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Viktoria Vorobyova (✉ vorobyovavika1988@gmail.com)

Nacional'nij tehnicnij universitet Ukraini Kiivs'kij politehnicnij institut imeni Igora Sikors'kogo

<https://orcid.org/0000-0001-7479-9140>

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Potential of Tomato Pomace Extract as a Multifunction Inhibitor Corrosion of Mild Steel

Victoria Vorobyova¹, Margarita Skiba²

¹Department of Physical Chemistry, National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Kyiv, Ukraine

²Ukraine University of Chemical Technology, Dnipro, Ukraine

Corresponding author: Victoria Vorobyova; vorobyovavika1988@gmail.com

Victoria Vorobyova: Vorobyovavika1988@gmail.com
<http://orcid.org/0000-0001-7479-9140>

Margarita Skiba <http://orcid.org/0000-0003-4634-280X>

ABSTRACT

The aim of this paper is to investigate tomato pomace extract (TPE) as multifunctional “green” vapor phase corrosion inhibitor for prevention of the atmospheric corrosion of mild steel and as corrosion inhibitor in neutral media of 0.5 M NaCl solution. The chemical profile of the TPE was analysed using gas chromatography mass spectrometry (GC-MS) and high performance liquid chromatography analysis (HPLC-DAD-MS). The major volatile constituents identified in tomato pomace extract were alcohols (12.5 %), fatty acids (23.78 %), aldehydes (41.6 %), ketones (8.65 %), and terpenoids (9.11 %). The predominant semi-volatile and high molecular weight chemical components in tomato pomace extract were phenolic acids and flavanols. The corrosion protection properties of the TPE as multifunctional corrosion inhibitor were studied using of accelerated corrosion tests (weight loss method) and electrochemical methods (polarization curves and linear polarization technique (LPR)). The mechanism of steel inhibition by TPE formulations was studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM) observations. The analysis confirmed that the growth of inhibitory properties is prolonged and corrosion rate is reduced after 40 - 48 h of exposure. Quantum-chemical calculations were used to predict the adsorption/inhibition properties of some of the main compounds of the extract.

Keywords – Green, inhibitor, corrosion, mechanism, SEM, AFM.

Declaration of interests

+The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Paper type Research paper

Introduction

The market for anti-corrosion means of protection (inhibitors) is expected to expand at a CAGR of more than 5% during the period of 2020 - 2027. The main factors stimulating the market include modernization of infrastructure and metalworking industry. In the same time regulations related to the solvents, rise in prices of raw materials etc. are expected to hinder the growth of the market studied. Consequently, it is an interesting and useful task to find the new sources for highlighting anticorrosive active compounds and to obtain “green” organic compounds for their further utilization as corrosion inhibitor. According to the literature, the extracts of horticultural crops (i.e., waste of agroforestry industry, food processing, fruit-based wastes) contain many green active compounds with promising

corrosion inhibition ability under different conditions. Food waste is considered as a sustainable and potentially renewable resource alternative to synthetic chemicals. Nowadays, scientists are developing more eco-friendly methods of corrosion protection that follow the principles of “green chemistry” [1-5]. Green and sustainable organic compounds can be simply obtained by extraction using organic solvents or water/organic solvent mixtures [6-7]. Research findings have shown that the use of a solvent system is promising, as it contributes to the extraction of a wider class of organic compounds from raw materials and subsequently makes it possible to provide multifunctionality of the inhibitory effect in neutral, alkaline and acid media. Moreover the presence of volatile organic compounds in the extract the possibility of using it as a volatile corrosion inhibitor. However, it should be noted that research is more aimed at studying the inhibitory effectiveness of plant extracts in an acid media and to a lesser extent in the neutral [1-3, 8-9]. As for the study of the effectiveness of “green” organic substances as vapor phase corrosion inhibitor of steel, only individual publications can be found [10]. There are some of publications showing the possibility of using menthol and Thyme as volatile corrosion inhibitors [10]. Most of the publications are the scientific result of the author's work [11-16]. The investigation presented herein had as its scope the development of polyfunctional corrosion inhibitor for the efficient protect of steel in various media [17]. The polyfunctional action of the extract can be achieved only then both volatile and higher molecular weight organic compounds from raw materials been extracted [18-20]. Moreover, the inhibitory efficiency and multi-functionality of the obtained extracts largely depends on the type of extractant/system of extractants chosen to extract organic compounds. Besides this, the mixture of solvent (Ethanol/water; acetone/water) provides a polarity variation capable of extracting compounds of different degrees of polarity [21-22].

Analysis of the agro-industrial sector of Ukraine shows that it is advisable to valorize tomato products (*Lycopersicon esculentum*. Mill.). Moreover, tomato is one of the most important vegetable crops cultivated worldwide. After the processing of tomato was formed a waste product called tomato pomace. Tomato pomace are a great source of phenolic compounds, as well as non-phenolic compounds (benzyl alcohol, saturated and unsaturated fatty acids, carotenoids and others) which have excellent redox properties [23-25]. Tomato pomace is the vegetable crop from tomato processing, comprised of skins, pulp, and seeds. Previous studies highlighted the potentiality of tomato pomace to be used as a promising source of eco-friendly organic compounds and antioxidants, nutrient-rich antioxidant ingredients (used as reductants for synthesis of Fe₃O₄/Au nanoparticles and as inhibitor corrosion of tin) that could be applied as functional compounds in various fields of chemical technologies [26-30]. The use of the "green" organic compounds such as extracted pectin, polyphenolic compounds from tomato peels as corrosion inhibitors have been widely reported by several authors [27]. In the literature, one can also find no information about possible applications of the tomato pomace and its extracted compounds as vapor phase corrosion inhibitor for prevention of the atmospheric corrosion of mild steel and as corrosion inhibitor in neutral media.

The prime target of the present work firstly is to determine the chemical composition of tomato pomace extract (TPE), obtained by mixes of the solvents, for recovering volatile organic compound (VOCs), semi-volatile and high molecular weight components. Secondly, is to evaluate the corrosion inhibition effect of TPE as “green” vapor phase corrosion inhibitor for prevention of the atmospheric corrosion of mild steel and as corrosion inhibitor in neutral media of 0.5 M NaCl solution.

Experimental

Materials and Methods

Steel planar specimens (St-3) having dimensions of 3.5 cm × 2.5 cm × 1.25 cm with a hole drilled at one end to enable suspension of the specimens, were used. The mild steel strips with the chemical composition 0.20% C, 0.43% Mn, 0.55 % Si, 0.016% S, 0.02% P and Fe balanced were used for the corrosion tests and electrochemical measurements. The mild strips were purchased from Rocholl, Aglasterhausen, Germany.

Tomato-processing by-products (peels/pomace) were received processing factory located in Nikolaev (Ukraine) from the company of the Chumak trademark. For this work, tomato peels were obtained upon industrial steam peeling of tomato fruits (*Solanum lycopersicum*) of the “Volove heart” variety.

Preparation and characterization of the tomato pomace extract

The by-product pomace (2 g) was mixed with 25 mL of solution 2-propanol/ethanol/water (v:v:v =50/20/30) in an extraction vessel. The mixture was placed in the ultrasound bath. Ultrasound-assisted extraction is a strategy to improve extraction since it can decrease the solvent consumption and extraction time. The extraction parameters were: temperature 50 °C and time 60 min. The final extract was then filtered in Whatman filter paper No. 1.

Gas chromatography–mass spectrometry analysis (GC–MS)

The composition of volatile substances of the extract was identified by gas chromatography coupled to mass spectrometry (GC–MS). A Shimadzu gas chromatograph (model GC 17A) equipped with flame ionization detector (FID), was operated under the following conditions: capillary fused silica column (CBP-5) (length, 25 m; internal diameter, 0.25 mm; film thickness, 0.22 µm), ion source temperature of 280°C. The GC–MS was operated in the electron impact ionization mode (EI) at 70 eV. The oven temperature was programmed as follows: the initial temperature of 50°C was maintained for 2 min, and then increased to 200°C at the rate of 10°C/min and held for 5 min. The percentage of each compound was determined from its peak area to the sum of the areas of all peaks. The identification of various components was carried out exclusively by a comparison of their retention time (RT) and mass spectral data with the RT, RI and mass spectral database of Wiley and NIST library. The compounds quantified on the basis of area under the peak and results were presented in percentage area.

HPLC-DAD-MS analysis

Identification and quantification of phenols were obtained by HPLC. The analysis was conducted in HPLC-Diode array detection (DAD) Agilent 2100 Series HPLC system (Agilent Technologies, Palo Alto, CA, USA) using a Zorbax Eclipse C18 column (4.6 × 100 mm, 3.5 µm). The column temperature was 35 °C and the flow rate was constant at 1.5 ml/min. The mobile phase was composed of 0.1 % (v/v) water : formic acid (mobile phase A) and acetonitrile (mobile phase B). The elution conditions were as follows: 0–15 min, B from 8 % to 30 % (5 min); 22–35 min, B from 30 % to 70 % (10 min); and 35–40 min, B from 70 % to 8 %. MS spectra were recorded using an Agilent 1290 Infinity LC System.

The UV-Vis spectra were acquired from 190 nm to 600 nm with a sampling rate of 1.0 and the highest scanning resolution (1 nm). MS spectra were recorded using an Agilent 1290 Infinity LC System equipped with an Agilent 6470A triple quadrupole using the separation conditions described above. The mass spectrometer operated in negative and positive ionization modes and spectra were recorded by scanning the mass range from m/z 50 to 1000. Nitrogen was used as drying, nebulizing and collision gas. Drying gas flow was 12 L/min at 350 °C. Nebulizer pressure was 50 psi and capillary voltages were 4000 V and 3500 V in positive and negative ionization modes, respectively. For the tandem MS (MS²), collision energy was set at 30 eV. The identity of polyphenols was ascertained using data from DAD and MS analysis, by comparison and combination of their retention times, UV-Vis and mass spectra. In addition identity for some compounds was confirmed with using authentic standards. Chromatograms were acquired at 280 and 320 nm and data analyzed using the Chromeleon software (Version 7.2 SR4).

Quantification was performed by HPLC–DAD according to an external standard method. Furthermore, the calibration curves, limits of detection (LOD) and quantification (LOQ) of the six target compounds were shown in Table 1. The

LOD and LOQ were evaluated by the residual standard deviation, with a residual range of 2–3 and 5–10, for LOD and LOQ, respectively.

Vapor phase inhibition test

The specimen preparation procedure was performed according to ASTM 31-72 standard. Mild steel coupons were used in the weight loss experiments. Before each experiment, the coupons were abraded and polished using emery papers (grades 220-1200), washed thoroughly with distilled water, degreased with acetone and finally dried. The tests were performed in a humidity chamber with periodic condensation of moisture. The anticorrosion films on steel surface are prepared by the vapor phase assembly [31] method. The method involved hung of a sample into the conical flask that contained VIC and immersion during of 12-72 hours. After inhibitor film-forming period gravimetric measurements inhibition test (vapor phase inhibition test) was conducted. The relative humidity (RH) one of the key factor that influence on the corrosion rate in atmospheric condition. Thus, the gravimetric measurements on condition of the periodic condensation of humidity from the various solution, these creates various relative humidity was carried out. According to the accelerated corrosion tests, samples of carbon steel were placed in a hermetically sealed vessel with distilled water or another more aggressive solution (3% NaCl and 1% NaNO₃) and a tank with the volatile inhibitor in a heat chamber, in which a mode of periodic moisture condensation (a test cycle at 40°C for 8 h and at 25°C for 16 h) was maintained. Solution of sodium chloride (3% NaCl that simulated a coastal atmosphere) as the most aggressive solution for studies the effectiveness of VIC in the condition of the periodic condensation of humidity during storage and transportation was selected. The influence of various RH on the effectiveness of VIC was studied. To form RH around 70% percent by the pressure of saturated water vapor as working solution to create an atmosphere with indicated humidity was used saturated aqueous solution of NaNO₃ (H = 67.3 - 70.1 % simulating high humidity and heat marine atmosphere environment) [32].

The total test time was 20 and 60 days. After the corrosion tests, the degree of corrosion damage was estimated the criteria of the ASTM D 610 - 95 standard. As inhibitors were investigated tomato pomaces extract (TPE) and mixes of TPE and 1% of APTES.

Corrosion rates and inhibitor effectiveness are calculated by means of the following equations:

$$CR = \frac{W_0 - W_1}{A \times \tau}, \quad (3)$$

$$IE = \frac{CR_1 - CR_2}{CR_1} 100, \quad (4)$$

where CR is the corrosion rate, g m⁻² h⁻¹; A is the sample area, m²; W₀ is initial weight of the sample, g and W₁ is sample weight after the immersion period, g; τ is the immersion period, h; CR₁, g m⁻² h⁻¹ and CR₂, g m⁻² h⁻¹ are the corrosion rates without and with inhibitor, respectively.

Assessment of the inhibitory effectiveness of the extract in 0.5 M NaCl solution

The initial weight of each coupon was taken (before immersion) using an analytical balance. Then, the specimens were immersed in 0.5 M NaCl solution without and with various dosages of the TPE. After the immersion period (26 days), the specimens were taken out, washed, dried and weighed again. All the experiments were performed in triplicate and the average weight loss values were recorded. The efficiency of inhibitors (IE, %) was estimated according to the degree of protection against corrosion. The 0.5 M NaCl solution was prepared by diluting sodium chloride into distilled water.

Electrochemical measurements

Electrochemical experiments were carried out in the conventional three-electrode cell with a platinum counter electrode (CE), a saturated calomel electrode (SCE) coupled to a fine Luggin capillary as the reference electrode (RE) and a working electrode (WE). The carbon steel working electrode was designed with a fixed exposed surface area of 0.385 cm². As a specific feature of our electrochemical investigations, we can mention the following fact: the disk-shaped surface of the end face of the working electrode was immersed in surface layers of the working solution by at most 1–2 mm [32]. This enabled us to perform more exact modeling of the atmospheric corrosion (AC) running on the metal surface in thin layers of condensed moisture. Preliminarily, within 24-48 hours, the sample in a closed container with TPE was exposed. After that, the sample was transferred to an electrochemical cell for research. The stimulated atmospheric corrosion solution was prepared by using double-distilled water which contains 7.1 g Na₂SO₄ /L.

In the study of the extract as corrosion inhibitor in a neutral medium (0.5 M NaCl) sample was immersed in solution that contained TPE (1000 ppm) and kept for 24-48 hours. After that, electrochemical studies were carried out.

The corrosion resistance of the films formed on the metal surface was evaluated by the electrochemical method of linear polarization technique (LPR), in order to study the process of corrosion in the conditions of moisture condensation on the metal surface. LPR method, used widely in corrosion process research, involves only slight polarization of the sample, typically in the order of ± 10 mV. When measuring the polarization resistance, the polarization resistance indicator was used [32-36].

The measurements in thin films of electrolytes required a special design of the corrosion sensor. Four coaxial steel rings (steel 20) of different diameters were assembled in a package and connected in pairs. The electrode has alternating zones of metal and dielectric. A dielectric, the hydrophilicity of which is close to the hydrophilicity of the metal, was used to provide the conditions for the more uniform condensation of moisture on the surface. The end surfaces of the electrodes with dielectric layers are the working surface of the sensor. The moisture film condensed on the end surface is an electrolyte that provides measurement of the polarization resistance at the metal - electrolyte interface. The working surface area of the sensor is 4 cm². In the experimental setup, sealed containers with the solution and sensors located above it were installed in a thermostat. The temperature of the solution in the thermostat was maintained higher (30 and 40°C) than the ambient temperature. Due to the temperature difference of the sensor surface, which was located above the water level in the thermostat, a film of moisture condensed on it. The working surface of the sensors was cleaned with sandpaper, degreased with Viennese lime and washed under running water. After washing and drying with filter paper, the electrodes were fixed on the lids and transferred to a thermostatic container. To create a film of moisture, the condensation of the vapor from the solution was carried out on the surface of the sensor, due to the difference in temperature of the solution and the ambient air. To perform the measurement, the measuring cable of the polarization resistance indicator was connected to the sensor contacts and during the experiment the instantaneous values of the polarization resistance R_p in kOhm. The influence of the nature of condensation was investigated based on the conditions of humidity, temperature and dew point, as well as the types of condensation, such as capillary, droplet and film condensation.

In the study of the extract as corrosion inhibitor in a neutral medium, a sensor of a different configuration was used [32-36]. The density of polarizing current was $i = 5 \mu\text{A}/\text{cm}^2$. The initial potential difference and Ohmic drop were automatically compensated. Polarization resistance values R_p were measured during the immersion time of the samples in an aggressive solution without and with tomato pomace extract (1000 ppm.).

Surface characterization

Scanning electron microscopy (SEM)

Surface analysis of the carbon steel samples was carried out in the without and after storing the electrode in the vapors with tomato pomace extract and TPE+APTES using FEI E-SEM XL 30 (Detection of secondary electrons). For SEM images, 1 cm² sample was taken.

Atomic force microscopy (AFM)

The AFM analysis was performed in tapping mode using AFM (Dimension icon Scan Asyst) supported by Nanoscope V. 1.80 software having spring constant of 42 N/m and tip radius 10 nm. The measurements were done at room temperature and a scan rate of 0.4 Hz over an area of 10 × 10 μm².

Computational studies

The geometry optimization of the molecules was calculated by using HyperChem 7 program package. The energy of the obtained conformers of molecules was minimized using the MM+ force field and PM3 parameterization. The geometry optimization was obtained by application of the restricted Hartree-Fock method (RHF) using MNDO approach. The energy of the highest occupied molecular orbital (E HOMO), and the HOMO – LUMO gap (E_{gap}), absolute hardness (η), chemical softness (σ) and electronegativity (χ), electrophilicity index (ω), vertical ionization potentials (IP_v), electron affinity (EA_v) were calculated with the help of Eq. (5)-(8). Vertical ionization potential (IP_v) was determined according to Koopmans' theorem: (IP_v = -EHOMO). Electron affinity was determined according to formula: EA_v = -ELUMO. Additionally, absolute hardness (η) and electronegativity (χ) for the compounds under study were evaluated from HOMO and LUMO energies using the following formulae:

$$\eta = (IP_v - EA_v)/2 \quad (5)$$

$$\chi = (IP_v + EA_v)/2 \quad (6)$$

The molecular electrophilicity index (ω) was calculated from the relationship between η and χ as:

$$\omega = \frac{\chi^2}{2\eta} \quad (7)$$

The chemical softness was calculated with the help of Eq 8:

$$\sigma = \frac{1}{\eta} \quad (8)$$

Results and Discussion

The elution profile of the compounds derived from the extracts was followed at 270 and 330 nm, the wavelength characteristics of the phenolic. The results of the HPLC analysis of the tomato pomace extracts (TPE) are presented in Tables 2 and Figures 1. The structures of the main phenolic compounds extracted are shown in Fig. 2. The most abundant compounds in tomato pomace extract obtained by solution of 2-propanol/ethanol/water were phenolic acids (hydroxybenzoic and hydroxycinnamic acids) and flavanols (kaempferol 3-O-glucoside, (+)-catechin and

quercetin). Peak 1 was detected at retention time 4.03 min with λ_{max} 280 nm was gallic acid with m/z 169 followed by MS2 fragmentation of m/z 125, 107, 97 and 79, as shown in Table 1. Caffeic acid was eluted at retention time of 4.03 min with 332 nm and identified with m/z 181. The fragmentation pattern was m/z 135, the loss of a formate (CHO_2) group from caffeic acid and m/z 163 by dehydration. The next peak obtained at 4.3 min was ferulic acid with m/z 193 followed by MS2 fragmentation of m/z of 134.

(Take in Tables 2 and Figures 1)

(Take in Figures 2)

The GC-MS analysis of tomato pomace extract (Table 3, Fig. 3) showed the presence of 21 volatile organic compounds (VOCs).

(Take in Figures 3)

It was found that the VOCs of the tomato pomace extract were mainly presented of alcohols (12.5 %), saturated and unsaturated fatty acids (23.78 %), aldehydes (41.6 %), ketones (8.65 %), and terpenoids (9.11 %). Of the aldehydes identified hexanal (9.6 %) and benzaldehyde (5.7 %) was the predominant aldehyde found in the tomato pomace extract. In the tomato pomace extract, the most significant compound was terpenoids such as thymol (4.8%) and ketones, namely 3-Octanone (6.18%), agreement previous studies on volatiles in tomato waste.

According to the GC-MS analysis after using the solution 2-propanol/ethanol/water as solvents volatile chemical components were extracted from tomato pomace and therefore is a potentially can be for use as a volatile corrosion inhibitor of steel. The structures of the main volatile compounds extracted are shown in Figure 4.

The analytical standards were unavailable for all of the separated peaks/compounds. Table 4 shows the content of selected compounds: quercetin, caffeic acid, chlorogenic acid, gallic acid and ferulic acid identified and quantified by HPLC-DAD-MS. Chlorogenic acid was detected as the main phenolic compound in tomato extracts.

(Take in Table 4)

More importantly, after using the solution 2-propanol/ethanol/water as solvents volatile, semi-volatile and high molecular weight chemical components were extracted from tomato pomace and therefore is a potentially can be for use as a multifunctional corrosion inhibitor of metals.

(Take in Figures 4)

Accelerated tests of corrosion-resistant carbon steel showed that the studied extract of tomato pomace provides a sufficiently high corrosion protection of steel with periodic condensation of moisture for 20 days (Figure 5). The film formed from the vapor-gas phase of tomato pomace extract depending on concentration provides a degree of protection of the metal under conditions of periodic condensation of moisture at the level of 70-98%.

(Take in Figures 5)

It should be noted that the corrosion rate to decreases with increasing the time film-formation. The inhibition efficiency (IE) increases in the range 27 – 93 % (Table 5). The inhibition efficiency after 72 h of TPE film-forming was higher than that after 12 and 48 h of TPE film-forming. This suggested that the corrosion protectiveness of TPE film-forming on the steel surface was enhanced by prolonging the TPE treatment.

The influence of the value of relative humidity during moisture condensation on the on inhibition efficiency of TPE was studied (Figure 6). It was found, the inhibition efficiency of TPE is less at the condensation of moisture on the steel surface from aqueous solution containing chlorides.

(Take in Table 5)

(Take in Figures 6)

The efficiency of various concentrations TPE in 0.5 M NaCl medium for a period of 26 days obtained via weight loss method is listed in Fig 7 indicating that the solution with 1000 ppm possessed maximum efficiency for inhibition. The effectiveness of inhibition increased with concentration.

(Take in Figures 7)

The immersion time is an important parameter in assessing the stability of corrosion inhibitive properties of organic compounds. Fig. 7 illustrates the effect of immersion time on the inhibitive performance of TPE. Immersion time was found to have a profound effect on the corrosion inhibition performance by the tomato pomace extract. It is evident from Fig. 7 that inhibition efficiency in 0.5 M NaCl containing TPE slowly increased up to the moment when it reached 30 h of immersion, and then it rapidly increased between 40 h and 48 h of immersion till reached its saturation. The inhibition performance is improved with the elongation of immersed time reaching the maximum value of 95 % for 48 h. The effect of immersion time in a 0.5 M NaCl solution with TPE on the weight loss rate indicated that TPE not only keeps its inhibitive activity for steel but also improves its effectiveness over the long-term immersion due to the synergistic influence of the main compounds which offer an additional protection.

These observations indicate that the inhibition efficiencies of the film formed in the vapour phase of tomato pomace extract may vary significantly over the exposure period of condensation of moisture. As shown in the figure 8, R_p of the sample after treatment in the volatile compounds of VCI is both increased firstly (1-12 h) and then slightly decreased. And then, the polarization resistance values increased from 5 to 20.1×10^{-3} Ohm after 12-18 h of immersion time. This period to the first stage of the formation of a protective film can be attributed. During 40-48 h, there is a significant increase in the value of R_p . It's the second stage of film formation. The data obtained are quite natural, since the plant extract contains volatile compounds with differences volatility and the evaporation of which can be prolonging for a certain time.

(Take in Figures 8)

The same behavior was shown in the case of the evolution of inhibition efficiency (%) in function of immersion time of TPE for the steel in 0.5 M NaCl solution (Fig. 9). Such time dependence means that the formation of a barrier layer on the surface is a continuous process which requires at least 45-48 hours.

The relatively poor protection afforded by tomato pomace extract on steel at the initial immersion compared to the results obtained at long exposure suggests that the formation of a highly protective and stable inhibitor layer on steel surface might need more time than 1-30 h to evolve completely. The authors obtained similar results related to the effect of immersion time on the inhibition performance of the grape pomace [38], rape cake [37] and raphanu scape [40], apricot pomace extract and *Centaurea cyanus* extract [41].

(Take in Figures 9)

Polarization measurements were performed to monitor the mechanism of anodic and cathodic partial reactions as well as identifying the effect of an inhibitor on each partial reaction. Polarization curves were measured after steel assembly time in the environment of volatile compounds of the tomato pomace extract, in 12 and 48 h of exposure. The anodic and cathodic corrosion current density curves in presence of film on the surface are shifted towards lower current density region as compared to the blank (Figure 10). When forming a protective film with volatile compounds of peach pomace extract, a significant effect is observed on the cathodic polarization curve after 48 hours of film formation. During the 12-hour exposure of the sample in an inhibitor atmosphere, iron oxidation products (lepidocrocite (γ -FeOOH), goethite (α -FeOOH), and maghemite (γ -Fe₂O₃)) are formed and the components are gradually adsorbed. The formation of electrochemically active corrosion products occurs a little later, therefore on the cathodic polarization curve there is no significant effect on the current density.

(Take in Figures 10)

The polarization plots for the steel samples exposed to the solution including TPE is illustrated in Figure 11. The polarization curves were provided for studying the inhibition mechanism of inhibitor after 48 h exposure of the samples in 0.5 M NaCl. It is generally accepted, that the corrosion mechanism of carbon steel in neutral NaCl aqueous medium can be expressed as the following typical reactions [41]:



Then, corrosion products including FeOOH, Fe₂O₃ and Fe₃O₄ would generate at the interface between steel and NaCl solution.

The cathodic polarization curve recorded immediately after steel immersion in testing solution shows typical trend of oxygen reduction with limiting current of $i = 0,39 \times 10^{-4} \text{A/cm}^2$. The region of the cathodic curve in the range from - 0.6 to - 0.9 V/SCE has occurred due to the diffusion-controlled oxygen reduction reaction [41-43]. As exposure progresses, the value of limiting current decreases and finally reaches $0.17 \times 10^{-4} \text{A/cm}^2$ after 48 h of exposure. So, the addition of extract reduces the corrosion rate of steel by forming a diffusion barrier on the surface of the metal.

However, the highest blocking ability of the surface film is reached only after the 48 h of exposure. Furthermore, the corrosion potential of the steel panels increased from -0.395 mV to -0.310 mV in the presence of TPE extract. At anodic polarization of an electrode active anodic dissolution of steel is observed. The anodic and cathodic corrosion current density curves in presence of film on the surface are shifted towards lower current density region as compared to the blank. It can be understood that in the attendance of TPE the anodic and cathodic reactions were suppressed compared to the blank sample, revealing the mixed anodic/cathodic inhibition activities of the TPE on the surface.

(Take in Figures 11)

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) was performed for surface study of uninhibited and inhibited mild steel samples. In order to understand the mechanism of film formation by tomato pomace extract, it was researched the morphology of steel surface. Fig. 12 shows the surface morphology of specimens after 48 hours immersion in the solutions with tomato pomace extract (1000 ppm). The steel immersed for 48 h in NaCl (Fig. 12 a) shows basically flower-like flakes with finger-like structures protruding in a random manner and bumpy surface. The close examination of the SEM images reveals that the specimens immersed in the inhibitor-containing solutions possess

smoother surfaces compared to those immersed in a blank 0.5 M NaCl solution, which are rough and coarse. This improvement of the surface morphology indicates the formation of a good protective film of TPE which is responsible for the inhibition observed. The surface morphology of the sample without exposure to volatiles of tomato pomace extract indicates formation of corrosion product. The following images are of the steel surface after 48 h of exposure for the film-forming of the tomato pomace extract. The formation of a protective film is evident.

(Take in Figures 12)

The samples after their exposure in a corrosive medium with TPE for 24 and 48 h using an atomic force microscope were investigated. It was found that a protective film with a thickness of more than 248 and 540 nm, respectively, is formed on the steel surface. The relevant average roughness (Ra) is 16.9 nm. In addition, after the increases time of film-forming to 48 h the corresponding value of Ra is reduced to 14.6 nm (Figures 13). Given the topography of the surface of films of organic compounds of plant extract and their thickness, the results of voltammetric studies and accelerated corrosion tests, it can be argued that the mechanism of their formation are based on a number of complex processes.

(Take in Figures 13)

This observation supported the formation of a protective barrier layer on the steel surface already after 24 h and 48 h exposure to the media of vapors with tomato pomace extract (Figures 14 and Figures 15). After 24 h exposure the surface of steel is almost completely by film was covered. When exposure time extends to 48 h, more filled film on the steel surface was observed.

(Take in Figures 14)

Figure 15 indicates that the thickness film of the steel surface after 48 h exposure at atmosphere the volatile compounds of TPE is up to 109.9 nm.

(Take in Figures 15)

The question of identifying bioactive molecules responsible for the inhibitory properties of plant extracts as inhibitors of metal corrosion is relevant. The obvious fact is that, the mechanism of inhibition by tomato pomace extract cannot be described by adsorption mechanism of individual molecules as it is often claimed since the extract contains compounds of various classes. In addition, by the gravimetric and polarization methods it was shown that the inhibition efficiency of the extract increases with time. Moreover, a complementary investigation of component composition of the solution containing 1000 ppm of TPE after 48 hours of immersion steel and washouts obtained from the metal surface preliminarily treated in volatile compounds of TPE during 48 h was carried out to clarify the inhibition mechanism of inhibitor. From GC-MS data of the component composition of the solution containing 1000 ppm of TPE after 120 hours of immersion steel and washouts obtained from the metal surface preliminarily treated in volatile compounds of TPE during 48 h, various classes of inhibitor-compounds were identified, namely the main components of the extract, the oxidized structures of the phenolic compounds and adduct of transformation (Fig. 16, 17). The transformation (polymerisation) products of the phenolic flavanol and aldehydes namely flavanol-aldehyde adducts

(Catechin-furfuraldehyde dimer (RT 4.34) Catechinc - syringaldehyde. Dimer (RT 7.2)), have also been identified It is rather difficult to determine which of these connections provide higher ability for inhibition corrosion (Table 6) [45].

(Take in Figures 16 and Table 6)

Chromatogram of the 2-propanol (Fig. 17, Table 7) washout obtained from the metal surface preliminarily treated with TPE after 48 h of film-forming indicates about presents of the main volatile compounds of TPE and products of oxidized of the thumol and limonene.

(Take in Figures 17 and Table 7)

The extracts of tomato pomace are a mixture of organic components, which results in the complex anticorrosion action. It is rather difficult to determine what components present in tomato pomace extract create their relatively high inhibition potency. Moreover, taking into account the formation of new components of the extract, such as transformation and oxidation adducts, it is important to theoretically evaluate their adsorption capacity in comparison with the main components. A theoretical calculation was conducted to investigate the inhibition activity of the main compounds of tomato pomace extracts and it's the transformation and oxidation adducts. The molecules structure of the main tomato pomace extract obtained after a geometric optimization procedure is presented in Fig. 18. The results of quantum-chemical calculations of the energy parameters of molecules are presented in Tables 8 and 9.

Research findings have shown that some descriptors relevant to adsorption/inhibition properties have also been computed: the energy of the highest occupied molecular orbital (EHOMO), the energy of the lowest unoccupied molecular orbital (ELUMO), and the HOMO–LUMO gap (H–L gap) [46-48]. It was reported that higher HOMO energies indicate better electron-donating properties of a molecule and is also the index predicting inhibition activity. The inhibition activities increase with the increasing energy of HOMO. The electron density distribution of HOMO enables the prediction of the adsorption centres at the molecules for the reaction with the metal surface. (Fig. 18). The EHOMO values for compounds increase in the following order: Caffeic acid, Chlorogenic acid, Ferulic acid, Gallic acid, (R)-(-)-carvone and Isopropyl palmitate. The negative amount of HOMO and negative amount of LUMO are equal to vertical ionization potential and vertical electron affinity, respectively [46-48].

(Take in Figures 18 and Table 8, 9)

A small energy gap between the HOMO and LUMO increases the anticorrosion activity. The energy gap values for compounds listed in Table 8 increase in the following order: Ferulic acid; Caffeic acid; Chlorogenic acid; Gallic acid, (R)-(-)-carvone and Isopropyl palmitate. According to Parr et al. ω is a global reactivity index related to the chemical hardness and chemical potential of the molecule. Chemical hardness (η) and softness (σ) are used to analyze the behavior of molecule within a biological system. The molecule characterized by a low hardness is classified as a reactive one and vice versa. It is obvious from Table 9 that compound Ferulic acid has the lowest hardness. The softness is the ability of a molecule to take the electrons which is related to the existing functional groups in the molecule. The calculated values of softness for the molecules are approximately the same. The absolute softness value is the smallest at isopropyl palmitate. Low value of absolute electronegativity as well as high value of chemical potential denotes the delocalization of electrons in the molecular system. It is obvious from Table 9 Chlorogenic acid that has the lowest absolute electronegativity. The electrophilicity index is a descriptor of the strength of electrophilicity. Moreover, the low values electrophilicity (~ 1.2 eV) for all compounds shows its high current of electron from the donor moiety to the

acceptor. Thus, the results of quantum-chemical results indicate that both individual compounds and transformation products have high adsorption activity.

Inhibition mechanism

There are several arguments that can be proposed to explain the inhibition mechanism or the observed higher amount of inhibition effect after 48 hours of corrosion measurements:

(a) The main compounds of tomato pomace extract have changed their structure over the immersion time in neutral solution during the corrosion measurement, and transformed to a new structurally different compound, which appears as the designated peaks in the chromatogram. This new compounds can be adsorbed onto the surface of mild steel or reenters the bulk solution.

(b) New compounds had formed a complex with other main compounds of tomato pomace extract before it got adsorbed onto the surface of mild steel. It is possible that all or a combination of some of the proposed explanations took place to produce the observed significant decrease of the corrosion rates after 48 -72 hours of the corrosion measurements. Furthermore, the inhibitory action of TPE in neutral media could be attributed to the adsorption and interactions of its components on the steel surface. This layer acts a self-protective barrier, characterized with the high degree of the protection. The new self-transformed protective layer provides better protective properties. Thus, the high inhibiting efficiency of TPE in respect to steel corrosion in a neutral solution is a consequence of the formation of a protective film with the participation of the main components of the extract and the products of their chemical transformations on the corroding steel.

(c) The mechanism of action of the extract as a volatile inhibitor of atmospheric corrosion is somewhat more complicated. Since, it is more likely that the oxidation of volatile substances of TPE occurs already on the metal surface, after their adsorption from the vapor phase.

The results of this study could open a new window for the understanding and development of the effective eco-friendly phytochemical based corrosion inhibitors. The results obtained would contribute of scientific research in the direction of the understanding, that in the plant extracts the main inhibitory compounds was caused there are not only individual organic compounds, but the products of their interaction, transformation and oxidation.

CONCLUSIONS

Our current study has described an experimental investigation of corrosion inhibition by TPE as corrosion inhibitors in neutral medium and in conditions of periodic condensation of moisture. The extraction from waste was a conventional extraction process using of solution 2-propanol/ethanol/water as the solvent. After all the investigations the following conclusions are obtained:

-Four dominant volatile compounds were identified, which are saturated and unsaturated fatty acids (23.78 %) and aldehydes (41.6 %). Mainly five semi-volatile and high molecular weight chemical compounds (Chlorogenic acid, Caffeic aci and Ferulic acid) were identified in tomato pomace extract from the HPLC-DAD-MS analysis data.

-For the first time, the extract of the tomato pomace, which contains some bio-active/eco-friendly compounds, was employed as organic eco-friendly inhibitors for steel corrosion mitigation in neutral medium and in conditions of periodic condensation of moisture. The inhibition efficiency obtained from plurality of experimental data is showing good agreement with each other and exhibit prolonged film-forming period up to 48 hour. The complex analysis showed that the inhibitor after prolonged time of film forming provide an excellent protection against corrosion that is complemented by the protective layer of the product polymerization between the components of the extract, oxidation

products of organic substances and the same was confirmed by GC–MS after exposing the plates to accelerated corrosion tests in neutral medium and the condition of condensation of moisture.

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References

1. N. Chaubey, Savita, A. Qurashi, et al., Frontiers and advances in green and sustainable inhibitors for corrosion applications: A critical review, *Journal of Molecular Liquids*. 321 (2018), 114385. <https://doi.org/10.1016/j.molliq.2020.114385>
2. S.H. Alrefaee, K.Y. Rhee, C. Verma, et al., Challenges and advantages of using plant extract as inhibitors in modern corrosion inhibition systems: Recent advancements, *Journal of Molecular Liquids*. 321 (2021), 114666. <https://doi.org/10.1016/j.molliq.2020.114666>
3. Hongyu Wei, B. Heidarshenas, L. Zhou, G. Hussain, Q. Li, K. (K.) Ostrikov, Green Inhibitors for Steel Corrosion in Acidic Environment: State-of-art, *Materials Today Sustainability*. 10 (2020), 100044. <https://doi.org/10.1016/j.mtsust.2020.100044>.
4. G. Vasyliiev, V. Vorobiova, Rape grist extract (*Brassica napus*) as a green corrosion inhibitor for water systems. *Materials today. Proceedings* 6 (2) (2019), 78-186. <https://doi.org/10.1016/j.matpr.2018.10.092>
5. G. Vasyliiev, V. Vorobyova, and T. Zhuk, Raphanus sativus L. Extract as a Scale and Corrosion Inhibitor for Mild Steel in Tap Water, *Journal of Chemistry*. 2020 (2020), 5089758. <https://doi.org/10.1155/2020/5089758>
6. S Pal, H Lgaz, P. Tiwari, I.M, Ji G Chung, , and R. Prakash Experimental and theoretical investigation of aqueous and methanolic extracts of *Prunus dulcis* peels as green corrosion inhibitors of mild steel in aggressive chloride media. *Journal of Molecular Liquids*. 276 (2018) 347–361. <https://doi.org/10.1016/j.molliq.2018.11.099>
7. Refait P, Rahal C., Masmoudi, M. Corrosion inhibition of copper in 0.5 M NaCl solutions by aqueous and hydrolysis acid extracts of olive leaf. *Journal of Electroanalytical Chemistry*. 859 (2020) 113834. <https://doi.org/10.1016/j.jelechem.2020.113834>
8. Y. Liu, Z. Song, W. Wang, L. Jiang, Y. Zhang, M. Guo and N. Xu, Effect of ginger extract as green inhibitor on chloride-induced corrosion of carbon steel in simulated concrete pore solutions. *Journal of Cleaner Production*. 214: (2019) 298–307. <https://doi.org/10.1016/j.jclepro.2018.12.299>
9. C. C. Ahanotu, I.B. Onyeachu, M.M. Solomon., I.S. Chikwe, O.B. Chikwe, and C.A. Eziukwu, *Pterocarpus santalinoides* leaves extract as a sustainable and potent inhibitor for low carbon steel in a simulated pickling medium. *Sustainable Chemistry and Pharmacy* 15 (2020), 100196. <https://doi.org/10.1016/j.scp.2019.100196>
10. S. Gangopadhyay, P.A. Mahanwar, Recent developments in the volatile corrosion inhibitor (VCI) coatings for metal: a review. *J Coat Technol Res*. 15 (2018) 789–807. <https://doi.org/10.1007/s11998-017-0015-6>
11. V. Vorobyova, O. Chygyrynets', M. Skiba, T. Zhuk, I. Kurmakova, and O. Bondar, A comprehensive study of grape cake extract and its active components as effective vapour phase corrosion inhibitor of mild steel, *Int. J. Corros. Scale Inhib.*, 7 (2018), 185–202. doi: 10.17675/2305-6894-2018-7-2-6
12. V. I. Vorobyova, M. I. Skiba, A. S. Shakun and S. V. Nahirniak, "Relationship between the inhibition and antioxidant properties of the plant and biomass wastes extracts – A Review," *Int. J. Corros. Scale Inhib.*, vol. 8, no. 2, pp. 150–178, 2019. doi: 10.17675/2305-6894-2019-8-2-1
13. V. Vorobyova, M. Skiba, and O. Chygyrynets', "A novel eco-friendly vapor phase corrosion inhibitor of mild steel," *Pigment & Resin Technology*, vol. 48, no. 2, pp. 337–349, 2018 <https://doi.org/10.1108/PRT-03-2018-0025>
14. V.I. Vorob'iova, O.E. Chyhyrynets, O.I. Vasyl'kevych, Mechanism of Formation of the Protective Films on Steel by Volatile Compounds of Rapeseed Cake. *Mater Sci* 50, 726–735 (2015). <https://doi.org/10.1007/s11003-015-9778-z>
15. O.E. Chyhyrynets, Y.F. Fateev, V.I. Vorobiova, et al. Study of the Mechanism of Action of the Isopropanol Extract of Rapeseed Oil Cake on the Atmospheric Corrosion of Copper. *Mater Sci* 51, 644–651 (2016). <https://doi.org/10.1007/s11003-016-9886-4>

16. V. Vorobyova, O. Chygyrynets, and M. Skiba, "4-hydroxy-3-methoxybenzaldehyde as a volatile inhibitor on the atmospheric corrosion of carbon steel," *Journal of Chemical Technology and Metallurgy*, vol. 53, pp. 336–345, 2018. https://dl.uctm.edu/journal/node/j2018-2/22_17_91_p_336_345.pdf
17. V. I. Vorobyova, M. I. Skiba, Surface modification of the mild steel by multifunctional self-assembling nanolayers from the natural organic compounds of apricot pomace extract, *Molecular Crystals and Liquid Crystals*, 1, 700 (2020) 63-76. <https://doi.org/10.1080/15421406.2020.1732553>
18. Y. P. Yee, S. N. Saud, & E. Hamzah, Pomelo Peel Extract as Corrosion Inhibitor for Steel in Simulated Seawater and Acidic Mediums. *Journal of Materials Engineering and Performance*. (2020). [doi:10.1007/s11665-020-04774-1](https://doi.org/10.1007/s11665-020-04774-1)
19. M. Magni, E. Postiglione, S. Marzorati, L. Verotta, S. P. Trasatti, (Green Corrosion Inhibitors from Agri-Food Wastes: The Case of Punica granatum Extract and Its Constituent Ellagic Acid. A Validation Study. *Processes*, 8(3) (2020), 272. [doi:10.3390/pr8030272](https://doi.org/10.3390/pr8030272)
20. J. Halambek, I. Cindrić, A. N. Grassino, Evaluation of pectin isolated from tomato peel waste as natural tin corrosion inhibitor in sodium chloride/acetic acid solution. *Carbohydrate Polymers*, (2020), 115940. [doi:10.1016/j.carbpol.2020.115940](https://doi.org/10.1016/j.carbpol.2020.115940)
21. S. Yahya, N. K. Othman, M. C. Ismail, Corrosion inhibition of steel in multiple flow loop under 3.5% NaCl in the presence of rice straw extracts, lignin and ethylene glycol. *Engineering Failure Analysis*. 100 (2020), 365–380. [doi:10.1016/j.engfailanal.2019.02.036](https://doi.org/10.1016/j.engfailanal.2019.02.036)
22. V. Vorobyova, M. Skiba, Peach Pomace Extract as Efficient Sustainable Inhibitor for Carbon Steel Against Chloride- Induced Corrosion, *Journal of Bio- and Tribo-Corrosion*. (2021), 7:11. <https://doi.org/10.1007/s40735-020-00450-y>
23. Z. Lu, J. Wang, R. Gao, F. Ye, and G. Zhao, Sustainable valorisation of tomato pomace: A comprehensive review, *Trends in Food Science & Technology*, 86 (2019), 172–187. <https://doi.org/10.1016/j.tifs.2019.02.020>
24. B.J. Allison, and C.W. Simmons, Valorization of tomato pomace by sequential lycopene extraction and anaerobic digestion", *Biomass and Bioenergy*, 105 (2017), 331–341. <https://doi.org/10.1016/j.biombioe.2017.07.019>
25. J. Pinela, M. A. Prieto, A. M. Carvalho, M. F. Barreiro, M. B. P. P. Oliveira, L. Barros, and I. C. F. R. Ferreira, Microwave-assisted extraction of phenolic acids and flavonoids and production of antioxidant ingredients from tomato: A nutraceutical-oriented optimization study, *Separation and Purification Technology*, 164 (2016), 114–124, <https://doi.org/10.1016/j.seppur.2016.03.030>
26. M. Sarno, and M. Iuliano, "Highly active and stable Fe₃O₄/Au nanoparticles supporting lipase catalyst for biodiesel production from waste tomato", *Applied Surface Science*, 474 (2019), 135–146. <https://doi.org/10.1016/j.apsusc.2018.04.060>
27. A. N. Grassino, J. Halambek, S. Djaković, S. Rimac Brnčić, M. Dent, and Z. Grabarić, Utilization of tomato peel waste from canning factory as a potential source for pectin production and application as tin corrosion inhibitor, *Food Hydrocolloids*, 52 (2016), 265–274. <https://doi.org/10.1016/j.foodhyd.2015.06.020>
28. Calvo, M.M., Dado, D. & Santa-María, G. Influence of extraction with ethanol or ethyl acetate on the yield of lycopene, β-carotene, phytoene and phytofluene from tomato peel powder. *Eur Food Res Technol*, 224 (2007), 567–571. <https://doi.org/10.1007/s00217-006-0335-8>
29. J. Nagarajan, H. Pui Kay, N. P. Krishnamurthy, N. R. Ramakrishnan, T. M. S. Aldawoud, C. M. Galanakis, and O. C. Wei, Extraction of Carotenoids from Tomato Pomace via Water-Induced Hydrocolloidal Complexation, *Biomolecules*, 10(7), (2020) 1019. <https://doi.org/10.3390/biom10071019>
30. B. Šojić, B. Pavlić, V. Tomović, S. Kocić-Tanackov, S. Đurović, Z. Zeković, and S. Škaljac, Tomato pomace extract and organic peppermint essential oil as effective sodium nitrite replacement in cooked pork sausages, *Food Chemistry*, 330 (2020), 127202. <https://doi.org/10.1016/j.foodchem.2020.127202>
31. H.L Zhang, T. F. Ma, L.X. Gao et al. Vapor phase assembly of urea–amine compounds and their protection against the atmospheric corrosion of carbon steel, *J. Coat. Technol. Res*, 17 (2020), 503–515, <https://doi.org/10.1007/s11998-019-00301-7>
32. S. Wan, Ze. H. Don, X. Guo, Investigation on initial atmospheric corrosion of copper and inhibition performance of 2-phenyl imidazoline based on electrical resistance sensors, *Materials Chemistry and Physics*, 262 (2021), 124321. <https://doi.org/10.1016/j.matchemphys.2021.124321>
33. Vasylyev, H.S. Measurement of polarization resistance with computer logging of results. *Mater Sci* 48 (2013), 694–696. <https://doi.org/10.1007/s11003-013-9556-8>
34. H.S. Vasylyev, Y.S. Herasymenko, Corrosion Meters of New Generation Based on the Improved Method of Polarization Resistance. *Mater Sci* 52 (2017), 722–731. <https://doi.org/10.1007/s11003-017-0015-9>
35. G. Vasylyev, Polarization Resistance Measurement in Tap Water: The Influence of Rust Electrochemical Activity. *J. of Materi Eng and Perform*, 26 (2017), 3939–3945. <https://doi.org/10.1007/s11665-017-2813-5>

36. Y.S. Herasymenko, H.S. Vasylyev, A two-step method for the evaluation of corrosion rate in metals. *Mater Sci.* 45(2009), 899–904. <https://doi.org/10.1007/s11003-010-9256-6>
37. V. Vorobyova, M. Skiba, I. Trus, and S. Frolenkova, Grape pomace extract as green vapor phase corrosion inhibitor, *Chemistry and Chemical Technology*, 12 (3) (2018), 410–418. <http://ena.lp.edu.ua:8080/handle/ntb/45180>
38. O.E. Chyhyrynets', V.I. Vorob'iova, Anticorrosion Properties of the Extract of Rapeseed Oil Cake as a Volatile Inhibitor of the Atmospheric Corrosion of Steel. *Mater Sci.* 49, (2013), 318–325. <https://doi.org/10.1007/s11003-013-9617-z>
39. V. Vorobyova, M. Skiba, Peach Pomace Extract as Efficient Sustainable Inhibitor for Carbon Steel Against Chloride-Induced Corrosion. *J. Bio. Tribo. Corros.* 7, 11 (2021). <https://doi.org/10.1007/s40735-020-00450-y>
40. G. Vasylyev, V. Vorobyova, and T. Zhuk, Raphanus sativus L. Extract as a Scale and Corrosion Inhibitor for Mild Steel in Tap Water, *Journal of Chemistry*, vol. 2020, p. 5089758, 2020 <https://doi.org/10.1155/2020/5089758>
41. R. Kusumastuti, R. I. Pramana, J. W. Soedarsono, The use of morinda citrifolia as a green corrosion inhibitor for low carbon steel in 3.5% NaCl solution. *AIP Conference Proceedings*, 1823 (2017), 020012. <https://doi.org/10.1063/1.4978085>
42. S. M. Zakir Hossain, S. A.Kareem, A. F .Alshater, H. Alzubair, S. A. Razzak, M. M.. Hossain, Effects of Cinnamaldehyde as an Eco-Friendly Corrosion Inhibitor on Mild Steel in Aerated NaCl Solutions. *Arabian Journal for Science and Engineering* (2019). doi:10.1007/s13369-019-04236-4
43. El-Taib Heakal, F., Deyab, M. A., Osman, M. M., and Elkholy, A. E. Performance of Centaureacyanus aqueous extract towards corrosion mitigation of carbon steel in saline formation water. *Desalination*. 425 (2018), 111–122. <https://doi.org/10.1016/j.desal.2017.10.019>
44. T. Tanaka, Y. Matsuo, Y. Yamada, I. Kouno, Structure of Polymeric Polyphenols of Cinnamon Bark Deduced from Condensation Products of Cinnamaldehyde with Catechin and Procyanidins. *Journal of Agricultural and Food Chemistry*, 56 (14) (2008), 5864–5870. <https://doi.org/10.1021/jf800921r>
45. O.E. Chyhyrynets, Y.F.Fateev, V.I. Vorobiova, M.I. Skyba, Study of the mechanism of action of the isopropanol extract of rapeseed oil cake on the atmospheric corrosion of copper *Materials Science*, 51(5) (2016). 644–651. <https://doi.org/10.1021/jf800921r>
46. K.O. Sulaiman, A.T. Onawole, O. Faye, D.T. Shuaib, Understanding the corrosion inhibition of mild steel by selected green compounds using chemical quantum based assessments and molecular dynamics simulations, *J. Mol. Liq.* 279 (2019) 342–350, <https://doi.org/10.1016/j.molliq.2019.01.136>.
47. D.I. Njoku, I. Ukaga, O.B. Ikenna, E.E. Oguzie, K.L. Oguzie, N. Ibisi, Natural products for materials protection: corrosion protection of aluminium in hydrochloric acid by Kola nitida extract, *J. Mol. Liq.* 219 (2016) 417–424, <https://doi.org/10.1016/j.molliq.2016.03.049>.
48. E.E. Oguzie, Y. Li, F.H. Wang, Corrosion inhibition and adsorption behavior of methionine on mild steel in sulfuric acid and synergistic effect of iodide ion, *J. Colloid Interface Sci.* 310 (2007) 90–98, <https://doi.org/10.1016/j.jcis.2007.01.038>.

Table 1: Analytical characteristics of the calibration graphs

Compound	Calibration curve		Method LOD ($\mu\text{g/g}$)	Method LOQ ($\mu\text{g/g}$)
	Linear range ($\mu\text{g/mL}$)	Correlation coefficient		
Caffeic acid	$y=11.04x + 14.43$	0.9998	3.13	9.12
Chlorogenic acid	$y=15.01x+22.24$	0.9995	0.41	1.12
Gallic acid	$y=3.72x - 25.46$	0.9988	1.23	3.69
Ferulic acid	$y=1.71x + 1.25$	0.9982	3.96	13.20
Quercetin	$y=14.68x - 1 8.25$	0.9997	1.11	3.03

Table 2: Characterization of the main of the TPE using their spectral characteristic in HPLC-DAD-MS

Peak	Rt/min	Mode of Ionization [M+H] ⁺ /[M-H] ⁻	Fragments MS2	UV-Vis max	Compound	Relative percentage (mean ± standard deviation)
Phenolic Acids						
1	4.03	-/169	125, 107, 97, 79	280	gallic acid*	8.8
2	6.08	-/181	135, 163	332	caffeic acid*	4.2
3	10.05	-/163	119	230, 310	p-Coumaric acid*	6.3
4	12.78	-/177	131, 164	280	trans-cinnamic acid	-
5	18.45	-/193	134	280	ferulic acid	-
6	19.10	-/353	191	320	neochlorogenic acid	-
7	20.20	-/353	191	244, 324	chlorogenic acid*	9.9
Flavanols						
8	22.82	-/447	284, 255, 227	265, 346	kaempferol 3-O-glucoside	-
9	28.56	-/289	245, 205	244, 276	(+)-catechin*	8.3
10	31.87	-/609	300.8, 299.9	280	Rutin	-
11	33.11	-/301	301, 151	254, 371	Quercetin*	-

Table 3: Component profile of tomato pomace extract

Name of compound	Retention time, min	Percentage (%)
2-Methyl-1-butanol (Alcohols)	4.70	1.7
Hexanal (Aldehydes)	4.72	8.7
2-Phenylacetaldehyde	4.74	3.6
3-Hexenol (Alcohols)	4.78	8.9
(E,E)-2,4-Hexadienal (Aldehydes)	4.83	2.7
Nonanal (Aldehydes)	5.12	4.1
1-Hexanol (Alcohols)	9.64	1.9
Benzaldehyde	10.9	5.7
D-Limonene	12.02	1.1
(E)-2-Hexenal (Aldehydes)	14.19	9.6
Acetic acid	16.68	2.3
Furfuraldehyde	19.85	1.9
5-(hydroxymethyl)furfuraldehyde	19.91	1.1
2-isopropyl-5-methylphenol (thymol)	20.95	4.8
Syringaldehyde	22.88	5.5
3-Octanone (Ketones)	25.56	2.7
Myristic acid	28.15	6.18
6-Methyl-5-hepten-2-one (Ketones)	29.45	2.47
Hexanoic acid	31.10	2.4
Hexadecanoic acid (Palmitic acid)	31.54	9.82
(9Z)-Octadec-9-enoic acid (Oleic acid)	31.87	8.72
(9Z,12Z)-9,12-Octadecadienoic acid (Linoleic acid)	33.46	2.94
(2E)-3,7-Dimethyl-2,6-octadien-1-ol (geraniol)	34.01	4.31
(E)-2-Octenal (Aldehydes)	38.24	4.42
2,6,6-Trimethyl-1-cyclohexene-1-carboxaldehyde (beta-Cyclocitral) (Aldehydes)	43.10	1.2
Lucopene	44.94	2.6
Quercetin	47.10	2.2

Table 4: Concentration of predominant compounds ($\mu\text{g/g}$)

Quercetin	Caffeic acid	Chlorogenic acid	Gallic acid	Ferulic acid
1.13 ± 0.11	2.03 ± 0.37	37.23 ± 0.80	10.2 ± 0.80	0.87 ± 0.013

Table 5: Calculated corrosion rates and inhibition efficiency of TPE

Film-forming time, h	Corrosion rates, g/m ² h ⁻¹	Inhibition efficiency (IE), %
12	0.1359	27.69
24	0.0929	50.55
30	0.0776	58.67
40	0.0457	75.64
48	0.0186	91.00
72	0.0131	93.01
without inhibitor	0.1879	–

Notes: periodic condensation of moisture for 20 days; TPE concentration 1000 ppm

Table 6 GC-MS analysis of the 0.5 M NaCl solution with addition of 1000 ppm tomato pomace extract and exposure for 120 hours

Compound	RT (min)	Percentage (%)
p-quinones	3.03	5.2
Benzaldehyde	3.48	0.9
Catechin-furfuraldehyde dimer	4.34	2.5
Catechin- syringaldehyde. dimer	7.2	4.8

Table 7 GC-MS analysis of the 2-propanol washout obtained from the metal surface preliminarily treated with TPE after 48 h film-forming

Compound	RT (min)	Percentage (%)
Phenylacetaldehyde	5.87	1.5
o-quinone	7.18	12.2
(R)-(-)-carvone	9.34	3.9
cis and trans isomers of (+)-limonene oxide	10.78	8.1
benzaldehyde	11.52	4.5
palmitic acid	15.54	2.1
Isopropyl palmitate	15.28	4.5
Octadecanoic acid, 10-hydroxy-, methyl ester	17.41	1.8
(9Z,12Z)-9,12-Octadecadienoic acid	17.89	5.5
Cinnamaldehyde	20.01	2.04

Table 8: Calculated quantum chemical properties for the most stable conformations of the major components of the tomatopomace extracts

Compounds	EHOMO, (eV)	ELUMO,(eV)	HOMO-LUMO gap (ΔE)
Chlorogenic acid	-9.0672	-0.976713	8.09
Caffeic acid	-8.8099	-0.8397997	8.06
Gallic acid	-9.6115	-0.7838859	8.82
Ferulic acid	-9.1099	-1.065813	8.04
(R)-(-)-carvone	-10.0573	-0.40178	9.648
Isopropyl palmitate	-11.1229	0.7147	11.83

Table 9: Calculated quantum chemical properties for the most stable conformations of the major components of the tomatopomace extract

Compounds	Ionization potential IP_v	Electron affinity EA_v	Electronegativity χ	Hardness η	Softness σ	Electrophilicity index ω
Chlorogenic acid	9.0672	0.9767	5.02	4.04	0.247	1.25
Caffeic acid	8.8099	0.8397	5.14	4.03	0.242	1.28
Gallic acid	9.6115	0.7838	5.11	4.41	0.223	1.29
Ferulic acid	9.1099	1.0658	5.08	4.02	0.248	1.27
(R)-(-)-carvone	10.057	0.4017	5.21	4.824	0.207	1.30
Isopropyl palmitate	11.1229	-0.7147	5.70	6.419	0.155	1.42

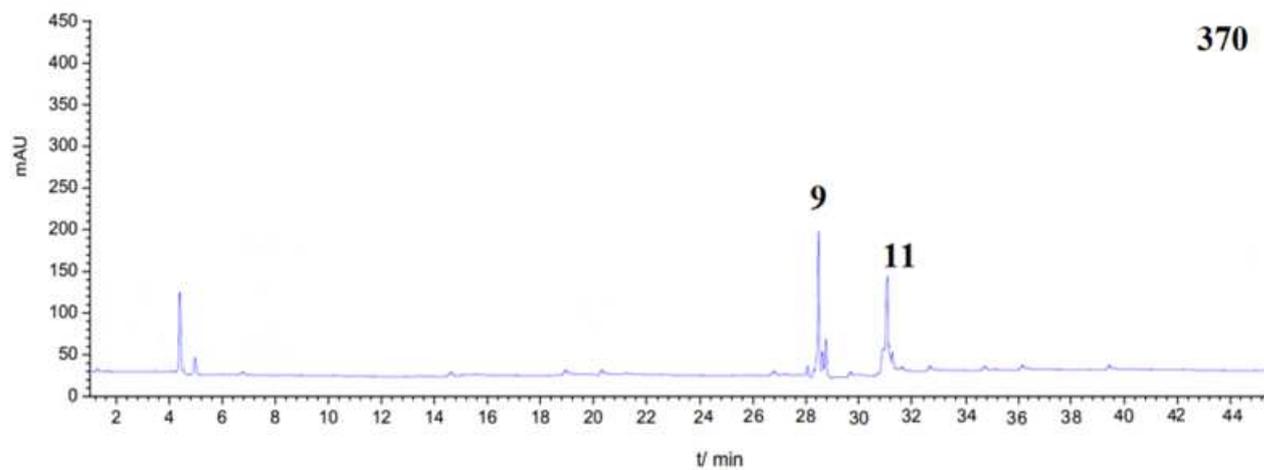
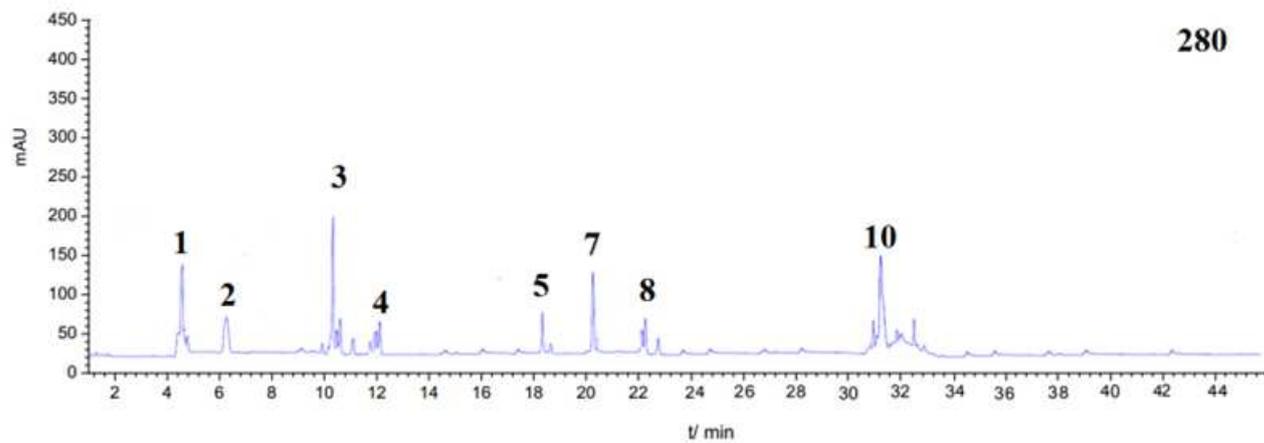
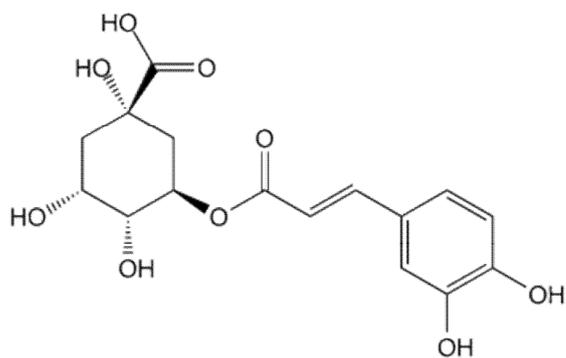
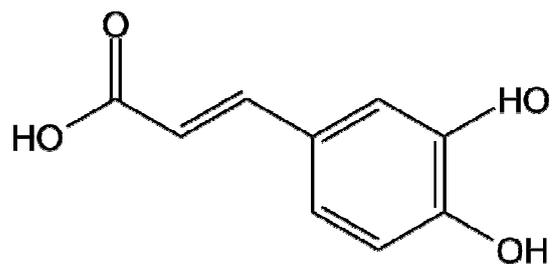


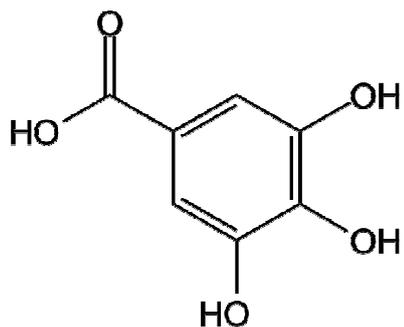
Figure 1: HPLC chromatograms at 280 and 370 nm of phenolic compounds in TPE obtained by solution of 2-propanol/ethanol/water



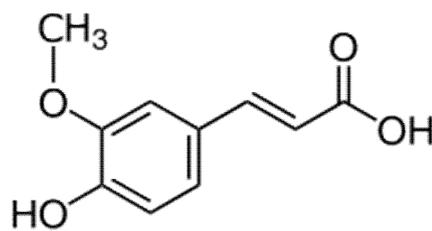
Chlorogenic acid



Caffeic acid



Gallic acid



Ferulic acid

Figure 2: Chemical structures of the main chemical constituents of tomato pomace extract.

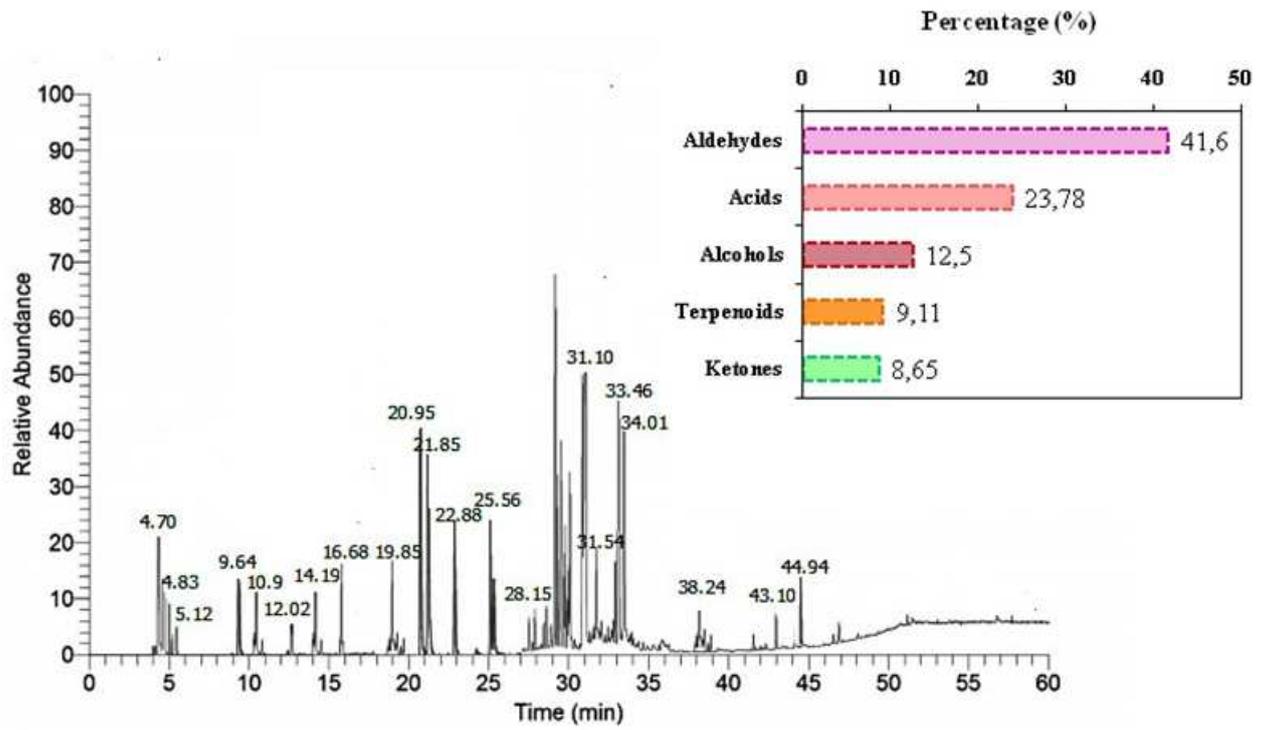


Figure 3: Chromatogram of GC-MS analysis of tomato pomace extract

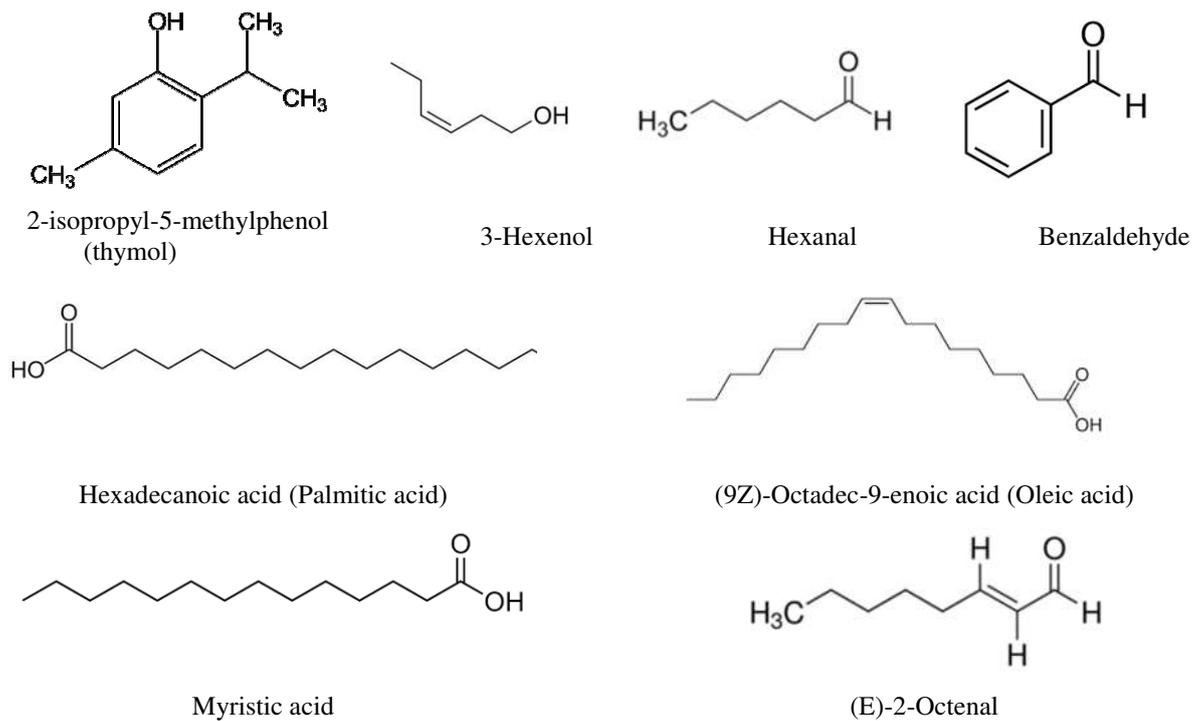


Figure 4: Chemical structures of the main volatile chemical constituents of tomato pomace extract.

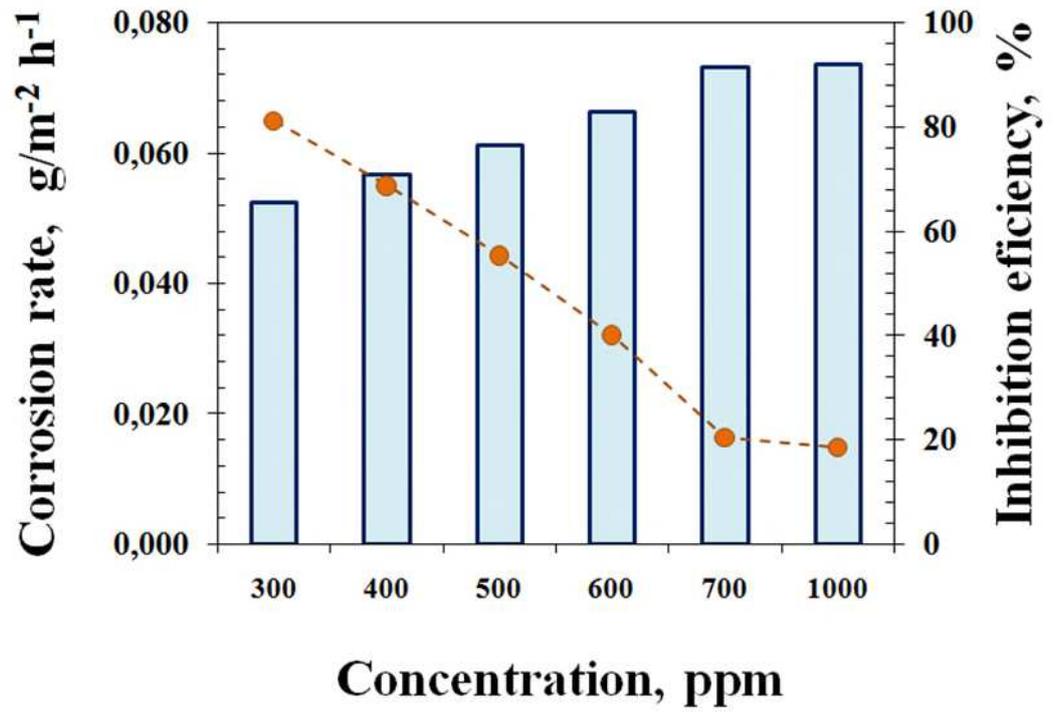


Figure 5: Calculated corrosion rates (g/m²×h) and inhibition efficiency (%) of TPE in conditions of periodic condensation of moisture (film-forming time 48 h; periodic condensation of moisture (distilled water) for 20 days)

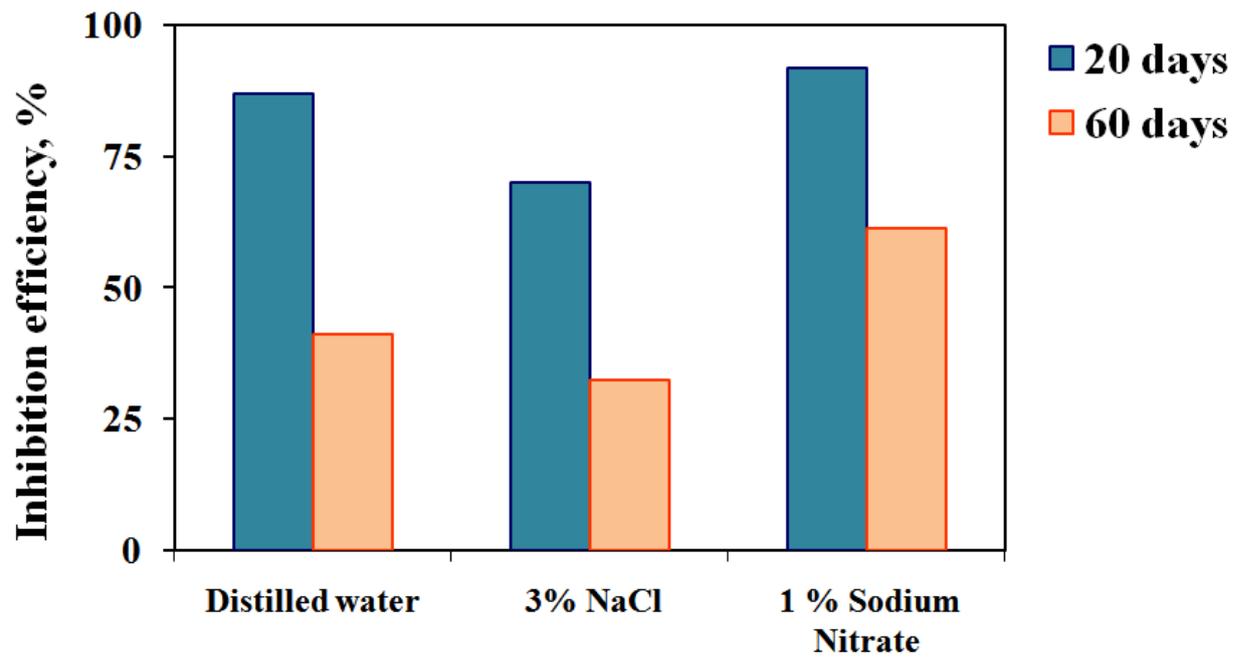
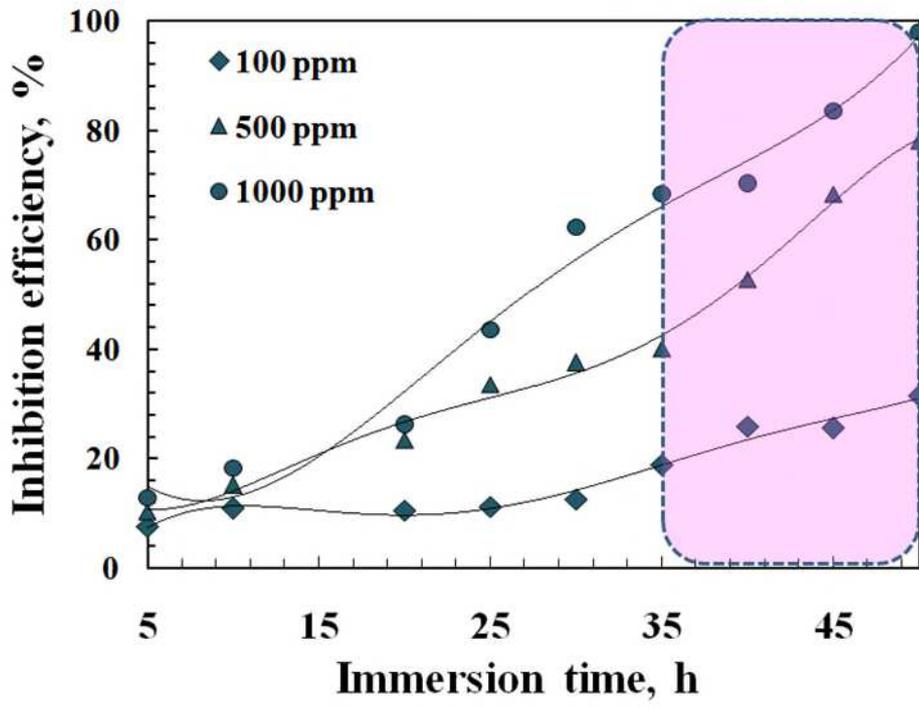
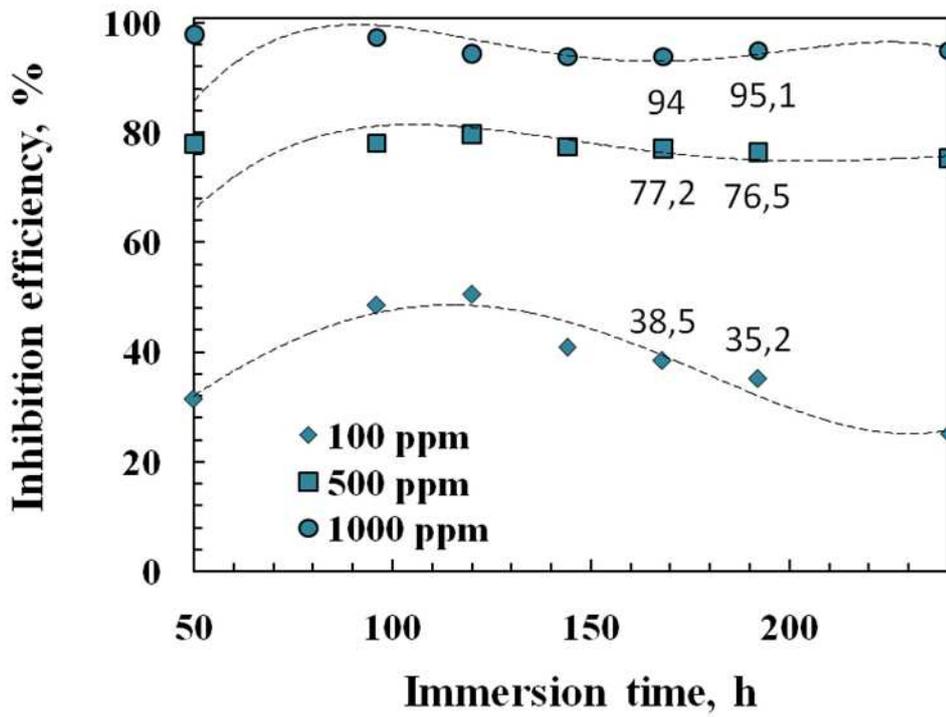


Figure 6: Calculated inhibition efficiency obtained for mild steel by weight loss measurements of after accelerated corrosion tests within 20 (a) and 60 days (b)



a



b

Figure 7: Effect of change in immersion time (5-45 h (a); 50-240 h (b)) on inhibition efficiency of TPE for the steel in 0.5 M NaCl solution with 100- 1000 ppm

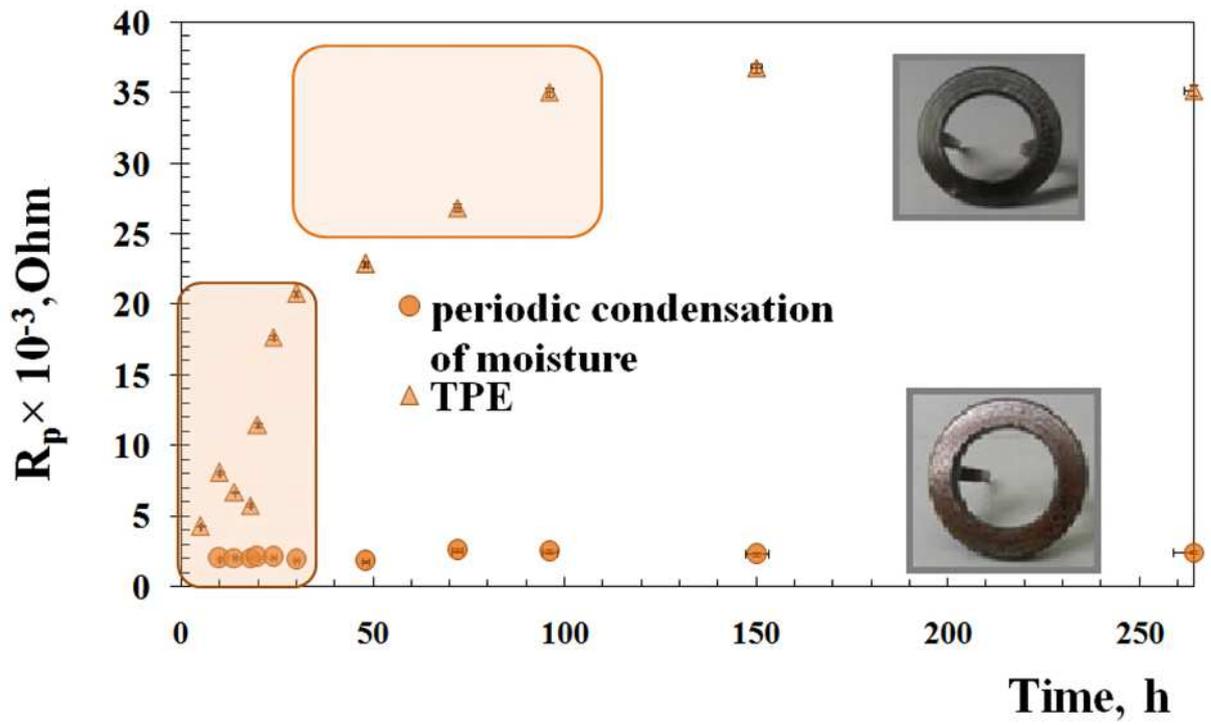


Figure 8: The relationship between LPR corrosion and immersion time mild steel in conditions of periodic moisture condensation after 48 hours of film formation.

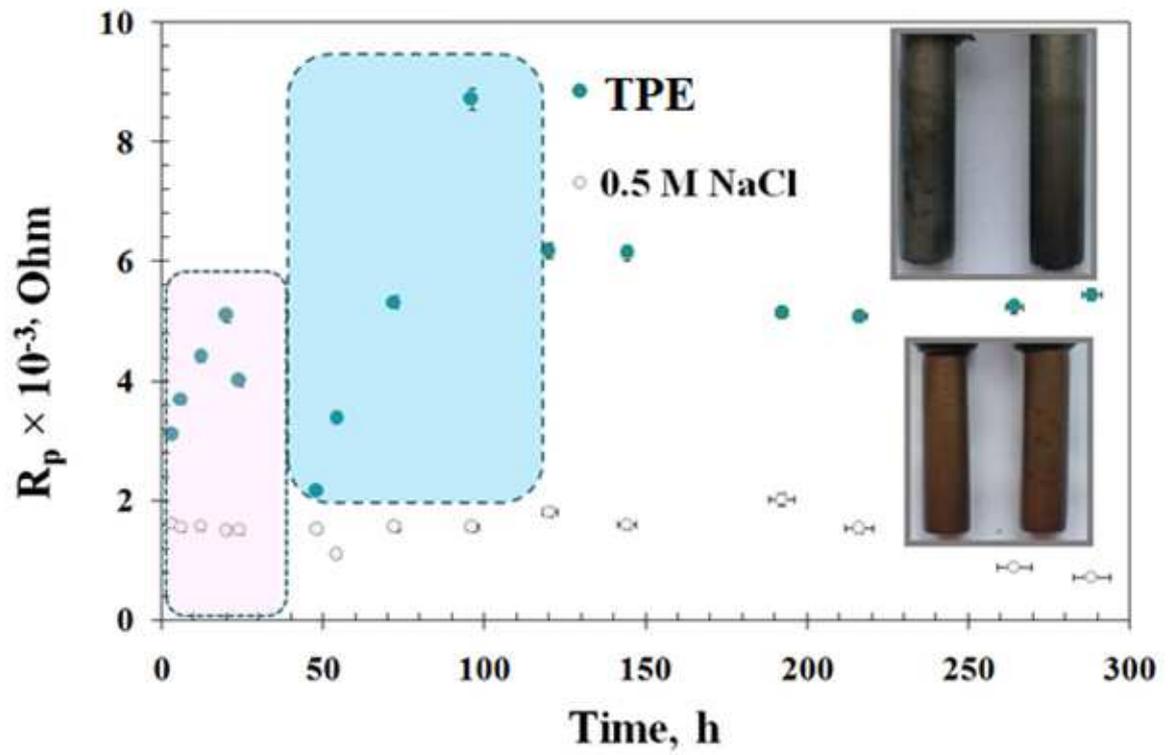


Figure 9: The relationship between LPR corrosion and immersion time mild steel in 0.5 M NaCl solution and with 1000 ppm tomato pomace extract.

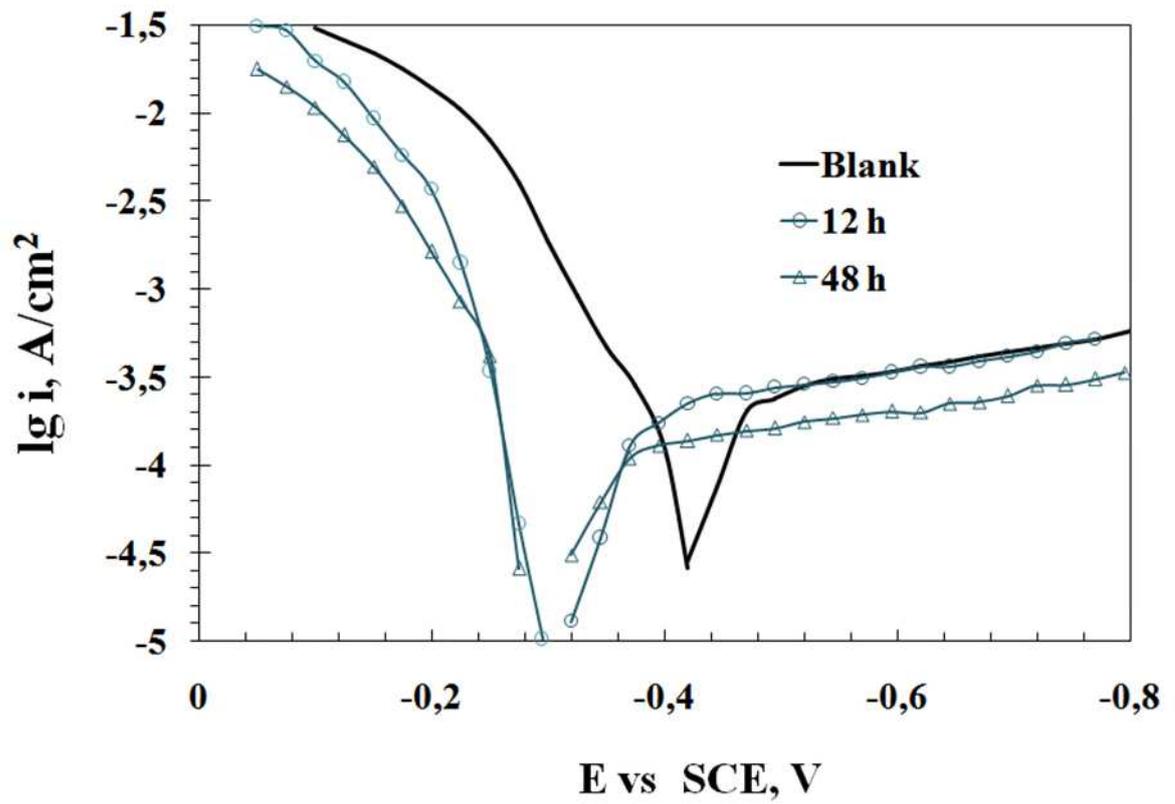


Figure 10 : Polarization curves of mild steel in 0.5 M Na_2SO_4 without (the blank sample) and with the film formed after 12 and 48 h in the vapour phase of TPE.

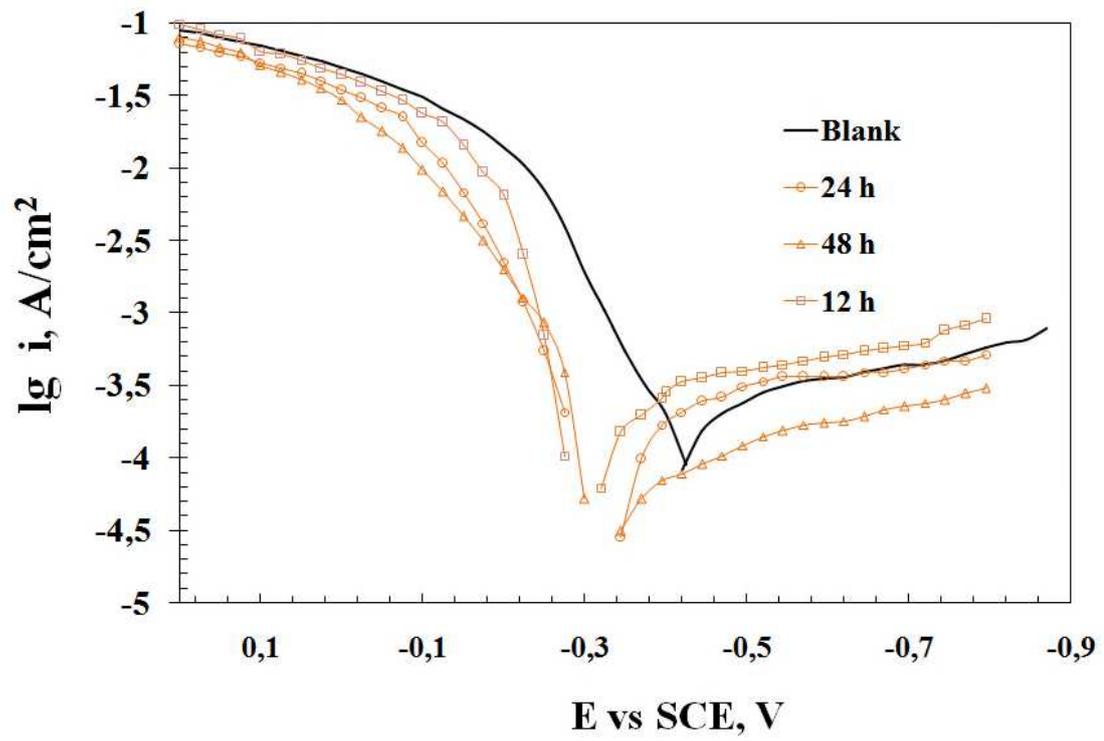
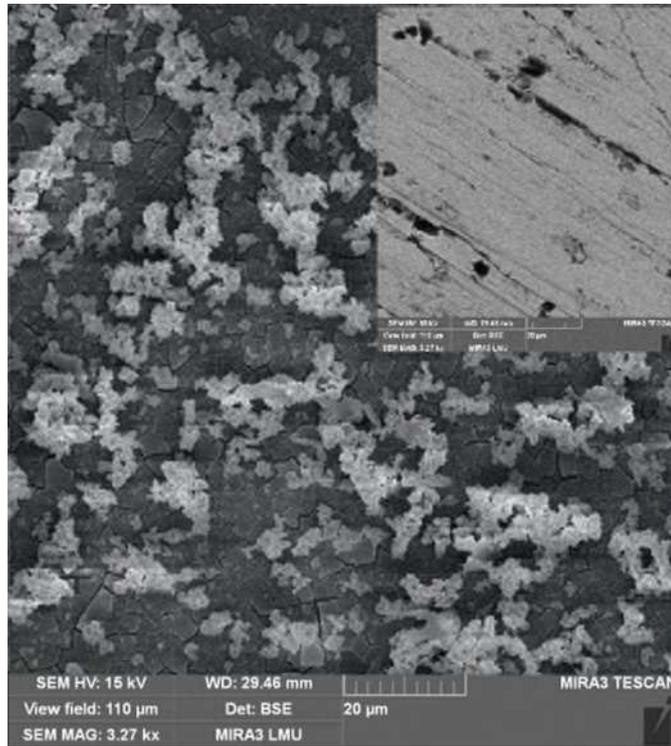
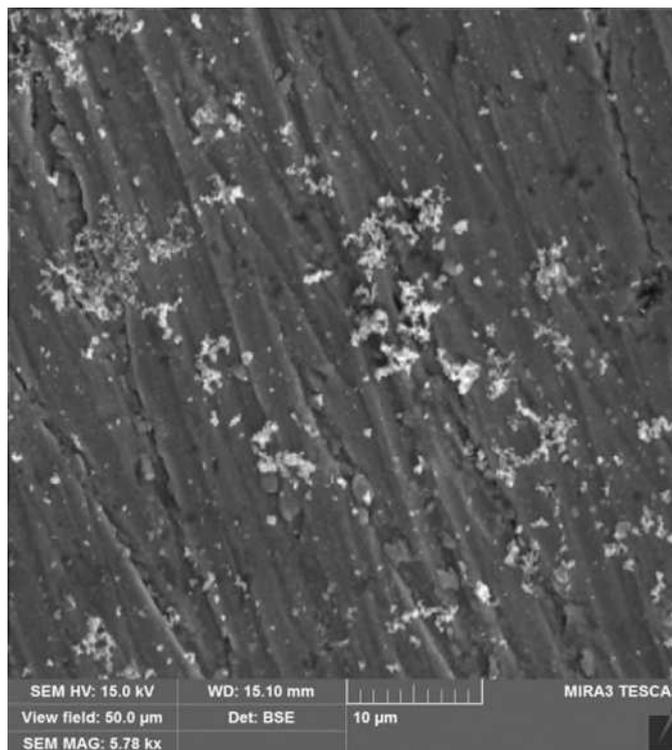


Figure 11 Polarization curves of mild steel in 0.5 M NaCl with tomato pomace extract

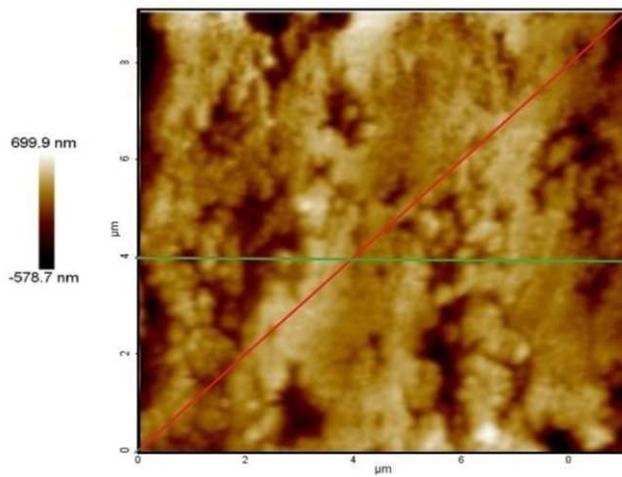


a

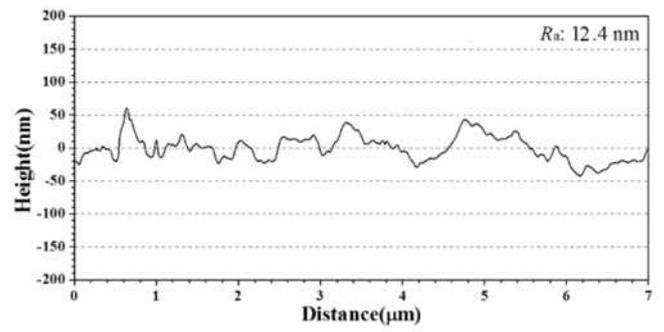


b

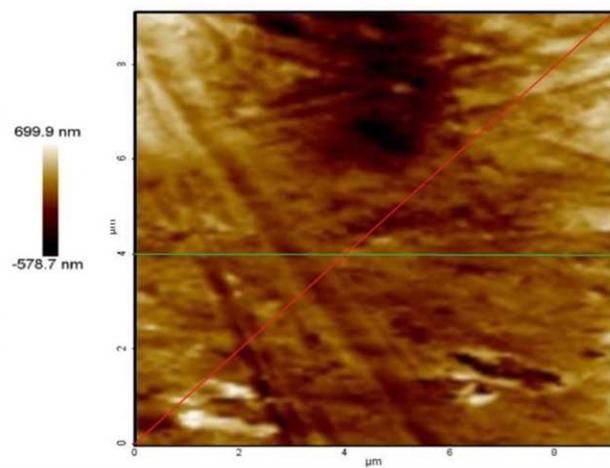
Figure 12. SEM image of steel after immersion in 0.5 M NaCl without (a) and with 1000 ppm of tomato pomace extract (48 h of immersion).



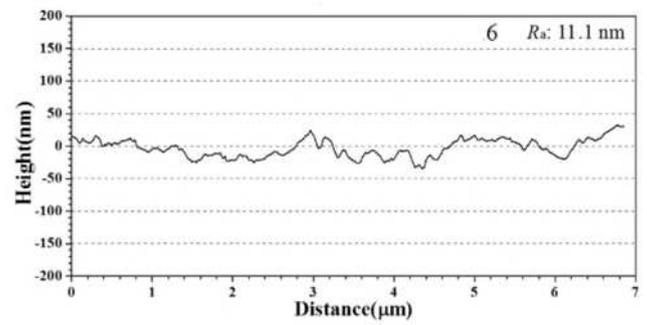
a



a1

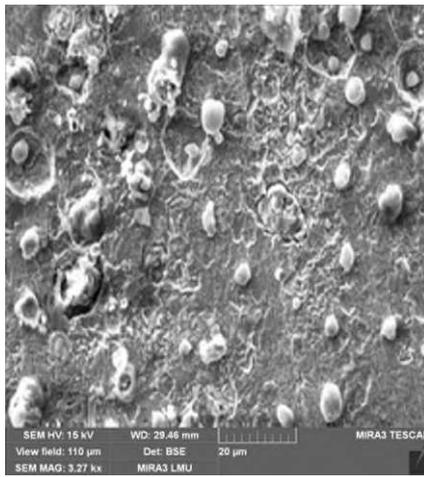


b

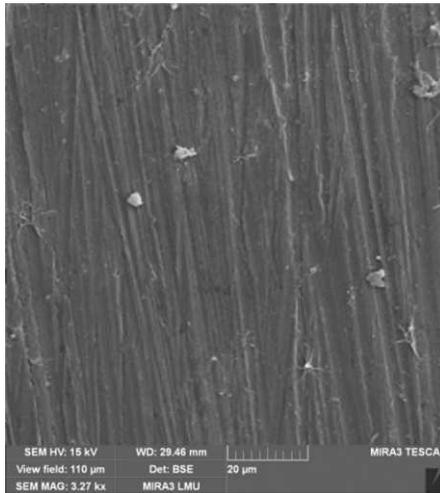


b1

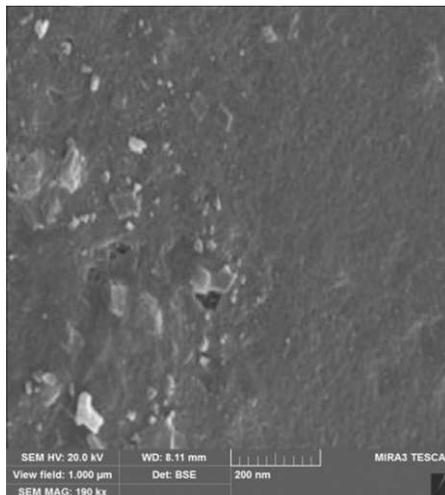
Figure 13. The two - dimensional AFM image of steel after immersion in 0.5 M NaCl 24 (a) and 48 h (b) with 1000 ppm of TPE. Panel is the height profile of the steel surface made along the marked lines on panel by the Nanoscope v 1.80 software.



a

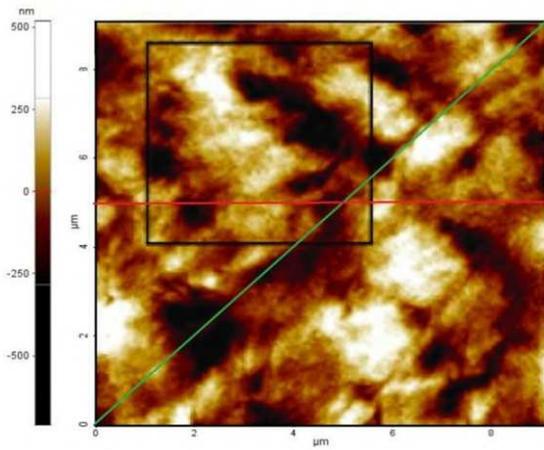


b

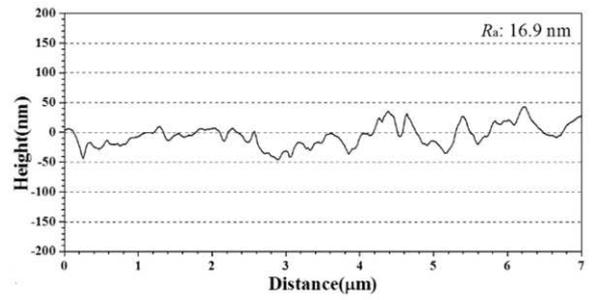


c

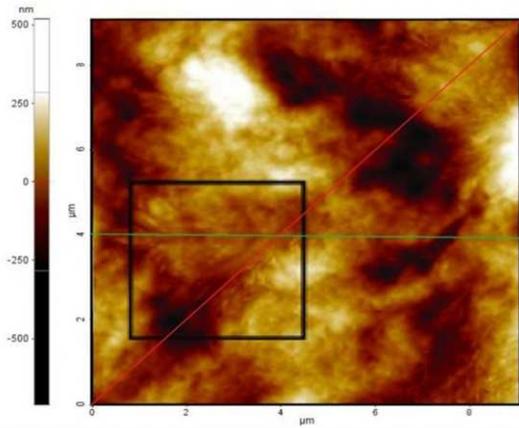
Figure 14. SEM image of steel after immersion in conditions of periodic condensation of moisture without (a) and after 48 (b, c) h exposure for PPE film-forming



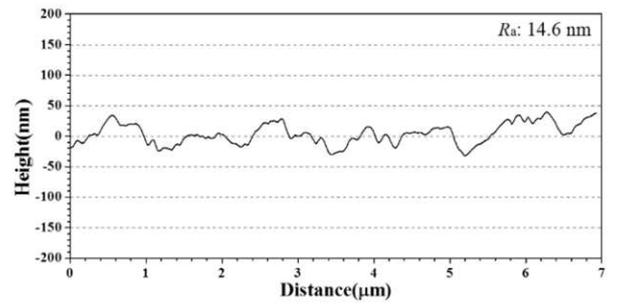
a



a1



b



b1

Figure 15 shows the 2-dimensional AFM photographs of steel sample after 24 (a) and 48 (b) hours of exposure for PPE film-forming. Panel (a1- b1) is the height profile of the steel surface made along the marked lines on panel by the Nanoscope v 1.80 software.

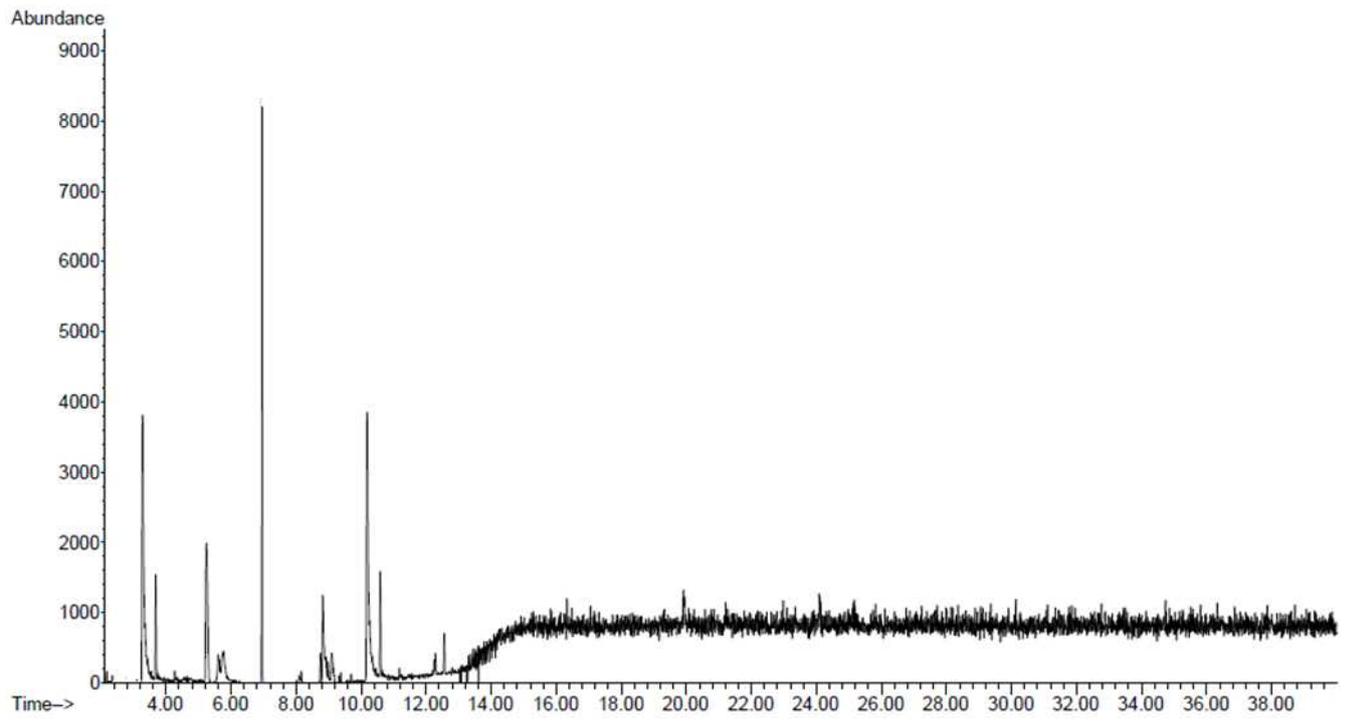


Figure 16. GC-MS chromatogram of the 0.5 M NaCl solution with addition of 1000 ppm tomato pomace extract and exposure for 120 hours.

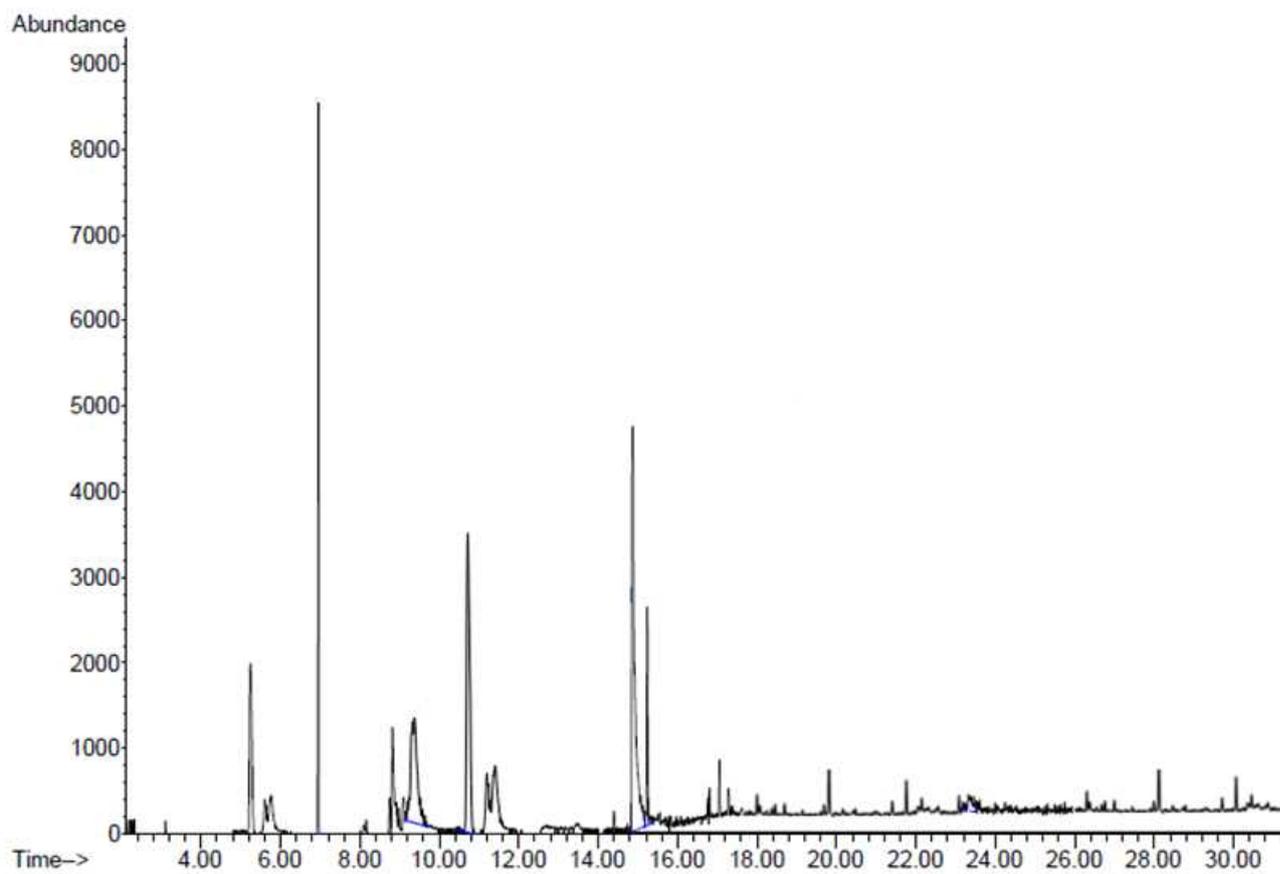


Figure 17. GC-MS of the 2-propanol washout obtained from the metal surface preliminarily treated with TPE after 48 h of film-forming.

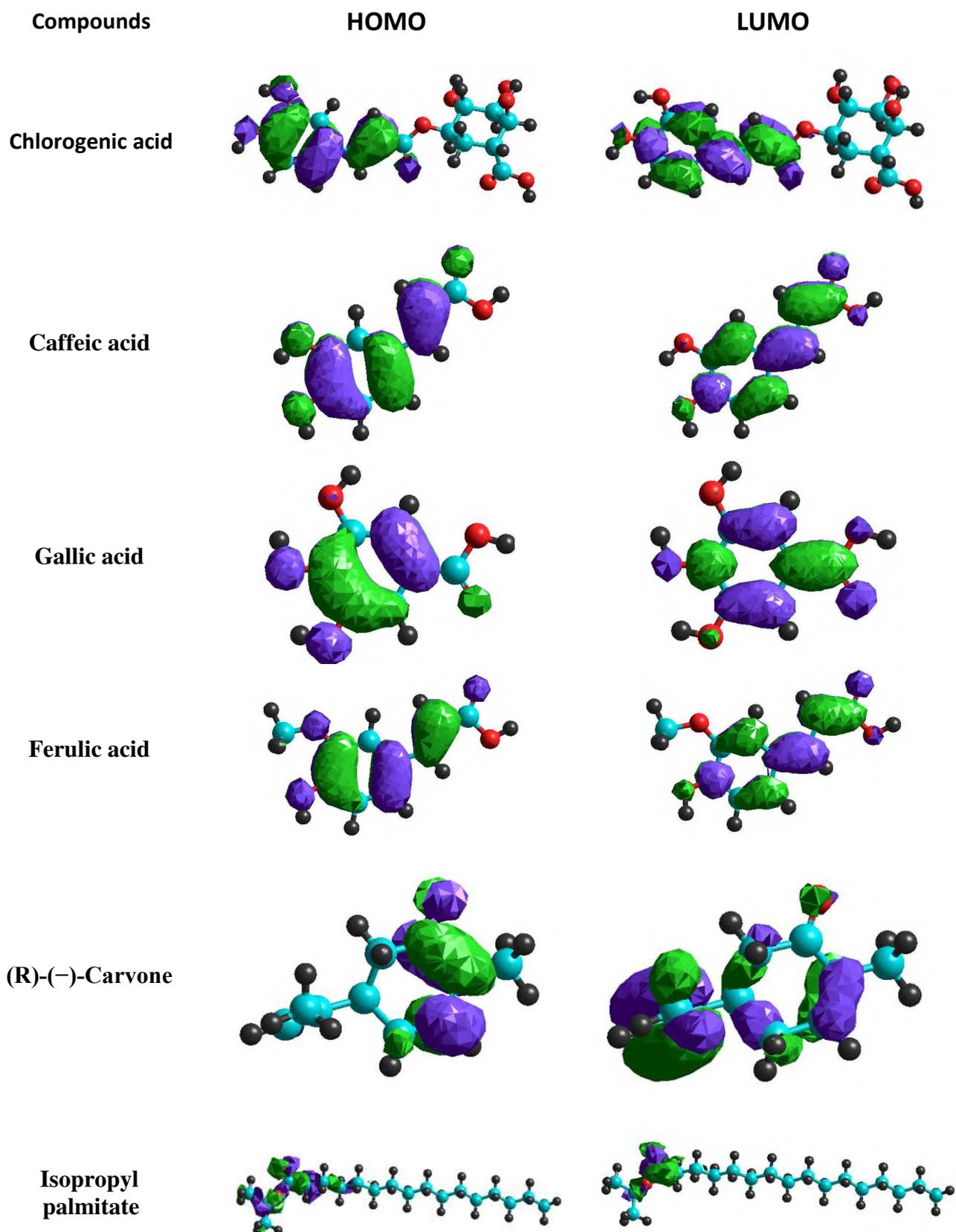


Figure 18 :The HOMO and LUMO orbital distribution of the tested molecules in the gas phase