

Green Corrosion Inhibitors from Agri-Food Wastes: The Case of Punica granatum Extract and Its Constituent Ellagic Acid. A Validation Study

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Giving a “new life” to wastes should be the golden rule for all production processes in the forthcoming future, aiming at making them more sustainable and environmentally friendly. In the corrosion science field, the ambitious circular economy paradigm has recently led to the employment of extracts from plants (and, in less extent, from agri-food wastes) as green inhibitors against corrosion of metals. However, in spite of the number of scientific papers published in the field, a deep revision of the scientific approach is needed both in the execution of experiments and in the critical analysis of the results. Starting from some discrepancies in published data, the corrosion inhibition effect induced by a well-characterized methanolic extract from wastes of fermented Punica granatum and by its main component (ellagic acid, EA) was validated. The corrosion behaviour of Armco® pure iron in the presence of small concentrations of ellagic acid and extract (containing ca. 10 μM and 100 μM EA) was studied by combining results from mass loss tests, at free corrosion potential, and from polarization tests, by linearly sweeping the potential applied to the metal substrate. Experiments were carried out both in acidic medium (typical for a general corrosion phenomenon) and in near-neutral chloride bearing solution (characteristic of a localized pitting corrosion phenomenon). Neat conflicts with already published data have been identified first in the solubility of the inhibitor and then in the inhibition efficiency (around 40% in a 0.05 M HCl). The very limited solubility in aqueous environment was identified as the main drawback, hindering any possible exploitation of ellagic acid and pomegranate extract as promising green corrosion inhibitors. Results point to the necessity to establish clear and rigorous good laboratory practices to follow while reporting results on such complex matrices like vegetable extracts.

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Article

Green Corrosion Inhibitors from Agri-Food Wastes: The Case of *Punica granatum* Extract and Its Constituent Ellagic Acid. A Validation Study

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Abstract: Giving a “new life” to wastes should be the golden rule for all production processes in the forthcoming future, aiming at making them more sustainable and environmentally friendly. In the corrosion science field, the ambitious circular economy paradigm has recently led to the employment of extracts from plants (and, in less extent, from agri-food wastes) as green inhibitors against corrosion of metals. However, in spite of the number of scientific papers published in the field, a deep revision of the scientific approach is needed both in the execution of experiments and in the critical analysis of the results. Starting from some discrepancies in published data, the corrosion inhibition effect induced by a well-characterized methanolic extract from wastes of fermented *Punica granatum* and by its main component (ellagic acid, EA) was validated. The corrosion behaviour of Armco[®] pure iron in the presence of small concentrations of ellagic acid and extract (containing ca. 10 μ M and 100 μ M EA) was studied by combining results from mass loss tests, at free corrosion potential, and from polarization tests, by linearly sweeping the potential applied to the metal substrate. Experiments were carried out both in acidic medium (typical for a general corrosion phenomenon) and in near-neutral chloride bearing solution (characteristic of a localized pitting corrosion phenomenon). Neat conflicts with already published data have been identified first in the solubility of the inhibitor and then in the inhibition efficiency (around 40% in a 0.05 M HCl). The very limited solubility in aqueous environment was identified as the main drawback, hindering any possible exploitation of ellagic acid and pomegranate extract as promising green corrosion inhibitors. Results point to the necessity to establish clear and rigorous good laboratory practices to follow while reporting results on such complex matrices like vegetable extracts.

Keywords: green corrosion inhibitors; ellagic acid; pomegranate extract; iron corrosion

1. Introduction

The biggest challenge of the present and near future is the preservation of our planet. Climate change, pollution and exhaustion of primary resources are hot topics in both political and scientific discussions. Circular economy, and the related green chemistry principles [1], represent a valuable route to reduce wastes, to favor a clever reuse of by-products and thus to decrease both pollution and dependence on primary resources.

The circular economy finds application in many fields. In the corrosion science, it has been causing an escalation of scientific papers aimed to find green corrosion inhibitors as alternatives to the more common, but toxic and harmful, ones (e.g., chromium and molybdenum compounds, nitrites,

amines) [2–5]. Corrosion inhibitors are compounds that, directly added in a small concentration into the aggressive solution with which the metal is in contact, slow down the irreversible interfacial reaction, *i.e.*, corrosion process, based on the concomitant advent of an oxidation reaction (*i.e.*, metal dissolution) and a reduction one (typically, hydrogen evolution or oxygen reduction) [6]. Inhibitors work through different mechanisms, often not straight to be interpreted (*e.g.*, protective oxide film, adsorbed blanketing layer, precipitation phenomena), resulting into anodic, cathodic or mixed effect [2,7]. The label “green”, or sometimes “eco-friendly”, is commonly added to the noun inhibitor if the molecule, in addition to meeting the previous definition of inhibitor, also has a biocompatibility in nature [5]. Part of this class of inhibitors are complex matrices like plant extracts due to their biological origin and, by extension, their single components like flavonoids, alkaloids, polyphenols and glycosides.

The relative simplicity of many extraction procedures, combined with the plenty of vegetable sources available even at very low prices, made the exploitation of plant extracts a new “trend” in the corrosion science. This “green turn” must surely receive praise but it is to be worth noting also the other side of the medal. A critical revision of the open literature concerning green corrosion inhibitors brings up to a constructive critique [3]. First of all, only a few works actually deal with extracts from natural residues, by-product or biomass wastes [3]. The majority use, as starting materials, pristine agri-food or plant sources, which means that biomass is still full of all its nutritious components. This largely adopted approach can arouse some ethical concerns and some doubts on the respect of the principles of both green chemistry and the circular economy. The second big drawback found out in the relevant literature is a sort of “superficial” approach. The critique regards (i) the characterization of the extract, which in many cases is completely missing, and (ii) the design of the experiments and the subsequent interpretation of the collected data (main concerns are for the electrochemical ones) that should demonstrate the validity of a given extract as corrosion inhibitor [3].

In this work, an attempt was made to valorise an extract from a biomass waste by employing it as a truly green corrosion inhibitor. The attention was focused on *Punica granatum* (pomegranate), as literature reported promising inhibition efficiencies for extracts obtained by both seeds and peels of fresh pomegranates [8,9]. Exploiting our specific expertise in the extraction of valuable compounds from biomass wastes [10–12], the residues resulting from the industrial fermentation process of pomegranates were selected as bio-waste material for this work. Ellagic acid (EA) is one the main components of pomegranate extracts [8–11] even if it can be found in other fruits like raspberries, strawberries, walnuts, pecans, etc. [13]. It is worth mentioning that yeast fermentation processes significantly improve (40-fold) the content of EA in pomegranate extracts with respect to extracts obtained directly from the lyophilized fresh fruit [10]. Ellagic acid, the dilactone of 2,2'-dicarboxy-4,5,6,4',5',6'-hexahydroxybiphenyl (Figure 1), is characterized by a biphenyl ring system that is constrained to near planarity by the ring-enclosure process resulting from the esterification between a carboxyl and a hydroxyl group belonging to a different phenyl ring. As a result, ellagic acid has an ideal C_{2h} symmetry group (resulting in two couples of diastereotopic –OH groups and two homotopic ester groups) and an extended π -electron system. Its conformational and chemical features, including the presence of oxygen atoms with free electron couples, make EA a valuable candidate as corrosion inhibitor [14]. This hypothesis seems to be supported by inhibition efficiencies around 90% reported in both 2 M HCl and 1 M H₂SO₄ solutions [9]. Other interesting medical and pharmaceutical applications of this polyphenol are as an antioxidant, anticarcinogen, and antimutagen [15].

The corrosion inhibition efficiency of pure ellagic acid (EA) and of the extract from the fermented pomegranate waste (FPW) was investigated employing pure iron substrates, selected as a reference, prototype material for any possible real application with carbon steel. Hydrochloric acid and sodium chloride were chosen as testing solutions, two typical corrosive environments in which the dissolution of the metal occurs via general and localized pitting corrosion phenomena, respectively. The first case study wants to reproduce the typical environment of a pickling process during which a ferrous metal is dipped into an acid bath, containing also a small concentration of a corrosion inhibitor, aiming at dissolving the corrosion products, naturally forming on the outermost layer of the handwork, just

before the finishing (galvanization, surface coating, etc.). The second aqueous medium mimics the near neutral fluids used, for example, in the cooling systems of industrial plants, where ground or, even, sea water is employed. In these fluids, some dissolved ions (*i.e.*, chlorides) are responsible for the metal corrosion. Evaluation of corrosion inhibition efficiency of EA and FPW extract was done combining mass loss tests and potentiodynamic polarization investigation.

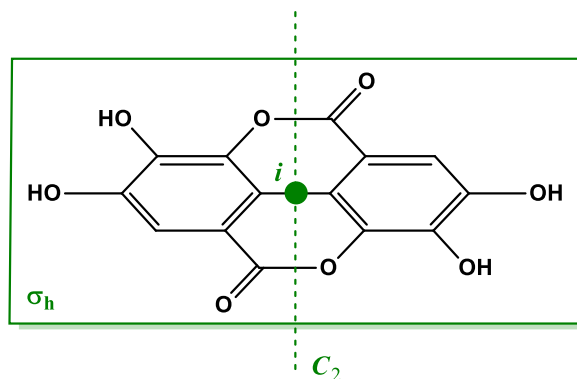


Figure 1. Tilted view of the structural formula of ellagic acid molecule, together with the three symmetry elements: centre of inversion (*i*), rotation axis of order 2 (C_2) and mirror plane (horizontal, σ_h).

2. Materials and Methods

2.1. Materials and Solvents

Ellagic acid ($\geq 96.0\%$, Fluka, Merck KGaA, Darmstadt, Germany), sodium chloride ($\geq 99.0\%$, Sigma-Aldrich, Merck KGaA, Darmstadt, Germany), hydrochloric acid (37% , Sigma-Aldrich, Merck KGaA, Darmstadt, Germany) and methanol ($\geq 99.9\%$, Sigma-Aldrich) were used as received, without any further purification. All aqueous solutions were prepared with Milli-Q water. Solutions of 0.05 M HCl were prepared by diluting properly the concentrated acid solution.

The iron samples (99.85% , Armco[®] pure iron, AK Steel International, West Chester, OH, USA) used for mass loss tests and electrochemical investigations were cut in the same forms of rod and plate, respectively. Mechanical polishing was performed using emery papers of 180 grit, 400 grit, 800 grit, 1200 grit. Then, the samples were thoroughly rinsed with Milli-Q water and, finally, cleaned with acetone and dried.

2.2. Extraction Procedure and Extract Characterization

Residues of the production of wine by yeast fermentation of pomegranates (supplied by Prela Alba Srl, an Italian agri-food company specialized in the production of fermented beverages) were employed as starting material for the extraction procedure. According to a previously reported procedure [10], the fermented pomegranate waste (FPW) was extracted with methanol (10 mL g^{-1}) at room temperature under vigorous magnetic stirring. After 1 h, the solvent was removed by centrifugation (7000 rpm, 15 min) and the residue was collected. The procedure was overall repeated for three times using 20 mL of methanol in the first run, reduced to 10 mL in the other two runs. The collected methanol extracts were taken, eventually, to dryness to give a red solid residue (*ca.* $10\text{ wt}\%$ yield) that was stored up at *ca.* $4\text{ }^\circ\text{C}$ until its utilization.

By a combination of HPLC, LC-MS, 1D and 2D NMR analyses, it is possible to state that the main component of the extract is ellagic acid ($38\text{--}40\text{ wt}\%$ by HPLC, with an external standard calibration). Minor species are succinic and citric acids (coming from fruit itself) and leucine, isoleucine, valine and 2,3-butandiol (from yeast metabolism). For all the corrosion tests involving FPW extract, an average content of EA equal to $39\text{ wt}\%$ was considered [10].

2.3. Spectrophotometry

UV-visible spectrophotometric analyses were carried out with a Shimadzu UV-360 Plus using quartz cuvettes (1-cm path wavelength) and scanning wavelength in the range 600–190 nm (resolution 1 nm). Absorbance versus concentration plots were obtained by recording absorbance of solutions containing different concentrations of ellagic acid (from 3.3 to 10 μM). Each analysed sample was prepared by directly spiking a suitable volume of the nominally 10 μM EA stock solution (prepared in water or in 0.05 M HCl, both containing 1 vol% methanol) into the corresponding blank solution.

2.4. Corrosion Tests

2.4.1. Mass Loss Investigation

Pure iron coupons for mass loss tests were minimum 2 cm \times 1.5 cm \times 0.4 cm, prepared as described above. A hole of 0.2 cm in diameter was drilled to hang the sample, through a Teflon[®] wire, in a 300 mL round-bottom glass test tube by blocking the wire to a glass hook attached to the stopper. The test tube was firstly filled with a suitable volume of the studied solution (inhibited or not) to assure a volume to surface ratio of ca. 7 mL cm⁻², and thermostated to the operative temperature. All solutions were naturally aerated. Finally, the sample was completely immersed into the stagnant solution and kept for 1 h; tests were repeated at least three-times for each of the operative conditions. At the end of the test, the sample was gently but firmly cleaned with a brush under running water to remove any deposited corrosion product, then rinsed with abundant Milli-Q water, acetone, and dried at 70–90 °C for 20 min. The sample was left to cool down into a dryer for around 15 min and, finally, weighted (W_{final}) through an analytical balance (Gibertini E42-B). The mass (expressed in grams) was compared with that of the pristine sample (W_{start}) to estimate the mass loss rate (v_w , Equation (1)) and the corresponding corrosion rate (v , Equation (2)) [16]:

$$v_w = \frac{(W_{\text{start}} - W_{\text{final}})}{A \cdot t}, \quad (1)$$

$$v = \frac{87600(W_{\text{start}} - W_{\text{final}})}{A \cdot t \cdot d}, \quad (2)$$

where A is the surface area of the sample (in centimeters), t is the exposure time (in hours), d is the density of iron (7.86 g cm⁻³), and 87600 is a numerical factor to express the corrosion rate in millimeter per year (mm y⁻¹). The corrosion inhibition efficiency (IE) of ellagic acid and pomegranate extract was estimated (Equation (3)) by comparing the mass loss rate with ($v_{w,\text{inh}}$) and without ($v_{w,\text{uninh}}$) their addition to the HCl or NaCl aggressive medium:

$$IE\% = \frac{v_{w,\text{uninh}} - v_{w,\text{inh}}}{v_{w,\text{inh}}} \cdot 100 \quad (3)$$

2.4.2. Potentiodynamic Polarization

The electrochemical investigation was carried out in a customized thermostated glass/quartz cell with a hole, 1 cm in diameter, in the middle of the flat bottom to allocate the working electrode. Potentiodynamic scans were performed in a classical three-electrode configuration including: as working electrode, a pure iron plate ca. 6 \times 3 \times 0.1 cm (exposed area 0.78 cm²) firmly attached to the drilled bottom of the cell through an adhesive layer (VHB transparent, A2 Soluzioni Adesive, Italy); as counterelectrode, a Pt spiral wire; as reference electrode an aqueous saturated calomel electrode (SCE) inserted into a glass jacket ending with a Luggin capillary placed next to the working electrode surface. After filling the cell with ca. 50 mL of the pre-thermostated working solution (0.01 M HCl or 0.01 M NaCl, with or without inhibitor), the open circuit potential (OCP) was recorded for 20 min and then the working electrode was polarized by sweeping the potential at 0.5 mV s⁻¹ from -300 mV

to + 300 mV vs. OCP. When a variation in the pH of the medium was expected for the addition of the inhibitor (*i.e.*, with the near neutral NaCl solution), recorded potentials ($E_{(vs. SCE)}$) were then referred to the reversible hydrogen electrode (RHE) as $E_{(vs. RHE)} = E_{(vs. SCE)} + 0.244 + 0.059\text{pH}$, where 0.244 V was taken as the potential of SCE with respect to the standard hydrogen electrode (SHE). In all tests, stagnant and aerated solutions were invariably used. At least two polarizations were performed for each of the tested conditions, to assure reproducibility of the reported current density *vs.* potential curves.

3. Results and Discussion

3.1. Spectrophotometric Investigation

The open literature reports very different solubility values for ellagic acid, with the threshold spanning from 7.2 mg dm⁻³ [17] and 10 mg dm⁻³ [13] in pure water to 1.2 g dm⁻³ in 2 M hydrochloric acid solution [9]. The *ca.* 100-fold increase in the solubility of EA moving from near neutral to strongly acidic medium seems quite anomalous. In fact, generally speaking, the solubility of a weak organic acid tends to increase by increasing pH of the medium, so by increasing the percentage of its dissociated form (*i.e.*, the conjugated base). This general trend has also been experimentally confirmed for ellagic acid: the equilibrium solubility of the species increases by two orders of magnitude by passing from pH 5.5 to 7.5 [13].

As a preliminary stage in the study of the corrosion inhibition effect of EA and of EA-enriched pomegranate extract, a spectrophotometric investigation of a commercially available sample of EA was carried out (i) to study the speciation of the molecule in the studied media and (ii) to assure the homogeneity of the batch solutions that are going to be used in the subsequent corrosion tests. A concentration of EA equal to 10 μM was chosen for the corrosion tests, a bit lower than the solubility limit [13,17]. A batch solution of ellagic acid in 0.05 M HCl (containing, nominally, 10 μM of EA) presented a visible suspension even after some days of vigorous agitation; as a confirmation, the UV-vis spectrum (not shown) was affected by a significant scattering of the incident beam. Considering the good dissolution ability of methanol [13], stock solutions of EA in 0.05 M HCl and in pure water were prepared by adding 1 vol% of the alcohol. Another promising candidate as co-solvent, polyethylene glycol (PEG300), was considered but, due to its too high intrinsic corrosion inhibition effect (see next section), was eventually discarded.

Spectra of the two EA stock solutions with 1 vol% of methanol are overlapped in Figure 2. Ellagic acid in 0.05 M HCl solution shows two main absorption bands centred at 250 nm and 367 nm, with a shoulder in between at around 300 nm, all attributable to π - π^* electronic transitions [18,19]. Being the pH of the working medium significantly lower than the reported pKa of ellagic acid (pKa = 6.54 [17], or pKa,1 = 5.42 and pKa,2 = 6.76 [20]), the spectral features just described can be associated to the fully protonated form of EA (*i.e.*, free ellagic acid). By moving from the acid to the near-neutral environment, a scarce shift of the position of the two main bands is recorded together with a slight reduction in the intensity of the higher energetic transition and a slight intensification of the lower one. Moreover, a new band around 275 nm grows up. According to a previous detailed spectrophotometric study on ellagic acid in a 7:3 mixed solvent of ethanol and water [19], all these features depict, for the near-neutral solution, the presence of the singly deprotonated form of EA.

The linearity of the maximum absorbance versus concentration response (Figure 2 and Supplementary Table S1) indicates compliance with the Beer–Lambert law and points to a solubility of EA up to 10 μM in both acid and near-neutral stock solutions.

3.2. Corrosion Inhibition of Iron in Hydrochloric Acid Solution

In this study, the corrosion behaviour of Armco® pure iron, immersed in HCl solutions with a concentration ranging between 5 mM and 1 M at a temperature ranging from 30 to 50 °C, has been studied. Mass loss results by un-inhibited hydrochloric acid solutions at 30 °C (Supplementary

Figure S1) showed that the most severe condition is for concentrations between 0.05 M and 0.2 M. All the subsequent investigations on the corrosion inhibition effect of pure ellagic acid and of the EA-enriched extract was carried out in 0.05 M HCl solutions.

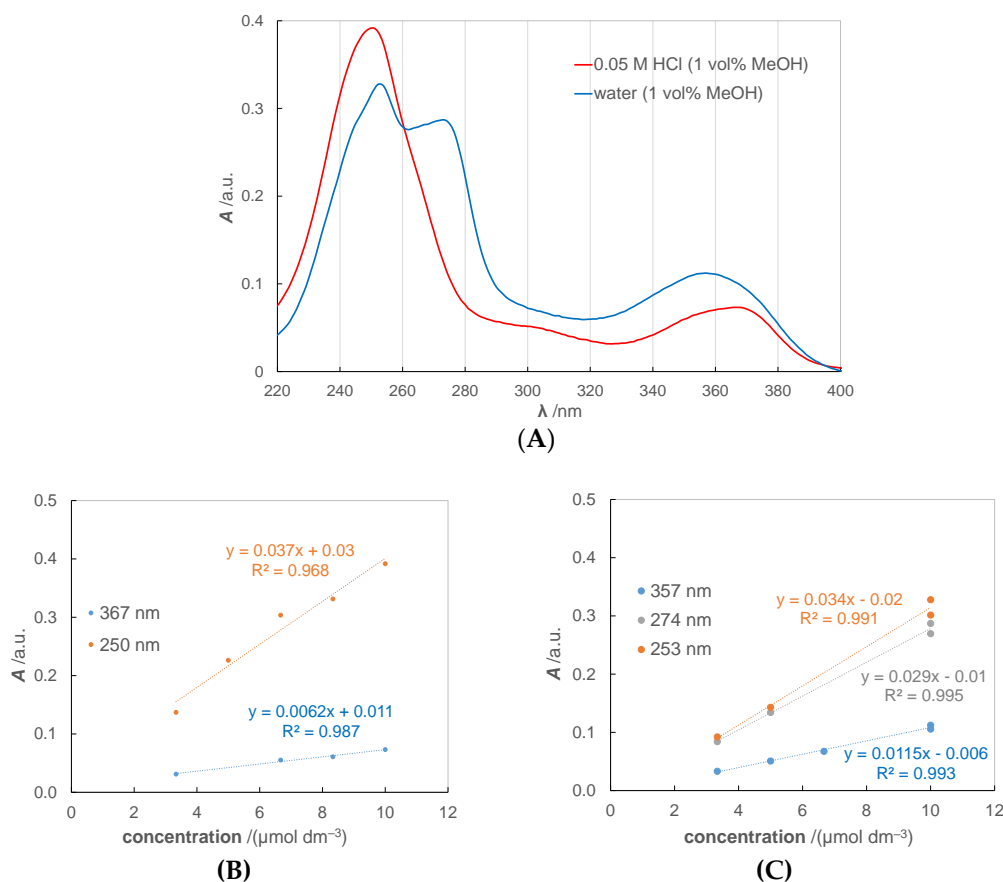


Figure 2. (A): UV-vis spectra of 10 μM ellagic acid in 0.05 M HCl solution (red line) and in water (blue line). Corresponding calibration plots in the acid (B) and in the near-neutral solution (C). In all analysed samples 1 vol% methanol is invariably present.

3.2.1. Choice of a Co-Solvent for Performing Corrosion Inhibition Tests

As discussed above, the highly recalcitrant solubility of ellagic acid in acidic solution (contrary to the 1.2 g dm⁻³ solubility previously reported [9]) forced to find a suitable organic co-solvent able to solubilize the polyphenol. Care must be taken to select a solvent that exhibits no significant corrosion inhibition effect by itself. Among possible candidates [13], methanol and polyethylene glycol 300 (PEG300) were evaluated by performing mass loss tests on iron coupons immersed in blank solutions made of 0.05 M HCl and 1 vol% of the co-solvent. Results are listed in Table 1.

PEG300 works itself as an effective corrosion inhibitor of iron (IE *ca.* 80%), in good agreement with the behaviour evidenced by polyethylene glycols of different molecular weights towards mild steel in acid solution, with PEG simply blocking at the metal surface [21]. The addition of 10 μM ellagic acid did not imply any significant change to the overall inhibition effect of the mix inhibitor system PEG300/EA (IE = 83 ± 4%, Table 1). It is a general assumption that the first step of the mechanism of the inhibition action is the adsorption of the inhibitor on the surface of the metal. The huge molar unbalance between PEG300 and EA drastically decreases the possibility by EA molecules to interact with the metal surface, being already most likely covered by the 3000-times more abundant PEG300.

On the other hand, methanol seems not to act as an inhibitor, but as an active agent slightly speeding up the corrosion of iron (see the negative value of IE%, Table 1). Such effect is however not detectable if judged through voltammetry technique (Figure S2). Thus, methanol was selected as the

co-solvent for the corrosion inhibition study in acidic medium, assuring a 10 μM threshold solubility to the ellagic acid. Methanol is also the election solvent for dissolving the extract obtained from the fermented pomegranate waste (FPW).

Table 1. Results of the corrosion tests (by mass loss determination, at least in triplicates) carried out by dipping iron coupons for 1 h at 30 °C in uninhibited and inhibited 0.05 M HCl solutions. Pure ellagic acid and FPW extract were considered as inhibitors.

Solution	Co-solvent	$v_w / (\text{mg cm}^{-2} \text{ h}^{-1})^a$	$v / (\text{mm y}^{-1})^b$	IE% ^c
0.05 M HCl	-	0.8 ± 0.1	9 ± 1	-
0.05 M HCl + 1 vol% co-solvent (blank)	PEG300	0.17 ± 0.03	1.9 ± 0.3	79 ± 5^d
	Methanol ^e	1.0 ± 0.1	11 ± 1	-25 ± 20^d
blank + 10 μM EA	PEG300	0.14 ± 0.03	1.5 ± 0.3	83 ± 4^d
	methanol	0.72 ± 0.07	8.0 ± 0.8	28 ± 10
blank + 8 mg/dm^3 FPW extract (ca. 10 μM EA)	methanol	0.86 ± 0.03	9.6 ± 0.3	14 ± 9
blank + 80 mg/dm^3 FPW extract (ca. 100 μM EA)	methanol	0.80 ± 0.04	8.9 ± 0.4	20 ± 9

^a Mass loss rate (Equation (1)). ^b Corrosion rate (Equation (2)). ^c Corrosion inhibition efficiency (Equation (3)).

^d Taking 0.05 M HCl solution as the uninhibited reference solution. ^e Reference solution, taken as the uninhibited one for IE% calculation (if not otherwise stated).

3.2.2. Investigation of the Performance of EA and FPW Extract as Corrosion Inhibitors

Mass Loss Test

The results of mass loss test with 10 μM EA added to the corroding medium clearly show a conflict with already published data [9]. Experiments provided a modest corrosion protection ability (IE = $28 \pm 10\%$, Table 1) with respect to the reported inhibition efficiency ranging from 60 to 90% by increasing EA content from 0.6 to 1.2 g dm^{-3} [9]. These last concentrations seem, according to both our solubility tests and with other literature data [13,17], very unlikely considering that are referred to a 2 M HCl solution (*i.e.*, more acid than our 0.05 M HCl medium, so a harder condition for the solubilisation of EA). The lower inhibition feature of EA reported in this work must be attributed to the quite low concentration of additive (*ca.* from 200 to 400-fold lower than the presumed concentration in [9]) that inevitably results in a poor coverage capability of the metal surface, assuming that the organic molecule should first adsorb onto the surface to exert its protection effect.

The inhibition features of the FPW extract was also tested by adding to the acid medium an amount containing a comparable quantity of ellagic acid, the last being considered the most active component for the inhibition action [9]. Also, in this case, the inhibition effect resulted quite poor, even decupling the extract concentration (Table 1). The absence of any visible white precipitate in the working medium nominally containing 100 μM EA could be attributable to some possible interactions with other constituents of the extract (*e.g.*, amino acids) that could convert the free EA species into a more soluble one.

Potentiodynamic Polarization

In order to have a more complete picture of the inhibiting action of EA and of FPW extract, mass loss data were complemented by means of an electrochemical investigation. Contrary to the “passive” mass loss test that evaluates only the overall “macroscopic” effect (*i.e.*, the mass loss) resulting from the redox phenomena that occur at the free corrosion potential (E_{corr}) self-defined by the metal/electrolyte system, polarizations allow to perform a more “active” investigation of the phenomenon. By changing the potential applied to the electrode (*i.e.*, the metal), the occurrence of anodic (oxidation) and cathodic

(reduction) reactions can be discerned and studied, separately. In this context, potentiodynamic polarization is a valuable and time-saving technique to study the corrosion behaviour of a given substrate in a given medium. Comparing the voltammetric patterns recorded in the free and the inhibited solution is possible not only to qualitatively identify any corrosion inhibition effect, but also to quantitatively rank the performance of inhibitors and to understand the action mechanism by evaluating some electrochemical key parameters. Most of the quantitative analysis performed on a voltammogram is based on the assumption of the validity of the Tafel equation (Equation (4))

$$\eta = E - E_{eq} = a \cdot \ln i_0 \pm a \cdot \ln i \quad (4)$$

where: $a = -\frac{RT}{(1-\alpha)nF}$ and “plus” sign, for the anodic reaction; $a = \frac{RT}{\alpha nF}$ and “minus” sign, for the cathodic one (with η = overpotential, defined as $E - E_{eq}$; E_{eq} = equilibrium potential (ca. E_{corr}); i_0 = exchange current density; R = gas constant; T = temperature, in kelvin; α = transfer coefficient; n = number of exchanged electrons per mole; F = Faraday constant).

In turn, the equation is an approximation (at high overpotentials) of the more general Butler-Volmer equation describing the current *vs.* potential relationship for reaction occurring under kinetics control (*i.e.*, without any mass transport limitation due to the diffusion of reagents/products) [22]. Particular care must be taken in considering the validity of such an approximation.

Potentiodynamic curves (Figure 3) were recorded for iron electrodes, in contact with each of the media investigated by mass loss tests, by scanning the potential in a cathodic-to-anodic direction within a window centered around the open circuit potential (corresponding to E_{corr}).

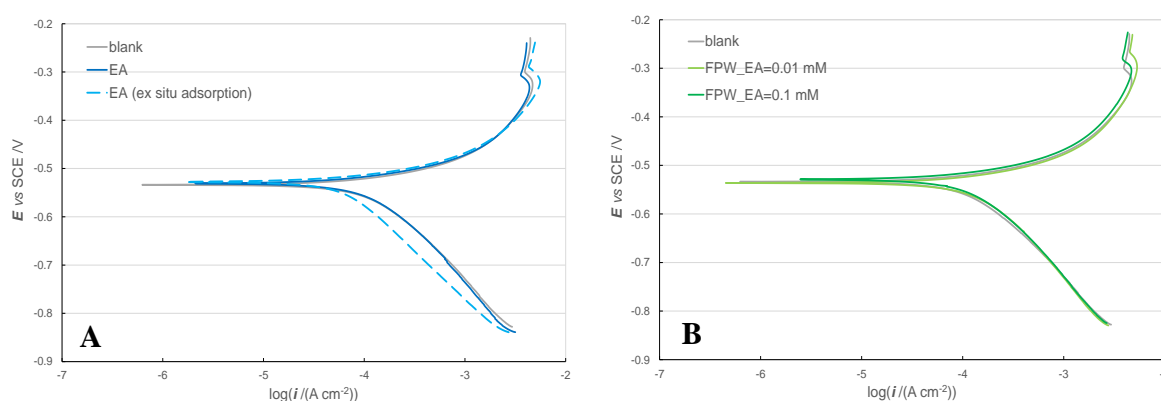


Figure 3. Potentiodynamic polarization curves (scan rate 0.5 mV s^{-1}) of Armco[®] iron electrodes in aerated 0.05 M HCl with 1 vol\% methanol (grey lines). (A): with the addition of $10 \mu\text{M}$ ellagic acid (solid dark blue) and after 2 h of ex-situ immersion in 1 mM EA methanolic solution (dashed light blue); (B): with the addition of different concentrations of FPW extract. Electrolyte temperature: $30 \text{ }^\circ\text{C}$.

Polarization curves recorded in each of the aggressive solutions modified with EA (in both pure form and from the vegetable extract) are near superimposable with the blank one, evidencing a very slight inhibition effect in good qualitative agreement with the results from mass loss investigation. In particular, no significant modification was detected neither in the corrosion potential (E_{corr} varies from -0.53 to -0.54 V vs. SCE) nor in the Tafel slope (from 220 to 240 mV dec^{-1}) of the cathodic branch corresponding mainly to hydrogen evolution reaction (Supplementary Table S2). Care was taken in selecting the Tafel region (from -0.65 to -0.75 V vs. SCE) [23,24], in order to assure to be in the activation control zone, that is at sufficiently high overpotentials ($>120 \text{ mV}$ at $25 \text{ }^\circ\text{C}$ [22]) to make the reverse reaction negligible with respect to the forward one. On the other hand, no linear portion, sufficiently wide and far from OCP, was detected in $E \text{ vs. } \log(i)$ plots for the anodic branch. Indeed, oxidation is characterized by a fast increase of the current density within a very narrow potential region (*ca.* 100 mV from OCP; active zone) followed by a near constant plateau value attributable to the formation of stable, insoluble corrosion product film.

The only significant difference in the polarization curves is for electrodes subjected to an *ex-situ* adsorption of ellagic acid by dipping into a 1 mM methanolic bath for two hours, before performing polarization scan (Figure 3A). The adsorption step, while keeping unchanged the corrosion potential, brought to a net modification in the cathodic branch when iron is exposed to HCl 0.05 M solution with 1 vol% methanol (*i.e.*, blank). The lower cathodic current densities lead to the estimation of a lower corrosion current density (i_{corr}) with respect to an untreated electrode in the same blank solution (Supplementary Table S2). Combining the i_{corr} value with that of the polarization resistance (R_p), obtained by i vs. E linear plot around OCP, an averaged 40% inhibition efficiency was evaluated according to the following two equations [24,25]:

$$IE\%_{(i_{\text{corr}})} = \frac{i_{\text{corr},\text{uninh}} - i_{\text{corr},\text{inh}}}{i_{\text{corr},\text{uninh}}} \cdot 100 \quad (5)$$

$$IE\%_{(R_p)} = \frac{R_{p,\text{inh}} - R_{p,\text{uninh}}}{R_{p,\text{inh}}} \cdot 100 \quad (6)$$

where “*inh*” and “*uninh*” subscripts refer, here, to an electrode previously dipped or not into the 1 mM ellagic acid solution, respectively. On the other hand, the near superimposable anodic branch with that of the reference condition could be due to the detachment from the metal surface of most of the originally adsorbed EA molecules, probably due to mechanical actions of H₂ bubbles generated during application of the more negative potentials.

The experimental results suggest that ellagic acid is intrinsically able to interact with the iron surface and to form a blanketing layer that, reducing the area of the free, reactive surface exposed to the aggressive solution, slows down the interfacial redox reaction rate that brings ultimately to the substrate corrosion. Such adsorption, supposedly governed by a weak donor–acceptor interaction between iron atoms and both oxygen-containing polar functional groups and π -electrons delocalized all over the flat molecular surface of ellagic acid, should involve the neutral, fully-protonated form of the polyphenol ($\text{p}K_a \gg \text{pH}$). Such considerations are perfectly in agreement with the good adsorbability of ellagic acid on iron reported in a previous computational study [8]. In particular, a high binding energy with a Fe(110) simulated surface was predicted by molecular dynamics, mainly due to molecular size and electronic structure considerations. The effective corrosion inhibition features of ellagic acid when adsorbed onto iron surface from a sufficiently concentrated solution, points out that the main drawback of this polyphenol to be employed as inhibitor is the too low solubility in an aqueous environment, which in turn significantly limits the number of molecules available to interact and cover the metal substrate.

3.3. EA and FPW Extract as Corrosion Inhibitors of Iron in Chloride-Based Near Neutral Solution

Inhibition of the corrosion of iron by ellagic acid and fermented pomegranate waste extract was further tested in aerated near neutral 0.05 M NaCl solutions, to maintain the same concentration of chlorides of the acidic medium. The higher pH should slightly improve the solubility of the polyphenol [13,17] and increase the dissociation percentage making available its negatively charged deprotonated form(s), being $\text{p}K_{a,1} = 5.42$ and $\text{p}K_{a,2} = 6.76$ [20]. Considering that aqueous neutral solutions containing chloride ions are generally responsible of localized corrosion of iron and steel, the investigation was performed only through electrochemistry, being the mass loss test specifically designed for environment responsible of general corrosion.

Comparing potentiodynamic curves of Armco[®] iron at constant Cl[−] concentration but at different pH, some differences can be detected (Figure S3). Contrary to acid solution where the cathodic reaction is supported by hydrogen evolution, as soon as the pH increases (*e.g.*, a near neutral NaCl solution) oxygen reduction acts as the main drain of electrons generated from the dissolution of the metal. One of the peculiarities of the oxygen reduction reaction is that it is generally subjected to a strong mass transport limitation, due to the limited solubility of O₂ gas in aqueous solutions (*ca.* 10 ppm, at room

temperature) that leads to high concentration overpotentials and, finally, to a diffusion-limited current density. According to this different mechanism and its intrinsic features, polarization curves in neutral or slightly acid solutions do not follow the Tafel law (Equation (4)) at the more negative overpotentials. The absence of a linear trend between potential and logarithm of current density characterizes also the anodic branch of the polarization curve of iron in 0.05 M NaCl. This is due to the rapid accumulation of corrosion products (*e.g.*, iron oxides/hydroxides) produced by the metal dissolution [26], resulting in a partially diffusion-controlled mechanism (not modelled by the Tafel equation).

Effect of the addition of 10 μM of EA to a 0.05 M NaCl solution is depicted in Figure 4A. Potentials are referred to reversible hydrogen electrode (RHE, see Experimental section for more details) to make the potential of reactions involving hydrogen (or hydroxyl) ions independent from the actual concentration of those species. The employment of the RHE scale is particularly important for the here discussed near neutral medium with respect to the HCl solution because the partial acid dissociation of EA (or of components of the FPW extract) slightly changes the actual pH of the medium (Table S3). Analysing the voltammetric curves in Figure 4A, the addition of EA results into a variation in the potentiodynamic pattern with respect to the blank, contrary to the acid case study. In particular, while the general shape of the curve remained almost unchanged, the addition of the polyphenol shifts the corrosion potential of iron to a 140 mV more positive value, pointing to an ennoblement of the metal (Supplementary Table S2).

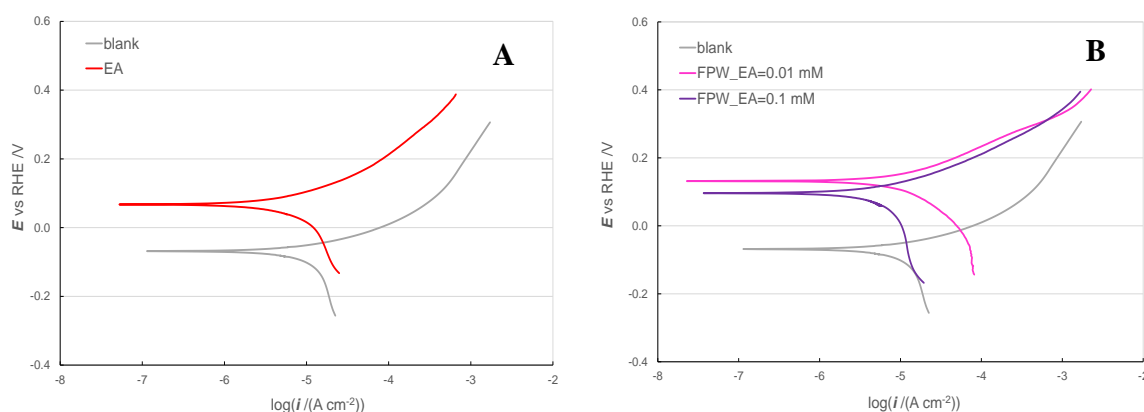


Figure 4. Potentiodynamic polarization curves (scan rate 0.5 mV s^{-1}) of Armco[®] iron electrodes in aerated 0.05 M NaCl with 1 vol% methanol (grey lines). (A): with the addition of 10 μM ellagic acid (red line); (B): with different concentrations of FPW extract. Electrolyte temperature: 30 $^{\circ}\text{C}$.

The different behavior of ellagic acid in HCl and NaCl solutions can be tentatively attributed to the different speciation of the molecule. As confirmed by spectrophotometric investigation (see related section), at the near neutral pH of a sodium chloride solution partially (or even fully) dissociated forms of EA are present. These are characterized by a net negative charge, contrary to the fully protonated EA, that makes oxygen atoms of the hydroxyl groups powerful anchoring sites prone to donate electrons to empty *d* orbitals of iron atoms. The π -conjugated structure, facilitated by the planar moiety, provides a further source of interaction. Moreover, negatively charged deprotonated EA can give rise to purely electrostatic interactions with the positively charged iron surface [14].

Independently from the actual mechanism of adsorption, the effect of EA resulted quite labile as confirmed by recording curves at increasing temperatures (Figure S4). In fact, already at 40 $^{\circ}\text{C}$ the aforementioned shift of E_{corr} almost vanished. This points out to an inhibition mechanism based on surface physisorption of the molecules that are easily detached by providing a small thermal energy.

The addition of the FPW extract to the same 0.05 M NaCl solution led to an effect similar to that of a comparable concentration of pure ellagic acid (Figure 4B and Supplementary Table S2), with an ennoblement of the corrosion potential (E_{corr} ca. 0.1 V vs. RHE) which is not significantly modified

by the quantity of the extract. The major effect caused by the extract concentration is on the cathodic branch, with an evident reduction of limiting current density by increasing the extract content.

4. Conclusions

The aim of this work was to valorize extracts obtained from agri-food industry by-products, exploring potential re-use as green corrosion inhibitors. A methanolic extract from fermented pomegranate waste was tested as a potential corrosion inhibitor of iron in both acid and near neutral chloride-based media, together with its main component: ellagic acid. The experimental work was aimed to validate results found out in the scientific literature that point out to ellagic acid and related pomegranate extract as very promising green inhibitors against the corrosion of steel [9]. As a first result, through a spectrophotometric investigation, this work proved that in an acid solution (0.05 M HCl) at least 1 vol% of an organic co-solvent is necessary to guarantee a solubility of 10 μM , so 400-folds lower than that reported in pure 2 M HCl.

Mass loss tests and electrochemical investigation performed in 0.05 M HCl solution agreed in identifying only a slight inhibition efficiency by the near-saturated ellagic acid solution (*ca.* 10 μM) and the extract. The same concentration of both pure ellagic acid and extract, when added to a near neutral 0.05 M NaCl solution, brought to an ennoblement of the metal, with a +130 mV displacement of the corrosion potential with respect to the blank solution. A modification of the cathodic branch was detected, especially by adding the pomegranate extract. The pH-dependent behaviour of the additives could be partly attributable to the different speciation of ellagic acid, as confirmed by the spectrophotometric study.

A higher inhibition efficiency (around 40%) in a 0.05 M HCl solution was calculated on the basis of corrosion current density and polarization resistance from potentiodynamic polarizations performed on iron electrodes previously dipped into a 1 mM EA methanolic solution. The increased efficiency after the *ex situ* treatment supports the thesis that EA is actually able to adsorb on iron surface and promote corrosion inhibition by forming a blanketing layer. The main drawback is the very limited solubility in aqueous environment, hindering any possible exploitation of both purified ellagic acid and pomegranate extract as green corrosion inhibitors.

This work also points to the importance of defining well-accepted, clear, and rigorous laboratory practices to follow when reporting results on vegetable extracts, being very complex and variable matrices. In particular, (i) providing a detailed composition of the extract employed in the corrosion inhibition tests and (ii) concerning the electrochemical study, assuring that the equations used to interpolate data can be truly applied in the specific situation (*i.e.*, all assumptions that make the equation valid are actually satisfied).

Supplementary Materials: The following are available online at <http://www.mdpi.com/2227-9717/8/3/272/s1>, Table S1: Statistical analysis of the calibration plots of EA in different media, from the visible spectroscopy study. Figure S1: Mass loss of Armco[®] iron coupons as a function of HCl concentration. Figure S2: Voltammetric curves of iron electrodes showing the effect of the addition of 1 vol% of methanol to aerated HCl 0.05 M solution. Figure S3: Comparison of the voltammetric behavior of iron electrodes in aerated 0.05 M HCl and 0.05 M NaCl solutions. Table S2: pH values of the solutions used in voltammetric investigation. Figure S4: Voltammetric curves showing the effect of the temperature on iron electrodes in aerated 0.05 M NaCl solution with and without EA.

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