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

Victoria Vorobyova1 · Margarita Skiba2

Received: 18 May 2021 / Accepted: 6 February 2022 / Published online: 22 February 2022 © The Author(s), under exclusive licence to Springer Nature B.V. 2022

Abstract

The aim of this paper is to investigate tomato pomace extract (TPE) as a multifunctional “green” vapor phase corrosion inhibitor for prevention from the atmospheric corrosion of mild steel and as a corrosion inhibitor in neutral media of 0.5 M NaCl solution. TPE would be an effective inhibitor with the efficiency of around 98% in both corrosive conditions. The chemical profile of the TPE was analyzed 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 [caffeic acid (2.03 ± 0.3 μg/g), chlorogenic acid (37.23 ± 0.80 μg/g), gallic acid (10.2 ± 0.80 μg/g)]. The corrosion protection properties of the TPE as multifunctional corrosion inhibitor were studied using 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 with the help of scanning electron microscopy (SEM) and atomic force microscopy (AFM) observations. TPE acts as a "pro-inhibitor" of the steel corrosion in neutral solution. The analysis confirmed that the growth of inhibitory properties is prolonged and corrosion rate is reduced after 40–48 h of exposure. The inhibition efficiency increases with increasing exposure time and reaches 98% after 48 h. Quantum-chemical calculations were used to predict the adsorption/inhibition properties of some of the main compounds of the extract and compounds formed as a result of chemical conversion. This work to contributes interpretation/explanation and understanding of the mechanism of action of green corrosion inhibitors in neutral solution.
Statement of Novelty

Tomato pomace extract was obtained for the first time by mixture of solvents as multifunctional “green” atmospheric corrosion inhibitor to be used in neutral media of 0.5 M NaCl solution. The results indicated that TPE acts as “pro-inhibitor” of the steel corrosion in neutral solution. Compounds formed as a result of chemical conversion in the electrolyte volume are then adsorbed on the metal surface or adsorbed on the metal/electrode surface and undergo various chemical transformations which causes secondary inhibition of the corrosion process and therefore “pro-inhibitor” action. The polymerization products have much more carbon atoms in the skeletal structure, they are arranged in an aromatic pattern and have some hydroxyl groups and additional aromatic groups. Such structures of compounds have a large ability of being strongly bonded to metal surfaces via oxygen heteroatom and π–π interactions.

Introduction

The market for anti-corrosion means of protection (inhibitors) is expected to expand at a CAGR (Compound annual growth rate) of more than 5% during the period of 2020–2027 [1]. The main factors stimulating the market include modernization of infrastructure and metalworking industry [2]. At the same time, solvent related regulations, rise in the prices of raw materials etc., are expected to hinder the growth of the market studied [3]. 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 [4–7]. 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” [8–15]. Green and sustainable organic compounds can be simply obtained by extraction using organic solvents or water/organic solvent mixtures [15–17]. 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 acidic media. Moreover, the presence of volatile organic compounds in the extract presents the possibility of using it as a volatile corrosion inhibitor. However, it should be noted that the research is more aimed at studying the inhibitory effectiveness of plant extracts in an acidic media and to a lesser extent in the neutral [1–7, 15]. As for the study of the effectiveness of “green” organic substances as vapor phase corrosion inhibitor of steel, only individual publications can be found [18–25]. There are some publications showing the possibility of using menthol, thyme, leaves and seeds of key lime as volatile corrosion inhibitors [18]. Thyme extract and menthol was used as volatile corrosion inhibitor for mild steel in sodium chloride environment with 100% relative humidity. It has also been found that menthol and thyme powder of concentration 1000 mg offered maximum inhibition efficiency of 78.64%, respectively. The mechanism of inhibition of corrosion is conditioned by adsorption of mono terpene compounds to the formation and maintenance of a protective film on the metal surface. Atmospheric corrosion of metals and corrosion in neutral aqueous media are the most common media. The low carbon steel is very sensitive against chloride containing solutions. The solution of 0.5 M NaCl simulates the actual environment of transmission pipelines, cooling tower systems and storage tanks.

The investigation presented herein had as its scope the development of polyfunctional corrosion inhibitor for the efficient protection of steel in various media. The polyfunctional action of the extract can be achieved only when both volatile and higher molecular weight organic compounds have been extracted from raw materials [26–28]. 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 [29, 30].

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 tomatoes, a waste product called tomato pomace is formed. Tomato pomace is 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 [31–35]. Tomato pomace is comprised of skins, pulp, and seeds. Previous studies highlighted the potential 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 [36–38]. Pectin extracted from tomato waste proved to be a potential corrosion inhibitor of tin in sodium chloride/acetic acid solution [28]. In addition, tomato peels contain volatile and semi volatile compounds, which can be used for the inhibition of the corrosion of steel at the atmospheric conditions and as a corrosion inhibitor in neutral media. However, in the literature, there is no information about possible applications of the tomato peels and the extracted compounds as vapor phase corrosion inhibitor for prevention from the atmospheric corrosion of mild steel and as corrosion inhibitor in neutral media. Therefore, their inhibition behavior deserves to be further determined.

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 compounds (VOCs), semi-volatile and high molecular weight components. Secondly, the aim is to evaluate the corrosion inhibition effect of TPE as “green” vapor phase corrosion inhibitor for prevention from 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 samples (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 samples, 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 were used for the corrosion tests and electrochemical measurements. The mild strips were purchased from RochollAglasterhausen, Germany.

Tomato-processing by-products (peels/pomace) were received from 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 the ratio of its peak area and the sum of the areas of all peaks. The identification of compounds was achieved by comparing the Kovats retention indices (RI) determined for each compound in sample with the RI described in the literature and by comparing the MS fragmentation with the mass spectra present in the NIST 14 spectral database (Mass spectrums are not shown for GC–MS analysis. The compounds quantified based on the area under the peak and results were presented in percentage form.

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 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. A UV–Vis and mass spectrum, 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 Chromleken software (Version 7.2 SR4).

Quantification was performed by HPLC–DAD according to an external standard method. The calibration curves, limits of detection (LOD) and quantification (LOQ) of the six target compounds are 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 stripes were used in the weight loss experiments. Before each

| Table 1 Analytical characteristics of the calibration graphs |
| --- | --- | --- | --- |
| Compound | Linear range (µg/mL) | Correlation coefficient | Method LOD (µg/g) | Method LOQ (µg/g) |
| --- | --- | --- | --- | --- |
| 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 | $y = 14.68x – 1.825$ | 0.9997 | 1.11 | 3.03 |
experiment, the stripes 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 were prepared by the vapor phase assembly [39, 40] method. The method involved hung of a sample into the conical flask that contained vial with VIC (tomato peels extract) and exposure during a certain time (12, 24, 72 h) for formation of the protective film on the steel surface. After inhibitor film-forming period gravimetric measurements inhibition test (vapor phase inhibition test) was conducted. The relative humidity (RH) is one of the key factors that influences 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 of the effectiveness of VIC in the condition of the periodic condensation of moisture during storage and transportation was selected. The influence of various RH on the effectiveness of VIC was studied. To form RH around 70% 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) [40].

The total test time was 20 and 60 days. After the corrosion tests, the degree of corrosion damage was estimated based on the criteria of the ASTM D 610–95 standard. Tomato pomace extract (TPE) and mixes of TPE and 1% of APTES were investigated as inhibitors.

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

$$CR = \frac{W_0 - W_1}{A \times \tau},$$  \hspace{1cm} (1)

$$IE = \frac{CR_1 - CR_2}{CR_1} \times 100,$$  \hspace{1cm} (2)

where CR is the corrosion rate, g/m² h; 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/m² h and CR₂, g/m² h 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 (before immersion) was taken using an analytical balance. Then the samples were immersed in 0.5 M NaCl solution with and without various dosages of the TPE. After the immersion period (26 days), the samples 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 was used 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, the sample in a closed container with TPE was exposed within 24–48 h. 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 a corrosion inhibitor in a neutral medium (0.5 M NaCl) sample was immersed in solution that contained TPE (1000 ppm) and kept there for 24–48 h. 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, which is 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 [41–44].

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 cm$^2$. 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 were taken. 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 [41–48]. The density of polarizing current was $i = 5$ μA/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 before 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 cm$^2$ 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 $10 \times 10$ μm$^2$.

**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 ($E_{\text{gap}}$), absolute hardness ($\eta$), chemical softness ($\sigma$) and electronegativity ($\chi$), electrophilicity index ($\omega$), vertical ionization potentials (IPv) and electron affinity (EAv) were calculated with the help of Eqs. (3)–(6). Vertical ionization potential (IPv) was determined according to Koopmans’ theorem: $\text{IPv} = -E_{\text{HOMO}}$. Electron affinity was determined according to formula: $\text{EAv} = -E_{\text{LUMO}}$. Additionally, absolute hardness ($\eta$) and electronegativity ($\chi$) for the compounds under study were evaluated from HOMO and LUMO energies using the following formulas:

$$\eta = (\text{IPv} - \text{EAv})/2$$

$$\chi = (\text{IPv} + \text{EAv})/2$$

The molecular electrophilicity index ($\omega$) was calculated from the relationship between $\eta$ and $\chi$ as:

$$\omega = \frac{\chi^2}{2\eta}$$

The chemical softness was calculated with the help of Eq. 6:

$$\sigma = \frac{1}{\eta}$$

**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 groups. The results of the HPLC analysis of the tomato pomace extract (TPE) are
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. It was gallic acid with m/z presented in Table 2 and Fig. 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. It was gallic acid with m/z presented in Table 2 and Fig. 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. It was gallic acid with m/z presented in Table 2 and Fig. 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. It was gallic acid with m/z presented in Table 2 and Fig. 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. It was gallic acid with m/z presented in Table 2 and Fig. 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. It was gallic acid with m/z presented in Table 2 and Fig. 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. It was gallic acid with m/z presented in Table 2 and Fig. 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. It was gallic acid with m/z presented in Table 2 and Fig. 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. It was gallic acid with m/z presented in Table 2 and Fig. 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. It was gallic acid with m/z presented in Table 2 and Fig. 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. It was gallic acid with m/z presented in Table 2 and Fig. 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. It was gallic acid with m/z presented in Table 2 and Fig. 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. It was gallic acid with m/z presented in Table 2 and Fig. 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. It was gallic acid with m/z presented in Table 2 and Fig. 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. It was gallic acid with m/z
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 separation of a formate (CHO₂) 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.

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

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%). Among the identified aldehydes 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 compounds were terpenoids such as thymol (4.8%) and ketones, namely 3-octanone (6.18%). This is in agreement with previous studies on volatiles in tomato waste.

According to the GC–MS analysis after using the solution 2-propanol/ethanol/water as solvent volatile chemical components were extracted from tomato pomace and therefore can be potentially used as a multifunctional corrosion inhibitor of metals.

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 (Fig. 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%.

It should be noted that the corrosion rate decreases with increasing the time of 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 inhibition efficiency of TPE was studied (Fig. 6). It was found that the inhibition efficiency of TPE is lesser in the conditions of the condensation of moisture on the steel surface from aqueous solution containing chlorides.

The efficiency of various concentrations of TPE in 0.5 M NaCl medium for a period of 26 days studied via weight-loss
Table 3 Component profile of tomato pomace extract

| Name of compound                                    | RT, (min) | RI  | Percentage (%) |
|-----------------------------------------------------|-----------|-----|----------------|
| 2-Methyl-1-butanol (Alcohols)                       | 4.70      | –   | 1.7            |
| Hexanal (Aldehydes)                                 | 4.72      | 780 | 8.7            |
| 2-Phenylacetaldehyde                                | 4.74      | 1047| 3.6            |
| 3-Hexenol (Alcohols)                                | 4.78      | 970 | 8.9            |
| (E,E)-2,4-Hexadienal (Aldehydes)                   | 4.83      | 1050| 2.7            |
| Nonanal (Aldehydes)                                 | 5.12      | 1108| 4.1            |
| 1-Hexanol (Alcohols)                                | 9.64      | 803 | 1.9            |
| Benzaldehyde                                        | 10.9      | 1003| 5.7            |
| D-Limonene                                          | 12.02     | 1031| 1.1            |
| (E)-2-Hexenal (Aldehydes)                           | 14.19     | 1200| 9.6            |
| Acetic acid                                         | 16.68     | 1090| 2.3            |
| Furfuraldehyde                                      | 19.85     | 1457| 1.9            |
| 5-(Hydroxymethyl)furfuraldehyde                    | 19.91     | 1226| 1.1            |
| 2-Isopropyl-5-methylphenol (thymol)                 | 20.95     | 1290| 4.8            |
| Syringaldehyde                                      | 22.88     | -   | 5.5            |
| 3-Octanone (Ketones)                                | 25.56     | 1240| 2.7            |
| Myristic acid                                       | 28.15     | -   | 6.18           |
| 6-Methyl-5-hepten-2-one (Ketones)                   | 29.45     | 1319| 2.47           |
| Hexanoic acid                                       | 31.10     | 1829| 2.4            |
| Hexadecanoic acid (Palmitic acid)                   | 31.54     | 2059| 9.82           |
| (9Z)-Octadec-9-enoic acid (Oleic acid)              | 31.87     | 2129| 8.72           |
| (9Z,12Z)-9,12-Octadecadienoic acid (Linoleic acid) | 33.46     | 2157| 2.94           |
| (2E)-3,7-Dimethyl-2,6-octadien-1-ol (geraniol)      | 34.01     | 1850| 4.31           |
| (E)-2-Octenal (Aldehydes)                           | 38.24     | 1442| 4.42           |
| 2,6,6-Trimethyl-1-cyclohexene-1-carboxaldehyde (beta-Cyclocitril) (Aldehydes) | 43.10 | 1220 | 1.2 |
| Lycopene                                            | 44.94     | -   | 2.6            |
| Quercetin                                           | 47.10     | -   | 2.2            |

RT retention time, STD standard compound; NIST 14, RI Kovats retention indices (RI) determined using a commercial hydrocarbon mixture (C9–C25) on the HP-5MS column

Fig. 3 Chromatogram of GC–MS analysis of tomato pomace extract
method is listed in Fig. 7 indicating that the 1000 ppm solution possessed the maximum efficiency for inhibition. The effectiveness of inhibition increased with concentration.

The immersion time is an important parameter in assessing the stability of corrosion inhibitive properties of organic compounds. Figure 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 and 48 h of immersion till reached its saturation. The
formation process of the protective layer can be classified into two steps, namely primary adsorption (1–30 h) as the first step and then a slow chemical transformation (polymerization) of the molecules that were adsorbed on the steel surface (40–50 h). 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 based 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 vapor phase of tomato pomace extract may vary significantly over the exposure period of condensation of moisture. As shown in the Fig. 8. Rp of the sample after treatment in the volatile compounds of VCI increased firstly (1–12 h) and then slightly decreased. And then, the polarization resistance values increased from 5 to $20.1 \times 10^{-3}$ Ohm after 12–18 h of immersion time. This period can be attributed to the first stage of the formation of a protective film. During 40–48 h there is a significant increase in the value of Rp. It is the second stage of film formation. The data obtained are quite natural since the plant extract contains volatile compounds with differences in volatility and the evaporation of which can be prolonged for a certain time.

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 h.

The relatively poor protection provided by tomato pomace extract on steel at the initial immersion compared to the results obtained at longer exposure suggests that the formation of a highly protective and stable inhibitor layer on steel surface might need more 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 [45], rape cake [46] and Raphanus cake [47], apricot pomace extract and Centaurea cyanus extract [49].

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 (Fig. 10). Polarization curves were measured after steel assembly time in the environment of volatile compounds of the tomato pomace extract, in 24, 48 h and 72 h of exposure. When forming a protective film with volatile compounds of tomato pomace extract, a significant effect is observed on the anodic polarization curve after 48 h of film formation (Table 6). During the 24-h exposure of the sample in an inhibitor atmosphere,
iron oxidation products [lepidocrocite ($\gamma$-FeOOH), goethite ($\alpha$-FeOOH) and maghemite ($\gamma$-Fe$_2$O$_3$)] 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. The limiting current on the cathode curves is almost independent on the time of film formation.

The OCP of the sample in the solution with tomato pomace extract was diminished in the initial immersion times (5–24 h). The OCP displaced toward positive values, which correspond to the coverage of anodic sites via extract molecules. On the other side, to increases of time immersion probably the formation of the transformation (polymerization) products over the cathodic sites of steel caused the OCP reduction. The potential reduction evidenced that the cathodic reaction was affected in the presence of the transformation (polymerization) products (Fig. 11).

The polarization plots for the steel samples exposed to the solution including TPE is illustrated in Fig. 12. The polarization curves were provided for studying the inhibition mechanism of the 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 [50, 51]:

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (7)$$

Then, corrosion products including FeOOH, Fe$_2$O$_3$ and Fe$_3$O$_4$ 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 $i = 0.386 \times 10^{-4} \text{A/cm}^2$. The region of the cathodic curve in the range from $-0.6$ to $-0.7 \text{V/SCE}$ has occurred due to the diffusion-controlled oxygen reduction reaction [50, 51]. The results obtained indicate that after 5 h of exposure in the solution there is an insignificant displacement of the stationary position and a small effect on the kinetics of particular electrode effects. Both anodic and cathodic reactions of the corrosion process are inhibited. After 24 h of exposure

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

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

Fig. 10 Polarization curves of mild steel in 0.5 M Na$_2$SO$_4$ without (the blank sample) and with the film formed after 24, 48 and 48 h in the vapour phase of TPE

Fig. 11 Variation of the open-circuit potential (OCP) of steel in 0.5 M NaCl with tomato pomace extract

Fig. 12 Polarization curves of mild steel in 0.5 M NaCl with tomato pomace extract

Fig. 10

Fig. 11

Fig. 12
of the electrode in the solution NaCl with TPE the anodic and cathodic corrosion current density curves are shifted towards lower current density region as compared to the blank (Fig. 12, Table 7). However, it can be observed that practically no effect on the cathodic process occurs, while the anodic reaction is inhibited more significantly. That is, the inhibitor molecules do not affect the blocking of metal in the areas where oxygen depolarization takes place but affect the areas where there is the reaction of the formation of Fe²⁺ cations. This means that within 24 h the adsorption of organic compounds capable of forming complex compounds with iron cations occurs on the metal surface, and the formed layer is protective. As exposure progresses, the value of limiting current decreases and finally reaches 1.82 × 10⁻⁴ A/cm² after 48 h of exposure. The decrease in the value of the limiting diffusion current is 2.1 times. Consequently, 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 decreased from −0.483 to −0.515 mV in the presence of TPE extract. 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. The Tafel curves indicated that the i_corr diminished to 20.8 × 10⁻⁴ A/cm² after 48 h of MS subjection to the electrolyte.

It can be understood that in the attendance of TPE the anodic and cathodic reactions were suppressed compared to the sample that was immersed in NaCl during 24 h, revealing the mixed anodic/cathodic inhibition activities of the TPE on the surface. Thus, within 48 h, a film is formed on the metal surface. It effectively blocks the access of oxygen to the metal surface. According to the accepted scientific knowledge of influence of corrosion inhibitors on kinetics of electrode reactions of corrosion, inhibition of corrosion process can be carried out both by initial compounds, and by products of their full/partial chemical transformation, which can occur both in electrolyte volume, and on a metal surface electrode. Therefore, compounds formed as a result of chemical conversion in the electrolyte volume are then adsorbed on the metal surface or adsorbed on the metal/electrode surface and undergo various chemical transformations which causes secondary inhibition of the corrosion process and therefore “pro-inhibitor” action. The results of electrochemical studies indicate that the tomato pomace extract acts as “pro-inhibitor” of corrosion of the steel in neutral solution. To confirm this hypothesis comparisons of the FTIR spectra of the tomato pomace extract and the surface after treatment with volatile compounds of TPE and after immersions in the neutral solution with extract were made.

Comparisons of the FTIR spectra of the tomato pomace extract and the surface after treatment with the vapor phase of the TPE show that there is a decrease in the intensity of oscillations in the range 1800–1580 cm⁻¹ (characteristic of aldehydes, monoterpene phenols and ketones compounds present on the IR spectrum of individual tomato pomace) and the intensity of the absorption band of the group C=O in the range of 1740–1720 cm⁻¹, which is characteristic of aliphatic aldehydes in the extract (Fig. 13). Also, since the composition contains compounds with a conjugation, the oscillation frequency is reduced: for aromatic aldehydes to 1710–1685 cm⁻¹, for unsaturated aldehydes to 1695–1660 cm⁻¹ [50, 51]. The peak in the range of 3000–3800 cm⁻¹ in the extract is due to C–H starching of π-system. The increase in the intense absorption of ν (O–H) and ν (C–O) in the range of 1420–1200 cm⁻¹ indicates the adsorption of terpenoids of the investigated extract on the steel surface. It should be noted that when treated individually with plant extract, a band of absorption of valence bonds in the region 2200–2100 cm⁻¹, which is characteristic of aliphatic aldehydes in the extract (Fig. 13). Also, since the composition contains compounds with a conjugation, the oscillation frequency is reduced: for aromatic aldehydes to 1710–1685 cm⁻¹, for unsaturated aldehydes to 1695–1660 cm⁻¹ [50, 51]. The peak in the range of 3000–3800 cm⁻¹ in the extract is due to C–H starching of π-system. The increase in the intense absorption of ν (O–H) and ν (C–O) in the range of 1420–1200 cm⁻¹ indicates the adsorption of terpenoids of the investigated extract on the steel surface. It should be noted that when treated individually with plant extract, a band of absorption of valence bonds in the region 2200–2100 cm⁻¹ at a frequency of 1984, 1952, 1944 cm⁻¹ and in the region 1800–1700 cm⁻¹, which are characteristic of ν (C≡C) groups, appears. This is more likely due to the partial polymerization of organic compounds on the metal surface during the formation of

| Holding time | E_corr versus SCE. V | Tafel coefficients. V | Corrosion current densities (I_corr). A/cm² 10⁻⁵ |
|--------------|---------------------|----------------------|-----------------------------------------------|
| Blank        | −0.534              | 0.09 − 0.14          | 2.49                                          |
| 5            | −0.512              | 0.11 − 0.14          | 1.69                                          |
| 24           | −0.485              | 0.12 − 0.14          | 0.43                                          |
| 48           | −0.515              | 0.11 − 0.14          | 0.83                                          |

Fig. 13 FT-IR-absorption of TPE (1) and IR spectra displayed on the surface of the steel, the treated volatile compounds of the TPE (2)
the protective film. The presence of these peaks verifies the presence of described functional groups containing oxygen heteroatoms along with the π-system in the structure of a partially polymerized film on the steel surface.

FTIR analyses were made on both the tomato pomace extract and the surface protective film formed on the steel operating electrode after immersion in neutral solution at a concentration of the inhibitor of 1000 ppm (Fig. 14). The peaks at 1206 cm\(^{-1}\) and 1372 cm\(^{-1}\) correspond to the ν (C=O), while the absorptions at 1692, 1714 cm\(^{-1}\) may be referred to C=C vibrations or aromatic ring ν (C=C). Absorption bands at 2910 cm\(^{-1}\) are attributed to C-H bonds in aldehydes. The intense bands between 1206 and 1020 cm\(^{-1}\) are linked to C–O stretching. Extended peak in the range around 1200–1400 cm\(^{-1}\) indicate that phenolic compounds were adsorbed on the steel surface. The presence of intense peaks in the range 2000–2100 cm\(^{-1}\) indicates the formation of new more complex compounds on the steel surface. It is possible that the formation of a partially polymerized type of film causes a high inhibition action.

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were performed for surface study of uninhibited and inhibited mild steel samples. In order to understand the mechanism of film formation by tomato pomace extract, the morphology of steel surface was researched. Fig. 15 shows the surface morphology of specimens after 48 h immersion in the solutions with tomato pomace extract (1000 ppm). The steel immersed for 48 h in NaCl (Fig. 15a) 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...
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.

The samples after their exposure in a corrosive medium with TPE for 24 and 48 h were investigated using an atomic force microscope. It was found that a protective film’s thickness is of more than 248 and 540 nm. Respectively, it is formed on the steel surface. The relevant average roughness ($R_a$) is 16.9 nm. In addition, after the increases time of film-forming to 48 h the corresponding value of $R_a$ is reduced to 14.6 nm (Fig. 16). Given the topography of the surface of films of organic compounds of plant extract and their thickness, the results of voltametric studies and accelerated corrosion tests, it can be said that the mechanism of their formation is based on a number of complex processes.

This observation confirms 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 (Figs. 17 and 18). After 24 h exposure the surface of steel is almost completely covered by film. When exposure time extends to 48 h more filled film on the steel surface is observed.

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

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. The author has shown in a number of works [5, 6] that a prolonged inhibition effect in neutral aqueous media of plant extracts was established. The scientific rationale for this process is described by competing adsorption processes, stepwise film formation and film instability. In the several new foundlings.

![Fig. 16](image)

**Fig. 16** 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.
in field of corrosion protection, namely, analysis of mechanism of "green" inhibitors action, with involvement of modern experimental techniques, it was shown that the process of inhibition by plant extracts is complex and phased with oxidation, chemical transformation of the extract components in the corrosive media (neutral aqueous media) or on the metal surface [7]. This is in fact a new view on the fundamental aspects of the mechanism of action of "green" inhibitors. Moreover, a complementary investigation of component composition was carried out to clarify the inhibition mechanism. To confirm the hypothesis on formation of new compounds in the electrolyte volume by chemical conversion, GC–MS analyses of the solution containing 1000 ppm of TPE after 120 h of immersion steel were carried out.

The solution containing 1000 ppm of TPE after 48 h of immersion steel and washouts obtained from the metal surface preliminarily treated in volatile compounds of TPE during 48 h was used. From GC–MS data of the component composition of the solution containing 1000 ppm of TPE after 120 h 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. The main components of the extract are the oxidized structures of the phenolic compounds and adduct of transformation (Figs. 19 and 20). The chemical conversion/transformation (polymerization) products of the phenolic flavanol and aldehydes namely flavanol-aldehyde adducts [catechin-furfuraldehyde dimer (RT 4.34) Catechin–syringaldehyde Dimer (RT 7.2)], have also been identified. It is rather difficult to determine which of these compounds provide higher ability for corrosion inhibition (Table 8) [52, 53]. According to the results, the tomato pomace extract can be attributed to corrosion inhibitors with "pro-inhibition" effect. The polymerization products have hyperbranched molecules with more carbon atoms in the skeletal structure, arranged in an aromatic pattern with hydroxyl groups and additional aromatic groups.

Chromatogram of the 2-propanol (Fig. 19, Table 9) washout obtained from the metal surface preliminarily treated with TPE after 48 h of film-forming indicates the presence of the main volatile compounds of TPE and oxidized products of the thymol and limonene.

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, considering 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
The molecule structure of the main tomato pomace extract obtained after a geometric optimization procedure is presented in Fig. 21. The results of quantum-chemical calculations of the energy parameters of molecules are presented in Tables 10 and 11.

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) [53–56]. It was reported that higher HOMO energies indicate better electron-donating properties of a molecule, and it 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 centers at the molecules for

Table 8 The electrochemical parameters of PDS extracted from the steel samples immersed in chloride solutions (0.5 M NaCl)

| Holding time | $E_{corr}$ versus SCE, V | Tafel coefficients, V | Corrosion current densities ($I_{corr}$) A/cm$^2$ | 10$^{-4}$ |
|-------------|--------------------------|-----------------------|-----------------------------------------------|--------|
| Blank       | $-0.534$                 | 0.07 − 0.18           | 78.8                                          |        |
| 5           | $-0.512$                 | 0.07 − 0.18           | 48.1                                          |        |
| 24          | $-0.485$                 | 0.09 − 0.19           | 34.6                                          |        |
| 48          | $-0.515$                 | 0.1 − 0.19            | 20.8                                          |        |
| 288         | $-0.545$                 | 0.1 − 0.16            | 27.4                                          |        |

Table 9 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) | RI    | Percentage (%) |
|---------------------------------------|-----------|-------|----------------|
| Phenylacetaldehyde                    | 5.87      | 1047  | 1.5            |
| o-quinone                             | 7.18      | 1340  | 12.2           |
| (R)-(-)-carvone                       | 9.34      | 1242  | 3.9            |
| cis and trans isomers of (+)-limonene oxide | 10.78     | 1125  | 8.1            |
| benzaldehyde                          | 11.52     | 1003  | 4.5            |
| palmitic acid                         | 15.54     | 1970  | 2.1            |
| Isopropyl palmitate                   | 15.28     | 1993  | 4.5            |
| Octadecanoic acid,10-hydroxy-methyl ester | 17.41     | –     | 1.8            |
| (9Z,12Z)-9,12-Octadecadienoic acid    | 17.89     | 2157  | 5.5            |
| Cinnamaldehyde                        | 20.01     | 2017  | 2.04           |

$RT$ retention time, $STD$ standard compound; NIST 14, $RI$ Kovats retention indices (RI) determined using a commercial hydrocarbon mixture (C9–C25) on the HP-5MS column
| Compounds                        | HOMO         | LUMO         |
|---------------------------------|--------------|--------------|
| Chlorogenic acid                | ![Image]     | ![Image]     |
| Caffeic acid                    | ![Image]     | ![Image]     |
| Gallic acid                     | ![Image]     | ![Image]     |
| Ferulic acid                    | ![Image]     | ![Image]     |
| \((R)-(−)\)-Carvone            | ![Image]     | ![Image]     |
| Isopropyl palmitate            | ![Image]     | ![Image]     |
| Catechin-furfuraldehyde dimer   | ![Image]     | ![Image]     |
| Catechin-syringaldehyde trimer  | ![Image]     | ![Image]     |

**Fig. 21** The HOMO and LUMO orbital distribution of the tested molecules in the gas phase
the reaction with the metal surface (Fig. 21). The EHOMO values for compounds increase in the following order: Catechin-syringaldehyde trimer, Caffeic acid, Catechin-furfuraldehyde dimer, 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].

It has been reported that the more stable molecular structure has the largest HOMO–LUMO energy gap. Therefore, an electronic system with a larger HOMO–LUMO gap should be less reactive than one having a smaller gap. This relationship is based on the Maximum Hardness Principle [57], which states that “there seems to be a rule of nature that molecules arrange themselves so as to be as hard as possible”. A small energy gap between the HOMO and LUMO increases the anticorrosion activity. The energy gap values for compounds listed in Table 10 increase in the following order: Ferulic acid, Caffeic acid, Chlorogenic acid, Catechin-furfuraldehyde dimer, (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].

According to Parr et al. [58] 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 11 that 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 for 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 11 that Chlorogenic acid 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. The amount of charge transfer, \( \Delta N \), between the molecules and the mild steel Fe surface as calculated is given in Table 11. According to this table, the positive values of the electron charge transfer (\( \Delta N \)) ensure the transfer of electrons from inhibitors to empty orbitals of metal atoms. According to Lukovits, if \( \Delta N < 3.6 \). Almost all molecules, except chlorogenic acid, can be assumed to possess charge transfer ability towards the metal surface [59, 60]. Thus, the results of quantum-chemical results indicate that both individual compounds and transformation products have high adsorption activity. However chemical researchers indicate that the transformation products have higher adsorption activity (Fig. 22).

**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 h of corrosion measurements:

The mechanism of inhibitory action in a neutral medium includes the first stage of the formation of a protective layer consisting of complex compounds of \( \text{Fe}^{2+} \) cations and organic substances of the extract. Further, high molecular weight polymeric structure products are formed in the solution and on the metal surface as a result of chemical interaction/transformation of the main substances of the extract, which block the surface from accessing oxygen. The major role of products of chemical transformation in corrosion protection is the formation of insoluble deposit on intermetallic inclusion. The presence of metallic cations in the environment like \( \text{Fe}^{3+} \) can facilitate the construction of a polymeric structure with a bigger molecular weight. The transformation (polymerization) products of the phenolic flavanol and aldehydes have much more carbon atoms in the skeletal structure, arranged in an aromatic pattern, plus some hydroxyl groups, methyl groups, and additional of aromatic groups. With such structures, the transformation products have a large ability of being strongly bonded to metal surfaces via oxygen heteroatom and \( \pi-\pi \) interactions.

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

(b) The results indicated that the tomato pomace extract acts as "pro-inhibitor" of corrosion of steel in neutral solution. 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 h 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 as 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. 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 to 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 the solution of 2-propanol/ethanol/water as solvent. After all the investigations the following conclusions are obtained:

- Four dominant volatile compounds were identified. These are saturated and unsaturated fatty acids (23.78%) and aldehydes (41.6%). Five semi-volatile and high molecular weight chemical compounds (Chlorogenic acid, Caffeic acid and Ferulic acid) were identified in tomato pomace extract from the HPLC-DAD-MS analysis data.
Fig. 22 Charges of heteroatom’s in optimized molecules
For the first time the extract of the tomato pomace, which contains of some bio-active/eco-friendly compounds, was employed as organic eco-friendly inhibitor for steel corrosion mitigation in neutral medium and in conditions of periodic condensation of moisture. If the steel samples are immersed in 1000 ppm TPE solution for 48 h, the inhibition efficiency is enhanced to 92.5% in the same corrosive environment. The inhibition efficiency obtained from plurality of experimental data shows good agreement with each other and exhibits prolonged film-forming period up to 48 h. The complex analysis showed that the inhibitor provides an excellent protection against corrosion after prolonged time of film forming. 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 in the condition of condensation of moisture.

Funding  This work was supported by the Ministry of Education and Science of Ukraine [Grant No. 2403. 2021].

Data Availability Availability of data and material.

Declarations

Conflict of interest 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.

References

1. Siti, Z.S., Abdul, H.Y., Siti, K.Z., Mustaffa, A.A.T., et al.: Plant extracts as green corrosion inhibitor for ferrous metal alloys: a review. J. Clean. Prod. 304, 127030 (2021). https://doi.org/10.1016/j.jclepro.2021.127030
2. Makhmatkulovich, K.K.: Classification of factors influencing the development of the engineering industry. Acad. Glob. Insci. Res. 2(5), 27–31 (2021). https://doi.org/10.17605/OSF.IO/CR5VW
3. Bobba, S., Carrara, S., Huisman, J., Mathieux, F., Pavel, C.: Critical raw materials for strategic technologies and sectors in the EU—a foresight study. European Commission, Brussels (2020). https://doi.org/10.2873/580811
4. Haddadi, S.A., Alibakhshi, E., Bahlakeh, G., Ramezanzadeh, B., Mahdavian, M.: A detailed atomic level computational and electrochemical exploration of the Juglans regia green fruit shell extract as a sustainable and highly efficient green corrosion inhibitor for mild steel in 3.5 wt% NaCl solution. J. Mol. Liq. (2019). https://doi.org/10.1016/j.molliq.2019.04.045
5. Mohammad, E.H.N.T., Pantea, G., Mohammad, R., Ghaseb, B., Bahram, R.: Theoretical and experimental assessment of a green corrosion inhibitor extracted from Malvaviscus triloba. J. Environ. Chem. Eng. 9(3), 105256 (2021). https://doi.org/10.1016/j.jece.2021.105256
6. Ramezanzadeh, M., Sanaei, Z., Bahlakeh, G., Ramezanzadeh, B.: Highly effective inhibition of mild steel corrosion in 3.5% NaCl solution by green Nettle leaves extract and synergistic effect of eco-friendly cerium nitrate additive: Experimental, MD simulation and QM investigations. J. Mol. Liq. 256, 67–83 (2018). https://doi.org/10.1016/j.molliq.2018.02.021
7. Majd, M.T., Ramezanzadeh, M., Bahlakeh, G., Ramezanzadeh, B.: Steel corrosion lowering in front of the saline solution by a nitrogen-rich source of green inhibitors: detailed surface, electrochemical and computational studies. Constr. Build. Mater. 254, 119266 (2020). https://doi.org/10.1016/j.conbuildmat.2020.119266
8. Mirlalrio, A., Vázquez, A.E.: Plant extracts as green corrosion inhibitors for different metal surfaces and corrosive media: a review. Processes 8(8), 942 (2020). https://doi.org/10.3390/pr8080942
9. Chaubey, N., Savita, R., Qurashi, A., et al.: Frontiers and advances in green and sustainable inhibitors for corrosion applications: a critical review. J. Mol. Liq. 321, 114385 (2018). https://doi.org/10.1016/j.molliq.2020.114385
10. Arefaee, S.H., Rhee, K.Y., Verma, C., et al.: Challenges and advantages of using plant extract as inhibitors in modern corrosion inhibition systems: Recent advancements. J. Mol. Liq. 321, 114666 (2021). https://doi.org/10.1016/j.molliq.2020.114666
11. Hongyu, W., Heidarshenas, B., Zhou, L., Hussain, G., Li, Q., O strikov, K.: Green inhibitors for steel corrosion in acidic environment: state-of-art. Mater. Today Sustain. 10, 100044 (2020). https://doi.org/10.1016/j.mtsust.2020.100044
12. Vasylijev, G., Vorobiova, V.: Rape graft extract (Brassica napus) as a green corrosion inhibitor for water systems. Mater. Today Proc. 6(2), 78–186 (2019). https://doi.org/10.1016/j.matpr.2018.10.092
13. Vasylijev, G., Vorobiova, V., Zhuk, T.: Raphanus sativus L. extract as a scale and corrosion inhibitor for mild steel in tap water. J. Chem. 2020, 5089758 (2020). https://doi.org/10.1155/2020/5089758
14. Pal, S., Lgaz, H., Tiwari, P., Chung, I.M., Ji, G., Prakash, R.: Experimental and theoretical investigation of aqueous and methanolic extracts of Prunus dulcis peels as green corrosion inhibitors of mild steel in aggressive chloride media. J. Mol. Liq. 276, 347–361 (2018). https://doi.org/10.1016/j.molliq.2018.11.099
15. 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. J. Electroanal. Chem. 859, 113834 (2020). https://doi.org/10.1016/j.jelechem.2020.113834
16. Liu, Y., Song, Z., Wang, W., Jiang, L., Zhang, Y., Guo, M., Xu, N.: Effect of ginger extract as green inhibitor on chloride-induced corrosion of carbon steel in simulated concrete pore solutions. J. Electrochem. Soc. 165, 100196 (2018). https://doi.org/10.1016/j.ijcorros.2018.10.092
17. Ostrikov, K.: Green inhibitors for steel corrosion in acidic environment: state-of-art. Mater. Today Sustain. 10, 100044 (2020). https://doi.org/10.1016/j.mtsust.2020.100044
18. Ahanotu, C.C., Onyeachu, I.B., Solomon, M.M., Chikwe, I.S., Chikwe, O.B., Eziukwu, C.A.: Pterocarpus santalinoides leaves extract as a sustainable and potent inhibitor for low carbon steel in 3.5% NaCl solution. J. Mol. Liq. 321, 114666 (2021). https://doi.org/10.1016/j.molliq.2020.114666
19. 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. J. Electroanal. Chem. 859, 113834 (2020). https://doi.org/10.1016/j.jelechem.2020.113834
20. Liu, Y., Song, Z., Wang, W., Jiang, L., Zhang, Y., Guo, M., Xu, N.: Effect of ginger extract as green inhibitor on chloride-induced corrosion of carbon steel in simulated concrete pore solutions. J. Clean. Prod. 214, 298–307 (2019). https://doi.org/10.1016/j.jclepro.2018.12.299
21. Ahanotu, C.C., Onyeachu, I.B., Solomon, M.M., Chikwe, I.S., Chikwe, O.B., Eziukwu, C.A.: Pterocarpus santalinoides leaves extract as a sustainable and potent inhibitor for low carbon steel in a simulated pickling medium. Sustain. Chem. Pharm. 15, 100196 (2020). https://doi.org/10.1016/j.scip.2019.100196
22. Gangopadhyay, S., Manwaner, P.A.: Recent developments in the volatile corrosion inhibitor (VCI) coatings for metal: a review. J. Coat. Technol. Res. 15, 789–807 (2018). https://doi.org/10.1007/s11998-017-0015-6
23. Vorobyova, V., Chygrynyets, O., Skiba, M., Zhuk, T., Kurmako, S.: 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, 185–202 (2018). https://doi.org/10.17675/2305-6894-2018-7-2-6
20. Vorobyova, V.I., Skiba, M.I., Shakun, A.S., Nahirniak, S.V.: Relationship between the inhibition and antioxidant properties of the plant and biomass wastes extracts—a review. Int. J. Corros. Scale Inhib. 8(2), 150–178 (2019). https://doi.org/10.17675/2305-6894-2019-8-2-1
21. Vorobyova, V., Skiba, M., Chygyrynets, O.: A novel eco-friendly vapor phase corrosion inhibitor of mild steel. Pigment Resin Technol. 48(2), 337–349 (2018). https://doi.org/10.1108/PRT-03-2018-0025
22. Vorobyova, V.I., Chyhyrynets, O.E., Vasyly'keych, O.I.: 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/s11003-015-9778-7
23. Chyhyrynets, O.E., Fateev, Y.F., Vorob’iova, V.I., 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
24. Vorobyova, V., Chyhyrynets, O., Skiba, M.: 4-hydroxy-3-methoxybenzaldehyde as a volatile inhibitor on the atmospheric corrosion of carbon steel. J. Chem. Technol. Metall. 53, 336–345 (2018)
25. Vorobyova, V.I., Skiba, M.I.: Surface modification of the mild steel by multifunctional self-assembling nanolayers from the natural organic compounds of apricot pomace extract. Mol. Cryst. Liq. Cryst. 1(700), 63–76 (2020). https://doi.org/10.1080/15421406.2020.1732553
26. Yee, Y.P., Saud, S.N., Hamzah, E.: Pomelo peel extract as corrosion inhibitor for steel in simulated seawater and acidic medium. J. Mater. Eng. Perform. (2020). https://doi.org/10.1007/s11665-020-04774-1
27. Magni, M., Postiglione, E., Marzorati, S., Verotta, L., Trasatti, S.P.: Green corrosion inhibitors from agri-food wastes: the case of Punica granatum extract and its constituent ellagic acid. A valid study. Processes 8(3), 272 (2020). https://doi.org/10.3390/pr8030272
28. Halambek, J., Cindrić, I., Grassino, A.N.: Evaluation of pectin isolated from tomato peel waste as natural tin corrosion inhibitor in sodium chloride/acetic acid solution. Carbohydr. Polym. (2020). https://doi.org/10.1016/j.carbpol.2020.115940
29. Yahya, S., Othman, N.K., Ismail, M.C.: Corrosion inhibition of carbon steel in multiple flow loop under 3.5% NaCl in the presence of rice straw extracts, lignin and ethylene glycol. Eng. Fail. Anal. 100, 365–380 (2020). https://doi.org/10.1016/j.engfailanal.2019.02.036
30. Vorobyova, V., Skiba, M.: 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
31. Lu, Z., Wang, J., Gao, R., Ye, F., Zhao, G.: Sustainable valorisation of tomato pomace: a comprehensive review. Trends Food Sci. Technol. 86, 172–187 (2019). https://doi.org/10.1016/j.tifs.2019.02.020
32. Allison, B.J., Simmons, C.W.: Valorization of tomato pomace by sequential lycopene extraction and anaerobic digestion. Biomass Bioenergy 105, 331–341 (2017). https://doi.org/10.1016/j.biombioe.2017.07.019
33. Pinela, J., Prieto, M.A., Carvalho, A.M., Barreiro, M.F., Oliveira, M.B.P.P., Barros, L., Ferreira, I.C.F.R.: Microwave-assisted extraction of phenolic acids and flavonoids and production of antioxidant ingredients from tomato: a nutraceutical-oriented optimization study. Sep. Purif. Technol. 164, 114–124 (2016). https://doi.org/10.1016/j.seppur.2016.03.030
34. Sarno, M., Iuliano, M.: Highly active and stable Fe3O4/Au nanoparticles supporting lipase catalyst for biodiesel production from waste tomato. Appl. Surf. Sci. 474, 135–146 (2019). https://doi.org/10.1016/j.apsusc.2018.04.060
35. Grassino, A.N., Halambek, J., Djkovć, S., Rimac-Brnčić, S., Dent, M., Grabarić, Z.: Utilization of tomato peel waste from canning factory as a potential source for pectin production and application as tin corrosion inhibitor. Food Hydrocoll. 52, 265–274 (2016). https://doi.org/10.1016/j.foodhyd.2015.06.020
36. Calvo, M.M., Dado, D., Santa-Maria, G.: Influence of extraction with ethanol or ethyl acetate on the yield of lycopene, β-carotene, phytoene and phytolfluene from tomato peel powder. Eur. Food Res. Technol. 224, 567–571 (2007). https://doi.org/10.1007/s00217-005-0335-8
37. Nagarajan, J., Pui Kay, H., Krishnamurthy, N.P., Ramakrishnan, N.R., Aldawoud, T.M.S., Galanakis, C.M., Wei, O.C.: Extraction of carotenoids from tomato pomace via water-induced hydrocolloidal complexation. Biomolecules 10(7), 1019 (2020). https://doi.org/10.3390/biom10071019
38. Šojić, B., Pavlić, B., Tomović, V., Kocić-Tanackov, S., Đurović, S., Zeković, Z., Škaljac, S.: Tomato pomace extract and organic peppermint essential oil as effective sodium nitrite replacement in cooked pork sausages. Food Chem. 330, 127202 (2020). https://doi.org/10.1016/j.foodchem.2020.127202
39. Zhang, H.L., Ma, T.F., Gao, L.X., et al.: Vapor phase assembly of urea–amine compounds and their protection against the atmospheric corrosion of carbon steel. J. Coat. Technol. Res 17, 503–515 (2020). https://doi.org/10.1007/s11998-019-00301-7
40. Wang, S., Don, Z.H., Guo, X.: Investigation on initial atmospheric corrosion of copper and inhibition performance of 2-phenyl imidazoline based on electrical resistance sensors. Mater. Chem. Phys. 262, 124321 (2021). https://doi.org/10.1016/j.matchemphys.2021.124321
41. Vasyl’ev, H.S.: Measurement of polarization resistance with computer logging of results. Mater. Sci. 48, 694–696 (2013). https://doi.org/10.1007/s11003-013-9556-8
42. Vasyl’ev, H.S., Herasymenko, Y.S.: Corrosion meters of new generation based on the improved method of polarization resistance. Mater. Sci. 52, 722–731 (2017). https://doi.org/10.1007/s11003-017-0015-9
43. Vasyliev, G.: Polarization resistance measurement in tap water: the influence of rust electrochemical activity. J. Mater. Eng. Perform. 26, 3939–3945 (2017). https://doi.org/10.1007/s11665-017-2813-5
44. Herasymenko, Y.S., Vasyl’ev, H.S.: A two-step method for the evaluation of corrosion rate in metals. Mater. Sci. 45, 899–904 (2009). https://doi.org/10.1007/s11003-010-9256-6
45. Vorobyova, V., Skiba, M., Trus, I., Frolenková, S.: Grape pomace extract as green vapor phase corrosion inhibitor. Chem. Chem. Technol. 12(3), 410–418 (2018). https://doi.org/10.23939/chcht12.03.410
46. Chyhyrynets’, O.E., Vorob’iova, V.I.: Anticorrosion properties of the extract of rapeseed oil cake as a volatile inhibitor of the atmospheric corrosion of steel. Mater. Sci. 49, 318–325 (2013). https://doi.org/10.1007/s11003-013-9617-z
47. Vorobyova, V., Skiba, M.: 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
48. Sarno, M., Iuliano, M.: Highly active and stable Fe3O4/Au nanoparticles supporting lipase catalyst for biodiesel production from
50. Kusumastuti, R., Pramana, R.I., Soedarsono, J.W.: The use of morindacitrifolia as a green corrosion inhibitor for low carbon steel in 3.5% NaCl solution. AIP Conf. Proc. 1823, 020012 (2017). https://doi.org/10.1063/1.4978085

51. Zakir Hossain, S.M., Kareem, S.A., Alshater, A.F., Alzubair, H., Razzak, S.A., Hossain, M.M.: Effects of cinnamaldehyde as an eco-friendly corrosion inhibitor on mild steel in aerated NaCl solutions. Arab. J. Sci. Eng. (2019). https://doi.org/10.1007/s13369-019-04236-4

52. Tanaka, T., Matsuo, Y., Yamada, Y., Kouno, I.: Structure of polymeric polyphenols of cinnamon bark deduced from condensation products of cinnamaldehyde with catechin and procyanidins. J. Agric. Food Chem. 56(14), 5864–5870 (2008). https://doi.org/10.1021/jf800921r

53. Chyhyrynets, O.E., Fateev, Y.F., Vorobiova, V.I., Skyba, M.I.: Study of the mechanism of action of the isopropanol extract of rapeseed oil cake on the atmospheric corrosion of copper. Mater. Sci. 51(5), 644–651 (2016). https://doi.org/10.1021/jf800921r

54. Sulaiman, K.O., Onawole, A.T., Faye, O., Shuaib, D.T.: Understanding the corrosion inhibition of mild steel by selected green compounds using chemical quantum based assessments and molecular dynamics simulations. J. Mol. Liq. 279, 342–350 (2019). https://doi.org/10.1016/j.molliq.2019.01.136

55. Njoku, D.I., Ukaga, I., Ikenna, O.B., Oguzie, E.E., Oguzie, K.L., Ibis, N.: Natural products for materials protection: corrosion protection of aluminium in hydrochloric acid by Kola nitida extract. J. Mol. Liq. 219, 417–424 (2016). https://doi.org/10.1016/j.molliq.2016.03.049

56. Oguzie, E.E., Li, Y., Wang, F.H.: Corrosion inhibition and adsorption behavior of methionine on mild steel in sulfuric acid and synergistic effect of iodide ion. J. Colloid Interface Sci. 310, 90–98 (2007). https://doi.org/10.1016/j.jcis.2007.01.038

57. Pearson, R.G.: Hard and soft acids and bases. J. Am. Chem. Soc. 85(22), 3533–3539 (1963). https://doi.org/10.1021/ja00905a001

58. Geerlings, P., De Proft, F., Langenaeker, W.: Conceptual density functional theory. Chem. Rev. 103, 1793–1874 (2003). https://doi.org/10.1021/cr990029p

59. Gece, G.: The use of quantum chemical methods in corrosion inhibitor studies. Corros. Sci. 50(11), 2981–2992 (2008). https://doi.org/10.1016/j.corsci.2008.08.043

60. Vasyliev, G.S., Gerasimenko, Yu.S., Poznyak, S.K., Tsybulskaya, L.S.: A study of the anticorrosion properties of carbonate deposits to protect low-carbon steel from the action of tap water. Russ. J. Appl. Chem. 87(4), 450–455 (2014). https://doi.org/10.1134/S1070427214040090

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.