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DOTTORATO DI RICERCA
IN SCIENZE DELLA TERRA

Dottorato di ricerca in: Scienze della Terra (XXXV ciclo)
Curriculum B: Scienze applicate per la protezione dell'ambiente e dei Beni Culturali

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1. Research activity

The main objective of the Project AMAART is to contribute to the development of an easy and affordable Preventive Conservation (PC) defined as all measures and actions aimed at avoiding and minimizing future deterioration or loss of cultural heritage from environmentally induced damage. Within the PhD Project AMAART, complementary research activities are being carried out to develop materials and devices for the mitigation and the monitoring of some of the most dangerous pollutants in museum environment.
Granting the optimal environmental conditions around art objects helps to minimize the pollutants amount in the microclimate inside the storage items and that derived from the emissions of the packaging materials (wood, paperboard, glue, etc.) thus eliminating the need for periodical interventions. Pollutant monitoring is important as a PC procedure in cultural heritage environments. The pollution monitoring tools designed for human safety applications can be used in museum environments but do have some important limitations. Art objects can visibly react to very low pollutant concentration, lower than that typically measured to assess a safe environment for human beings. Furthermore, since the market is focused on the purification of the indoor air from the pollutants affecting human health, targeted tools for the monitoring and the mitigation of those pollutants most dangerous for art objects are not yet available.
The Project AMAART is conducted in cooperation with the ISMN (Istituto per lo Studio dei Materiali Nanostrutturati) of CNR (Consiglio Nazionale delle Ricerche) and in parallel with the H2020 Project APACHE (Active & intelligent PAckaging materials and display cases as a tool for preventive conservation of Cultural Heritage - GA N.81449, starting on 01/01/2019, duration 42 months, http://www.apacheproject.eu/).
Within the APACHE Project, the high-technology company IONVAC built an airlock for the set-up of some environments, adding a pre-determined amount of pollutant and setting the relative humidity to test the sensors developed and designed by CNR-ISM for the detection

of low concentration of selected pollutants. The tests have been carried out using copper and zinc sensors and the impedance signals with each environment variation set was monitored by the CNR-ISM researchers. The sensors were characterized after the exposure to the pollutants in the airlock by means of optical microscopy and infrared spectroscopy (Micro-FTIR) to study their degradation process and lifetime as well as any similarity with the coupons exposed to similar environments.

As regards the mitigation of pollutants' concentration, a study of the materials with high absorption capacity towards the selected pollutants was carried out and ceramic foams (c.f.) were chosen as porous substrate to be used as support of active species suitable for the chemisorption of some organic volatile compounds. The specific properties of monolithic structures can offer an alternative to conventionally prepared pellets or powders (Vesna Tomašić et al.2006) and their structures exhibit very high porosities with good interconnectivity. In this study, the monoliths were functionalized with fillers to improve their absorption capacity (monoliths catalyst). Tests using NaOH as filler chemisorbent for the mitigation of formaldehyde and acetaldehyde concentration were conducted. After the ceramic foams impregnation, the monoliths were sampled and FEG-SEM analysis (figure 2 a and b) were carried out to verify the consequent increase in its roughness and decrease in its grain sizes as well as ATR-FTIR (figure 2 c) analysis to check any chemical reactions.

Tests to check the effectiveness of the NaOH treated monoliths in the mitigation of formaldehyde and acetaldehyde concentration were carried out, putting the ceramic foams as such, and after the treatment with NaOH, in a sealed vessel with a given volume of pollutant. An easy and cheap monitoring of the environmental museum condition is usually achieved using coupons that work as long-term passive monitors to reveal the possible surrounding pollution. Metal coupons grant a fast-response and allow an easy trace back of the most dangerous indoor pollutants like, for instance, volatile organic compounds, because of the role they play on metal oxidation (C.M. Grzywacz et al. 2006) (T. Prosek et al. 2013). The possible mitigation action of the ceramic foams was therefore verified analysing the corrosion products developed on metal coupons inserted in the sealed vessel. Two different coupons (a copper plate and a bronze disk -555B) were chosen as dosimeters.

The coupons were analysed by means of ATR-FTIR and the presence of degradation products was observed. The amount of corrosion products developed on the coupons surface due to the reaction of the metal with the pollutants, was checked to measure the corrosion progress in each sample. To compare this parameter, the intensity of one of the peaks ascribed to the presence of the detected degradation product was calculated and plotted for every ATR-FTIR spectrum.

Other ceramic foam treatments were performed to enhance the mitigation ability such as washcoating, which results in the formation of the required secondary support layer for the fillers, and an L-cysteine treatment to favour the chemisorption of some pollutants.

2. Research products

a) Publications (ISI journals)

Gabriel M. Ingo, Monica Albini, Angel D. Bustamante, Alva Sandra del Pilar Zambrano, Arabel Fernandez, Chiara Giuliani, Elena Messina, Marianna Pascucci, Cristina Riccucci, Maria Paola Staccioli, Gabriella Di Carlo, Luca Tortora, Microchemical Investigation of Long-Term Buried Gilded and Silvered Artifacts From Ancient Peru, (2020) Frontiers in Chemistry 7:230.

Monica Albini, Stefano Ridolfi, Chiara Giuliani, Marianna Pascucci, Maria Paola Staccioli and Cristina Riccucci, Multi-Spectroscopic Approach for the Non-invasive Characterization of Paintings on Metal Surfaces (2020) Frontiers in Chemistry 8:289.

Chiara Giuliani, Elena Messina, Maria Paola Staccioli, Marianna Pascucci, Cristina Riccucci, Leonarda Francesca Liotta, Luca Tortora,Gabriel Maria Ingo and Gabriella Di Carlo, On-Demand Release of Protective Agents Triggered by Environmental Stimuli, (2020) Frontiers in Chemistry 8:304.

Elena Messina, Chiara Giuliani, Marianna Pascucci, Cristina Riccucci, Maria Paola Staccioli, Monica Albini, Gabriella Di Carlo, Synergistic Inhibition Effect of Chitosan and L-Cysteine for the Protection of Copper-Based Alloys against Atmospheric Chloride-Induced Indoor Corrosion, Int. J. Mol. Sci. 2021, 22(19).

Debora Kelen Silva da Conceição, Kauana Nunes de Almeida, Elsa Nhuch, Maria Grazia Raucci, Chiara Santillo, Martina Salzano de Luna, Luigi Ambrosio, Marino Lavorgna, Chiara Giuliani, Gabriella Di Carlo, Maria Paola Staccioli, Tiago Falcade, Henri Stephan Schrekke, The synergistic effect of an imidazolium salt and benzotriazole on the protection of bronze surfaces with chitosan-based coatings, Silva da Conceição et al. Herit Sci (2020) 8:40

b) Abstracts

14-23 September 2021 - XXVII Congresso nazionale della Società Chimica Italiana. Poster contribution “Active and monitoring materials for the environmentally safe storage and exhibition of works of art”, Maria Paola Staccioli, Valerio Serpente, Daniele Trucchi, Marco Girolami c, Cristina Riccucci, Gabriella Di Carlo

14-23 September 2021 - XXVII Congresso nazionale della Società Chimica Italiana.” Poster contribution “Corrosion protection in Concrete Heritage: from material design to in situ validation”, £lena Messina, Maria Paola Staccioli, Simone Pagnani, Francesca Boccaccini,Cristina Riccucci, Gabriel M. Ingo, Gabriella Di Carlo

2-3 December 2021. Secondo Training Pubblico presso il Centro Conservazione e Restauro "La Venaria Reale” Project H2020 Active & intelligent PAckaging materials and display cases as a tool for preventive conservation of Cultural Heritage” Oral presentation titled “Multifunctional materials based on chitosan for the removal of degrading species in museum storage/display environments” (presenting author).