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Dense carbon dioxide technologies applied to the conservation of cultural heritage: A review

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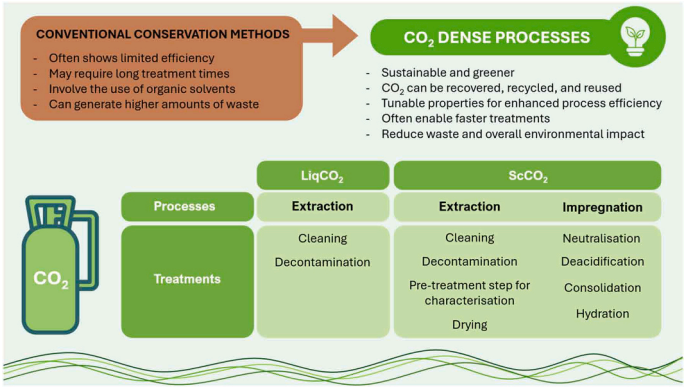
HIGHLIGHTS

- Comprehensive review of liqCO_2 and scCO_2 application in heritage conservation.
- CO_2's potential for safer and greener conservation processes.
- This study reviews trials, noting CO_2 method successes, limits, and research needs.

GRAPHICAL ABSTRACT



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ABSTRACT

Cultural heritage conservation is a complex and challenging field, involving a wide variety of materials with distinct properties, degradation behaviours and specific requirements, often demanding non-standardised methodologies. Conventional treatments frequently rely on hazardous products, raising concerns about user safety and environmental impact. In response, green chemistry principles have gained prominence, advocating for safer and more sustainable practices by replacing toxic products with less harmful alternatives, thereby mitigating risks to conservators, the environment, and heritage assets. Carbon dioxide (CO_2), owing to its tuneable and non-toxic properties, has emerged as a green solvent alternative to traditional solvent-based methods in the conservation field. Therefore, this research reviews the application of dense CO_2 technologies (liquid and supercritical) in conservation processes including cleaning, decontamination, degreasing, hydration,

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stabilisation, and consolidation, across a wide array of materials like textiles, wood, leather, metal, glass, paper and plastics. Drawing on experimental trials and case studies, key achievements, challenges, and emerging trends are highlighted, encouraging further research into these promising and sustainable CO_2-based technologies.

1. Introduction

The conservation of cultural heritage involves complex decision-making due to the diversity of materials, each with unique characteristics, needs, and degradation pathways [1,2]. Conservation treatments require case-by-case assessment, which frequently involves non-standardised methodologies [3]. Commonly used products and techniques have been adapted from other fields to meet specific requirements for conservation [1]. Nevertheless, treatments often involve the use of hazardous products, an issue sometimes overlooked by heritage professionals [3–5]. To address this challenge, the conservation field is increasingly aligning with the principles regulating green chemistry, promoting safer and more sustainable practices by minimising the use of reagents and waste while enhancing conservation treatments' efficiency [3,6,7]. Thus, whenever possible, toxic solvents are replaced with less harmful alternatives [1,3,5–7], and the use of multi-functional reagents and materials is increasing, as this approach allows accomplishing more with fewer resources [6].

Carbon dioxide (CO_2), naturally available as a gas, is considered low-priced, non-toxic, non-flammable, chemically inert, and does not further contribute to the greenhouse effect [8,9]. When compressed, it gains liquid-like densities, and depending on the pressure and temperature, can exist as a liquid or a supercritical fluid. As shown in Fig. 1, liquid CO_2 ($liqCO_2$) forms at pressures above the vapor pressure (0.52 MPa) between −56.6 °C and 31.1 °C. When heated in a closed vessel, it transitions to the supercritical region, which occurs above the critical point (7.38 MPa, 31.1 °C) [10,11]. In its liquid or supercritical form, CO_2 can act as an environmentally benign solvent, contributing to green chemistry practices [12]. Dense CO_2 is effective for precision cleaning, removing soil, grease and contaminants due to its low surface tension, liquid-like high density, excellent wettability and gas-like properties, such as lower viscosity and higher diffusivity [10,12]. Nonpolar organic compounds are removed through dissolution and detachment, whereas the removal of highly polar contaminants is limited by CO_2's low dielectric constant, a drawback that can be mitigated by using suitable co-solvents. Liq- and $scCO_2$ processes tend to be less effective for removing inorganic materials, large particles, and hydrophilic compounds. However, the drag force generated by the CO_2 flow must be sufficient to overcome adhesion forces. Consequently, cleaning efficacy primarily relies on the system's chemistry and the specific treatment conditions [10,11]. High crosslinked polymers are typically very robust and largely inert to dense CO_2; however, it may induce plasticisation, brittleness, swelling and distortion in low-crystallinity amorphous polymers [10,11,13].

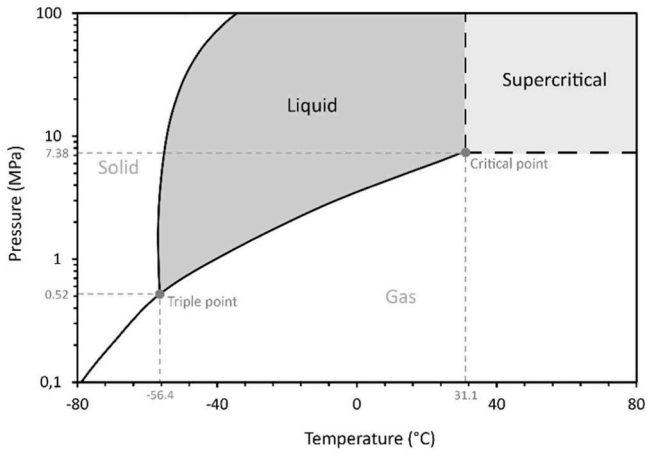

Fig. 1. Pressure-temperature phase diagram of carbon dioxide with triple and critical points identified. Adapted from [8].

Fundamental components of the apparatus include CO_2 cylinders, a compression pump, and a high-pressure stainless-steel chamber, varying in size and complexity [10,13–15]. Co-solvents can be added to the reactor before or during treatment [16,17]. Depending on the substrate and contaminants, treatment durations range from 30 min to 24 h [10,11,13], with treated items leaving the chamber dry [10,11,13]. Overall, it is a complex system that requires high technical expertise [10,11].

The application of $liqCO_2$ and $scCO_2$ in heritage conservation has gained increasing attention due to their proven effectiveness and greener advantages. These technologies have been successfully applied in processes including cleaning, decontamination, degreasing, hydration, drying, stabilisation and consolidation across a wide range of materials, including textiles, wood, leather, metal, glass, and paper, demonstrating their potential as sustainable alternatives to conventional conservation methods [13,17–21]. Despite promising outcomes, CO_2-based methods remain underexplored in this field, which may be attributed to the high cost and scale limitations of high-pressure reactors or to a general lack of awareness of the potential of these technologies. Currently, no recent review comprehensively covers CO_2 technologies in conservation. This study focuses specifically on dense CO_2 processes, aiming to fill this gap by reviewing published experiments and case studies, highlighting major achievements, challenges, and emerging trends to support their broader application in conservation practices. Other CO_2-based technologies, including gaseous and solid CO_2 (in both snow and dry ice forms), have been successfully applied to cultural heritage, with several studies reported in the literature. Although closely related, they are not addressed here, as they will be the subject of another review article.

2. Liquid CO_2

In conservation, $liqCO_2$ is predominantly used for extraction processes, mainly for cleaning, chemical decontamination and microbiological decontamination purposes. Accordingly, the following sections are structured around these three extraction treatments. *Cleaning* refers to the removal of soil, dust, residues, conservation materials, and alteration products or foreign matter from surfaces. *Chemical decontamination* involves the removal of substances such as pesticides and heavy metals. *Microbiological decontamination* targets contamination caused by living organisms, including bacteria, viruses, fungi, and algae. It should be noted that decontamination processes (both chemical and microbiological) may also result in a certain degree of surface cleaning, as the applied conditions are often similar.

Table 1 summarises the reviewed studies on the application of $liqCO_2$ technology in conservation treatments, organised by treatment type, substrate or collection treated, target material or contaminant, specific objects treated, and corresponding reference.

2.1. Cleaning

The dry method of $liqCO_2$ cleaning, which does not require direct handling of the samples during treatment, has been used for decades to clean overlubricated collagen-based materials [13,18,22]. Historically, leather objects were treated with oil and fatting agents, often leading to discolouration, dryness and brittleness [18]. Cleaning trials for degreasing were conducted under sequential experimental parameters:

Table 1
Summary of the application of liquid carbon dioxide ($liqCO_2$) technology to heritage assets for different treatment procedures (cleaning, and chemical and microbiological decontamination), according to material/collection treated, target material or contaminant, specific objects treated, and corresponding reference.

Treatment procedure	Material/collection	Target	Treated Items	Reference
Cleaning	Glass	Soil	Buttons and beads in different colours (Staatliche Museen zu Berlin - Museum Europäischer Kulturen and Firma Twist)	[22]
	Leather	Oil/fatty agents	19th-century bookbinding, 18th-century chair seat, and 18th- and 19th-centuries gilt leather	[18]
		White efflorescence	Ancient Egyptian leather specimen (Staatliche Museen zu Berlin (SMB) - Museum für Byzantinische Kunst)	[22]
			Wavy and hardened leather patches (Stiftung Preußische Schlösser and Gärten Berlin-Brandenburg)	
		Wax/grease	18th-century gilded leather hanging	[13,15,23]
			Seal gut parka	[13,23]
			Imitation of gold leather wallpaper (Landesamt für Denkmalpflege Sachsen)	[22]
	Metal	Soil	Buttons and zipper (Staatliche Museen zu Berlin - Museum Europäischer Kulturen and Firma Twist)	[22]
	Plastic	Soil and efflorescence	Coloured buttons, sequins and Bakelite box (Staatliche Museen zu Berlin - Museum Europäischer Kulturen and Firma Twist)	
		-	Unsoiled poly(methyl methacrylate) (PMMA) of historical value	[14]
	Textiles	Dust/soil/residues	Hangings (in warp knitting technique) and embroidery fragment (Ethnografisches Museum Belgrad)	[22]
			Silk fabrics of a maniple and fringes from a processional umbrella (Stiftung Stift Neuzelle)	
			Wool-coloured uniform fragments (Deutsches Historisches Museum, Berlin)	
			18th-century religious scapulary from Virgin and Child from Palácio das Necessidades (Portugal)	[16]
			Undyed and dyed silk samples	[24]
			Silk mock-ups	[25]
	Wood	Residues from previous conservation treatments/soil	Wooden epitaph fragment (Cathedral in Zwickau, Germany)	[13,23]
			Coated wood panel sample (Landesamt für Denkmalpflege Sachsen)	[22]
Chemical Decontamination	Protein-containing objects	Pesticides and heavy metals	Boot made of polar hare fur and hair from a bison robe (Staatliche Museen zu Berlin – Ethnologisches Museum)	[22]
			18th-century bundle of feathers (Fasanenschlösschen Moritzburg)	
	Textiles		Chilean Patagonia woollen blanket	[13,23]
			Silk Neuzelle pilgrim's coat (Neuzelle Monastery, Germany),	[26]
			Fragments of an ancient Egyptian tunic (14th century BC), mummy bandage (4th−7th century AD) and antique woollen cloth (Staatliche Museen zu Berlin - Museum für Byzantinische Kunst)	[22]
			Wool mousseline mock-ups	[27]
			Dyed woollen sock and silk shoe (Swiss National Museum)	[28]
	Wood		Pinewood panel (Staatliche Kunstsammlungen, Dresden, Germany),	[13,23]
			Historical xylotheque (Museum Waldenburg, Germany)	[29]
			European Cherry Tree mock-up samples	[27]
			Pharmacy and Baroque drawer (Swiss National Museum)	[28]
Microbiological Decontamination	Textiles	Living organisms	Two antependia (1885 and 1888)	[30]

25 °C and 6.4 MPa with and without rotation of the sample holder, and 26 °C and 6.6 MPa with drum rotation, for approximately 30 min. The tested samples included a 19th-century bookbinding, an 18th-century chair seat, and 18th- and 19th-century gilt leather. Results showed successful removal of fats, particularly neatsfoot oil, although the extent of extraction varied with the type of leather. Moreover, drum rotation and prolonged treatments enhanced extraction. According to the authors, the extracted fat was considered minimal, with no surface damage observed. Thus, additional trials involving modifications to the experimental setup (temperature, pressure or co-solvents use) are recommended [18]. An ancient Egyptian leather specimen retained its appearance and stiffness after a 30-minute treatment (at 20–25 °C and pressure between 5.7 and 6.4 bar), while showing reduced white efflorescence and weight loss, suggesting an effective extraction. Similarly treated wavy and hardened leather patches showed reduced white efflorescence. Other tested leather fragments also maintained their pre-treatment flexibility and softness [22].

Further leather objects were treated in $liqCO_2$ at 15–20 °C and at 5–6 MPa for half an hour to 24 h [13,15,23]. For the 18th-century gilded leather hanging containing synthetic wax, Montan wax, Vaseline (petroleum jelly), and possibly beeswax, the results indicated only partial effectiveness in removing waxes [13,15,23]. $LiqCO_2$ cleaned the leather's backside and reduced surface tackiness. Microscopically, small white spots observed on the surface suggested partial beeswax solubilisation. The process proved safe for proteinaceous materials (stable shrinkage temperature and pH) and effective in removing fat. However, some flaking of the paint layer on the surface of the hanging was observed, possibly a consequence of the treatment or handling [13,23]. Under the same $liqCO_2$ treatment conditions, an imitation of a gold leather wallpaper displayed small bubbles in the gold lacquer post-treatment [22]. Also, a wrinkled translucent seal gut parka, previously greasy and sticky with waxy deposits, became pliable and no longer sticky after treatment, while its appearance was preserved. Weight and thickness reduction confirmed the removal of unwanted materials [13,23].

$LiqCO_2$'s ability to remove past conservation materials and clean ethnological wood objects has also been studied. A wooden epitaph piece treated with linseed oil showed signs of oil degradation and migration of its oxidation products. After 24 h in $liqCO_2$ (at 15–20 °C and at 5–5.5 MPa), the cleaning was deemed unsuccessful [13,23]. Following the same conditions, experiments were conducted in coated wood panels with layers of paint, varnish and other products. The results showed that most panels retained their pre-treatment appearance. Varnished panels and those having written paper glued to the backside were kept unchanged; one panel experienced slight surface lifting at the edge. Regarding the cleaning effect, a reduction in weight was observed, confirming its effectiveness [22]. Unger [31] reported that $liqCO_2$ and $scCO_2$ extraction of mixtures of vegetable oils and resins yielded disappointing results, but the addition of co-solvents enhanced performance [31]. However, optimal treatment parameters remain undefined.

Regarding textile cleaning, $liqCO_2$ (at 20–25 °C and 5.7–6.4 MPa, for 30 min) safely removed dust from warp knitted hangings and an embroidery fragment, with no visible changes [22]. Likewise, damaged silk fabrics from a maniple recovered colour and appearance, and the corroded metal threads of the braids remained unchanged. Although the cleaning of fringes from a processional umbrella was considered safe, it was only partially successful. Experiments on wool-coloured uniform fragments (containing corroded buttons and metallic threads) showed successful cleaning without affecting colour, texture, tactile properties or dimensions, nor corroding the metallic components [22]. $LiqCO_2$ cleaning was also applied to heavily soiled fragments of an 18th-century religious silk garment and mock-up samples dyed with metal ions identified in the original textile [16]. Treatment was carried out for 2 h at 25 °C and 20 MPa using a mixture of 97.83 % $liqCO_2$, 1.66 % isopropanol, and 0.51 % H_2O. Additional sequential trials were performed with $scCO_2$ (see section 2.1.1), but results for each treatment step were reported separately, allowing conclusions to be drawn for $liqCO_2$ extractions conducted with 98.35 % CO_2 and 1.66 % isopropanol. Under these latter conditions, residue reduction was limited to 10 %. The addition of water improved dirt removal above 50 %, though overall efficiency remained low. This procedure also caused greater weight variation, suggesting increased material loss. Despite a decrease in specimens' luminosity, colour hue remained unchanged [16]. In addition to soiling removal, $liqCO_2$ was also tested (at 25 °C and 20 MPa, with small amounts of methanol) for removing a hydrophobic and oleophobic conservation coating for silk artefacts. This coating comprises a water-based emulsion of silane, siloxane and organic polymer with the addition of silica (SiO_2) nanoparticles. Its reversibility was also assessed using $scCO_2$, see section 2.1.1. $LiqCO_2$ with 5 % v/v methanol resulted in 73.2 % removal, but higher methanol concentrations reduced the cleaning effect, suggesting that CO_2 played a role in the coating extraction. Post-treatment with compressed air improved removal to 100 % (which alone would not have the same effect), confirming the method's complete reversibility [25].

Further studies involving sequential experiments using $scCO_2$ and $liqCO_2$ on a Medallion carpet [25,32] are discussed in section 2.1.1. Additionally, a study was conducted on undyed and dyed silk samples that were artificially stained with olive oil, rabbit skin glue, and beetroot paste. This experiment was performed at 30 °C and 15 MPa, for 60 min. Several other conditions in $scCO_2$ were employed and are further discussed in section 2.1.1. The trials using $liqCO_2$ demonstrated a higher cleaning effectiveness comparable to that achieved with $scCO_2$ [24].

The impact of $liqCO_2$-treatment on glass, metals and plastics was also assessed [14,22]. In a research conducted by Unger *et al.*, experiments were performed on glass buttons and beads, metallic buttons and a zipper, coloured plastic buttons and sequins, and in a Bakelite box [22]. Post-treatment (at 20–25 °C and 5.7–6.4 MPa, for 30 min), all the specimens retained their appearance and dimensions, with no damage observed. In addition, it effectively reduced soiling and efflorescence on the Bakelite box [22]. Conversely, thick poly(methyl methacrylate) (PMMA) samples exposed to 25 °C and 7 and 10 MPa (for 60 and 30 min) experienced severe irreversible damage, including fractures, cracks, reduced surface hardness, and swelling near the edges [14]. Although weight and dimensions recovered over 35 weeks, surface hardness and visual integrity were compromised, confirming $liqCO_2$'s unsuitability for PMMA [14].

In summary, $liqCO_2$-cleaning proved to be highly effective for collagen-based materials, yet caution is required with specimens featuring paint or lacquer, which may be damaged [13,22,23]. The success of this technology for textiles was inconsistent [22], suggesting material-specific responses. For wood and PMMA, this technology was found ineffective and unsafe [13,14,22,23]; as for the latter material, the polymer crystallinity may have some influence on the treatment outcome. Therefore, tailored treatment conditions based on material chemistry and structure are crucial for successful cleaning [10,11]. The conditions applied to each material/collection, along with the corresponding outcomes, are summarised in Table 2.

2.2. Chemical decontamination

The effectiveness and suitability of $liqCO_2$ in extracting pesticides from wooden ethnographic objects were studied. A pinewood panel, damaged by insects and exhibiting white efflorescence (crystals of dichlorodiphenyl trichloroethane, DDT), was analysed, revealing additional commercial pesticides: Lindane (γ-hexachlorocyclohexane) and pentachlorophenol (PCP). After treatment with $liqCO_2$ at 15–20 °C and 5–6 MPa for 30 min to 24 h (exact duration not specified for this item), the wood's colour intensified, DDT efflorescence disappeared, and significant reductions in DDT and Lindane concentrations were observed [13,23]. This indicates that $liqCO_2$ can dissolve surface-level DDT crystals and some portion of pesticides present in the wood matrix. However, PCP content remained unchanged, and residual pesticide

Table 2
Summary of liquid carbon dioxide ($liqCO_2$) cleaning trials conducted on cultural assets, according to the given treatment conditions (reactor type/volume, sample container size, temperature, pressure, exposure/compression/depressurisation times, CO_2 flow, co-solvents), material treated, and the main outcomes for each material, with corresponding references.

Treatment conditions given by the authors (vol., volume; T, temperature; P, pressure; *ct*, compression time; *et*, exposure time; *dt*, depressurisation time; Ø, diameter)	**Material**	**Results**	**Reference**
Amsonic autoclave (Ø45 cm×59 cm (depth)) with retractable and rotatable wash basket (42 ×23 x 18 cm) and integrated ultrasonic transducer; T = 20–25 °C, P = 5.7–6.4 MPa, *et* = 30 min	Glass	No damage observed	[22]
	Leather	Reduced white efflorescence; small bubbles formed in gold lacquer-covered leather	
	Metal	No damage or corrosion detected	
	Plastic	Bakelite: Effectively reduced soiling	
	Textile	Hangings and embroidery: Safely and effectively removed dust	
		Silk: Recovered colour and appearance; corroded metal threads unchanged; only partially cleaned fringes	
		Wool: Successfully cleaned; colour, texture, dimensions, and metallic components unaffected	
	Wood	Weight reduction confirmed cleaning effect, slight surface lifting observed in one panel edge	
Autoclave vol. = 50 L, 6 kg $liqCO_2$ per test; T = 25 °C, P = 6.4 MPa, *et* = 30 and 36 min, with and without rotation of the sample holder, respectively; and T = 26 °C, P = 6.6 MPa, *et* = 30 min, drum rotation ≈ 75 rpm in both directions); post cleaning with a CO_2 cycle	Leather	Successfully removed fats, with extraction efficiency varying by leather type	[18]
UniClean apparatus; T = 15–20 °C, P = 5–6 MPa; *et* = 30 min to 24 h		Calf or kid leather: Partially removed waxes and reduced tackiness; flaking occurred on painted leather surfaces	[13,15,23]
		Seal gut: Leather became pliable and non-sticky; weight and thickness reduction confirmed cleaning effect	[13,23]
Chamber vol. = 33 mL; T = 25 °C, P = 7 and 10 MPa, CO_2 flow = 10 mL/min, *ct* = ≈ 15 min, *et* = 60 and 30 min, and *dt* = 20 min	Plastic	PMMA: Severely damaged	[14]
Laboratory-scaled cell vol. = 4.5 mL; T = 25 °C, P = 20 MPa, compression CO_2 flow = 0.98 g/min; *et* = 2 h (with and without co-solvent), CO_2 (or a CO_2 + co-solvent) flow = 1.5 mL/min; co-solvents = 98.35 % $liqCO_2$ + 1.66 % isopropanol, and 97.83 % $liqCO_2$ + 1.66 % isopropanol + 0.51 % H_2O; post cleaning with CO_2 to remove residues	Textile	Silk: Residue reduction limited to 10 % when isopropanol is used; water and isopropanol improved removal to > 50 % but overall efficiency is low; higher weight loss observed, suggesting material loss	[16]
T = 30 °C, P = 15 MPa, *et* = 60 min, *dt* = 30 min		Silk: Effective in cleaning olive oil, rabbit skin glue, and beetroot paste stains	[24]
Reactor vol. = 40 mL; T = 25 °C, P = 20 MPa, co-solvent = none or methanol (5 and 10 % v/v); post-treatment, some samples were air blown (2 min) to remove residues		Coated silk: Treatment with 5 % MeOH achieved 73 % removal; higher MeOH% reduced efficiency; post-treatment compressed air aided removal to 100 %, confirming reversibility	[25]
UniClean apparatus; T = 15–20 °C, P = 5–5.5 MPa, *et* = 24 h	Wood	Unsuccessful removal of polymerised linseed oil and its oxidation products	[13,23]

concentrations were still considered hazardous, suggesting that the procedure should either be repeated or that a more successful method involving $scCO_2$ should be used [13,23]. A historical xylotheque containing hazardous pesticides underwent $liqCO_2$ decontamination at 15–20 °C and 5–6 MPa, for 2 h. Most specimens maintained their shape, colour and properties; however, resin-rich woods exhibited resin exudates at the end grain and around knot zones. Nevertheless, DDT levels decreased on both surfaces and cross-sections, though extraction was incomplete for the latter - treatment optimisation could enhance removal [29].

Following the previous experiments, Lombardo *et al.* [27] investigated optimal lab-based conditions for removing biocides from museum objects using $liqCO_2$. European Cherry Tree veneer samples, artificially contaminated with an acetone solution of common chlorinated biocides (including Lindane, DDT, PCP, and Permethrin), were treated at 6 MPa and 20 °C. To find the optimal conditions, the treatment parameters varied in exposure time (10, 30, 60 and 120 min), number of cycles (1, 2, 3 and 5), basket (sample holder) rotation (50 and 500 U/min) and co-solvent usage (none, 5 % (v/v) ethanol, 5 % (v/v) methyl tert-butyl ether, 5 % (v/v) water and 5 % (v/v) acetone) [27]. Results indicated that biocide reductions range from 42 % to 77 % after a 30-minute single cycle. Longer treatments and additional cycles improved decontamination. Despite basket rotation having a limited impact (regardless of the velocity), the addition of co-solvents like ethanol, acetone, and methyl tert-butyl ether significantly enhanced extraction, particularly for PCP and Lindane; water was almost ineffective. Due to potential risks to museum items, co-solvents were excluded from standard procedures. Therefore, a recommendation of three 30-minute cycles was made, acknowledging possible residual biocides in deeper wood layers [27]. These conditions were tested in real collection objects using the same equipment [28]. A pharmacy drawer (consisting of softwood, paper, ink, paint and a metal handle) and a Baroque drawer (made of oak, spruce and walnut with a gilded brass handle) underwent $liqCO_2$ decontamination. Biocide-free model samples of different woods (coated or uncoated) and paper were also treated to assess potential physical and chemical changes. Results were considered acceptable, besides minor changes in smell and texture (likely due to beeswax fatty acids solubilisation). The pharmacy drawer showed a significant extraction of PCP (94 %), the only biocide identified, and a slight reduction in chlorine content. No observable alterations occurred in wood, shellac coating, label, or metallic handle, though minor paint loss was noted on the front, and the lining paper became uneven. The Baroque drawer exhibited significant reductions in chlorine counts (91 %), Lindane (95 %), and DDT (85 %), with complete removal of biocide crystals. Although the appearance of the drawer, veneer, and metallic handle remained unchanged, blisters appeared on the front, likely caused by pressure changes. Overall, the treatment effectively reduced chlorine content, though coated and polychrome wood samples may experience alterations [28].

The decontamination of textiles was tested at 15–20 °C and 5–6 MPa for 30 min to 24 h (exact duration not specified for this item) on a Chilean Patagonia woollen blanket contaminated with organo-chlorine pesticides and heavy metals (mercury and arsenic) [13,23]. The white wool blanket with dyed threads exhibited moth holes, soiling, and greasy brittle fibres. Although DDT concentration significantly decreased after $liqCO_2$, Lindane, mercury and arsenic levels were not reduced to a safe extent. Nevertheless, this process also resulted in soil removal, brightening colours and improving fibre softness and elasticity [13]. A silk Neuzelle pilgrim's coat, embroidered with multi-coloured silk yarns and different metal threads, presented similar contamination [26]. Decontamination trials (at 12–15 °C and 4–5 MPa, for four cycles, each 54 min) were first performed on sacrificial samples from a silk *crêpeline* lining to determine the optimal treatment conditions. Three extraction methods were tested: $liqCO_2$ with detergent (not specified), and dry extraction (micro vacuuming) followed by $liqCO_2$ (with and without detergent). The decontamination was carried out in a closed system (about two-thirds liquid, one-third gaseous). The most effective method for DDT and Lindane removal was dry extraction followed by $liqCO_2$ without detergent, although differences between methods were minor. As no damage was observed, the extraction of contaminants was conducted on the historical object. Pre-treatment, the mantle was covered with silk fabric, folded on itself, and placed in a perforated polyethylene box secured to the drum with cable ties. After about an hour in $liqCO_2$, no dimensional changes or displacement of fabric layers occurred; the mantle appeared refreshed, less dusty, and slightly shinier, with no dye bleeding. Moreover, metal threads remained unchanged, and original marks and stains were preserved. The only change observed was the appearance of wax stains, possibly due to the detachment of wax flakes and the dissolution of dirt particles embedded in the wax. Further research is needed to optimise conditions for reducing pesticides and heavy metals (the latter are assumed to be mechanically mobilised rather than dissolved), as their heterogeneous distribution hinders conclusive results [26].

$LiqCO_2$ decontamination (at 20–25 °C and 5.7–6.4 MPa, for 30 min) was also applied to fragments of an ancient Egyptian tunic (14th-century BC), a mummy bandage (4th-7th century AD) and an antique woollen cloth. No macroscopical changes were observed post-treatment. A weight decrease was noted, suggesting soiling and biocide removal or potential loss of material (brittle fibres and consolidants), though not all specimens underwent thorough analysis to confirm extracted materials [22].

Additional studies on wool items involved artificially contaminated wool mousseline mock-ups treated in a laboratory-scale apparatus (at 6 MPa and 20 °C, for 10 and 30 min). Analysis revealed reproducible results, with nearly 100 % extraction of tested biocides, except for slightly lower PCP removal, for both 30- and 10-minute exposures. The exceptional biocide removal was attributed to the thin and permeable nature of wool, which enables both chemical and mechanical contaminant removal. Even though 10-minute treatments showed slightly higher effectiveness, single 30-minute cycles were deemed ideal for real objects, particularly for thicker fabrics [27]. Experiments on contaminated collection objects, a dyed woollen sock and a silk shoe (also containing bast fibres and goat leather), were conducted using the same apparatus and conditions, but only with a 30-minute extraction. $LiqCO_2$ treatment produced similar results for both objects: chlorine levels remained unchanged, while the pre-treatment presence of Chlorpyrifos became undetectable post-treatment, suggesting its removal. No macroscopic physical or chemical alterations were observed [28].

An ethnographic boot made of polar hare fur, contaminated with biocides and heavy metals, and heavily soiled and deformed, underwent $liqCO_2$ at 20–25 °C and 5.7–6.4 MPa, for 30 min [22]. Biocide analysis confirmed reductions in DDT and Lindane; no conclusions could be drawn regarding PCP. As for heavy metals, mercury levels significantly decreased; as for arsenic, conclusive statements would require initial higher contamination levels. Further tests on hair from a bison robe indicated similar success in reducing biocides and heavy metals [22]. The decontamination treatment made the fur and leather softer and more elastic, with no dimensional deformation; the pre-existing folds and creases remained unchanged. The fur's whitish colour lightened, and the restoration patch and interior leather tear were preserved. Additionally, coloured 18th-century feathers in precarious condition, exhibiting broken knots, light damage and heavy soiling, were decontaminated using $liqCO_2$ under the same conditions. Post-treatment biocide analysis indicated reductions in DDT, arsenic and mercury content, although not to a safe extent. Moreover, as previously noted, the treatment also induced a cleaning effect, while the visual appearance of the feathers remained unchanged, weight variation confirmed the dirt removal [22].

The overall results indicate that $liqCO_2$ effectively reduces pesticides, especially DDT, and moderately extracts Lindane due to its solvency. Heavy metals removal was inconsistent; their reduction mainly resulted from physico-mechanical detachment rather than solubilisation. While

results were promising for wooden objects, outcomes on textiles, particularly for heavy metals, were variable [13,15,22,26]. Based on the experimental results, Unger *et al.* [22] provided valuable insights into the factors influencing the removal efficiency of biocides and heavy metals, particularly contaminant concentration in the object, the method used to apply the organic and inorganic biocides, and whether these compounds are bound to or deposited on the surface of the object. Nonetheless, decontamination can be enhanced by incorporating additional steps, such as complementary cleaning methods, and/or compounds (e.g. surfactants and co-solvents) [13,15,22,26,30]. Table 3 summarises the treatment conditions applied to different materials, along with the main outcomes reported in the reviewed studies.

2.3. Microbiological decontamination

LiqCO_2 was tested on two biologically contaminated antependia (from 1885 and 1888) made of wool cloth decorated with textile appliques and embroidery [30]. Both severely deteriorated due to inadequate storage conditions, with mould and dry rot infestation. Preliminary trials were performed on inoculated wool samples and sacrificial fragments using the Amsonic-elCO_2 cleaning system, varying treatment times (30 min, 1 h, and 8 h), the use of mechanical processes (such as ultrasound), and depressurisation duration (short or long), though pressure and temperature values were not reported. These tests showed no adverse effects and a reduction in mould, thereby validating the method [30].

Following the positive results, a historical antependium was cleaned in the same apparatus. As a pre-treatment step, microbial infestation and extensive mycelium were mechanically removed using tweezers, spatulas and soft brushes. Damaged areas were covered with silk, folded on themselves, and wrapped in thick polyester fleece. After a 1-hour treatment with slow depressurisation (without mechanical assistance), no visual alterations were detected. In addition, dust and soil were effectively removed, and the discoloured outer edges remained unaltered. Some whitish mycelial residues were still visible on the surface but were easily removed with a brush. Analysis revealed a reduction in colony-forming moulds, yeasts and bacteria [30].

3. Supercritical CO_2

The use of scCO_2 in cultural heritage conservation incorporates a broader and more diversified range of applications compared to liqCO_2, involving both extraction and impregnation processes. Therefore, this section is organised around these two key approaches, each further subdivided. Extraction procedures are structured into *Cleaning* (including treatments where scCO_2 and liqCO_2 were used sequentially), *Decontamination* (chemical and microbiological), *Pre-treatment for analytical characterisation*, *Degreasing* and D*rying*. In contrast, the impregnation processes are grouped according to the material treated (such as paper, wood, stone, and foams) since, in most cases, the intervention pursues simultaneous objectives (e.g., neutralisation, deacidification and strengthening), making categorisation by treatment type less appropriate. Table 4 provides an overview of the reviewed studies, organised by treatment purpose and type, substrate or collection treated, target material or contaminant, specific objects treated, and corresponding reference.

3.1. Extraction applications

3.1.1. Cleaning

ScCO_2 has been studied as a dry-cleaning method for removing dust, soil, stains, as well as residues from previous interventions [13,16,25,36,37].

ScCO_2 cleaning (at 40 °C and 20 MPa, for 60, 90 and 130 min, with and without Tergitol® NP-9 surfactant) was applied to heavily soiled fragments of an 18th-century religious silk garment and mock-up samples dyed with metal ions identified in the original textile [16,36]. The treatment neither removed the metal ions from the mock-up nor caused significant weight loss or shrinkage. Similar results on the scapulary fragments confirmed the method's safety for fragile silk. Particulate extraction ranged from 50 % to 70 %, increasing with flow rate and exposure time. The incorporation of a surfactant (Tergitol® NP-9, 0.1 % v/v) in scCO_2 reduced extraction power. Although less effective than wet cleaning, scCO_2 caused no damage or material loss [36]. A sequential cleaning in scCO_2 (40 °C and 20 MPa, for 2 h) followed by liqCO_2 (25 °C and 20 MPa, for 2 h), with and without isopropanol and/or water as co-solvents, was tested on the most soiled fragments. ScCO_2 alone achieved 25 %-35 % extraction, unaffected by isopropanol addition. Further extraction in liqCO_2 with isopropanol was not so effective; however, the addition of water improved dirt removal above 50 %. Sequential scCO_2 and liqCO_2 cleaning (without co-solvents) achieved 35 % and 53 % extraction, respectively, the latter likely due to liqCO_2's higher density [16]. In sum, scCO_2 cleaning may remove 50–70 % of dirt from moderately soiled samples [36], but only 25–35 % from heavily soiled ones. Further treatment with liqCO_2 can enhance removal by 50 % for highly soiled specimens, while co-solvents aid extraction of polar particles by 20 % [16].

Another study with a similar sequential approach treated a fragment from a Persian Medallion carpet (comprising silk, wool, naturally dyed fibres and metal threads), presenting extensive colour fading, fibre degradation, material loss, oxidised metal threads and heavy soil. Trials were conducted in liqCO_2 with ethanol and water as co-solvent (at 25 °C and 20 MPa), followed by scCO_2 (at 40 °C and 20 MPa). This CO_2 cleaning approach was found to penetrate the knotted-pile structure effectively, removing dirt without damaging the metal threads (contrary to wet-cleaning procedures), causing no colour bleeding or significant material loss [32].

An innovative approach used scCO_2 combined with a Pickering emulsion mechanism [37]. This involved pre-impregnating textiles with a water suspension of calcium oxide, forming calcium hydroxide, which reacts with CO_2 to form calcium carbonate ($CaCO_3$), stabilising CO_2-in-water emulsions. Depending on the soil composition, the emulsion can aid extraction. Trials were conducted on undyed and dyed cotton and silk samples artificially stained with mixtures containing olive oil, beeswax, carbon black, rabbit skin glue, and beetroot paste. Undyed samples underwent one scCO_2 cycle with varying pressure and exposure time (at 40 °C and 20, 27, 34 MPa, for 30–120 min), while dyed samples were exposed to a second cycle (at 40 °C and 20 MPa, for 10 min, with water) to remove residual $CaCO_3$ particles. Undyed cotton samples exhibited 70–90 % olive oil stain removal at 20 or 27 MPa, but efficiency dropped at 34 MPa - possibly due to both high pressure and rapid depressurisation, leading to a higher cooling effect during expansion and partial freezing of water, causing it to redeposit on the fabric. Rabbit skin glue and beetroot paste showed 76–95 % and 80–96 % removal, respectively, whereas beeswax and carbon black removal were less effective (50 % and 20 %, respectively). Treatment duration had minimal impact on the removal of olive oil, rabbit skin glue and beetroot paste stains. Mechanical properties were largely unaffected, though tensile strength decreased after treatment. Furthermore, cleaned textiles demonstrated greater thermal stability than water-treated samples and slower decomposition compared to untreated samples. Dyed specimens showed similar results, with better olive oil removal from cotton than silk. Extraction efficiency for rabbit skin glue and beetroot paste was consistent across dyed textiles. Moreover, introducing a two-stage depressurisation (at equal or even higher pressures) improved olive oil and rabbit skin glue removal by approximately 10 %. Occasionally, soil removal was higher in cotton, possibly due to the greater fibre swelling caused by water, allowing deeper CO_2 penetration and superior extraction. Post-cleaning, dyed samples resembled their non-soiled counterparts, especially silk-treated samples. Macroscopically, cotton fibres seemed slightly unwoven and with a slight loss of consistency post-cleaning, while silk fibres maintained the original

Table 3
– Summary of liquid carbon dioxide ($liqCO_2$) chemical decontamination trials conducted on cultural assets, according to the given treatment conditions (reactor type/volume, sample container size, temperature, pressure, exposure/depressurisation times and co-solvents used), material treated, and the main outcomes for each material, with corresponding references.

Treatment conditions given by the authors (vol., volume; T, temperature; P, pressure; *ct*, compression time; *et*, exposure time; *dt*, depressurisation time; Ø, diameter)	**Material**	**Results**	**Reference**
Amsonic autoclave (Ø45 cm×59 cm (depth)) with retractable and rotatable wash basket (42 ×23 x 18 cm) and integrated ultrasonic transducer; T = 20–25 °C, P = 5.7–6.4 MPa, *et* = 30 min	Protein-containing objects	Polar hare fur: Reduced DDT, Lindane, and mercury; inconclusive for PCP and arsenic Hair from bison robe: Reduced biocides and heavy metals; fur became softer, lighter, and more elastic, with no deformation Feathers: Reduced DDT, arsenic, and mercury (not to safe levels); appearance unchanged; weight loss confirmed cleaning	[22]
	Textiles	Wool and other unspecified textiles: No visible changes; weight loss indicated soil and biocide removal.	
Amsonic autoclave; T = 15–20 °C, P = 5–6 MPa, *et* = 2 h	Wood	Timber: Most samples unchanged; resin-rich woods showed resin exudation; DDT reduced but not fully removed, especially in cross-sections	[29]
Two connected autoclaves vol. = 1 L, cylindrical metal baskets; T = 20 °C, P = 6 MPa, static phase; *et* = 10, 30, 60 and 120 min, cycles = 1–5, rotation = 50 and 500 U/min; co-solvents = none or 5 % (v/v) ethanol, methyl tert-butyl ether, water, or acetone		Cherry Tree: 42–77 % biocide reduction; longer exposures and additional cycles improved decontamination; co-solvents increased extraction (especially for PCP, Lindane); water ineffective; three 30-min cycles recommended	[27]
Two connected autoclaves vol. = 1 L, cylindrical metal baskets; T = 20 °C, P = 6 MPa, *et* = three 30 min cycles		Unspecified softwood containing paper, ink and paint: Reduction in PCP and slightly in chlorine content; minor paint loss and uneven lining paper Oak, spruce and walnut: PCP, Lindane, and DDT were greatly reduced (85–95 %); no major visual changes were observed, besides blistering on the surface	[28]
Two connected autoclaves vol. = 1 L, cylindrical metal baskets; T = 20 °C, P = 6 MPa, *et* = 10 and 30 min	Textiles	Wool: Nearly complete biocide removal (slightly lower for PCP); 30-min cycles recommended for real objects	[27]
Two connected autoclaves vol. = 1 L, cylindrical metal baskets; T = 20 °C, P = 6 MPa, *et* = 30 min		Dyed camel and sheep wool, and silk, bast fibres: Chlorpyrifos fully removed; chlorine unchanged; no visible or chemical alterations observed	[28]
	Leather	Goat leather: Chlorpyrifos fully removed; chlorine unchanged; no visible or chemical alterations observed	
UniClean apparatus; T = 15–20 °C, P = 5–6 MPa; *et* = 30 min to 24 h	Textiles	Wool: DDT reduced; Lindane, Hg, and As not reduced to a safe extent; cleaning improved appearance, softness, and elasticity	[13,23]
	Wood	Pine wood: DDT removed; Lindane reduced; PCP unchanged; residues still hazardous.	
Cleaning Enterprises facility, vol. = 250 L (Ø70 ×40 cm (depth)), capacity = 17 kg, sample holder Ø = 37 cm; T = 12–15 °C, P = 4–5 MPa, cycle = 54 min (incl. *ct*, *et* and *dt*); rotation = 40–45 rpm; extraction sequence: 1 cycle of long bath (600 s), 2–4 cycles of rinsing baths (300 s each); unspecified detergent added for sacrificial samples; post-depressurisation rest = 10 min	Textiles	Silk: No shrinkage or dye bleeding; fabric cleaner and shinier; metal threads unchanged; but wax stains appeared, possibly from dissolved residues	[26]

Table 4
Summary of the application of supercritical carbon dioxide ($scCO_2$) technology to heritage assets for different processes: extraction and impregnation. Extraction treatments include cleaning, chemical and microbiological decontamination, pre-treatment extraction for analytical characterisation, and degreasing. Impregnation procedures include neutralisation/deacidification, strengthening, hydrophobisation, hydration, and consolidation. Cleaning trials combining sequential use of $scCO_2$ and liquid carbon dioxide ($liqCO_2$) on heritage assets are reported in the last row. Organised by carbon dioxide (CO_2) technology used, treatment purpose and procedure, material/ collection treated, target material or contaminant, specific objects treated, and corresponding reference.

CO_2 technology	Treatment purpose	Treatment procedure	Material/ collection	Target	Treated Items	Reference
$ScCO_2$	Extraction	Cleaning	Calcium carbonate-containing objects	Soil	Cowry shells	[33]
			Cellulose-based objects		Blades of grass and calabash (Ethnological Museum in Berlin, Germany)	[33,34]
					Cedar bast	[33]
			Ceramic		Ceramic tile (Ethnological Museum, Berlin, Germany)	[34]
			Composite/ Miscellaneous		Brass bell with glass beads	[33]
			Metal		Copper cone	[33]
			Plastic		HDPE, HIPS, PVC and XPS mock-ups	[35]
					PMMA mock-ups	[14,35]
			Protein-containing objects		Horsetail hair and fragment of leather (Ethnological Museum, Berlin, Germany)	[33,34]
					Parchment, parrot skin, ermine fur, cow blind gut, pig stomach, beetle wings, guinea fowl feathers, bear hair, wild boar bristles, spoon made of horn, bones, and human and jaguar teeth	[33]
			Textiles		18th-century religious silk scapulary fragments from Virgin and Child (Palácio das Necessidades, Lisbon, Portugal)	[16,36]
				Rabbit skin glue, carbon black soil, beeswax, olive oil and beetroot paste	Silk and cotton mock-ups, with and without applied natural dyes	[24,37]
				Conservation coatings	Silk mock-ups	[25]
			Wood	Soil	Wooden epitaph fragment (Cathedral in Zwickau, Germany)	[13,23]
		Chemical Decontamination	Composite/ Miscellaneous	Pesticides and/or heavy metals	Composite object (leather, hair, cotton and wood)	[13,33,34]
					Ethnographic objects (wood, feathers, leather, skins, vegetable fibres, textiles, etc.)	[38,39]
			Protein-containing objects		Fur coat from the Samojades and bundle of Amazon feathers	[13,33,34]
					Chrome-tanned leather and brightly dyed feathers	[40]
			Textiles		Dyed cotton, wool, linen and silk mock-ups	[41]
					Cotton, tapa and wool tissues (Ethnological Museum, Berlin, Germany)	[13,33,34]
			Wood		Mock-ups of different types of wood, without and with different primers and coatings	[38,39,42]
					Not specified museum objects with coatings applied	[38,39]
					Mock-ups of limewood and pine sapwood coated with different combinations of coatings	[43,44]
		Microbiological Decontamination	Leather	Living organisms	Historical leather and model vegetable-tanned sheepskin leather (Auschwitz-Birkenau State Museum)	[45]
			Paper		Ancient paper	[46]
					1922 s-hand book	[47]
					Banknotes	[48]
					Historical paper and model wood paper (Auschwitz-Birkenau State Museum)	[45]
			Textiles		Silk and cotton mock-ups, with and without applied natural dyes	[24]

(*continued on next page*)

Table 4 (*continued*)

CO_2 technology	Treatment purpose	Treatment procedure	Material/ collection	Target	Treated Items	Reference
					Historical and model cotton (Auschwitz-Birkenau State Museum)	[45]
		Pre-treatment step	Bones and human remains	Contaminants for accurate plasma oxidation and carbon dating	Canopic jar contents	[49]
					Archaeological bones (Pleistocene cave site of Zafarraya, Malaga, Spain)	[50]
			Ceramic		Archaeological ceramics (Bobartia Road Midden, South Africa, Ust' Karenga, Popovskii Lug and Shamanka II - Russian Federation)	[51]
			Textiles		Mock-ups of linen embalmment fabrics	[49,52]
					Linen gauzes from an Egyptian child and bovine mummies, and historical Russian textiles	
			Wood		Wood/charcoal samples	[49]
		Degreasing	Protein-containing objects	Oils and fats	Caribou fur (Ethnological Museum, Berlin, Germany)	[13,33,34]
					Whale bones (Research Center of Marine Mammals at La Rochelle, France and Museum of Skeleton at Île-Verte, Canada)	[53]
		Drying	Composite/ Miscellaneous	Water and methanol	Wood samples with adhering bark, wood or bone and metal containing objects, and a sword handle and a compass (Duart Point site, West Scotland, National Museum of Scotland)	[54]
					Knife handles (Makeshift Warship)	[55]
			Cork		Cork bung and a bottle cork	[54]
					Wine bottle corks from a sank French frigate found in the Machault site (Canada), cork bungs from whale oil barrels of a sank Spanish Basque galleon found in the San Juan site (Canada), cork bottle inside a flacon bottleneck from the shipwreck believed to be the Queen Anne's Revenge (USA), and waterlogged canteen corks from the H.L. Hunley confederate submarine (USA)	[56]
			Metal		Spear shaft from Nydam Mose (Denmark)	[57]
					Corroded iron artefacts	[58]
			Protein-containing objects		Bone samples, an antler and birch bark	[54]
					Osteological remains from the 1997–2000 excavation in La Marmotta (Anguillara Sabazia, Rome, Italy)	[59]
			Wood		Mesolithic wood sample (English Heritage)	[57]
					Waterlogged elm from the mediaeval "Poznań" bridge (Lednica Lake, Poland)	[60]
					Gunstocks recovered from a Civil War blockade runner and a board from a 19th-century shipwreck	[57]
	Impregnation	Neutralisation/ deacidification and/or strengthening	Paper	-	Acidic paper	[61–63]
					Sacrificial samples from the Russian National Library	[64]
					Samples from a 1956 journal	[65]
					Samples from a 1989 New York Times newspaper	[66]
					Samples from 1953 and 1982 journals	[19]
		Strengthening and hydrophobisation			Hanji (traditional Korean paper)	[20]
		Hydration	Wood	-	Historic hard and softwood and modern hardwood samples	[67]
		Consolidation	Historic buildings	-	Solubilisation of fluorinated polymers to be applied to monuments	[68,69]
					Accelerate the production of frescoes	[70]
			Plastic		Consolidation of foam-based objects	[17,71,72]
Sequentially $scCO_2/liqCO_2$ or $liqCO_2/scCO_2$	Extraction	Cleaning	Textiles	Soil	18th-century religious silk scapulary fragments from Virgin and Child (Palácio das Necessidades, Lisbon, Portugal)	[16,36]
					Persian carpets (Palace of the Dukes of Bragança, Guimarães, Portugal)	[32]

integrity and knitting configuration [37].

Following the previous approach and conditions, five other methodologies were tested on undyed cotton: (1) pure $scCO_2$, (2) $scCO_2$ with isopropanol, (3) $scCO_2$ with water (4) pre-impregnation in water and further $scCO_2$ extraction, and (5) pre-impregnation in a silica (SiO_2) particle dispersion followed by $scCO_2$. All methods effectively removed olive oil, but the best results, particularly for olive oil, beetroot, and rabbit skin glue stains, came from pre-impregnation with water or $CaCO_3$ particles followed by $scCO_2$. Noting that, if water was used as a co-solvent rather than a pre-extraction step, the cleaning capacity would be significantly decreased. Pure $scCO_2$ was the most efficient method for beeswax removal. A detailed explanation of the cleaning mechanism is provided in the paper, covering the solubility of different soils, their interaction with water and CO_2, and the role of $scCO_2$ and the immersion step in enhancing cleaning efficiency [37].

A follow-up study investigated the impact of impregnating silk textiles with $Ca(OH)_2$ dispersion at two concentrations (5 % and 35 % w/w) in $scCO_2$ (at 40 °C and 10, 12, 15 and 20 MPa, for 60 min); an additional rising step was conducted to remove $CaCO_3$ residues. A trial in pure $liqCO_2$ (30 °C and 15 MPa) was also conducted for comparison (as described in section 1.1). The results indicate that the removal of olive oil was significantly affected by pressure rather than dispersion concentration, with better removal rates achieved without the pre-impregnation step (seen in both $scCO_2$ and $liqCO_2$ treatments), followed by experiments with lower $Ca(OH)_2$ concentrations. In contrast, for rabbit skin and beetroot stains, the cleaning effect was improved with 5 % $Ca(OH)_2$. To assess possible soil and stain migration, natural undyed silk samples were joined to dyed soiled and unsoiled samples. At 20 MPa (with 5 % $Ca(OH)_2$), colour transfer occurred; at 15 MPa, the cochineal-dyed sample stained the undyed fabric, but to a lesser extent [24]. According to the obtained results, the authors optimised the cleaning process of [37] by reducing the experimental pressure to 15 MPa (at 40 °C) and the $Ca(OH)_2$ concentration to 5 % w/w [24].

In addition to soiling removal, $scCO_2$ was also tested for removing conservation coatings from textiles. A new hydrophobic and oleophobic coating for silk artefacts was designed using a water-based emulsion of silane, siloxane and organic polymer with the addition of silica (SiO_2) nanoparticles. Its reversibility was assessed using $scCO_2$ at 40 °C and 20 MPa, with methanol. Pure $scCO_2$ removed only 37.4 % of the coating, yet 5 % v/v methanol improved extraction to 72.4 %, and 63.7 % for 10 % v/v. $LiqCO_2$ has shown the best cleaning effect, with post-treatment compressed air enhancing removal (see section 1.1.) [25].

In addition to textiles, $scCO_2$ has also been explored to clean plastics, though results are inconsistent [14,35]. During the POPART project, $scCO_2$ was tested (at 31.1 °C and 7.39 MPa) on high-density polyethylene (HDPE), high-impact polystyrene (HIPS), poly(methyl methacrylate) (PMMA), poly(vinyl chloride) (PVC) and expanded polystyrene (XPS). Tests induced stress cracking in both PMMA and HIPS; for the latter, opacity was also observed. Also, discolouration was detected for HDPE, and PVC became deformed and stiffened [35]. Further investigation into PMMA revealed that CO_2 treatments induced irreversible changes, regardless of the conditions used (i.e., CO_2 technology and exposure time) [14]. In addition to the glossy surface and the rounded corners common to all samples, $scCO_2$-treated samples (at 55 and 35 °C and 28 MPa for 60 or 30 min) presented major alterations in weight, volume, and appearance as a result of extensive bubbling in the samples' bulk. Additionally, optical boundaries contouring the edges, surface scratches, potential crazing, cracks, and a drastic decrease in hardness were identified. The long-term assessment revealed that CO_2 desorption was similar for all PMMA samples and occurred within a few days. Most samples returned to their original weight and dimensions within 35 weeks, except for those treated at 55 °C and 28 MPa (60 min), which remained swollen. Hardness values increased and became similar for all samples after 35 weeks, but remained lower than control values [14].

For cellulose-based materials, $scCO_2$ proved more promising [13,23,34]. Blades of grass and a calabash (adorned with beads, thread and wax) were cleaned at 25 MPa and 40 °C for 3 h [33,34]. After extraction, both soiled blades of grass [13,33,34] and the interior of the calabash brightened; for the latter, no decorative elements were damaged or removed [33,34]. Likewise, a cedar bast cleaned in $scCO_2$ (in the same conditions) retained its flexibility and lightened visibly [33]. Following the unsuccessful removal of linseed oil from a wooden epitaph fragment in $liqCO_2$ (section 1.1.), the extraction in $scCO_2$ was tested (at 28 MPa and 40 °C with and without co-solvents). Like $liqCO_2$, $scCO_2$ also failed to remove linseed oil and its oxidation products from the specimen, even with co-solvents like methanol, acetone, or DMSO (which, at best, reached ~20 % efficiency but is unsuitable for use in heritage) [13,23].

Protein-containing materials (e.g., horsetail hair and leather fragments) treated at 40 °C and 25 MPa, for 3 h, retained flexibility and elasticity, although the leather's epidermis became rougher [33,34]. Furthermore, the cleaning effectiveness was not as remarkable as in the materials previously presented [34]. Further testing on parchment, parrot skin, ermine fur, cow blind gut, pig stomach, beetle wings, guinea fowl feathers, bear hair, wild boar bristles, spoon made of horn, bones, and human and jaguar teeth, revealed no changes in visual appearance and mechanical properties [33]. The objects with the most weight loss after treatment were pig stomach and cow blind gut. For the ermine fur and parrot skin, the leather became rougher, corroborating [34] results, and for the latter, loss in flexibility was also observed. Although no damage was observed, the cleaning effect was considered very low [33].

As for inorganic materials, a ceramic tile bonded with animal glue, with several cracks and previous retouching, was cleaned at 40 °C and 25 MPa. Although the treatment preserved the ceramic's stability and retouching appearance without new cracks or adhesive loss, the cleaning was ineffective [34]. The adhesive's retention is relevant, as these materials ensure the structural stability of intervened objects. Nevertheless, the article mentions (not in detail) tests on animal-glued wooden dummies which swelled, softened, and hardened after treatment (unlike those with polyvinyl acetate (PVAc)-based glue) [33,34]. Similarly, objects like a copper cone, brass bell with glass beads, and cowry shells were unaffected by $scCO_2$ (at the same conditions) but resulted in ineffective cleaning [33].

Overall, according to Aslanidou *et al.*, $scCO_2$ cleaning is highly effective on organic materials with strongly structured surfaces [37]. Moreover, the porosity of the materials greatly influences cleaning effectiveness, as extraction is enhanced in materials with high porosity and open pores [33]. The cleaning process does not appear to negatively impact textile mechanical properties, nor dyes and metal threads. Except for cotton fibres, which may become slightly more unwoven [37]. For cellulose-based materials, the treatment was highly successful [13,34]. However, for plastics, the cleaning treatment induced stress cracking, discolouration and deformation, deeming CO_2 unsuitable for low-crystallinity and amorphous polymers [14,35]. Moreover, while macroscopically $scCO_2$ treatment did not induce damage to ceramic and protein-containing materials, it resulted in minimal to no cleaning effect [34]. Table 5 summarises the experimental conditions given by the authors and the main outcomes revised in this section. Ultimately, cleaning effectiveness depends on the substrate and soil type. As stated in several studies, it is crucial to test different methods and conditions to administer a well-considered treatment [37]. Notwithstanding, sequential treatments with $scCO_2$ and $liqCO_2$ (without or with carefully selected co-solvents) offer enhanced cleaning performance while maintaining conservation safety standards [16,32,36].

3.1.2. *Chemical decontamination*

Several researchers, including Arnulf von Ulmann, Erich Jelen, Helene Tello and Achim Unger have applied $scCO_2$ for contaminants extraction from museum objects [15,23,34,41,42].

An inquiry into the use of pesticides in German museums found that approximately 300000 fabrics are contaminated with DDT, dichlorodiphenyldichloroethane (DDD), and dichlorodiphenyldichloroethylene

Table 5
Summary of supercritical carbon dioxide ($scCO_2$) cleaning trials conducted on cultural assets, according to the given treatment conditions (reactor type/volume, sample container volume, temperature, pressure, exposure/compression/depressurisation times, CO_2 flow, co-solvents), material treated, and the main outcomes for each material, with corresponding references.

Treatment conditions given by the authors (vol., volume; T, temperature; P, pressure; *ct*, compression time; *et*, exposure time; *dt*, depressurisation time; →, followed by)	**Material**	**Results**	**Reference**
Chamber vol. = 10 L, basket vol = 7 L; T = 40 °C, P = 25 MPa; CO_2 flow = 20 kg/h; *ct* = 34 min, *et* = 3 h, *dt* = 1–2 h	Cellulose-based objects	Blades of grass and calabash (containing beads, thread and wax): Visibly cleaned and no damage was observed	[33,34]
		Cedar bast: Visibly cleaned and retained its flexibility	[33]
	Composite/Miscellaneous Inorganic	Brass bell with glass beads: Ineffective cleaning; no damage	
		Cowry shells: Ineffective cleaning; no damage	
		Copper cone: Ineffective cleaning; no damage	
		Ceramic tile: Preserved ceramic stability and retouching appearance; ineffective cleaning	[34]
	Protein-containing objects	Horsetail hair and fragment of leather: Poor cleaning effect; retained flexibility and elasticity; leather became rougher	[33,34]
		Parchment, parrot skin, ermine fur, cow blind gut, pig stomach, beetle wings, guinea fowl feathers, bear hair, wild boar bristles, spoon made of horn, bones, and human and jaguar teeth: Low cleaning effect; visibly unchanged; retained mechanical properties except for ermine fur and parrot skin, which became rougher, and the parrot skin showed loss in flexibility	[33]
Kemi Rens chamber; T = 31.1 °C, P = 7.39 MPa	Plastic	HDPE, HIPS, PVC, PMMA and XPS: Damaged and altered sample surfaces	[35]
Chamber vol. = 33 mL, T = 35 and 55 °C both at P = 10 and 28 MPa; CO_2 flow = 10 mL/min; *ct* ≈ 15 min, *et* = 30 and 60 min, *dt* = 20 min		PMMA: Severely damaged	[14]
Laboratory-scaled cell vol. = 4.5 mL; compression CO_2 flow = 0.98 g/min; *et* = 2 h, CO_2 (or a CO_2 + co-solvent) flow = 1.5 mL/min; T = 40 °C, P = 20 MPa ($scCO_2$) and T = 25 °C, P = 20 MPa ($liqCO_2$); sequential cycles: (1) $scCO_2$ → 98.35 % $scCO_2$ + 1.66 % isopropanol → 98.35 % $liqCO_2$ + 1.66 % isopropanol → 98.13 % $liqCO_2$ + 1.64 % isopropanol + 0.23 % H_2O; (2) $scCO_2$ → $liqCO_2$ (no co-solvent); post-cleaning with CO_2	Textiles	Silk: $ScCO_2$ removed 25–35 % of residues, adding a cycle in $liqCO_2$ increased removal to ~50 %, especially for heavily soiled samples; co-solvents improved polar particle extraction by ~20 %	[16]
Laboratory-scaled cell vol. = 4.5 mL; T = 40 °C, P = 20 MPa; CO_2 flow ≈ 2 g/min; with/without 0.1 % (v/v) Tergitol® NP−9 surfactant; *et* = 60, 90, and 130 min; historical samples treated in 33 mL cell		Silk: Safe for fragile fragments; removed 50–70 % of particulates, particularly with increasing flow rate and exposure time; surfactant reduced efficiency; less effective than wet cleaning, but caused no damage or material loss	[36]
Laboratory-scaled cell vol. = 33 mL, CO_2 flow = 1.5 mL/min, *et* = 2 h; $liqCO_2$ (98.13 % CO_2 + 1.64 % ethanol + 0.23 % H_2O), T = 25 °C, P = 20 MPa; rising cycle with $liqCO_2$ → $scCO_2$, T = 40 °C, P = 20 MPa		Silk, wool, naturally dyed fibres and metal threads: Effectively removed dirt; no colour bleeding, metal thread damage, or significant material loss observed	[32]
Textiles pre-impregnated with $Ca(OH)_2$: T = 40 °C, P = 20, 27 and 34 MPa; *et* = 30–120 min; dyed samples: additional cycle T = 40 °C, P = 20 MPa, *et* = 10 min, chamber containing 5 mL H_2O; *dt* procedures: (1) single-step, 1–5 MPa drop + gradual 5 min release; (2) two-step ≈ 1 MPa drop after *et* = 30 min → repressurised → held 30 min → gradual *dt*		Silk and cotton with and without natural dyes: Overall, the colour of both undyed and dyed samples remains largely unaffected by the treatment duration; colour restoration occurs in most cases (particularly for silk samples); two-step depressurisation improved olive oil and rabbit skin glue removal by ~10 %; mechanical properties largely preserved, slight tensile strength loss in cotton (undyed samples); cotton fibres slightly loosened, silk fibres intact (dyed samples)	[37]
T = 40 °C, P = 20, 27 and 34 MPa; *et* = 30–120 min; six procedures tested: (1) $scCO_2$; (2) $scCO_2$ + isopropanol; (3) $scCO_2$ + H_2O; (4) pre-impregnation in H_2O → $scCO_2$; (5) pre-impregnation in a silica dispersion → $scCO_2$; (6) pre-impregnation in $CaCO_3$ dispersion → $scCO_2$		Undyed cotton: Olive oil, beetroot, and rabbit skin glue effectively removed, best results achieved with pre-impregnation with water or calcium carbonate particles followed by $scCO_2$; water as co-solvent is less effective; pure $scCO_2$ most efficient for beeswax removal	
T = 40 °C, P = 10, 12, 15 and 20 MPa; *et* = 60 min, *dt* = 30 min; trials: (1) $scCO_2$; (2) pre-impregnation in H_2O (10 min) → $scCO_2$; (3) pre-impregnation in $Ca(OH)_2$ dispersion (5 % and 35 % w/w, 10 min) → $scCO_2$ → rinsing cycle in $scCO_2$ with 5 mL H_2O (10 min) to remove $CaCO_3$ residues		Silk: Best olive oil removal when trails are conducted without pre-impregnation; 5 % $Ca(OH)_2$ improved rabbit skin and beetroot cleaning; minor colour transfer from dyed soil samples occurred at 20 and 15 MPa; optimal process at 15 MPa and 5 % $Ca(OH)_2$	[24]
Cell vol. = 40 mL, T = 40 °C, P = 20 MPa; co-solvent = methanol (5 and 10 % v/v); post-treatment, some samples were air blown (2 min) to remove residues		Coated silk: 37 % of the coated removed with pure $scCO_2$; 5 % MeOH enhanced removal to 72 %; 10 % MeOH extracted 64 %	[25]
T = 40 °C, P = 28 MPa; co-solvents: none and 3 % acetone, 3 % methanol, or 3 % DMSO	Wood	Unsuccessful removal of polymerised linseed oil and its oxidation products even with co-solvents	[13,23]

(DDE). Between 2000 and 2001, a project involving the Deutsche Bundesstiftung Umwelt (Osnabrück), the University of Applied Sciences (Köln), and the Laboratory in the Germanisches Nationalmuseum (Nürnberg) tested $scCO_2$ for pesticide removal from historic textiles. Cotton, wool, linen and silk samples dyed with indigo and madder were artificially contaminated with *Hylotox* and treated at 40 °C and 25 MPa for 60 min. Only 5–10 % of pesticides remained in the textiles post-treatment (no differentiation between the fabrics' nature). No changes or induced damage in the fabrics' fibres were noted, nor changes in colour; however, differences in smell and touch were reported, possibly due to the contaminant's extraction [41]. Further trials for pesticides and heavy metals extraction were conducted on cotton, tapa (made of birch bark), and wool tissues, at 35 MPa and 40 °C for 7 h [13,33,34]. Activated carbon was used to trap both liquid and gaseous substances during extraction and to avoid equipment contamination. While a slight weight loss occurred, fabric flexibility and stability remained intact [13,33,34]. The decontamination resulted in a significant extraction of mercury and DDT, while for Lindane and PCP, which were present in lower concentrations, it was less pronounced [13]. The decontamination rate for mercury was higher than 76 % for tapa and wool tissues, and 70 % for cotton. DDT extraction exceeded 81 % for tapa and cotton [13,34]. Among the three textiles, cotton had the highest concentrations of arsenic, and $scCO_2$ treatment was found ineffective for this contaminant [33,34].

In the study of the Chilean Patagonia woollen blanket, the decontamination in $liqCO_2$ was ineffective in extracting heavy metals (see 1.2. Decontamination). However, the authors suggest that it may be possible to reduce the contaminants with $scCO_2$ (unknown conditions), as its low viscosity and surface tension make it an ideal solvent for extracting contaminants [13,23]. This thought is supported by another study [34], although they only share a common material basis, and once again, only mercury content was successfully reduced.

$ScCO_2$ was also applied to collagen-containing materials at 35 MPa and 40 °C for 7 h [13,34,73]. Different model samples of a fur coat from the Samojades were treated following three methods: (1) pure $scCO_2$, (2) $scCO_2$ with ethanol and (3) $scCO_2$ with ethanol and the chelating agent trimercaptotriazine 15 (TMT 15). Treatments (1) and (2) preserved the appearance and stability of the specimens but reduced flexibility. In contrast, treatment (3) led to brittleness and strength loss. All the treatments cause slight dryness and a degreasing effect [34]. These trials showed that, like with $liqCO_2$, $scCO_2$ treatment of oil- and fat-containing materials can extract free fatty acids and their degradation products (issue deepened in 2.1.5. Degreasing: extraction of oils and fats), especially when modifiers are used. As for arsenic, it was only significantly removed when modifiers were used, with an extraction of 37.5 % for both ethanol alone or combined with TMT 15 [13,33,34]. Mercury, DDT and Lindane content reduced despite the use of modifiers; in fact, the extraction was higher for mercury and Lindane (and approximately the highest for DDT) in pure $scCO_2$ [13,34]. At the same conditions, a bundle of Amazon feathers and a composite object containing leather, hair, cotton and wood, were also decontaminated in $scCO_2$ with ethanol and TMT 15 [33,34,73]. The physical stability and appearance of the specimens were preserved after treatment [34]. In the feathers, mercury and DDT were reduced by over 90 % [13,34]. However, unlike with the fur, the arsenic content was not reduced, even with modifiers [33,34]; possibly due to its low initial content [13]. However, for the composite object, the arsenic concentration was already high, so the authors suggest that an error may have occurred in analytical measurements [13,34]. Mercury content of the composite object was reduced by 62.8 %, but no definitive conclusions could be made for DDT as its content was already low [33,34]. Remarkably, the wood part of the object exhibited a strong cleaning effect [34]. As for the treatment of rawhide, pure $scCO_2$ was not significantly effective, as the level of contaminants was already lower before treatment [13,34].

Zimmt *et al.* [40] explored the use of acetone to enhance the extraction of polar organic pesticides, particularly high molecular weight compounds insoluble in pure $scCO_2$. Chrome-tanned leather and brightly dyed feathers artificially contaminated with "Ortho Diazinon, 25 % active material" were treated in $scCO_2$ at 50–60 °C, and 10–25 MPa, for 2 min with small quantities of acetone introduced into the reactor without direct contact with samples. Toxicological screening using rat lung epithelial cell cultures indicated that complete pesticide removal could be achieved with 1 % v/v acetone (100 % cellular metabolic activity, so no cell damage occurred), while 0.1 % v/v acetone resulted in approximately 75 % extraction, pure $scCO_2$ retained about 50 % of the active ingredient in the pesticide. The study demonstrated significant improvement in decontamination with minimal damage to the leather and dyed feathers with short treatment durations and small amounts of acetone [40]. In a theoretical paper, the authors discussed $scCO_2$'s potential for decontaminating ethnographic assets, highlighting the benefits of pure $scCO_2$ and the use of co-solvents like acetone and methanol to address pesticide insolubility in CO_2. The authors emphasise that well-designed processes and testing different pesticides and additives would enable museums to decontaminate items at reasonable costs [74].

Wooden items have also been successfully treated with $scCO_2$, which diffuses deep into the wood tissue without swelling, effectively removing contaminants from deeper layers [38,39,42]. Different wood types (spruce, birch plywood, fir/pine, lime and cherry wood), without and with different primers (gesso-ground, glue, crayon, and pumice and shellac) and coatings (egg tempera, resin oil, shellac glue, etc.) were tested at 40 MPa and 100°C, with special attention to the pressurisation and depressurisation stages [42]. Particularly, to prevent damage from the expanding gas [38,39,42]. DDT and Lindane removal rates reached 75 % and 90 %, respectively, without notable mass or dimensional changes. The casein tempera and glue-bound coatings were not affected by exposure to $scCO_2$, but gilded and shellac-coated samples showed surface roughening and tarnishing, respectively. These adverse effects could be mitigated by lowering experimental conditions, though it may impact biocide removal effectiveness [42]. Experiments on wooden museum objects with coatings (paints, varnishes and glues) demonstrated successful $scCO_2$ decontamination (at 40–60 °C and 40 MPa) without damaging the wood [38,39]. The extraction exceeded 90 % for DDT and Lindane (regardless of wood type). In addition, the article mentioned that other contaminated objects, such as ethnographic objects composed of wood, feathers, leather, skins, vegetable fibres, textiles, etc., were also treated, revealing the viability of this technology [38,39].

A more focused study examined $scCO_2$'s impact on multi-coated wood species [43,44]. Limewood and pine sapwood mock-ups were coated with different combinations of commonly used coatings (shellac, bone glue, Naples yellow, etc.), artificially contaminated with Hylotox 59 (containing DDT and Lindane) and treated at 45 °C and ~20.7 MPa. Post-treatment analysis indicated alterations in luminosity levels in 15 out of 31 samples, particularly in those containing Naples yellow, shellac and bone glue. Naples yellow-containing samples darkened after treatment, while shellac-containing samples showed inconsistent changes - some brightened, others darkened, and some remained unchanged. Only a few bone glue-containing samples exhibited changes in luminosity. Regardless of coating combinations, $scCO_2$ extraction effectively removed DDT from all mock-ups, with removal rates ranging from 27.4 % to 87.6 %. The authors emphasise that future work should focus on optimising conditions and exploring the impact of coatings on extraction effectiveness, especially for impermeable wood species [43].

Overall, the decontamination process is complex and demands expertise, particularly during the pressurisation and depressurisation phases. The availability of pilot plants for additional testing is restricted, and adapting them to cultural assets is challenging. Additionally, building new facilities is costly, with long payback periods [22]. Nevertheless, the reviewed studies confirmed the viability of $scCO_2$ to extract contaminants from cultural objects made of different materials [13,34,38,39,42]. Organic pesticides are generally well-extracted, while

inorganic pesticide removal requires co-solvents or chelating agents [13,33,34,40]. Through literature results, Unger *et al.* [22] compared the performance of liqCO_2 and scCO_2 for removing contaminants, reporting comparable depletion rates for DDT and lindane. In contrast, for inorganic contaminants such as arsenic and mercury, the observed reduction was attributed not to a solvent effect, but to a physico-mechanical detachment attributed to the blowing effect of liqCO_2 [22]. A summary of the experimental conditions given by the authors and the main outcomes of this section is presented in Table 6.

3.1.3. Microbiological decontamination

Biodeterioration is still an underestimated issue in cultural heritage preservation. Studies have shown scCO_2's potential for inactivating microorganisms [24,46,47].

In a pioneering study from 1999, it was found that in scCO_2, the morphology of spores of different fungi identified in ancient papers can be partially destroyed, moreover, the addition of methanol as a co-solvent resulted in complete spore inactivation [46]. ScCO_2 with ethanol (at 40 °C and 15 MPa, for 1 h) removed fungi from a 1922 s-hand book. Among 294 treated samples, *Aspergillus niger* was the most prevalent fungi found, followed by *Aspergillus flavus*. Fungal activity was significantly reduced using 4 % and 8 % ethanol concentrations, with no damage to paper fibres [47]. A more recent study tested two scCO_2 processes on historical and model paper for microbial inactivation: 20 min at 11 MPa and 40 °C, with hydrogen peroxide (H_2O_2); and 3 h at 20.5 MPa and 40 °C without co-solvent. Treated samples experienced binder extraction (more prominent in the second procedure), which may have induced fibre jaggedness, mechanical stress, and visible colour change. These adverse effects rendered scCO_2 disinfection unsuitable for these samples [45].

ScCO_2 has also proven effective in cleaning modern banknotes contaminated by bacterial colonies and soiled [48]. The effectiveness in removing oxidised sebum and motor oil from artificially soiled banknotes (at 60 °C and 11–14 MPa, for 1–3 h) set the tone for testing on naturally soiled and contaminated banknotes in circulation (60 °C and 34 MPa for 3 h). ScCO_2 extraction effectively cleaned the notes (even while in note straps) without compromising printing contrast and quality, while removing common organism colonies, such as *Micrococcus luteus* and yeast. The assessment for changes caused by the treatment in security features, such as threads, lenticular arrays, watermarks, UV emissive inks, and fibres, showed no significant alterations in appearance and functionality, aside from partial dissolution of pigments in United Kingdom banknotes. In addition, machine-readable features, such as magnetic inks and capacitive structures, remained unchanged. Therefore, this treatment could reduce the disposal of banknotes due to soil and shredding [48].

Regarding leather materials, model vegetable-tanned sheepskin and historical samples were treated under two scCO_2 conditions: 20 min at 11 MPa, 40 °C, with H_2O_2; and 3 h at 20.5 MPa, 40 °C, without co-solvent [45]. The model sample showed surface delamination and detachment after the first condition, likely due to H_2O_2, as the second condition only caused minor cracks. Historical leather exhibited fewer visible changes after treatment with H_2O_2, though surface loosening was noted upon treatment without co-solvent. Colour alterations and lipid extraction occurred in both treatment conditions; thus, the method was deemed unsuitable for heritage leather disinfection. In the same study, model and historical cotton samples underwent identical treatments. H_2O_2-treated model samples showed surface damage, whereas fibre morphology remained intact when no co-solvent was used. Both treatment conditions removed aluminosilicates and organic contaminants from model and historical samples, although sulphides appeared after treatment under the second condition. Historical cotton also exposed significant colour alteration, leading to the same conclusion regarding unsuitability for heritage assets [45].

A study following the cleaning approach of [24,37], based on the Pickering mechanism (see 2.1.1. Cleaning), showed the scCO_2 potential for disinfecting silk infected with *Aspergillus Niger* fungi [24]. Undyed silk samples artificially contaminated were treated at 40 °C and 15 MPa for 1 h. Results revealed that pure scCO_2 was the least effective, while pre-impregnation in water achieved 97.5 % disinfection and removed fungal stains. Pre-impregnation in $Ca(OH)_2$ dispersion showed slightly lower decontamination rates but led to the lowest microbial load, due to pH increase, yielding the extermination and constraining the growth of these microorganisms. Following the results, the authors present a microorganism decontamination protocol [24].

Overall, impregnation in ethanol or water followed by scCO_2 was found to enhance microbiological decontamination of ancient papers and textiles [46,47]; nevertheless, further research is needed to validate these procedures. The conditions applied in each reviewed study, along with the corresponding outcomes, are summarised in Table 7.

3.1.4. Pre-treatment for analytical characterisation

ScCO_2 extraction has also been explored to remove contaminants from burial and embalming textiles, bones, and archaeological ceramics, either as a pre-treatment for radiocarbon dating (^{14}C) [49,50,52] or to extract organic residues, such as lipids, for further studies and characterisation [51].

Contamination during or after excavation, especially from conservation materials, can compromise radiocarbon analysis and lead to inaccurate dating [49,50]. Conventional decontamination methods (using organic solvents and acid-base treatments) can damage fragile artefacts and induce further contamination during laboratory handling [49,50,52]. Preliminary trials were performed (at 40 °C, 20.7 and 41 MPa, with methanol) on model linen treated with embalming and preserving organic compounds (beeswax, coconut and frankincense oil, humic acids, abietic acid, myrrh, glycerol, etc.) showed successful extraction of beeswax, coconut oil, and humic acids. Higher pressures were found to enhance contaminants removal, although humic acids and frankincense oil extraction remained below 50 %. The highest rate of removal was attributed to glycerol, with approximately 98 % [49]. Experiments were then extended to linen gauzes from an Egyptian child and bovine mummies, and Russian textiles containing lipids (at 40 °C, 20.7 MPa, 41 MPa and 62 MPa, with methanol). Egyptian gauze analyses revealed a polymer similar to a polyglycerol derivative, used in ancient Egyptian funeral rituals, though it could also be a result of long-term hydrolysis of oil and fat triglycerides. Moreover, the gauzes were also found to be covered with wax-like and/or animal fat and vegetable oils. ScCO_2 treatment induced changes in colour and dimension, with the fibres expanding slightly and the texture becoming open and unwoven. The Russian textiles showed a linear contaminant removal with pressure, and the extraction of an unidentified polymer and palmitic acid [49,52].

Further investigation was conducted to assess the suitability of scCO_2 (involving similar conditions) to prepare wood/charcoal samples, and study the content of a Canopic jar prior to ^{14}C dating [49,52]. For wood and charcoal, scCO_2 treatment improved ^{14}C dating accuracy despite incomplete decontamination. As for the extraction of the contents from the Canopic jar, from the resin fractions, a great amount of contaminants was removed [52]. Both studies indicate that scCO_2 with an alcoholic co-solvent effectively removes organic contaminants, offering a non-destructive pre-analysis treatment for burial specimens [49,52].

This methodology was also used to extract exogenous carbon from archaeological bones [50]. At 50 °C and 30 MPa (with ethanol for 3 h), compounds extracted from Pleistocene cave bones (Zafarraya, Malaga, Spain) included soil organic materials (e.g. non-collagenous proteins, nitrates, or humic acids) and/or degraded collagen. Furthermore, scCO_2 also effectively removed PVAc from previous conservation treatments. This approach matched, and in some aspects, surpassed standard solvent wash methods (confirmed by ^{14}C dating), providing faster results with fewer steps and no toxic chemicals, making it a safe alternative [50].

In another application, scCO_2 was used to decontaminate archaeological ceramics from lipids. Twelve archaeological specimens from

Table 6
Summary of supercritical carbon dioxide ($scCO_2$) chemical decontamination trials conducted on cultural assets, according to the given treatment conditions (reactor type/volume, temperature, pressure, exposure/compression/depressurisation times, CO_2 flow, co-solvents), material treated, and the main outcomes for each material, with corresponding references.

Treatment conditions given by the authors (vol., volume; T, temperature; P, pressure; *ct*, compression time; *et*, exposure time; *dt*, depressurisation time; →, followed by)	**Material**	**Results**	**Reference**
Cell vol. = 150 mL, T = 40 °C, P = 35 MPa; CO_2 flow = 2 kg/h; *ct* = 15 min, *et* = 7 h, *dt* = 1 h; co-solvent = ethanol; chelating agent = trimercaptotriazine 15 (TMT 15)	Composite/Miscellaneous	Composite object (leather, hair, cotton and wood): Preserved appearance and stability; mercury reduced by 62.8 %; no arsenic reduction (possible analytical error); wood component showed strong cleaning effect	[13,33, 34]
Cell vol. = 150 mL, T = 40 °C, P = 35 MPa; CO_2 flow = 2 kg/h; *ct* = 15 min, *et* = 7 h, *dt* = 1 h; trials: (1) $scCO_2$, (2) $scCO_2$ + ethanol, (3) $scCO_2$ + ethanol + TMT 15	Protein-containing objects	Fur: Pure $scCO_2$ and $scCO_2$ + ethanol preserved appearance but reduced flexibility; adding TMT 15 caused brittleness and strength loss; arsenic removal reached 37.5 % with co-solvent and TMT 15; mercury, DDT, and Lindane extraction was highest in pure $scCO_2$	
Cell vol. = 150 mL, T = 40 °C, P = 35 MPa; CO_2 flow = 2 kg/h; *ct* = 15 min, *et* = 7 h, *dt* = 1 h; co-solvent = ethanol; chelating agent = TMT 15		Feathers: Preserved appearance and stability; mercury and DDT reduced by > 90 %; arsenic content unaffected even with modifiers	
Cell vol = 150 mL, T = 40 °C, P = 35 MPa; CO_2 flow = 2 kg/h; *ct* = 15 min, *et* = 7 h, *dt* = 1 h		Raw hide: Low decontamination effect	[13,34]
Cell vol. = 200 mL, T = 50–60 °C, P = 10–25 MPa; *et* = 2 min, *dt* = 1 min; co-solvent: acetone 0.1–1 % (v/v)		Chrome-tanned leather and brightly dyed feathers: Complete pesticide removal achieved with 1 % v/v acetone (no cell damage); 0.1 % v/v acetone yielded ~75 % extraction; pure $scCO_2$ removed ~50 %; effective decontamination with minimal damage	[40]
Chamber vol. = 5 L, T = 40 °C, P = 25 MPa, *et* = 60 min	Textiles	Dyed cotton, wool, linen and silk: Effectively removed 90–95 % of pesticides; no fibre or colour changes observed	[41]
Cell vol. = 150 mL, T = 40 °C, P = 35 MPa; CO_2 flow = 2 kg/h; *ct* = 15 min, *et* = 7 h, *dt* = 1 h		Cotton, tapa and wool tissues: Significant extraction of mercury (>70 % for all) and DDT (>81 % for tapa and cotton); lower removal of Lindane and PCP; $scCO_2$ ineffective for arsenic; slight weight loss, but fabric flexibility and stability preserved	[13,33, 34]
Unknown conditions		Wool: Reduced mercury content	[13,23]
Cell vol. = 150 mL, T = 100 °C, P = 40 MPa; with special attention to the pressurisation and depressurisation stages	Wood	Spruce, birch plywood, fir/pine, lime and cherry wood without and with different primers and coatings: Effectively removed DDT (75 %) and Lindane (90 %) without mass or dimensional changes; casein and glue coatings unaffected, while gilded and shellac-coated samples showed minor roughening and tarnishing	[38,39, 42]
Industrial cell vol. = 200 L, T = 100 °C, P = 40 MPa		Coated wood: Successful removal of DDT and Lindane (>90 %); no damage	[38,39]
90.8 mm× 1036 mm vessel, T = 45 °C; compression rate = 0.07 MPa/s up to 20.7 MPa; static hold = 10 min → dynamic flow = 94.4 mL/min for 20 min; depressurisation rate = 3.45 MPa/min		Limewood and pine sapwood coated with different combinations of coatings: Effectively removed DDT (27.4–87.6 %); luminosity changes in samples with Naples yellow, shellac, or bone glue	[43]

Table 7
– Summary of supercritical carbon dioxide ($scCO_2$) microbiological decontamination trials conducted on cultural assets, according to the given treatment conditions (reactor type/volume, temperature, pressure, exposure/depressurisation times, CO_2 flow, co-solvents), material treated, and the main outcomes for each material, with corresponding references.

Treatment conditions given by the authors (vol., volume; T, temperature; P, pressure; *et*, exposure time; *dt*, depressurisation time; →, followed by)	**Material**	**Results**	**Reference**
Two different conditions and chambers were used: (1) Qarboon industrial chamber vol. = 83 L, equipped with oscillation, rotation, and ultrasound mixing; T = 40 °C, P = 11 MPa, *et* = 20 min; 200 H_2O_2; (2) Qarboon laboratory-scale chamber vol. = 0.5 L; T = 40 °C, P = 20.5 MPa, *et* = 3 h	Leather Paper Textile	Vegetable-tanned sheepskin leather: Caused lipid extraction and damage, making the method unsuitable for heritage materials Unsuitable for disinfection; induced binder extraction, mechanical stress, and colour change Cotton: H_2O_2 caused surface damage and colour alteration; both conditions removed contaminants but formed sulphides, confirming the method's unsuitability	[45]
Chamber vol. = 10 mL, T = 40 °C, P = 15 MPa, *et* = 1 h; co-solvent = ethanol (4 % or 8 % w/w) injected during treatment; samples rinsed 3x before and after $scCO_2$ T = 60 °C, P = 34 MPa, *et* = 3 h	Paper	Effectively reduced fungal activity (mainly *Aspergillus niger* and A. *flavus*) using 4 % and 8 % ethanol; no damage to paper fibres observed Effectively removed microbial colonies and yeast without affecting print quality or machine-readable features; safe cleaning/extraction method for banknotes	[47] [48]
T = 40 °C, P = 15 MPa, *et* = 1 h, *dt* = 30 min; trials: (1) $scCO_2$; (2) pre-impregnation in H_2O (10 min) → $scCO_2$; (3) pre-impregnation in $Ca(OH)_2$ dispersion (5 % and 35 % w/w, 10 min) → $scCO_2$	Textile	Undyed and dyed silk and cotton: Pre-impregnation in water achieved 97.5 % disinfection and removed fungal stains; $Ca(OH)_2$ pre-treatment slightly less effective but yielded lowest microbial load due to increased pH	[24]

different sites (seven from Bobartia Road Midden, South Africa and five from Ust' Karenga, Popovskii Lug and Shamanka II - Russian Federation) were treated at 50 °C and 30 MPa, with ethanol and water for 90 min. The substances extracted mainly contained free fatty acids attributed to plant and/or animal lipids. Compared to traditional lipid extraction involving crushed ceramic fragments combined with organic solvents, this methodology was found to be more efficient, yielding higher extraction rates and the removal of additional molecules, including free fatty acids. The ratio of unsaturated/saturated free fatty acids was found to increase with $scCO_2$ extraction, having removed more unsaturated free fatty acids, possibly because it is able to break stable organo-metallic complexes. Considering the results, the authors give a note addressing the suitability of this procedure as a pre-analysis method to remove exogenous organics prior to radiocarbon and rehydroxylation dating [51].

In summary, $scCO_2$ extraction with alcoholic co-solvents effectively removes organic contaminants, including conservation residues, offering a non-destructive pre-analyses treatment for burial specimens and archaeological artefacts [49,52]. Moreover, compared to traditional pre-treatment methods, $scCO_2$ yielded similar results, but with the added benefits of being faster, requiring only a single step and mitigating the use of hazardous chemicals. This makes it a viable and efficient alternative treatment [50,51]. Table 8 summarises the treatment conditions given by the authors and the main outcomes of $scCO_2$ extraction as a pre-treatment step for analytical characterisation.

3.1.5. Degreasing

As previously mentioned in *2.1.2 Chemical decontamination* and *2.1.4 Pre-treatment for analytical characterisation*, the removal of fatty acids and fat degradation products from protein-containing materials has been observed as a secondary effect of $scCO_2$-based treatments [13,34]. However, some studies have specifically focused on the use of $scCO_2$ for degreasing purposes. For instance, a caribou fur treated in $scCO_2$ (at 25 MPa and 40 °C, for 3 h) showed effective degreasing of the skin and softening of the fur, while preserving structural stability. However, slight differences in the haptic properties and some yellowish residues (possibly saturated aldehydes from long-term fur and skin damage) were observed. Ultimately, the treatment successfully extracted fatty acid degradation byproducts within the glycerides rather than fat, protein residues, water and dust [13,33,34].

Furthermore, $scCO_2$ was tested for degreasing lipid-rich osteological whale bones [53]. Cetacean vertebrae skeletons from the Research Center of Marine Mammals at La Rochelle (France) and fin whale metacarpus skeletons from the Museum of Skeleton at Île-Verte (Canada) underwent two 24-hour cycles (first at 30 MPa and 37–39 °C and second at 30 MPa, 36–38 °C, with ethanol). Although the treatment caused no visible alterations to the bones, it proved ineffective, extracting only small amounts of lipids [53].

3.1.6. Drying

$ScCO_2$ extraction has been used for drying susceptible archaeological items, namely waterlogged wood, cork, metal, bone and composite materials. In a handbook for the conservation of wood artefacts, the use of $scCO_2$ to dry waterlogged wood is reviewed [75], detailing the process and listing treated artefacts made of wood, cork, bark, and bone [54]. Very briefly, since water is insoluble in $scCO_2$, it is first replaced with methanol, which is further exchanged for CO_2 [54,55]. Unlike traditional treatments, $scCO_2$ drying significantly reduces treatment time (from weeks to days) while preserving the object's dimensions and shape [54,55]. A broken spear shaft and an extremely fragile Mesolithic wood were treated at 12 MPa and 50 °C with methanol for 30–36 h (after being submerged for 4 weeks in 200 mL of methanol). The results showed minimal shrinkage with no distortion. The fragile wood sample became stable and handleable, with minor "normal shrinkage", due to cellulose molecules' relaxation, forming a stable structure. Additionally, treated wood was found to remain stable after three years in

Table 8
– Summary of supercritical carbon dioxide ($scCO_2$) used as a pre-treatment step for further analytical characterisation of cultural assets, according to the given treatment conditions (reactor type/volume, temperature, pressure, exposure times, CO_2 flow, co-solvents), material treated, and the main outcomes for each material, with corresponding references.

Treatment conditions given by the authors (vol., volume; T, temperature; P, pressure; *et*, exposure time; →, followed by)	**Material**	**Results**	**Reference**
Waters® MV−10 ASFE system, T = 50 °C, P = 30 MPa; co solvent = 50 % ethanol, flow = 2 mL/min, *et* = 3 h	Bones and human remains	Effectively removed humic residues and PVAc from bones; improved ^{14}C dating with a faster and non-toxic method	[50]
Two different conditions and chambers were used: (1) Jasco®Semi-Prep SFC-SP−2086 vessel vol. = 10 mL; (2) Waters® MV10 vessel vol. = 5 mL; T = 50 °C, P = 30 MPa; CO_2 + 16 % (v/v) ethanol + water (95:5), flow = 2.3 mL/min, *et* = 90 min	Ceramic	Extracted free fatty acids efficiently; increased the unsaturated/saturated ratio; suitable as pre-analysis for radiocarbon and rehydroxylation dating	[51]
T = 40 °C, P = 20.7 MPa; co-solvent = methanol 10 % (v/v), variable flow rate and *et*	Human remains	Improved ^{14}C dating accuracy as effectively removed organic contaminants	[49]
T = 40 °C, P = 20.7 and 41 MPa; co-solvent = methanol 10 % (v/v), variable flow rate and *et*	Textile	Linen with preserving organic compounds: Effectively extracted beeswax, coconut oil, glycerol and humic acids; removal increased with pressure.	
T = 40 °C, P = 20.7, 41 and 62 MPa; co-solvent = methanol 10 % (v/v), variable flow rate and *et*		Ancient linen: Altered colour and dimensions; caused fibre expansion and a looser texture Unspecified Russian textile: pressure-dependent contaminant removal; extracted unidentified polymer and palmitic acid	[49,52]
T = 40 °C, P = 20.4 MPa; $scCO_2$ + 10 % (v/v) methanol, flow ≈ 1.4 mL/min, vol. CO_2 = 84 mL	Wood	Improved ^{14}C dating accuracy despite incomplete decontamination	[49]

environments from 30 % to 70 % relative humidity (RH) [57]. Following the same conditions, three marine archaeological wood-based artefacts (two gunstocks recovered from a Civil War blockade runner and a board from a 19th-century shipwreck) were treated [57]. Post-treatment, the samples became lighter (resembling natural wood) and some cracked due to advanced degradation [57]. $ScCO_2$ drying of severely degraded waterlogged elm from the mediaeval "Poznań" bridge (Lednica Lake, Poland), performed at 31.1 °C and 7.38 MPa, was found to be one of the most effective approaches for stabilising wood dimensions. It resulted in shrinkage below 10 % (one of the lowest), while preserving a high cell wall surface area and well-defined porous structure (resembling natural wood). Additionally, a notable increase in pore sorption volume was observed [60].

In the review conducted by Kaye *et al.* it is mentioned that a large collapsing cork bung (previously treated with PEG) and a bottle cork $scCO_2$-dried retained their dimensions without distortions [54]. Similarly, 23 archaeological corks were successfully treated using this technology: 8 wine bottle corks from a sank French frigate (Machault site, Canada); 8 cork bungs from whale oil barrels from a sank Spanish Basque galleon (San Juan site, Canada); a cork bottle inside a flacon bottleneck from the shipwreck (possibly the Queen Anne's Revenge, USA); and 6 waterlogged canteen corks from the H.L. Hunley confederate submarine (USA) [56]. The treatment was performed following the approach used for wood, but dried at 12.2 MPa and 55 °C. The treatment was deemed complete when no more methanol was extracted. Treated corks appeared lighter, maintained structural features, and while some shrinkage occurred in wine corks and whale oil bungs, no significant distortions were evident. Notably, the most degraded samples, including the canteen corks and the cork in the highly brittle flacon bottleneck, maintained their dimensions. For one specific bung, stress cracks were observed, but these could already have been there before treatment, masked by swelling and sediments. Further assessment of cork intercellular connection walls after drying confirmed the stability of the cell structure and the cleaning effect of $scCO_2$ [56].

As for protein-containing materials, Kaye *et al.* reviewed that birch bark samples treated under similar conditions showed some shrinkage and hardened, while jet and shale samples experienced severe delamination. Regarding bone $scCO_2$-drying, samples showed no cracking, though some shrinkage occurred; as for a treated antler, no changes were observed [54]. Osteological remains from La Marmotta (Italy) were dehydrated at 50 °C and 18 MPa with 7 % methanol, followed by a 2-hour methanol extraction to remove residues (at 50 °C and 20 MPa). The treatment resulted in successful water extraction and preserved the shape and dimensions of the bone, yet some traces were lost, and new striae were formed [59].

Regarding composite materials, archaeological wood samples with adhering bark maintained their integrity, showing minimal distortion after treatment (12 MPa and 50 °C with methanol) [54]. As for marine composite artefacts comprising wood or bone and metal were effectively dried without disassembly under the same conditions. Moreover, a sword handle (Duart Point site, Scotland) comprising wood, iron and a fibre padding with silver and gold wires, successfully endured $scCO_2$ drying, showing only slight shrinkage without cracks [54]. Additionally, eleven knife handles (comprising wood, metal, textile and leather) from the Makeshift Warship, presenting cracks and corrosion, were effectively dried and stabilised in $scCO_2$ (40 °C and 9 MPa, for 24 h) [55]. A challenging case study involved a compass base from the Duart Point excavation, which had a lead righting weight prone to corrosion in dry methanol solution. Therefore, treatment was carried out in $scCO_2$ at 12 MPa and 50 °C with methanol. Disassembly was unfeasible, so a copper alloy pin, contacting the lead weight, served as a sacrificial anode during solvent exchange and drying. This conservation methodology was highly successful, maintaining the items' dimensions and surface details without causing damage [54].

Overall, $scCO_2$ drying offers distinct advantages over traditional drying methods. It is a faster, compatible with fragile and composite

Table 9
– Summary of supercritical carbon dioxide ($scCO_2$) drying trials conducted on cultural assets, according to the given treatment conditions (reactor type/volume, temperature, pressure, exposure/depressurisation times, CO_2 and co-solvent flow, and co-solvents used), material treated, and the main outcomes for each material, with corresponding references.

Treatment conditions given by the authors (vol., volume; T, temperature; P, pressure; *et*, exposure time; *dt*, depressurisation time; Ø, diameter)	**Material**	**Results**	**Reference**
Autoclave vol. = 20 L (Ø20 × 65 cm), T = 50 °C, P = 12 MPa; methanol; slow depressurisation and cooling to room temperature	Composite/Miscellaneous	Wood samples with adhering bark, wood or bone and metal: Successfully dried with minimal shrinkage or distortion; dimensions and surface details preserved without damage	[54]
Samples submerged in methanol before $scCO_2$; T = 40 °C, P = 9 MPa, *et* = 24 h; calcium chloride to absorb methanol; *dt* = 6 h		Wood, metal, textile and leather: Effectively dried and stabilised	[55]
Samples pre-submerged in 250 mL incremental water/methanol mixture; final submersion with 20 g of dry sodium sulfate; $scCO_2$ trials: Thar Technologies stirred cell vol. = 250 mL, T = 55 °C, P = 12.2 MPa; 60 mL methanol, flow = 0.3 mL/min; *et* = until no methanol collected; *dt* = 6 h	Cork	Became lighter and retained structural integrity; minor shrinkage in wine corks and bungs; highly degraded samples retained their dimensions; cell structure remained stable; effective cleaning and drying	[56]
Two plant units were used: Muller vol. = 3 L & Luwar vol. = 8 L; Trials: (1) $scCO_2$ + 7 % methanol (w/w), T = 50 °C, P = 18 MPa, *et* = 2 h 40 min, flow: CO_2 = 20 kg/h, methanol = 1.8 kg/h; (2) $scCO_2$, T = 50 °C, P = 20 MPa, *et* = 2 h, CO_2 flow = 20 kg/h	Human remains	Successful water extraction; preserved bone shape and dimensions; formation of new striae	[59]
Samples: pre-submerged in 200 mL methanol; final submersion with 20 g of dry sodium sulfate; wrapped in polyester cloth in methanol; $scCO_2$ trials: T = 50 °C, P = 12 MPa, 50 mL methanol, flow = 0.25 mL/min, *et* = 30–36 h; *dt* = 6 h (≈2.03 MPa/h)	Metal Wood	Minimal shrinkage; no distortion Mesolithic wood: Became stable and handleable; minor shrinkage; stable after 3 years under 30–70 % RH Archaeological wood: became lighter, resembling natural wood; some exhibited cracking	[57]
E3000 Series Critical Point Dryer, T = 31.1 °C, P = 7.38 MPa; sample pre-submerged ~4 weeks in ethanol + 3 days in acetone		Waterlogged elm: Effective for dimensional stabilisation; shrinkage below 10 %, preserved porous structure and cell wall integrity	[60]

artefacts, requires no disassembly, and yields minimal modifications. Furthermore, extracted substances can be collected and analysed, enhancing the practical value of the process [54–56,58,59]. Table 9 gathers the conditions described in the reviewed studies and the main outcomes.

3.2. Impregnation applications

3.2.1. Treatment of paper (neutralisation/deacidification, strengthening and hydrophobisation)

$ScCO_2$ is a promising alternative for paper neutralisation/deacidification and strengthening [19,62,63,66]. As degradation increases acidity, it leads to cellulose depolymerisation and, consequently, damage. Traditional deacidification methods rely on impregnating the paper with alkaline agents dissolved in organic solvents, which may compromise the paper's strength [63,64,66]. $ScCO_2$ provides a less invasive approach, acting as a solvent and carrier for alkaline agents, thereby neutralising acidity and stabilising pH. Moreover, it could also be used to carry and diffuse strengthening agents into the paper's structure [19,20,64,66].

One of the earliest applications, developed by Perrut *et al.*, combined $scCO_2$ with ethanol for paper deacidification and reinforcement, successfully increasing pH, reducing yellowing, and enhancing porosity, enabling better reinforcing agent diffusion [61].

Several studies confirm $scCO_2$'s effectiveness in deacidification. Treatment with alcoholic solutions of magnesium alkoxides (methoxide and ethoxide) and magnesium methoxycarbonate (MMC, 8–30 wt%) was used to neutralise the acidity and extend the storage time of 100 % sulfite cellulose papers (pH of 5.5 and 6.3). Experiments were performed at 30–60 °C and 7–20 MPa in different steps of approximately 30 min: (1) extraction in $scCO_2$ with methanol (1 wt%), (2) 4/5 neutralisation cycles, (3) 4/5 $scCO_2$ wash cycles. The results showed that an effective neutralisation requires repeated treatments (one cycle leads to lower basicity) with 8 wt% methanolic solution of MMC, achieving a pH of 10.5 and a base stock of 300 mg-equiv kg^{-1}. Optimal conditions for this type of paper were identified at 11–13 MPa and 38–40 °C, with a CO_2 pumping rate of 300 cm^3 min^{-1} and a stirrer for agitation. This methodology was found to reduce the consumption of organic solvents and neutralising agents by nearly two orders of magnitude [62].

The effect of MMC was further explored in solutions containing Freon and alcohol in subcritical and $scCO_2$ (35–38 °C, 7–12 MPa) for the treatment of printed papers. Sacrificial samples included: 100 % sulfite pulp (5.9–6.4 pH); newsprint (8.8 pH); naturally aged printing paper (5.0–5.2 pH); mid-20th-century printed materials, books, and magazines (2.5–5.3 pH); and 2003–2005 newspapers (6.5–7.3 pH). The best results were achieved with alcohol solutions of MMC, ensuring a minimum 75-year preservation potential. Additionally, it is possible to adjust the alkali reserve level by varying the MMC concentration and the degree of CO_2 saturation. Ultimately, treatment in $scCO_2$ (at 35–38 °C, 10–11 MPa) and subcritical CO_2 (at 10–15 °C, 5–5.5 MPa) were found effective in achieving the minimum pH and alkali reserve values to neutralise the acidic paper [64].

Other alkali agents, such as magnesium acetate and bicarbonate, calcium hydroxide and propionate, and borax, were also tested for deacidification and strengthening acidic papers through $scCO_2$ [19,65,66]. A 1956 journal underwent a 30-minute pre-extraction at 35 °C and 7–13 MPa, followed by 40–120 min deacidification at 35–45 °C and 16–22 MPa with magnesium acetate and calcium hydroxide in water-ethanol solutions. $ScCO_2$ treatment notably enhanced pH levels and alkaline reserves without altering the paper's appearance, unlike immersion, and improved their mechanical strength [65]. Similarly, a 1989 newspaper treated with a borax solution of water and alcohol in $scCO_2$, following the previous approach (pre-extraction in the same conditions and deacidification at 40 °C and 20–22 MPa for 40 min), not only deacidified and reinforced the paper, but also cleaned it [66]. Further tests compared calcium propionate and magnesium bicarbonate

(in ethanol solutions) in $scCO_2$ (at 35–45 °C, 16–22 MPa, 20–30 min) to neutralise and strengthen 1953 and 1982 journal papers. In this case, a pre-treatment extraction was also conducted (35 °C and 7–13 MPa, for 30 min). Treatment with magnesium bicarbonate yielded higher pH and alkaline reserve, while calcium propionate gave better mechanical results. In both cases, $scCO_2$ shortened deacidification time compared to immersion [19]. A related study used calcium carbonate ($CaCO_3$, at 40°C and 22 MPa for 3 h) for deacidification and ethanol solutions of PEG or catechol for strengthening (at 40°C and 15 MPa for 1 h and 30 min). This neutralising agent presented a major improvement over previous ones (which are toxic and poorly soluble in $scCO_2$). It not only increased the pH of water extracts but also established a significant alkaline reserve within the paper. Regarding the strengthening treatments, while PEG proved ineffective, catechol improved most mechanical properties of artificially aged papers, likely due to hydrogen bonding with cellulose chains, effectively reinforcing the paper's structure [63].

Shin *et al.* explored $scCO_2$ as a medium for acetic anhydride mixtures to acetylate Hanji, a traditional Korean paper, to enhance its strength and hydrophobicity. Trials were carried out at 20 MPa with varying temperatures (120, 140 and 160 °C), exposure times (2, 4, 6, and 8 h), and acetic anhydride concentrations (10 %, 20 % and 30 % mol/mol, corresponding to corresponding to 90 %, 80 % and 70 % mol/mol of CO_2). At ~120 °C and 20 MPa, with 10 % (mol/mol) of acetic anhydride, and a reaction time of 4 h, $scCO_2$-mediated acetylation outperformed other acetylation processes. Despite minimal discolouration, under these conditions, surface hydrophobicity and tensile strength were enhanced within hours [20].

Overall, $scCO_2$ proved to be a versatile tool for paper conservation, enabling deep penetration of neutralising, strengthening and hydrophobic agents, reducing treatment time, minimising visual alterations, and enhancing strengthening effects [19,20,62–64,66]. Table 10 gathers the conditions described by the authors in the reviewed studies and the main outcomes for paper neutralisation/deacidification, strengthening and hydrophobisation.

3.2.2. Hydration and consolidation of wood

$ScCO_2$ was used to hydrate historic hard and softwood and modern hardwood samples to assess its conservation potential to increase moisture content and bending strength [67]. Experiments were performed on maple, white and red oak, zebrano and keruingat (for the hardwood species) and Scots pine (for the softwood species), on a 25 mL cell at 50 °C and 20 MPa for 45 min, with and without methanol as a co-solvent (2.5 and 5.0 mol%). A tissue saturated with distilled water or methanol solution was added to the chamber alongside the wood samples. Both pure $scCO_2$ treatment and methanol-modified treatment increased the moisture content, with 5.0 mol% solution yielding significant increases. Although higher co-solvent percentages slightly decrease mechanical strength (without reaching values below the initial strength), most samples exhibited improved bending strength. Additionally, while pure $scCO_2$ resulted in a lower moisture content increase, it still demonstrated the possibility of hydration in the presence of water. Among wood species, hardwoods responded better to $scCO_2$ hydration than softwoods, regardless of the specimens' age. Notwithstanding, the samples' age can significantly impact moisture absorption, especially in decayed softwood [67].

Consolidation trials in $scCO_2$ with poly(ethylene glycol) (PEG) and other consolidants were reviewed by Kaye *et al.,* and the results show very low consolidant retention [54].

Overall, the findings highlighted the potential of $scCO_2$ to stabilise the moisture content of historic wood while enhancing its mechanical strength [67].

3.2.3. Procedures to preserve stone and produce frescoes on historical buildings

Another application of $scCO_2$ in heritage conservation involves historical buildings and monuments. It has been used as an eco-friendly solvent for stone surface protective materials, providing a safer alternative to chlorinated fluorocarbon solvents previously used for solubilising fluorinated polymers, known for their hydrophobicity, stability to corrosive acids and UV radiation. Trials were performed in a 40 mL cell at 25–50 °C and 27.6 MPa, with a stirrer added to aid polymer solubilisation. The study was conducted with six fluorinated polymers and an elastomer, showing that all but the elastomer were soluble in $scCO_2$, with solubility decreasing with increased molecular weight, number of alkyl or polar groups, and hydrogen content. $ScCO_2$ thus allowed safe application of fluorinated polymers via spray, eliminating the need for harmful solvents [68]. Subsequently, Tuminello *et al.* tested a new application technology based on CO_2, acting as a solvent and spray agent for applying fluorinated resins to protect stones. In this experiment, a UNICARB® spraying application apparatus (by Union Carbide Corporation) intended for stone conservation was used. New fluorinated resins, namely perfluoropolyethers (PFPEs), were designed and tested in a collaboration between The DuPont Company and Consiglio Nazionale Delle Ricerche (CNR) to produce more effective water and oil-repellent coatings (no procedure conditions were specified). The PFPEs were dissolved in $scCO_2$, showing the viability of this technology. The resins were found to be water-resistant, breathable, long-lasting, and to have a protective effect against airborne pollutants. The novel spray process with CO_2 was deemed suitable to produce a thin and homogeneous coating without altering the appearance of the stone [69].

Another notable use of $scCO_2$ was in accelerating the production of frescoes, significantly reducing the time required for carbonation. Traditionally, frescoes relied on atmospheric CO_2 to carbonate calcium hydroxide in lime plaster, a slow process. In this investigation, calcium hydroxide was employed to form a protective coating over pigments on lime plaster, while a warm press method creates a calcium hydroxide base body. Three methods were tested, each ending with $scCO_2$ treatment at 50 °C and 9.5 MPa for 60 min. The first method, which involved only a warm press of calcium hydroxide and $scCO_2$ treatment, did not successfully retain the applied pigment, indicating insufficient carbonation. In the second method, calcium hydroxide or calcium carbonate powder was sprinkled over the pigment, followed by a second warm press and $scCO_2$ treatment. This approach was effective in immobilising the pigment but resulted in a whitening effect. The third and most effective method involved mixing pigment with calcium hydroxide powder (1:1), prior to application to the base body, followed by warm pressing and $scCO_2$ treatment. This produced an efficient carbonation layer that uniformly covered the pigment, like natural frescoes, while preserving the original red colouration of the pigment as the warm press step decreased the whiteness. Therefore, this fresco production method significantly accelerated the carbonation of calcium hydroxide [70].

3.2.4. Consolidation of foam-based objects

A pioneering study within the "PlasCO_2: Green CO_2 Technologies for the Cleaning of Plastics in Museums and Heritage Collections" project assessed the potential of $scCO_2$ technology as a safe and effective method to consolidate degraded synthetic latex-based foams, focusing also on designing a conservation treatment for a pair of heavily degraded goalkeeper gloves from *Museu Benfica - Cosme Damião* [17,71,72]. Mock-ups replicating the degradation of professional football player Robert Enke's gloves were produced using modern commercial materials. Various consolidants were tested, namely two ethylene-vinyl acetate copolymers such as EVA (pure) and Evacon-R™ (diluted and undiluted), polyvinyl acetate (PVAc), Paraloid™ B72 (PB72) and Regalrez™ 1094. The mock-up samples underwent $scCO_2$ treatments at 40 °C and 20–28 MPa for 120 min. The results indicate that $scCO_2$ treatment did not cause visible damage or significant changes in dimensions or chemistry, but consolidation success varied with experimental conditions. Some consolidants were not soluble in $scCO_2$, though all expanded into white amorphous rubbers during depressurisation, suggesting possible CO_2 sorption. Although both PVAc and Regalrez™

Table 10
– Summary of supercritical carbon dioxide ($scCO_2$) impregnation treatments applied to paper assets, according to the given treatment conditions (reactor type/volume, temperature, pressure, compression/exposure time, co-solvents and deacidification, strengthening and hydrophobisation agents used), treatment type (neutralisation/ deacidification, strengthening and hydrophobisation), and the main outcomes for each treatment, with corresponding references.

Treatment conditions given by the authors (vol., volume; T, temperature; P, pressure; *ct*, compression time; *et*, exposure time; →, followed by)	**Treatment type**	**Results**	**Reference**
T = 30–60 °C, P = 7–20 MPa, with a magnetic stirrer; $scCO_2$ extraction with methanol 1 wt% → 4–5 neutralisation cycles with alcoholic solutions of magnesium alkoxides (methoxide and ethoxide) and magnesium methoxycarbonate (8–30 wt%) → 4–5 wash cycles with $scCO_2$; *et* ≈ 30 min each	Neutralisation/ deacidification	100 % medium-porous sulfite cellulose (pH 5.5 and 6.3): Effective neutralisation after repeated cycles with 8 wt% methanolic MMC; optimal conditions at 11–13 MPa and 38–40 °C; reduced solvent and reagent use by nearly 100x	[62]
Reactor vol. = 480 mL, T = 35–38 °C, P = 7–12 MPa, *et* = 4 h; magnesium methoxicarbonate 7–30 wt% in alcoholic solution; post-treatment: neutralisation in subcritical conditions, T = 10–15 °C, P = 5–5.5 MPa, for recrystallisation of neutralising agent		100 % sulfite pulp (5.9–6.4 pH), newsprint (8.8 pH), naturally aged printing paper (5.0–5.2 pH); mid−20th-century printed materials, books, and magazines (2.5–5.3 pH) and 2003–2005 newspapers (6.5–7.3 pH): Alcohol-based MMC in $scCO_2$ and subcritical conditions achieved effective paper neutralisation and ≥ 75-year preservation potential	[64]
$ScCO_2$ extraction: T = 35 °C, P = 7–13 MPa, *et* = 30 min → deacidification: 40–120 min, T = 35–45 °C, P = 16–22 MPa; magnesium acetate and calcium hydroxide in water-ethanol solutions (50:50 v/v); magnetic stirrer	Neutralisation/ deacidification and strengthening	Highly acidic paper: Increased pH and alkaline reserve; improved mechanical strength	[65]
$ScCO_2$ extraction: T = 35 °C, P = 7–13 MPa, *et* = 30 min → deacidification: *et* = 40 min, T = 40 °C, P = 20–22 MPa; borax solutions; magnetic stirrer		Highly acidic paper: Deacidified, reinforced, and cleaned	[66]
$ScCO_2$ extraction: T = 35 °C, P = 7–13 MPa, *et* = 30 min → deacidification: *et* = 20–30 min, T = 35–45 °C, P = 16–22 MPa; calcium propionate or magnesium bicarbonate in ethanol solutions; magnetic stirrer		Highly acid papers: Magnesium bicarbonate yielded higher pH and alkaline reserve; calcium propionate enhanced strength; $scCO_2$ reduced deacidification time compared to immersion	[19]
Reactor vol. = 300 mL; $scCO_2$ extraction: T = 40 °C, P = 20 MPa, *et* = 30 min → deacidification: *et* = 3 h, T = 40 °C, P = 22 MPa, calcium carbonate in ethanol; strengthening treatment applied to acidic papers: *et* = 1.5 h, T = 40 °C, P = 22 MPa, 50 mL ethanol solution containing 40 % (w/w) poly(ethylene glycol) (PEG 400) or catechol		Neutral (hardwood chemical pulp and from a 50 % chemical pulp ±50 % softwood chemical pulp neutral cotton linter, respectively) and acidic papers: $CaCO_3$ improved pH and alkaline reserve compared to other alkaline agents; catechol enhanced paper strength, while PEG was ineffective	[63]
Reactor vol. = 25 mL, P = 20 MPa; varying T, *et*, and acetic anhydride concentrations: (1) T = 120 °C: *et* = 2, 4, 6 and 8 h, acetic anhydride 10 % (mol/mol), for *et* = 8 h also 20 % and 30 % were tested; (2) T = 140 and 160 °C: *et* = 8 h, acetic anhydride 10, 20, 30 % (mol/mol); magnetic stirrer	Strengthening and hydrophobisation	$scCO_2$ acetylation at 120 °C, 20 MPa, 10 % acetic anhydride and 4 h enhanced surface hydrophobicity and tensile strength	[20]

Table 11
– Summary of supercritical carbon dioxide ($scCO_2$) consolidation trials conducted on foam-based materials, according to the given treatment conditions (reactor type/volume, temperature, pressure, exposure/compression/depressurisation times, co-solvents and consolidating agents used), type of foam, and the main outcomes for each material, with corresponding references.

Treatment conditions given by the authors (vol., volume; T, temperature; P, pressure; *ct*, compression time; *et*, exposure time; *dt*, depressurisation time)	**Type of foam**	**Results**	**Reference**
Laboratory-scale reactor vol. = 33 mL, T = 40 °C, *et* = 120 min, discontinuous mode, with varying pressures: (1) P = 20 MPa, *ct* = 10 and 15 min, *dt* = 5, 15 and 25 min; (2) P = 28 MPa, *ct* = 10 and 15 min, *dt* = 10 and 15 min. For (1) 2 mL Evacon-R™ (25 % v/v in water), 1 mL Evacon-R™, 0.75 g Paraloid™ B72 (PB72) and 0.75 g EVA; for (2) 0.3 g EVA, 0.47 g PB72, 0.5 mL Evacon-R™, 0.5 g poly(vinyl acetate) (PVAc) and 0.5 g Regalrez™ 1094 were tested as consolidants	Latex-based foams	Caused no significant changes to the foams; successful consolidation varied with experimental conditions; only PVAc and Regalrez™ solubilised; PVAc deposited mainly on degraded areas; one sample (40 °C, 28 MPa, 120 min) showed slight shrinkage and stiffness; results required optimisation	[71]
Laboratory-scale reactor vol. = 33 mL, T = 40 °C, *et* = 120 min; varying P, *ct*, *dt*, PVAc MW, and the use of co-solvent (ethanol): (1) P = 28 MPa, PVAc MW 167 000, no ethanol, *ct*/*dt* = 7–11 min; (2) P = 36 MPa: PVAc MW 167 000 (no ethanol, *ct* = 8 min, *dt* = 2 min) and PVAc MW 83 000 (without ethanol, *ct* = 4–8 min, *dt* = 4.5–10 min; and with 1 mL ethanol, *ct* = 4.5–10 min, *dt* = 1–4.5 min). Magnetic stirrer used to aid consolidant solubilisation		No visual, dimensional, or chemical changes at higher pressures and faster depressurisations; PVAc MW 167,000 at 28 MPa and 40 °C consolidated one foam but was not reproducible; PVAc MW 83,000 at 36 MPa, 40 °C, and 5 min depressurisation led to reproducible results with uniform consolidation and enhanced cohesion; longer depressurisation less effective	[17]
Laboratory-scale reactor vol. = 33 mL, T = 40 °C, P = 25 MPa, *et* = 60 min, *dt* = 30 sec, static mode; consolidant: 0.25 mL mixture of 3-aminopropyl(diethoxy)methylsilane (APDEMS) and n-octyltrimethoxysilane (OTMS) (1:1 v/v), with magnetic stirring bar	Polyester-based polyurethane (PUR-ES) foams	No visual changes; 16 % weight gain and uniform in-depth consolidant distribution; $scCO_2$ formed a thin film without blocking pores, improving flexibility and structural reinforcement over spray application	[21]

were solubilised in $scCO_2$, only PVAc was detected on the sample surfaces, yet only in the degraded portions of the foam. This may be attributed to the precipitation of the consolidant on the foam during depressurisation, the highly porous morphology of the degraded surface, or chemical bonds between the consolidant and the degraded surface being favoured over less degraded areas. One PVAc-treated sample (at 40 °C and 28 MPa for 120 min) showed reduced dimensions and increased rigidity (by touch). While promising results were achieved, the authors stated that additional research was necessary to ensure reproducibility and effectiveness [71].

Further investigation involved testing PVAc with different molecular weights (MW, 83,000 and 167,000) at 40 °C and 28 and 36 MPa, for 120 min, along with 1–11 min of depressurisation. Ethanol was used in some trials to enhance consolidant solubility. No visual, dimensional, or chemical alterations were identified at higher pressures and faster depressurisations. A satisfactory result for MW of 167,000 was only obtained in one sample (without co-solvent, at 40 °C and 28 MPa, with a compression of 10 min, 120 min of exposure and 10 min depressurisation), as no reproducible results were achieved. In this sample, the consolidant maintained the original appearance and flexibility of the foam while increasing the surface cohesion. It was detected on the top surface, within the core, and in lateral layers of the treated sample. However, similar trials failed to reproduce these results. Increasing pressure to 36 MPa and reducing depressurisation to 2 min led to poor outcomes. For MW of 83,000, increasing the pressure up to 36 MPa (at 40 °C) leads to reproducible results, with optimal conditions requiring 5 min of depressurisation. These conditions enable homogenous impregnation of the consolidant within the foam, enhancing cohesion and reinforcing the structure without altering its appearance. Reducing depressurisation to 2–5 min caused surface deposits, while longer times led to poor consolidation [17].

$ScCO_2$ was also explored to consolidate polyester-based polyurethane (PUR-ES) foams with a 50/50 mix of alkoxysilanes: 3-aminopropyl(diethoxy)methylsilane, APDEMS; and n-octyltrimethoxysilane, OTMS. Compared with traditional spray application (10 % v/v in hexamethyldisiloxane), $scCO_2$-assisted treatment (at 40 °C, 25 MPa, 60 min) caused no visual changes but resulted in greater weight gain (16 %). ATR-FTIR and SEM-EDS analyses showed a more consistent and in-depth distribution of the consolidant in the samples treated via $scCO_2$, while spray-treated samples exhibited inconsistent and mostly superficial deposition. Microscopically, $scCO_2$ consolidation produced a thin and textured film covering the cell struts without obstructing the cell windows. Handling of the samples also revealed improved flexibility in $scCO_2$-treated samples, suggesting enhanced structural reinforcement and greater consolidation effectiveness than spray application [21]. Ongoing doctoral research by Soares continues to explore the potential of this technology.

Overall, $scCO_2$-assisted consolidation shows strong potential as an alternative to traditional methods for treating synthetic latex-based and PUR-ES foams ($scCO_2$ conditions and main results are summarised in Table 11).

4. Discussion and conclusion

Cultural heritage conservation seeks continuous improvement of the methodologies and materials used. With the growing demand to reduce the use of hazardous products, research is increasingly focused on developing *greener* solutions [3,6]. Among these, CO_2 technologies have emerged as a sustainable option, providing safer and often more efficient treatments for cultural heritage [19,36,37].

This review showed a broader and more diverse use of $scCO_2$ in cultural heritage conservation compared to liquid CO_2, which can be attributed to the unique properties of $scCO_2$. Above the critical point, CO_2 exhibits liquid-like densities combined with gas-like diffusivity and viscosity, allowing it to penetrate complex porous matrices while efficiently dissolving and transporting solutes. Small variations in

temperature and pressure within the supercritical region enable fine-tuning of its solvent power, transitioning between gas-like and liquid-like behaviour [10,76]. This tunability, together with its broad solvation capacity for non-polar and some polar low-molecular-weight compounds, allows for adjustment of solvent strength and selective interaction with target substances compared to liqCO_2 [10,77]. Consequently, scCO_2 can be effectively adapted for many processes, offering advantages in efficiency and penetration that may not be achievable under liqCO_2 conditions.

It is important to recognise that the outcomes reported in the reviewed studies cannot always be directly compared or reliably interpreted regarding the reasons behind specific results. The studies involved a wide variety of materials (including glass, metal, textiles, leather, wood, cork, human remains, plastics, etc.) with differences in composition, structure, degradation state, and contaminant interactions. Additionally, the experimental conditions varied significantly, including factors such as pressure, temperature, exposure time, compression and depressurisation rates, co-solvents, and pre- or post-treatments. These variables greatly influence the effectiveness of treatments; even within the same study, different outcomes can be observed, and detailed explanations for these differences are often lacking. As a result, this review focused on reporting outcomes based on the specific conditions of each study rather than drawing possibly inaccurate connections between different articles. Therefore, the use of dense CO_2 processes in cultural heritage and the outcomes obtained from each treatment on different materials are summarised as follows. LiqCO_2 has emerged as an effective cleaning method for metals, glass [22] and collagen-based materials (caution is necessary for specimens with paint or lacquer layers due to potential damage) [13,22,23]. Similarly, it was effective in removing fat/oil residues from leather-based materials [18,22], though results were inconsistent for the removal of wax [13,23]. The effectiveness of liqCO_2 for textiles varies across studies, likely reflecting differences in textile composition (e.g., wool, silk, embroidery), treatment parameters, and the specific contaminants targeted. While liqCO_2 safely and effectively cleaned some textiles [22,24], in other cases, it resulted in material loss and failed to remove contaminants [16]. Moreover, for plastics, liqCO_2 proved highly effective in cleaning a Bakelite box [22]. However, Bartoletti *et al.* reported contrasting results for PMMA sheet cleaning, suggesting that, among multiple factors, the effectiveness of the treatment may depend on the polymer's degree of crystallinity [14]. These findings indicate that further studies are needed to evaluate its application across the diverse morphologies and properties of plastic materials. Lastly, it has proven ineffective in removing intervention residues (oils, paint, varnishes and resins) from wood [13,22,23,31]. In terms of collections chemical decontamination - namely the removal of biocides and heavy metals - while liqCO_2 significantly reduced contaminants in wooden items, results on textiles were again inconsistent, particularly for the removal of heavy metals [13,15,22,26]. Interestingly, liqCO_2 was able to reduce moulds, yeasts and bacteria from textiles, albeit not entirely [30].

The use of scCO_2 in cultural heritage has been focused on two main processes: extraction and impregnation. It proved highly effective in cleaning cellulose-based materials [13,34,73] and textiles (undyed, naturally dyed and embroidered with metal threads) [16,24,32,36,37]. However, a study noted it induced damage to cotton fibres [37]. It was ineffective in cleaning wood [13,34], protein-containing materials, ceramics and metals [33,34], and damaged plastics (PMMA, HDPE, HIPS, PVC and XPS) [14,35]. When addressing chemical decontamination treatment, scCO_2 was highly effective for textiles [13,33,34], wood (even with coatings applied) [38,39,43] and collagen-containing objects [13,34]. However, modifiers such as ethanol and chelating agents are required for the removal of arsenic [13,33,34,40,74]. For microbiological decontamination, although pure scCO_2 was effective in contemporary papers [48], it was partially effective for ancient papers and some textiles. In these cases, the addition of co-solvents was essential to enhance the decontamination rate [24,46,47]. In extraction applications, scCO_2 has been successfully used on burial specimens and archaeological artefacts to remove contaminants as a pre-treatment step for plasma oxidation and carbon dating [49–52]. It has also been applied for degreasing, showing successful results for protein-containing materials [13,34], but ineffective for osteological bones [53]. As a drying treatment, it was effectively used on composite objects and metals without causing distortions [54,55,57]. It was also successful on cork, even for highly degraded samples [56], and preserved the porous structure and dimensional stability of wood [57,60]. However, changes were observed when treating human remains [59]. As for impregnation processes, it has been successfully used for neutralising/deacidifying [19,62–66] and strengthening paper [19,63,65,66], as well as in a hydrophobisation process [20]. Moreover, scCO_2 hydration of wood has shown effective results, especially for hardwood [67]. Regarding consolidation treatments, this technology was found suitable for stones [69] and highly effective for foam-based materials, allowing for an in-depth distribution of the consolidant within the foams [17,21,71,72]. Sequential treatments with both liquid and scCO_2, have also been employed on textiles to enhance cleaning effectiveness, with and without co-solvents, yielding promising results [16,32,36,37].

More specifically, in the past 5 years, research has increasingly focused on treating plastics, paper, textiles, wood and composite materials [17,20,21,27,28]. Moreover, CO_2-based treatments have been centred in applications like cleaning (both in liq- and scCO_2 [14]), decontamination and disinfection (using liqCO_2 [27,28]), consolidation/impregnation [17,20,21,70–72] and drying [60] (via scCO_2). These studies highlight the growing interest in these technologies and the effort to provide substantial evidence of their outcomes so that they can be used as standard methodologies.

Although exposure to CO_2 at low concentrations poses few risks to humans, the use of large volumes of CO_2 presents unique hazards. Surprisingly, none of the reviewed studies provide specific recommendations or safety protocols, despite the experiments involving pressurised equipment and potentially large CO_2 volumes. This lack of information represents a critical omission, as safety procedures are essential not only to protect operators but also to ensure that these treatments can be realistically applied in conservation practices. In the event of a gas leak, CO_2, being denser than air, can accumulate near the floor and gradually rise, creating a severe risk of asphyxiation. For this reason, laboratories must be equipped with proper ventilation or CO_2 recovery systems, and large-scale facilities should include CO_2 sensors for continuous monitoring. Furthermore, such treatments should only be conducted by trained personnel using appropriate protective equipment (particularly safety glasses) and following rigorous high-pressure safety procedures. In addition to these safety considerations, the reviewed literature shows considerable variability in the level of methodological detail reported. Some studies provide thorough descriptions of specimen protection for the treatment, such as wrapping them in fabrics or securing them within the chamber to prevent damage and sample loss [26,30,35,56,57], a feature that does not represent standard practices. In contrast, some authors omit fundamental parts of the methodology, such as key procedure conditions. In addition to the reactor volume, essential parameters, including pressurisation time, temperature ramping, depressurisation protocols, and other variables that strongly influence the phase behaviour of CO_2, are often not reported. This lack of information significantly limits the reproducibility of treatments and the possibility of scaling up processes, particularly when co-solvents or impregnation agents are used. These omissions highlight the need for closer collaboration between conservation professionals and specialists in physical chemistry and thermodynamics, in order to establish more rigorous and standardised protocols for the application of dense CO_2 in cultural heritage conservation. The volume of the chambers reviewed varied widely, ranging from 4.5 mL (laboratory scale apparatus [16]) to 83 L (industrial facility [45]). Many different chamber sizes are available, and they can also be designed to meet the specificities of cultural heritage. Although costs significantly influence decisions regarding the

acquisition of such facilities, given that they can be highly expensive [22,23], some authors state that the costs are reasonable [74], showing that it can reduce the consumption of conservation materials by nearly two orders of magnitude [62]. Furthermore, comparisons with traditional methods showed that CO_2-based treatments can enhance the long-term stability of paper and some textile specimens [37,63,64]. This can lead to a reduction in short-term treatments, making the conservation procedures more sustainable. Considering all these factors, CO_2 technologies emerge as attractive alternatives and could represent a worthwhile long-term investment. Nevertheless, it is important to point out that most studies do not include long-term assessments of the treatments performed, reinforcing the idea that CO_2-based methods remain a niche in cultural heritage. Despite the success achieved with several applications, additional research is needed to address this information gap.

While this review focuses only on dense CO_2 technologies, it is worth noting that CO_2 in gaseous and solid phases have also been explored for heritage applications. Solid CO_2, namely in the form of dry ice and snow, has been the subject of growing interest for its potential for cleaning. A subsequent review will gather the experiments conducted with these CO_2 technologies, highlighting their outcomes and assessing their relevance to the conservation field.

CRediT authorship contribution statement

Joana Lia Ferreira: Writing – review & editing, Methodology, Funding acquisition, Conceptualization. **Isabel Pombo Cardoso:** Writing – review & editing, Funding acquisition. **Teresa Casimiro:** Writing – review & editing, Methodology, Funding acquisition, Conceptualization. **Angelica Bartoletti:** Writing – review & editing, Writing – original draft, Investigation. **Carolina Viana:** Writing – review & editing, Writing – original draft, Investigation. **Inês Soares:** Writing – review & editing, Writing – original draft, Visualization, Methodology, Investigation, Funding acquisition, Conceptualization.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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