RETASTE Conference Abstracts
Vol. 3 RETASTE-NOV-462-Oral
Athens, Greece, 27-29 September, 2023

rethink food resources, losses, and waste 2023

From Food Waste to Metal Protecting Agents: the Case of Green Inhibitors and of Bio-based Polymer Coatings

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Abstract

The ever-growing demand for raw materials necessary to satisfy the hunger of modern society is one of the biggest issues that global policies have to face and solve in the near future. The corrosion protection is one of the areas in which the new paradigm of the circular economy can be applied. Among the available technological solutions, corrosion inhibitors and polymeric coatings represent two interesting springboards for the applied research, not only for the huge market potentialities, but also for their need of very high amount of raw materials, mostly derived from petrochemical industry and/or connected to environmental issues. Thus, it is expected the related market to be restricted in the next future by environmental regulations, asking for novel sustainable alternatives. The imminent request of a green turn in the corrosion protection market can be satisfied by exploiting biomass from the significant amount of food waste produced worldwide. Here we present the rationale and the main results of two research lines designed to satisfy this need, with a focus on green inhibitors and bio-based polymer coatings.

i) Green inhibitors from waste of processed fruits and vegetables

Waste from edible fruits and vegetables usually still contain macromolecules and redox active compounds of low nutritional impact but having characteristics, like the presence of heteroatoms and instaurations, well desired for adsorption onto metal surfaces. These features can induce a corrosion protection effect resulting from a combination of active and passive mechanisms of action. In this work, extracts from waste of pomegranate (Magni et al., 2020) and cynara derived from industrial processing were obtained using different extraction protocols. Leafs of Moringa oleifera were also considered in the comparative study. The resulting complex mixtures were firstly analysed through chromatographic (GC-MS and HPLC-UV) and spectroscopic (FTIR) techniques. Through dedicated libraries, the main families of compounds were identified by the

chromatograms: carbohydrate, short-chain acids and saturated/unsaturated fatty acids, the relative amount being modulated by the extraction medium, too. Additionally, starting from available literature, a quantification of some specific target molecule(s) for each extract was also performed (flavonoids, chlorogenic acids, etc.). Finally, the corrosion inhibition efficiency of the natural extracts towards metal specimens (Armco® iron, Fe >99.8 wt.%) was assessed by mass-loss measurements (dipped sample in a stationary solution) and through electrochemical investigation (open circuit potential, dynamic electrochemical impedance spectroscopy and anodic potentiodynamic polarization). The aggressive media was 1 M HCl aqueous solution, mimicking the conditions of the pickling treatment for carbon steel handworks. Comparable performance for the three natural extracts were detected, independently by the quite different nature of the vegetable matrix. In all cases, a maximum in the inhibition efficiency up to 86-97% was detected after 10-24 h of exposure of the metal specimens to the corrosive environment spiked with a comparable amount of extract. For longer exposure, a decrease in the inhibition efficiency was invariably detected for all the extracts and for the control sample (hexamethylenetetramine solution, a synthetic organic corrosion inhibitor). After 72h, the inhibition efficiency was reduced levelling between 76-80%. A more detailed time-resolved investigation of the decreased protective features of the inhibitors over time has been possible through electrochemistry, and the related results will be discussed. Degradation (and hence modification) of the chemical composition of the extract has been deduced. Lastly, but not less important, we will discuss how our data provide evidences that the main anticorrosive component in such extracts is not a single molecule (as stated in many related articles) but derives from a synergism between a plethora of compounds belonging to the above-cited main families of compounds.

ii) Polymer coatings from tomato peel waste

The project aims at the valorization of tomato peels, an abundant agricultural waste in Italy that is currently exploited only in few low added-value chains (animal feed, waste-to-energy). In this work, the attention will be focused on the utilization of the cutin monomer, derived from the depolymerization of tomato peels, as curing agent of some naturally-derived epoxydized prepolymers for the preparation of corrosion protection coatings for carbon steel (Figure 1, left). First, the innovative approach will be discussed evidencing improvements and advantages with respect to the few analogous examples in literature, in term of both extraction of pure cutin monomer (purity >93 wt.%, with a total yield of 35 wt.%) and formulation of bio-based coatings. Then, the focus will be shifted on the electrochemical assessment of the protective features of the coatings under natural and accelerated aging conditions, and on the correlation with their thermal, physical and mechanical properties. The performance of the fully naturally derived coatings has been compared with that i) of control coatings (partially natural ones), with either the pre-polymer or the hardener being petrol-based, and ii) of a benchmark coating, made of bisphenol A diglycidyl ether and phthalic anhydride (fully petrol-derived). With the optimized formulations, the protective performance of cutin-derived fully bio-based coatings outperform both reference coatings, with value of |Z|0.01Hz > 109 Ω cm2 even after accelerated cyclic electrochemical tests lasting 7 days.

Keywords: biowaste, corrosion, inhibitors, polymer coatings, electrochemistry

References

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Acknowledgments: Mirko Magni thanks FSE-REACT-EU PON “RICERCA E INNOVAZIONE” 2014-2020 and Engitec Technologies SpA for co-funding his current researcher position. Fondazione Cariplo is also thanked for the financial support to the tomato-derived coatings project named “CutToPro” (grant No. 2021-0651)