test methods used to assess the NPs leaching from nano-enabled products are ISO 2812-2:2007 [30] (nowadays replaced by ISO 2812:2018 [74]) and ISO 12457-3:2004 [31], applied to nano-based paints and paints debris, respectively. As far as nano-based wood preservatives, AWPA E11-97 [43] and EN 84-1997 [45] have been employed.

In addition to these standards, two further standard leaching test methods could contribute to NPs leaching investigation. The first one is EN 16105:2011 [75], a standard method for the determination of the leaching of substances from coatings, validated by Schoknecht et al. [76], by carrying out an interlaboratory comparison with eight EU participants. Panels of



extruded polystyrene were coated with different coatings and exposed in intermittent contact with water over 1 h, to simulate the alternation of rain events and dry seasons. Analysis of leached substances were conducted by applying high-performance liquid chromatography (HPLC) combined with UV detection, liquid chromatography-mass spectrometry (LC/MS) and LC/MS/MS. Results revealed that the procedure described by this standard leaching test method was suitable to investigate the potential released substances with good reproducibility.

Furthermore, the Technical Committee CEN/TC 351 “Construction products: assessment of release of dangerous substances,” developed some technical specifications concerning the release of hazardous materials under Construction Products Regulation. Among these specifications, as mentioned in Bandow et al. [77], CEN/TS 16637-1:2018 [78] allows identifying suitable leaching tests for the release of dangerous substances from construction products into soil, surface water and groundwater. Bandow et al. [77] stated that, since lab-scale experiments usually employed artificial conditions (e.g., deionized water, which has no buffering capacity and it is prone to changes of the pH value if products with high alkaline or acidic potential are investigated), standardized leaching test conditions have not to be considered as a simulation of reality but rather as inputs for data modeling. Moreover, they underlined that, due to the matrix complexity, a complete release assessment of hazardous substances from construction products should combine chemical analytical methods with standardized ecotoxicity tests, referring to the CEN/TR 17105:2017 guidance [79].

Since all these standards involve a partial or full immersion of test samples to obtain a leachate to be analysed, their applicability to cultural heritage could be limited to specific mock-up samples, such as treated building façades or artworks that need artificial specimens opportunely prepared which reproduce the original ones. Moreover, some other standard test methods evaluating, e.g., abrasion and corrosion resistance or tensile and flexural properties on mock-up samples could also be potentially useful to indirectly provide insights on NPs leaching, becoming potential alternatives to standard leaching test methods. In general, all these standard test methods show applicability limitations related to the size of the treated sample (especially for immovable artworks) and to their artistic value.

In addition to standard methods, non-standard procedures reported in Table 2 could be a valuable support to NPs’ leaching evaluation. In particular, besides non-standardized immersion methods used, which represent a worst-case scenario, other weathering conditions such

as water spray or outdoor runoff have been tested, which constitute an alternative exposure scenario.

Moreover, according to some studies performed by the National Institute of Standards and Technology (NIST), as reported in Jacobs et al. [80], NPs’ leaching as a function of UV dose exposure, combined with simulated washings of rainwater by applying a water spray protocol described in Sung et al. [81], could be another alternative for estimating NPs’ leaching at more realistic environmental conditions. This approach could provide the advantage of simulating further exposure scenarios by testing several UV irradiations ( $W/m^2$ ) and wavelengths as well as relative humidity ranges, representative of different real environmental conditions. However, one of the main limitations of this approach could be related to the complexity of the experimental design, also considering the costs of the equipment needed (e.g., climate chamber, UV lamps).

To advance the environmental exposure assessment of NPs from nano-enabled products, not necessarily limited to the field of cultural heritage, taking into account the complexity and the variety of the nano-based products available on the market, besides all the conventional parameters of a standard leaching test (e.g., the size of the sample under testing, the chemistry of the leaching solution or the duration of the test), the main information of a study designed for an NPs’ leaching evaluation should include: (i) the initial amount of NPs present in the product; (ii) the amount of nano-based product applied; (iii) the area of the surface treated; (iv) the time considered for the leaching test; (v) the cumulative loss of targeted species in the leachate (as for example  $mg/m^2$  or  $\%/m^2$ ), (vi) the form of the released substances in the leachate (i.e., ionic form, free NPs or matrix fragments containing NPs). A good starting point could be the review by Koivisto et al. [29], in which the NPs release was expressed by  $mg/m^2$  and, similar also to Froggett et al. [28], there was a clear distinction of release among ionic forms, matrix containing NPs, NPs alone and matrix alone. Lastly, as suggested by Bandow et al. [77], a standardized leaching test, by describing the analytical methods used to detect any NPs, alone or embedded in their matrix, should also give indications on performing standardized ecotoxicological tests to allow a comparison of the results.

Moreover, if we consider analytical issues, a tiered multi-method approach could be proposed to estimate the NPs’ leaching, suitable to balance the degree of detail in leachate characterization and operational costs. For example, a preliminary assessment to qualitatively verify the presence of NPs in the leachate could be performed by employing simple-to-use and fast techniques, such as ICP-OES or UV-Vis, following the procedure reported

by Lopez-Ortega et al. [32] and Regiel et al. [82]. A more comprehensive NPs' leaching evaluation could instead be achieved by the combination of spICP-MS with TEM/SEM + EDX techniques (such as described, e.g., by Pantano et al. [46] or Neubauer et al. [52]), to clearly distinguish the form potentially present in the leachate, i.e. ions, free NPs and the matrix containing NPs.

From the information collected through this literature review we might argue that, within the boundaries of the tested experimental conditions, the presence of free NPs detected in the leachate is very limited and does not provide evidence for expected significant concentrations in environmental media. Nevertheless, case-by-case conclusions based on a deep knowledge of tested materials/products and specific environmental conditions and proved through robust experimental methods are needed to effectively inform risk assessment and management.

The information extracted and elaborated from literature together with the recommendations provided in this work, concerning the methodological approach for leaching testing as well as possible analytical solutions, could provide useful inputs to guide the assessment of human health and ecological exposure due to releases from nano-enabled products. This review focused on nanotechnology applications for cultural heritage conservation but possible benefits to wider fields are foreseen (including the potential release of nano and microplastics from commercial thermoplastic products), with the appropriate adaptations based on the types and applications of nano-enabled products, potential environmental conditions and aging and weathering processes of interest, different exposure targets. Once release mechanisms and exposure scenarios are better characterized, this information could contribute to the development of innovative, safe and sustainable nano-enabled products, within a Safe by Design perspective to ensure an effective risk management of nanocomposite materials.

#### Abbreviations

A4F: Asymmetric flow field flow fractionation; AAS: Atomic absorption spectroscopy; ASTM: American Society for Testing and Materials; AUC: Analytical ultracentrifugation; AWWA: American Wood Protection Association; CLP: Classification, labelling and packaging; DLS: Dynamic light scattering; DW: Deionized water; EDX: Energy dispersive X-ray; EIS: Electrochemical impedance spectroscopy; EPA: Environmental Protection Agency; FEG-SEM: Field emission scanning electron microscopy; FEG-TEM: Field emission gun-transmission electron microscopy; FTIR: Fourier-transform infrared spectroscopy; HTCC: [(2-Hydroxy-3-trimethylammonium) propyl] chitosan chloride; ICP-AES: Inductively coupled plasma atomic emission spectroscopy; ICP-MS: Inductively coupled plasma-mass spectrometry; ICP-OES: Inductively coupled plasma-optical emission spectrometry; ISO: International Organization for Standardization; ITS: Integrated testing strategy; LLDPE: Linear low-density polyethylene; L/S: Liquid to solid; MWCNT: Multi-walled carbon nanotubes; NP: Engineered nanoparticles; OECD: Organisation for Economic Co-operation and Development; PVP: Poly(vinylpyrrolidone); REACH: Registration, evaluation, authorization of chemicals; RPM: Rotation per minute; spICP-MS: Single particle inductively coupled plasma-mass spectrometry; SERs: Surface

enhanced Raman spectroscopy; TGA: Thermogravimetric analysis; ToF-SIMS: Time of flight-secondary ion mass spectrometry; TXRF: Total reflection X-ray fluorescence; UV-Vis: Ultra violet-visible spectroscopy; XRD: X-ray diffraction; XRF: X-ray fluorescence; XPS: X-ray photoelectron spectroscopy; XAFS: X-ray absorbance fine structure.

## Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s12302-021-00493-z>.

**Additional file 1: Table S1.** Information about estimated amount of species detected after leaching experiments by employing standard leaching test methods used in studies included in Table 1.

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#### Authors' contributions

All authors helped in conceptualization of this review. AB, EB, LC and VC worked on data curation and data analysis. ES and AM recruited funding. AB, EB, LC, VG and ES were involved in the application of the methodology. EB, ES, EG and AM supervised the work and they contributed to the validation. AB, EB, LC and VC wrote the original draft. All authors helped in reviewing and editing the final draft. All authors read and approved the final manuscript.

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#### Availability of data and materials

Data sharing is not applicable to this article as no datasets were generated or analysed during the current study.

#### Declarations

##### Ethics approval and consent to participate

Not applicable.

##### Consent for publication

Not applicable.

##### Competing interests

The authors declare that they have no competing interests.

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