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# Corrosion inhibition of carbon steel in acidic medium by orange peel extract and its main antioxidant compounds

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ABSTRACT

Chemical compounds of orange peel extracts were identified and their antioxidant activities were determined. The inhibiting effect on acidic steel corrosion brought by the extract and selected antioxidant compounds (neohesperidin, naringin, ascorbic acid) was evaluated separately by electrochemical methods. Whatever the extract concentration, a significant inhibition is observed, whereas selected antioxidant compounds show only a slight effect. Both electrochemical impedance spectroscopy results and scanning electron microscopy observations after immersion reveal that the inhibiting efficiency of orange peel extract is not only due to the antioxidant activity of its compounds but also to the precipitation of a surface film.



## 1. Introduction

Corrosion inhibition of steel in acidic media is a topic of great interest in industry. Actually, hydrochloric acid is widely used for descaling, pickling of metals or chemical cleaning. In order to avoid important metal loss, the addition of corrosion inhibitors is required. Corrosion inhibiting efficiency of natural antioxidant products on metals has begun to be extensively studied from the end of the nineteenth century in replacement of the extensive use of very efficient inorganic inhibitors (such as phosphates, chromates, nitrites) or organic molecules (as polyamines, long-chain carboxylates, imidazole and derivate compounds). Actually, their production is not only expensive but also often toxic, and regulated by toxicological and ecological standards (as the REACH regulation and the water European directives on the waste water reject [1]). Consequently, some organic molecules extracted from food by-products appear as an alternative in the field of corrosion inhibition due to their biodegradability and easy availability. Various natural substances have been tested as corrosion inhibitors of steel in acidic media [2–3]. Among these, plant extracts [4–8], leaf extracts [9], fruit peel extracts [10–13] or even coffee ground [14] or honey [15] have shown their efficiency. The corrosion inhibition ability of plant extracts is generally attributed to the presence of secondary metabolites containing antioxidant polyphenolic compounds constituents like alkaloids, flavonoids, or condensed tannins [8,12,16]. The protection efficiency depends on the substrate, the active organic molecules and the corrosive media. The model of Langmuir-type adsorption of monolayers on metal surfaces and the precipitation of a conversion film are the two mechanisms used to explain the protection. However, due to the large variety of molecules contained in natural extracts, the inhibition mechanisms remain largely unknown.

In this work, the corrosion inhibition efficiency of maltaise orange peel extract on carbon steel in hydrochloric acid is investigated [10,17]. Actually, orange peel remaining after juice extraction constitutes almost 50% of the total fruit mass [18]. This waste is valuable since it is a rich source of phenolic compounds. Especially, flavonoids possess a significant antioxidant activity already used in the fields of functional food, cosmetic and pharmaceutic [19].

The aim of this paper is to correlate the antioxidant activity of selected molecules extracted from orange peel and the corrosion inhibition efficiency of the natural extract. For this purpose, the phenolic compounds were identified and quantified by HPLC. The corrosion inhibition efficiency of the orange peel extract and of selected phenolic compounds (neohesperidin, naringin) as well as the one of ascorbic acid was characterized by using electrochemical

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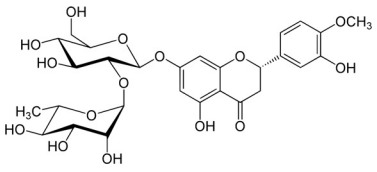
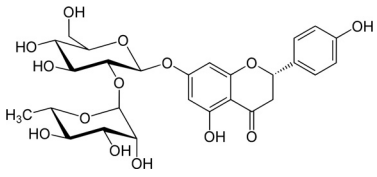
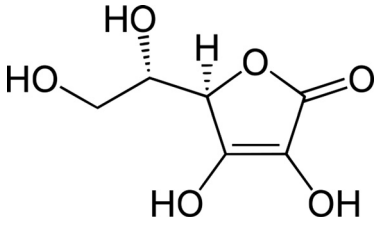
**Table 1**
Chemical formulae of compounds tested as corrosion inhibitors.

| Neohesperidin | Naringin | Ascorbic acid |
|---|---|---|
|  |  |  |

methods (corrosion potential measurements, polarization curves and electrochemical impedance spectroscopy) and was compared to their antioxidant activity evaluated by ABTS test. The electrochemical behavior analysis and microscopic surface observations after immersion in the acidic corrosive medium were combined to discuss the role of the antioxidant molecules in the corrosion protection brought by the extract.

## 2. Experimental

### 2.1. Preparation and characterization of the orange peel extract

Orange peels (Citrus sinensis, "Maltaise" variety in commercial maturity) were freeze-dried (Christ alpha 1-2 LD, −50 °C, 0.001 mbar, 72H) and finely ground using a coffee grinder (size of particles of ~0.315 mm) and stored at −18 °C in vacuum packaging bags. The extracts were prepared from 5 g of peel powder with 150 mL of a mixture ethanol/water (80/20 vol.%) by mechanical stirring at 35 °C. After centrifugation and filtration (0.2 μm), the extracts were stored at 4 °C [20].

Total phenols (TP) and total flavonoids (TF) contents of the extract were determined by spectrophotometric analysis, according to the methods described by Singleton et al. [21] and Zhishen et al. [22] respectively. The results were expressed as gallic acid equivalent (mg $L^{-1}$) for TP and rutin equivalent (mg $L^{-1}$) for TF.

Identification and quantification of the phenolic compounds contained in the extract were performed by using a High Performance Liquid Chromatography (HPLC) analytical system (Elite LaChrom, VWR-Hitachi) equipped with a diode array detector and a mass spectrometer. Both extract and standards were injected on a reversed-phase $C_{18}$ column and eluted at 40 °C using a gradient program with a mobile phase consisting of water-acetic acid 2% (solvent A) and methanol-acetic acid 2% (solvent B) [20]. Ascorbic acid was titrated by a procedure described by Tabart et al. [23].

The antioxidant activity of the extract and of its main antioxidant constituents was determined by ABTS test [24]. The free radical scavenging activities were determined by decolorization rate of 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) radical cation ($ABTS^{\bullet+}$) in presence of antioxidant compounds. The antioxidant activity was evaluated by measuring absorbance at 734 nm using a spectrofluorometer (SAFAS flx Xenius) exactly 1 min after mixing of the antioxidant compound with $ABTS^{\bullet+}$ and again after 15 min. The results were compared to the antioxidant activity of Trolox (commercial name for 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) which is commonly used as standard antioxidant molecule to measure the antioxidant capacity of foods and beverages [24]. The results are expressed as Trolox Equivalent Antioxidant Capacity (TEAC) in μM Trolox equivalent.

### 2.2. Electrochemical experiments

Steel specimens (composition C: 0.32–0.39 wt.%, Mn: 0.5–0.8 wt.%, S: <0.035 wt.%, P: <0.035 wt.%, Si: max 0.4 wt.%) of 3 $cm^2$ areas were used as working electrodes for electrochemical measurements. The exposed surface was abraded using SiC paper until 1200 grit. After rinsing with distilled water, the working electrode was mounted at the bottom of a three-electrodes cell, facing to a platinum grid (5 $cm^2$) used as counter electrode. The reference electrode was a KCl-saturated calomel electrode (SCE), mounted at a fixed distance of the working electrode (2 cm). Electrochemical tests were performed with air bubbling and at room temperature using a Versastat4 Potentiostat driven by Versastudio software.

Due to the low water solubility of the flavonoid compounds tested as corrosion inhibitors, the electrochemical characterisations were carried out in a corrosive electrolyte, 0.1 M HCl, prepared in a water/ethanol (50/50 vol.%) solvent. It has been shown that iron corrosion mechanisms are similar in water–alcohol acidic solutions and in pure aqueous acidic solution [25]. The orange peel extract (diluted to 10 and 50 vol.%) and selected pure antioxidant compounds ($10^{-5}$ M) were comparatively studied in this corrosive electrolyte. The chemical formulae of the chosen inhibiting molecules are given in Table 1: naringin, neohesperidin (purchased from Extrasynthese) and ascorbic acid (purchased from Sigma–Aldrich). In all cases, the pH of the corrosive electrolyte containing extract or pure antioxidant molecules was adjusted to 1 by adding 10 mL of 1 M HCl to 90 mL of the water/ethanol solvent.

For electrochemical measurements, the following experimental sequence was used:

a) Measurement of the open-circuit potential ($E_{oc}$),
b) Measurement of the electrochemical impedance spectra every 2 h for a duration of 8 h, with a 20 mV amplitude around the open-circuit potential maintained at its initial value during the data acquisition over all the frequency range (from 100 kHz to 5 mHz). The impedance data were analysed with ZSimpWin3.21 software, using a non-linear least squares fitting routine [26]. The charge transfer resistance $R_{ct}$ was evaluated in each case and the inhibition efficiency $\eta$ was estimated using relation (1) [27]:

$$\eta(\%) = \frac{R_{ct} - R^0_{ct}}{R_{ct}} \times 100 \quad (1)$$

where $R^0{}_{ct}$ is the charge transfer resistance calculated without inhibitor in the corrosive medium.

- Anodic and cathodic polarization curves were independently recorded after 8 h of immersion in the corrosive medium with a scan rate of 1 mV $s^{-1}$.

### 2.3. Surface analysis

To investigate the modification of steel surfaces in the corrosive medium, steel pieces (1 cm × 1 cm) were immersed during 10 days in the corrosive electrolyte without or with inhibitor (orange peel