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Review Article

A Review on Conservational Methodologies of Tangible Cultural Artifacts from Environmental Corrosion

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Abstract

Tangible cultural heritage are invaluable assets inherited from our ancestors, encompassing transformative skills, culture, tradition, knowledge and practice, passed down by generations to generation. It is said to say that, these assets are on the brink of deterioration, and vandalism from both pernicious natural forces and relentless time laps. There is an urgent need of preserving and transfer of these treasures to the future generations. The main objective of our study is to provide basic knowledge for the conservation of cultural artifacts. With this investigation, we lay stress on the significance of cultural artifacts, delve the factors influencing corrosion, talk about cleaning methods and stressing the use of inhibitor or protective coating to shield them from further decay. In this study emphasizes the urgent need of development of new methodologies and strategies to safeguard these assets from ruinous events. In addition, it also present ongoing efforts applied in transmission and preservation of these metallic artifacts in their original form.

Keywords: Conservation, Corrosion, Cultural Heritage, Preservation, Artifacts, Prevention

Introduction

Cultural heritage has tangible assets such as artifacts, monuments, buildings and, intangible include customs, practices, knowledge, and skills, that was handed down from each generation to the next generation. The tangible cultural artifacts are a legacy of physical artifacts, inherited from the past, and play a role as a bridge between past and future through developed approaches by the collection of present data heritages (Eppich and Grinda 2019). However, there were many threats to cultural heritage such as natural disasters, armed conflicts, inadequate management, and lack of resources, which always captured the significant attention of the world. Perhaps, another protentional threat involved in the deterioration of cultural heritage is climate change which exacerbates the expected rate of decay. Climate change influences the frequency and intensity of destructive events including drought, flood, and land-slides, which aggravate the physical, chemical, and biological processes involved in decaying by affecting the chemical composition and structure of the material (Sesana, Gagnon et al. 2021). Therefore, a sustainable approach and considerable struggle were needed for the conservation and maintenance of tangible cultural artifacts. In addition to the preservation of remains of the past for the benefit of future generations, a common heritage policy and legislation were needed in global policies.

The conservation of monuments and works of art appeared in Europe first time in the 15th century, which was addressed in 1907 as international law. Moreover, the international treaties and texts were first time developed by UNESCO and other international agencies in 1954. According to article 4 of the UNESCO World Heritage Convention, it was stated that the duty of each state party of the convention is to play their role in the identification, protection, conservation, presentation, and transmission of cultural and natural heritage to the future generation (Högberg and Holtorf 2021). Therefore, there is an urgent need to take action to actively preserve historical, archaeological, and art objects from further decay, corrosion, and deterioration. However, significant preservation challenges have been observed based on diversity in the originating area of cultural heritage metals. Since the last decades, it's become a mandatory task to address such challenges, to which science has provided the answer by developing innovative materials and methodologies. This article will focus on details studies of developed methodologies and futuristic approaches for the conservation of metal artifacts from corrosion (Watkinson 2010).

Conservation of cultural heritage

Cultural heritage is a powerful catalyst of regeneration for future generations, which, needs significant efforts for its protection and management of related information. Because, it shows the degree of development of civilization, that is passed from different stages in prehistoric periods. Conservation and restoration of cultural heritage has been accepted as a poorly documented discipline, which poses a hurdle in establishing new standardization approaches for the prevention of elements of heritage (Watkinson 2010). In fact, cultural heritage contributes positively for the attractiveness of the regions. However, it also provides the basis for marketing strategies, creates opportunities for employment, generates fiscal revenues, and provides a foundation for creativity and innovation. Therefore, it is necessary to develop awareness among people by organizing different activities such as seminars and conferences. In this case, research and academic organizations are seamlessly, playing their role very actively by generating concrete solutions and strategies with the collaboration of disciplinary and interdisciplinary institutions to tackle the complex factor stimulating the sustainability crisis (Yarime et al., 2012). To be acknowledged, Raadvad Center established 6-month educational training to produce skilled craftsmen, while the Royal Academy of Fine Arts, and School of Architecture was educating architects which played an important role in the restoration process. The main aim of educational institutes was to give skills to the students with an understanding of architectural, historical and technical knowledge, which helps in the investigation, and analysis of specific features of the excavation site (Pickard 2001). In addition, Italy and the French Ministry of Foreign Affairs promoted the mission with a cultural corporation which deal with both universities and research centers to engage in projects focused on ethnology, ethnography, archaeology, and history (Declich and Pennaccini 2014).

Corrosion

Archeological metals objects constitute our main information source about valuable cultural remains from past generations, their corrosion behavior, and destructive damage to metal samples (Bertholon 2007). Corrosion to ancient metallurgy is a destructive attack by chemical or electrochemical reactions in extensive environmental conditions, which can be found in everyday life. Hence, metals are destroyed by converting them into oxides or other corrosion products (Robinson 1982). Most often knowledge about corrosion is not studied right after the excavation of archeological metals, especially when equilibrium is reached over the centuries. Moreover, many factors influence the rate of corrosion after excavation such as; exposure to oxygen pressure after removal from many geological layers of buried artifacts, rainfall as outdoor exposure, organic pollutants indoors (Bernard and Joiret 2009) and microbiologically influenced corrosion (MIC) (Telegdi et al., 2017) also deteriorate them. Different species of metal oxidizing and reducing bacteria, such as Sulfur-oxidizing, Iron-reducing, Iron and Manganese-Oxidizing bacteria include Sphaerotilus, Pseudomonas aeruginosa, Gallionella, Leptothrix, and Crenothrix deteriorate metallic objects. The most critical situation is the presence of MIC forming microorganisms, which don’t show their presence, however, deteriorate the surface. This microorganism oxidizes the ferrous iron into ferric iron such as Fe(OH)3 or make ferric chloride, which causes pits on the metal surfaces. Another corrosive metabolite excreted by the microbes is organic acid such as acetic acid and butyric acid, inorganic acid (sulfuric acid), and other metabolites like fatty acids as a byproduct. These acid-producing bacteria show fermentative activities which help in lowering the pH of the biofilm into acidic and act as a major cause of corrosion (Telegdi et al., 2017, Al-Shamari, et al., 2013, Burt et al., 2015). Therefore, the conservation of each piece of our heritage needs much care as well as the utilization of corrosion inhibitors to make them able to both archeological studied and displayed to the public. Hence conservation and restoration treatments of artifacts become the main purpose of conservation professionals. Of great importance, what types of new coating material and corrosion inhibitors could be more suitable and have long-term protective impacts on them? Different types of suitable protective techniques and materials have been applied for diagnoses and treatment of metallic artifacts from heritage to restore their shape, collect their surface and fabrication detail (Watkinson 2010). Environment, alloy composition and the mechanisms of ionic, and electron transfer during corrosion dictate the nature of the corrosion layer as well as the passiveness or instability of the corrosion products formed

Conservation of Metal
Cleaning

To restore the excavated historical artifacts to their original surface, professionals have to face very common problems of removing the incrustation covering. This hard layer of crust is made up of stones, soil, and oxides, which need special treatment for its removal. Cleaning is a very difficult process in the conservation of cultural artifacts using conventional methods like hard abrasives. For the most part, we lost the details about revealing the original surface of the object using such treatments as morphology of artifacts. As a matter of course, cleaning become the most delicate, important, and active role of action in the preservation and conservation of the aesthetic appearance of cultural artifacts. Moreover, the behavior of post-corrosion became the most severe problem after the excavation of metal, which survived for thousands of years buried in the soil. The rate of catalytic effect of chlorides corroded the metal in a few years completely after its unearthing. In the past, metal objects were commonly used in ornaments, coins military items *etc* (Baglioni, Poggi et al. 2021). Thus, different type of unwanted materials is required to be removed including dirt, paint, stain, salts or materials that were used by the previous restoration process, to restore the original artistic surface without vandalizing it. However, the traditional approach to the cleaning process requires the removal of a wide variety of very selective materials such as natural protein, polysaccharides and synthetic resins include, acrylic, and vinyl (Baglioni, Poggi et al. 2021). However, the traditional approach of cleaning by using non-confined materials such as cotton swabs or brushes or poorly confined materials containing polymers such as polyacrylic acid or cellulose left some deteriorative effects such as scarce, lack of safety to artwork, possible leftover residues of polymers on the surface (Wolbers 2000, Stulik 2004, Baglioni, Poggi et al. 2021).

Therefore, recent advances are required to preserve cultural heritage by using such material that overcomes the limitation and reduceds the drawbacks of usage of cleaning materials. In recent years, nanoscience and materials revolutionized the cleaning of historical artifacts (Mastrangelo, R., et al., 2024). Nanostructured fluids (NSFs) as a colloidal system have peculiar properties of surfactants, solubilized the non-polar, low molecular weight molecules such as fatty acid, triglycerides, and hydrocarbons in the inside of hydrophobic micelles core (Baglioni, Poggi et al. 2018, Bartoletti, Maor et al. 2020). Which was found responsible for detergency in artistic surfaces. It was found that water-based NSFs showed promising results in the dewetting process by removing hydrophobic polymeric coatings of adhesives, varnishes, consolidants etc. As solvent and surfactants interact synergistically in NSFs material and show hydrophilic properties. Which swollen up and softened the coating films consisting of polymeric aqueous latex containing a significant quantity of amphiphilic additives (Baglioni, Montis et al. 2017, Baglioni, Montis et al. 2018, Baglioni, Alterini et al. 2019). In addition, it was found that nonionic surfactants have more dewetting ability compared to ionic. Similarly methyl capped ester ethoxylates showed more hydrophobicity compared to ethoxylates (Baglioni, Montis et al. 2017, Baglioni, Poggi et al. 2018, Baglioni, Alterini et al. 2019, Baglioni, Guaragnone et al. 2020, Bartoletti, Maor et al. 2020). Moreover, polymer-based gels have also shown controlled cleaning of sensitive surfaces. Highly viscous polymeric dispersions and gels formed by confining the liquid systems such as gellan or agarose were used recently in restoration practices, however, had some limitations on usage at irregular surfaces (Domingues, Bonelli et al. 2013, Casoli, Di Diego et al. 2014, Mastrangelo, Chelazzi et al. 2020).

To overcome such limitations, highly viscoelastic polymers or a combination of polymers, having a gel or gel-like network containing a structure of covalent or physical bonding, with highly effective, homogenous adhesion properties and control in the release of solvent are required. Recently, poly (hydroxyethyl methacrylate) based gel in combination with linear chains of polyvinylpyrrolidone makes a semi-interpenetrated network, which was used as a highly retentive, viscoelastic gel, loaded with aqueous solutions. These pHEMA/PVP-based gels are 2 mm thick sheets, easy to handle, and have been successfully utilized for the delicate cleaning of canvas, murals, and paper artifacts. They selectively remove unwanted layers from water-sensitive surfaces (Domingues, Bonelli et al. 2013, Bonelli, Montis et al. 2018, Chelazzi, Giorgi et al. 2018).

Prevention

The prevention of historical metallic artifacts involves employing measures to protect and safeguard these items from deterioration, damage, or loss due to environmental effects (temperature, humidity), mishandling, or security lacks. For indefinite preservation of historical artifacts, there has been a need to use stabilizing material for conservation purpose rational for many years. Since unstable metals are merely prevented from corrosion compared to metals which are inherently stable in ambient conditions, however, require some degree of the environmental control. Therefore, any change in environment could accelerate the decaying process, which favors the conservation process by intervening using protective materials to attain stability (Ashley-Smith 2013). Various strategies are implemented to ensure the longevity and preservation of these valuable objects.

Conservation by coating

The conservation of metallic artifacts through coating involves the application of protective layers on the metal surface to shield it from environmental factors that are involved in the deterioration process. Moreover, the protective layer of coatings material should be stable and not affect the surface color or damage the surface, because of external forces (Heat, Light and Moisture). To maintain the integrity and aesthetics of metallic artifacts, various coating such as lacquers, waxes, or other specialized protective layers were applied in ancient times. Moffet *et al*, stated the use of two layers of Incralac ((benzotriazole, methyl methacrylate copolymer) and one finishing layer of Renaissance wax (microcrystalline-polyethylene wax mixture) as a corrosion protection layer on the Benin commemorative figure in 1948 made up of bronze, belongs to hollow cast male head from late 15^{th} to 16^{th} century. However, adverse effect of environment and low mechanical strength was observed (Moffett 1996).

Some other examples of coating material are Paraloid B-72, an acrylic resin consisting of a 7:3 ratio of ethyl methacrylate and methyl acrylate (Feller 1961). Moreover, polyvinyl acetate emulsion and Primal AC-33 compounds are widely used for repairing and protecting metallic artifacts. Although, these acrylic resins undergo photo-oxidation reactions has been found to damage the surface of artifacts by the effect of sunlight (Koob 2009). These coating of acrylic resins become so unstable that these protective layers turn yellow with the passage of time, and even start to crack with the effect of light and heat (Davison 1984, Winther, Bannerman et al. 2015). It is common to coat metal (tin, zinc, copper lead, and their alloys) surfaces with Azole compounds (thiazole, benzotriazole, imidazole, and thiadiazole), amines, and Schiff bases as corrosion inhibitors (Hollander and May 1985). However, these protective heterocyclic compounds were found less toxic, more effective, and stable for copper and its alloys in neutral and alkaline media but less protective in acidic conditions (Khan, Shanthi et al. 2015). According to some already published studies, plant extracts, and oil were preferred over wax among natural protective coating, which also has antibacterial and antifungal properties (Behpour, Ghoreishi et al. 2012). In addition, amino acids like cysteine derivatives, methionine, glycine, tannin, or Isatin make complexes with metal surfaces and work as corrosion inhibitors (Barouni, Kassale et al. 2014). Some positive results have been found with the carboxylate group containing derivatives as a non-oxidizing inhibitor of metal artifacts. In addition, coting of objects made up of aluminum with poly(3-octylpyrrole) and copper, bronze, and silver with poly(3-amino-1,2,4,- triazole) compound has also shown effective results (GENÇER 2021). Another class of polymer as coating material containing flour group such as polyvinylidene (PVDF) has proven to be optimal for protection are often associated with silane. These fluoropolymers also show water-repellence properties as well as the presence of a C-F bond makes them more resistant and highly photo-stable (Sadat-Shojai and Ershad-Langroudi 2009, Figueira, Silva et al. 2015).

However, low adhesion properties to metal surfaces were also reported which can be enhanced by the addition of other components such as paraloid B-44 as acrylic polymer. The major hindrance while using fluoropolymer is their insolubility in common solvents as well as their removal problem (Muresan, Oniciu et al. 1992, Aufray, Josse et al. 2019, Masi, Josse et al. 2019). Therefore, these polymers need further modification to overcome these obstacles. The combination of sol-gel silica methyltrimethoxysilane (MTMS with fluoropolymer 3-glycidoxypropyltrimethoxysilane (GPTMS) gives a remarkable example applied on copper alloy by Bescher and Mackenzie. The properties of cross-linking the organic (Si-O) part and inorganic part permit the opening of the epoxy ring and allow the material to adhere to the surface of metallic artifacts (Ling, Maiqian et al. 2008, Meng, Mueller et al. 2014). Hence, siloxanes and fluoropolymers showed a high affinity with transition metals, which makes them good coating material alternatives to BTA. However, these formulations are not considered as best choice as they need a specialized operators to synthesize and apply, especially their removal becomes challenging if applied to archaeological artifacts (Artesani, Di Turo et al. 2020). Advancements in the field of nanotechnology opened new doors in the protection of heritage artifacts using nanoscale material to reduce cracks inside the artifacts, protect the surface by developing chemical resistance and enhance the mechanical strength (Moffett 1996, Figueira, Silva et al. 2015).

A study proposed by Faraldi *et al* (Faraldi, Cortese et al. 2017) showed excellent coating of diamond-like carbon (DLC) nanostructure with 200 nm thickness on the surface of the bronze sample. Moreover, no extraneous compound was observed on the surface after the removal of coating, which shows no modification to the surface. However, the limitation of DLC coating was its deposition by plasma-enhanced chemical vapor (PECVD) methodology, which needs proper expertise and because of the small chamber, the size of the object also does matter. The use of layered double hydroxide (LDH) has also shown promising results by slowing down the process of photo degradation of coating material. It was observed that the coated material 2-mercaptobenzothiazole (MTB) in polyvinyl alcohol show photo-aging under UV radiation, which is encapsulated into LDH nanocarrier forms limits the process of photo aging (Salzano de Luna, Buonocore et al. 2018)). Recently, bio-based corrosion inhibitors and green coating materials have proven novel coating materials for the conservation of artifacts from corrosion, fungal attack, and deterioration. Studies on extracts of plants or organisms (El-Haddad 2013), or their amino acid-based products (Ismail 2007, Wang, Wang et al. 2015) had shown anti-corrosive properties such as biofilm of oxalic acid formed on bronze material by using a fungal strain which protects the copper corrosion by converting it into a less soluble and more stable form. Albini *et al*, produce a biofilm by dispersing *Beauveria bassiana* a fungal species of class *Soradariomycetes*, into the water with supplementation of nutrients and jellifying agent. After two weeks of the experiment, samples were cleaned with fungal residues obtained from bio-patina. The authors compared the results with BTA-based treatment and found that bio-based treatment was most effective against corrosion (Albini, Letardi et al. 2018, Sloggett 2022). It was observed that biofilm converted all the atacamite ($Cu_2Cl(OH)_3$), into a homogeneous layer of copper oxalate which protects the metal surface from corrosion.

Ethical consideration

Prior to all above, it is most important to establish guidelines based on ethical and moral values to conserve cultural and historical artifacts (Caple 2008). Because, the conservation of historical cultural artifacts does not only need technical expertise but also ethical consideration, to ensure the authenticity, integrity, transparency, accountability, sustainability with respect, equity, exclusivity, and legality in the acquisition of artifacts. There are some national guidelines, which both guide and constrain conservation practices ethically. These generic rules help to minimize the intervention with objects, and develop reversibility in conservational agents and treatment methodologies to maximize the retention of cultural integrity with complete information on objects (Watkinson 2010).

Conclusion

In conclusion, the conservation of historical cultural artifacts necessitates a delicate balance between preserving their authenticity and ensuring their longevity for future generations. In this endeavor, the implementation of new strategies and the development of new material to be used in cleaning artifacts, inhibiting of corrosion, and coating the surface are essential. However, ethical considerations must guide these conservation efforts, prioritizing respect for cultural heritage, and transparency, and sustainability. To uphold the integrity of these historical treasures, we also need to develop reversible conservation methodologies, transparent decision-making strategies, and allow them to be accessible to diverse audiences by prioritizing equity and inclusivity. Insurance of these steps will benefit the all-marginalized communities and stakeholders. In essence, the conservation of metallic artifacts still demands a holistic approach, which integrates ethical consideration and technical expertise, which can safeguard these invaluable treasures of human history for generations to understand the past and go deep down to shape future sustainability and inclusivity.

Conflicts of Interest

The authors declare no conflict of interest.

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