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Enhancing pitting corrosion inhibition of AISI 304 stainless steel using a green frankincense-modified ferric chloride solution

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To inhibit pitting corrosion of AISI 304 stainless steel (SS), the effect of different percentages of frankincense addition to a 0.5 M ferric chloride solution was explored in this work for the first time. The samples were investigated for pitting corrosion susceptibility via electrochemical noise (EN) tests, where the current and potential noises were recorded for 10000 seconds, and potentiodynamic polarization. The frequency domain of EN data was analyzed using power spectral density (PSD). Frankincense addition to the ferric chloride solution effectively reduced the pitting corrosion of AISI 304 SS. The pitting inhibition was concluded from the high fluctuations in current noises over the test period, its decreasing amplitude, the greater positive potential, the lower current values, and the lower spectral noise and noise resistances with increasing frankincense additions. Optical microscope images supported pitting inhibition with frankincense addition, where pits decreased in number per mm^2 and size. A significant decrease in the pit size and pits mm^{-2} was observed with the 10 wt.% frankincense addition. It was attributed to the adsorption of the inhibitor on the stainless steel surface, inhibiting the adsorption of chloride ions. Additionally, frankincense addition reduced the corrosion current and increased the corrosion potential positively.

Keywords: *304 stainless steel, electrochemical noise (EN), frankincense, pitting corrosion, green inhibitor, polarization*

1. Introduction

There are various methods to control the corrosion of materials, such as protective coatings, cathodic or anodic protection, design and selection of proper materials, and organic and inorganic corrosion inhibitors [1]. Corrosion inhibitors are chemical compounds predominant in different fields because of their high efficiency, facile feasibility [2], and reasonable cost [3]. The work mechanisms of inhibitors are whether they adhere to the material's surface [4] and/or form a uniform protective layer against corrosive agents [5]. Such corrosives include but are not limited to hydrochloric acid [6], NaCl [7], nitric acid [8], and ferric chloride ($FeCl_3$) [9].

Organic inhibitors [10] and inorganic inhibitors [11], such as chromate [12], molybdate [13], and nitrate [14], are widely used in many industries to control the corrosion of metals. The use of organic inhibitors, especially against pitting corrosion of stainless steel (SS), has caught researchers' attention [15]. Early research [16] showed that many organic compounds could protect stainless steel against pitting corrosion. Garz and Glaser [17] showed the use of benzyl-n-propyl sulfide (BPS) inhibited the pitting corrosion of pure nickel and Cr–Ni SS in 0.5 M NaCl under conditions that allow the formation of SH^- and $BPSH^+$ ions. Also, other researchers showed the effectiveness of organic inhibitors against pitting corrosion [16]. However, due to the inhibitors' environmentally toxic nature, most recent attention has been on eco-friendly inhibitors to replace traditional ones. Green inhibitors are ecologically friendly [18], biodegradable [19], don't contain heavy metals [20], and are inexpensive [21].

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Different green inhibitors were investigated to reduce the pitting corrosion of AISI 3xx SS. It was reported in the literature that Thymus vulgaris plant extract, one of the green inhibitors used to reduce pitting corrosion, has an inhibition effect of 304 SS up to 62.15% in the HCl [22]. The use of Santolina chamaecyparissus extract in 3.5% NaCl solution was studied by Shabani-Nooshabadi et al. [23], and they found that it had an inhibition efficiency on AISI 304 SS of up to 83.6%.

Additionally, many reports were found in the literature on the use of green inhibitors for different metal/environment couples [24]. Suyun Caoa et al. [25] investigated the effect of ionic liquid inhibitors on the corrosion inhibition of carbon steel in HCl. They observed an enhancement in inhibition efficiency as the concentration increased, attributing it to the inhibitor's adsorption on the metal surface. Yujie Qiang et al. [26] studied derivatives of indazole inhibitors on the corrosion of copper in NaCl solution. They found that the adsorption of the inhibitor on the copper surface improved the corrosion resistance. Other researchers found improved corrosion inhibition efficiency of copper in NaCl solution by utilizing triazole and imidazole inhibitors [27]. Other examples of green inhibitors include Schiff bases [6], benzimidazole derivative [28], and ionic liquids [29], which were used for inhibiting the corrosion of mild and carbon steels in a hydrochloric acid medium. The inhibition was attributed to the adsorption of inhibitor [25] and the formation of a protective film on the steel surface [6]. Such protective films suppress corrosion attacks by blocking the active sites on the metal surface [26]. Another inhibitor, N-lauroylsarcosine, was found to inhibit localized corrosion in AISI 304 and 316L stainless steels in nitric acid by adsorption of the inhibitor on the steel surface [8]. Dithiocarbamate-modified glucose, an eco-friendly inhibitor, was effectively adsorbed on the surface of copper in NaCl solution leading to excellent anti-corrosion performance [30]. The addition of meat extract as an inhibitor improved the pitting corrosion resistance of mild steel in hydrochloric acid by the adsorption of the extract on the steel surface. The meat extract was prepared by boiling water containing meat for five hours, followed by further heating of the water-free meat to form a concentrate [31].

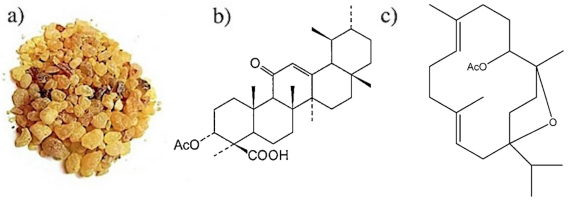


Fig. 1. a) Frankincense olibanum resin, b) the structure of β-boswellic acid, one of the main active components of frankincense [35], and c) incensole acetate [36]

Furthermore, it is to be emphasized that the aforementioned green inhibitors had to undergo various synthesis techniques before being used. The novelty of this study is the use of frankincense. Frankincense, an organic material, is employed in this study as a potential green inhibitor for mitigating pitting corrosion and is advantageously utilized as received without further processing. This work will be the first to examine the possible use of frankincense as a pitting inhibitor for AISI 304 SS in a ferric chloride solution.

Figure 1a shows frankincense/olibanum, a water-soluble aromatic resin obtained from genus Boswellia trees, forming heavy, thick, and dense solutions depending on the added quantity [2]. Frankincense can be produced from different types of Boswellia, giving resins of various grades, which are hand-sorted, based on harvesting time [32]. Frankincense consists of several chemical compounds like $C_{20}H_{32}O_4$ (6%), gum (30–36%) [33], alpha-boswellic acid, phellandrene, incensole acetate [34], 3-acetyle-beta-boswellic acid (Fig. 1b), which is one of the main active components of frankincense [35], and $C_{21}H_{34}O_3$, (Fig. 1c) [34].

Stainless steel has excellent corrosion resistance, especially the AISI 3xx series, so it has many applications, such as for medical instrumentation and tools [37] or in food plants [38], the oil industry [39], and marine infrastructure [40]. However, AISI 3xx SS can be subjected to localized pitting corrosion. Pitting corrosion can be caused by exposure to aggressive chloride anions [41]; it is

initiated when chloride anions are introduced into the working environment and reach a critical value, forming a thin layer of chloride ion-rich electrolyte on the stainless steel surface [42]. However, the adsorption of an inhibitor on a steel surface and the formation of a protective film could reduce or inhibit the pitting corrosion, as mentioned earlier.

Ferric chloride is a highly corrosive and aggressive solution that is commonly used in laboratory experiments and industrial applications to simulate harsh acidic environments. It has a high solubility in water, making it easy to prepare and work with. Additionally, $FeCl_3$ is particularly corrosive towards 304 stainless steel, making it a suitable solution for testing the effectiveness of various inhibitors in protecting the AISI 304 steel against pitting corrosion [43].

Several monitoring techniques can be used to investigate pitting corrosion in metals, including, but not limited to, linear polarization resistance, impedance spectroscopy, potentiodynamic polarization, and electrochemical noise (EN). In this work, the potentiodynamic polarization and EN will be utilized. The potentiodynamic polarization will be used to measure the inhibition efficiency and the pitting tendency as applied by others [44].

One of the advantages of the EN technique is that it is a non-destructive method, i.e., it does not alter the metal surface. It is also well known that the EN technique can be used to investigate localized corrosion of metallic materials through the acquisition and analysis of EN data and signals. Electrochemical noise is physiochemically related to the equilibrium state of the electrochemical processes. It depends on fluctuations detected in current and electrochemical potential associated with the difference between the kinetics of the partial reactions of the anode and cathode [45]. The electrochemical current noise (ECN) between two nominally identical electrodes is measured by a zero-resistance ammeter (ZRA). The electrochemical potential noise (EPN) of the electrically coupled electrodes is measured by a high-impedance voltmeter using a reference electrode [46]. The ECN and EPN signals correspond to the time-varying components filtered from the original current and potential signals. Therefore, in this work, and for the first time, the possible use of frankincense as an inhibitor against pitting corrosion in AISI 304 SS will be investigated via electrochemical noise measurements. The investigation will be conducted on the SS samples immersed in a pitting-aggressive environment, i.e., chloride anion-rich ferric chloride solution, and with different percentages of frankincense addition in the solution. Furthermore, the effect of frankincense addition on pit formation and size will be examined by utilizing an optical microscope.

2. Experimental and materials

2.1. Materials

AISI 304 SS disks (1.13 cm diameter x 0.5 cm, Goodfellow) were cut from a bar to investigate pitting inhibition. The chemical composition of the AISI 304 SS is shown in Table 1. The total area of the steel discs exposed to the testing solution was 1 cm^2 based on the assembly of the corrosion cell. Each specimen was ground with silicon-carbide papers with grit numbers 120, 220, 320, 400, and 600 sequentially. Finally, the samples were rinsed with distilled water, degreased with acetone, and dried with hot air.

Ferric chloride powder (Sigma Aldrich) was used for the preparation of a 0.5 M solution using distilled water, resulting in a pH of 1.8. This medium was used as the testing solution to represent severe pitting exposure conditions of AISI 304 SS. Frankincense was added by 2.5 wt.%, 5 wt.%, 7.5 wt.% and 10 wt.% to the solutions. These additions aimed to study the effect of added frankincense on pitting corrosion inhibition of AISI 304 SS, where the immersion time of the samples in each testing solution was 10,000 seconds (166 minutes). It is to be mentioned that the concentrations investigated in this work were chosen

Table 1. Chemical composition of AISI 304 stainless steel

Element	C	Cr	Ni	Mn	P	Si	S	Fe
Wt. %	0.07	18.25	8.2	1.8	0.044	0.77	0.032	balance

arbitrarily, and based on any pitting trends, other concentrations could be investigated.

2.2. Electrochemical noise and potentiodynamic polarization measurements

Autolab PGSTAT 30 was used to perform EN measurements. Electrochemical noise measurement was used to study the effect of frankincense addition on the pitting behavior of AISI 304 SS. The schematic of the utilized experimental setup is shown in Figure 2.

Three electrode connections were used in the electrochemical current noise (ECN) measurement, i.e., two identical AISI 304 SS working electrodes (WE1 and WE2) and a saturated calomel reference electrode (SCE) were connected, as shown in Figure 2. In the ECN test, the small fluctuations in current and voltage signals generated between the two identical working electrodes and the reference electrode were measured according to the ASTM G-199 standard [5].

The generated electrochemical current noise (ECN) between the two working electrodes (WE1 and WE2) was recorded at the same potential of the two electrodes to measure the electrochemical potential noise (EPN) versus the SCE, which was monitored simultaneously.

Recording of ECN was performed continuously for 10,000 seconds with a data-recording interval of 0.5 seconds. All tests were run just after immersion of the samples into the ferric chloride solution containing different amounts of frankincense, and the same procedure was applied for all frankincense concentrations. A low-pass filter was applied to eliminate peaks less than 10 nA.

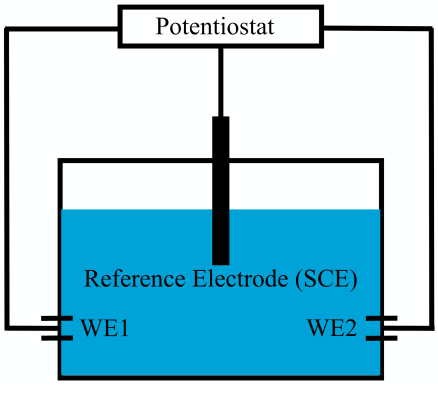


Fig. 2. EN experimental setup

Autolab PGSTAT 30 was also used to perform the potentiodynamic polarization of the AISI 304 steel in 0.5 M ferric chloride solution and in the solution with added frankincense of the abovementioned concentrations. The polarization cell setup consisted of AISI 304 steel as the working electrode, platinum as the counter electrode, and SCE as the reference electrode. The area of the steel subjected to the solution was 1 cm^2, and the applied polarization rate was 1 mV/sec.

2.3. Microscopical examination of the pits

The potential formation of pits on the tested specimens, before and after testing in the frankincense-free ferric chloride solution and in ferric chloride solutions containing frankincense, was observed with an optical microscope (MEIJI ML 7100). The optical microscope images were analyzed with ImageJ to measure any change in pits per mm^2 or their size as a result of frankincense addition. The reported measurements were the average of 20 readings from three randomly selected regions of each sample.

3. Results and discussion

EN current and potential noise values versus immersion time of the samples in the testing solution were recorded for frankincense-free ferric chloride solution (Fig. 3), and for the ferric chloride solution with 2.5 wt.%, 5 wt.%, 7.5 wt.%, and 10 wt.% of frankincense addition (Fig. 4). The recording of the current and potential EN signals of the samples was started immediately after immersion in the testing solution and lasted for 166 minutes. Figure 3a showed that there was a sharp increase in current noise indicating high susceptibility to pitting corrosion. The mean EN signal of the current noise record for the inhibitor-free solution was calculated from Figure 3a and found to be 6×10^{-2} A, while Figure 3b was used to calculate the mean EN signal of the potential record and was -3.8×10^{-3} V vs. SCE.

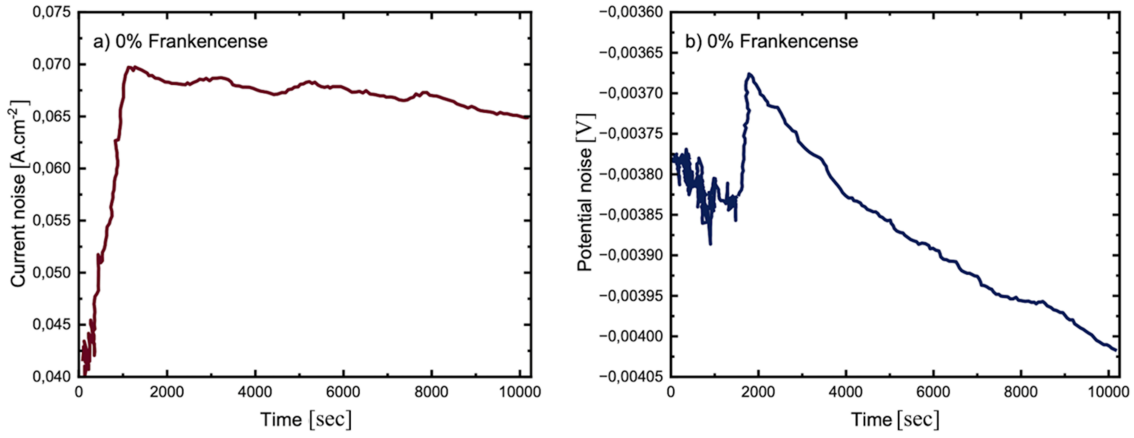


Fig. 3. Current and potential EN noise values recorded for an inhibitor-free solution

The effect of frankincense addition on pitting inhibition of AISI 304 SS in ferric chloride solution was investigated by comparing the mean current and potential noise records for the frankincense-free solution (Fig. 3) to that with different percentages of frankincense additions (Fig. 4). The mean current and potential noise values were calculated from the recorded current and potential noise values in Figures 3 and 4. It was found that frankincense addition resulted in a decrease in the mean current noise records (Fig. 4a, c, e, g) and a shift in the mean potential noise records toward more positive values (Fig. 4b, d, f, h). These trends in mean current and potential noises with frankincense additions were represented in Figure 5, where it was seen that the lowest mean current noise and the highest (more positive) mean potential noise were recorded for the 10% of frankincense addition. The mean current and potential noise values with the 10 wt.% of frankincense addition were 7.9×10^{-4} A and 1.3×10^{-2} V, respectively.

It is established that the primary step in pitting corrosion of stainless steel, including AISI 304 SS, is the adsorption of chloride ions to the stainless steel surface. On the other hand, the adsorption of inhibitors to a stainless steel surface is the main inhibition effect [47] that competes with the adsorption of chloride ions [48]. Inhibition of pitting depends on the interaction between inhibitor species on the metal surface and reducing the dissolution process of a passive film on the metal surface [49]. Forming a surface film that contains inhibitors decreases the active surface area of stainless steels. Therefore, when the stainless steels are exposed to chloride ions, their susceptibility to pitting, which is greatly influenced by the inhibitor adsorption on the surface of AISI 304 SS, would decrease. As mentioned above, Figure 5 shows the effect of added frankincense on mean current noise and mean potential noise. It is found that the mean current noise was decreased with increasing the wt.% of the added frankincense. However, the mean potential noise increased positively with the wt.% of the added frankincense. The positive increase in the mean potential noise suggested that adding frankincense, which has an emulsifying effect, can act as a barrier to the chloride ions' adhesion to a metal surface, reducing localized pitting corrosion.

Additionally, the emulsifying effect of frankincense would increase the viscosity of the solution, therefore slowing down the diffusion rates and the adsorption of chloride ions into the metal surface and inhibiting pitting corrosion. The effect of both β-boswellic acid and incensole acetate constituents of frankincense on pitting inhibition is not well understood, and this may need more investigation.

However, it was observed from the inset of Figure 5 that the mean potential noise increased negatively up to 5% of frankincense addition, and then the trend changed to more positive potentials afterward. The negative increase in mean potential noise between the frankincense-free solution

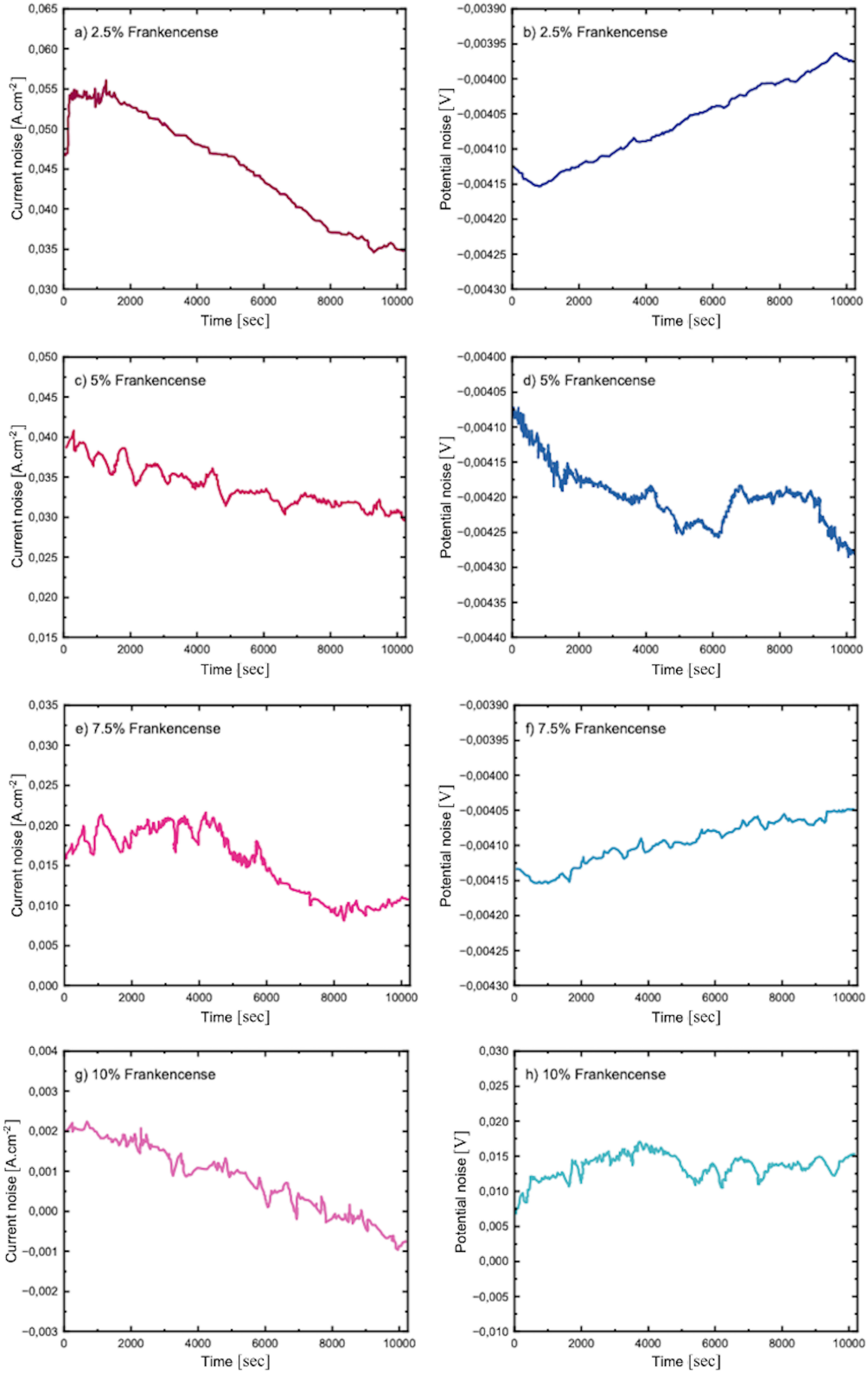


Fig. 4. Current and potential electrochemical noise values recorded for a-b) 2.5 wt.%, c-d) 5wt. %, e-f) 7.5 wt.%, and g-h) 10 wt.% of frankincense addition, respectively

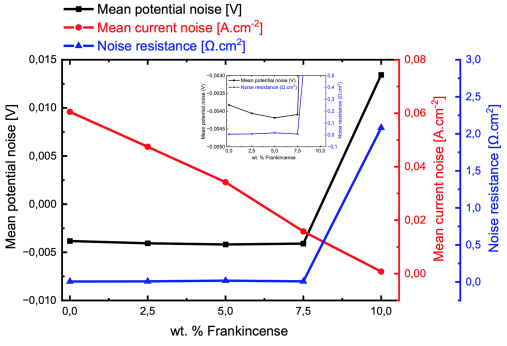


Fig. 5. The effect of frankincense addition on mean potential noise, mean current noise, and noise resistance (R_n)

and the solution with a 5% addition was negligible (10%) compared to the positive increase in mean potential noise. The positive increase in mean potential noise between the 5% and 10% of frankincense addition was 420%. Nevertheless, there are a few possible reasons for recording more negative mean potential noise at the low concentrations of frankincense addition. One reason could be the incomplete adsorption of the inhibitor on the metal's surface. The high solubility of the inhibitor in the solution at low concentrations may slow down the inhibitor's adsorption on the metal surface, which might be another reason for the more negative potential values recorded at low concentrations of frankincense addition. Additionally, the interaction of the inhibitor with other species in the testing solution may form other compounds that may be ineffective in inhibiting pitting corrosion. These possible reasons suggest that at concentrations higher than 5% of frankincense addition, better adsorption of the inhibitor and formation of a protective film on the metal surface led to an increase in the potential noise to more positive potentials, suggesting more resistance to pitting corrosion. Because the solution with the 10% frankincense addition showed the highest positive potential, it is suggested that film adsorption and the formation of the protective film were optimized at this concentration.

Furthermore, Figure 4 shows that the current and potential noises fluctuated irregularly. With increases in the frankincense concentration, the ECN plots (Fig. 4a, c, e, g) visually showed a decrease in noise amplitudes of the fluctuations. Current fluctuations can be pictured as birth-death transients or a sudden change in current values in a zigzag form. The decrease in current fluctuations' amplitudes observed in this work agrees with the findings of A. Ehsani et al. [44], who investigated the effect of Thymus vulgaris plant extract on the pitting of AISI 304 SS in 1 M HCl. The finding of this work also agrees with the work of Kannan et al. [50] and Y. Chen et al. [51]. They investigated the inhibition effect of benzimidazoliumtetrafluroborate ionic liquid and benzotriazole on the corrosion of carbon steel and copper in 1 M HCl and 0.1 M NaCl, respectively. Those researchers reported that the decrease in fluctuations' amplitudes with increasing inhibitor concentrations was associated with improved pitting corrosion resistance [51]. Additionally, The EPN plots (Fig. 4b, d, f, h) showed a shift in the mean potential noise to more positive values, as mentioned above and represented in Figure 5. Therefore, the observed trends in the ECN and EPN plots of this work may indicate an increase in the metal's passive state, which may be associated with slowing down in pitting corrosion.

It is to be addressed that the electrochemical potential noise in Figure 3b shows disturbance up to 2,000 seconds. This disturbance could be attributed to the formation of unstable pits, a behavior that was not observed in the solution with frankincense addition in Figures 4b, d, f, and h. This observation could potentially reinforce the efficiency of frankincense in reducing pitting corrosion.

Moreover, it was visually observed from Figures 3 and 4 that the number of fluctuations, i.e., birth-death transients, were increased with frankincense addition. The increase in fluctuations may be attributed to an activation-controlled process, i.e., metastable pitting behavior. The metastable behavior of pits, with frankincense addition, would indicate the occurrence of more uniform corrosion rather than pitting. Pitting is more damaging than uniform corrosion because it acts as a stress concentrator, leading to premature failure of the metal when pits are stable and penetrate deep into the

Table 2. The values of the I_{mean} and V_{mean} were calculated from the data recorded in Figures 3 and 4 for AISI 304 SS at different percentages of frankincense addition to ferric chloride solution. The noise resistance (R_n) was calculated from σ_V and σ_I according to Equation (1)

% of frankincense addition	I_{mean} (A.cm^{-2})	V_{mean} (V)	σ_I (A.cm^{-2})	σ_V (V)	R_n (Ω.cm^2)
0	6.05×10^{-02}	-3.82×10^{-03}	9.70×10^{-03}	5.82×10^{-05}	6.00×10^{-03}
2.5	4.75×10^{-02}	-4.06×10^{-03}	6.79×10^{-03}	5.69×10^{-05}	8.37×10^{-03}
5	3.42×10^{-02}	-4.19×10^{-03}	2.64×10^{-03}	4.72×10^{-05}	1.79×10^{-02}
7.5	1.58×10^{-02}	-4.10×10^{-03}	3.99×10^{-03}	3.12×10^{-05}	7.82×10^{-03}
10	7.90×10^{-04}	1.34×10^{-02}	8.65×10^{-04}	1.80×10^{-03}	2.08

metal. Therefore, the higher fluctuations recorded with increasing frankincense addition suggested less susceptibility (more inhibition) to pitting as compared to testing in a solution with low concentrations of frankincense addition. This finding agrees with the work of A. Ehsani et al. [44] mentioned above.

The above finding could be supported by calculating the noise resistance. The noise resistance is used to study pitting corrosion, and it measures the resistance to current noise in metals. The noise resistance is defined mathematically as [52],

$$R_n = \frac{\sigma_V}{\sigma_I}, \tag{1}$$

where σ_V is the standard deviation of the mean voltage noise values and σ_I is the standard deviation of the mean current noise values. Table 2 represents the values of the mean current noise (I_{mean}), mean potential noise (V_{mean}), σ_V, and σ_I, which were calculated from the data recorded in Figures 3 and 4 in addition to R_n. Figure 5 shows that R_n values increased with increasing frankincense addition. Therefore, the obtained higher noise resistance and slower corrosion rate suggested effective inhibition of frankincense to pitting corrosion. This finding agrees with the work of Ehsani et al. [53]. They found that the mean current noise decreased, the mean potential noise shifted to more positive values, and R_n increased with the increasing concentration of the Thymus vulgaris crude plant extract inhibitor. Similar results were also obtained by Kannan et al. [50]. They found that the amplitude of the current noise decreased and the noise resistance (R_n) increased with increasing inhibitor concentration, indicating better inhibition. The increase in noise resistance with the formation of a coating on the surface of aluminum was reported by Yong-Jun Tan et al. [54]. They observed a dramatic decrease in corrosion rate due to the formation of a protective passive film.

The sharp increase in noise resistance after 7.5 wt.% frankincense addition observed in Figure 5 might be attributed to the formation of new cations and anions by the dissolution of frankincense in the ferric chloride solution. The presence of such new ions in the solution might hinder the ability of Cl^- ions to reach the AISI 304 SS surface, causing a lower pitting tendency. However, the exact nature of the formed solution after adding the frankincense is still not understood and needs further investigation. Nevertheless, the noise resistance behavior of the solution may indicate that the critical weight percentage of frankincense addition is 7.5 wt.%. After this percentage, the mean potential noise and the noise resistance started increasing sharply, indicating reduced pitting susceptibility.

Next, the Fast Fourier transform (FFT) algorithm was applied to the EN data to transform the time domain into a frequency domain for making power spectral density (PSD) plots. The PSD plots were used to analyze the EN data. However, because the accuracy of EN measurements can be affected by direct current (DC) trends caused by the instability of test electrodes during the testing, the trends were removed before calculating the PSD as recommended elsewhere [55]. The removal of the DC noise trends from raw EN data was performed as Tan et al. [54] explained via a modified moving average removal (MAR) method. Figure 6 shows typical PSD plots, which represent spectral noise resistance, i.e., impedance

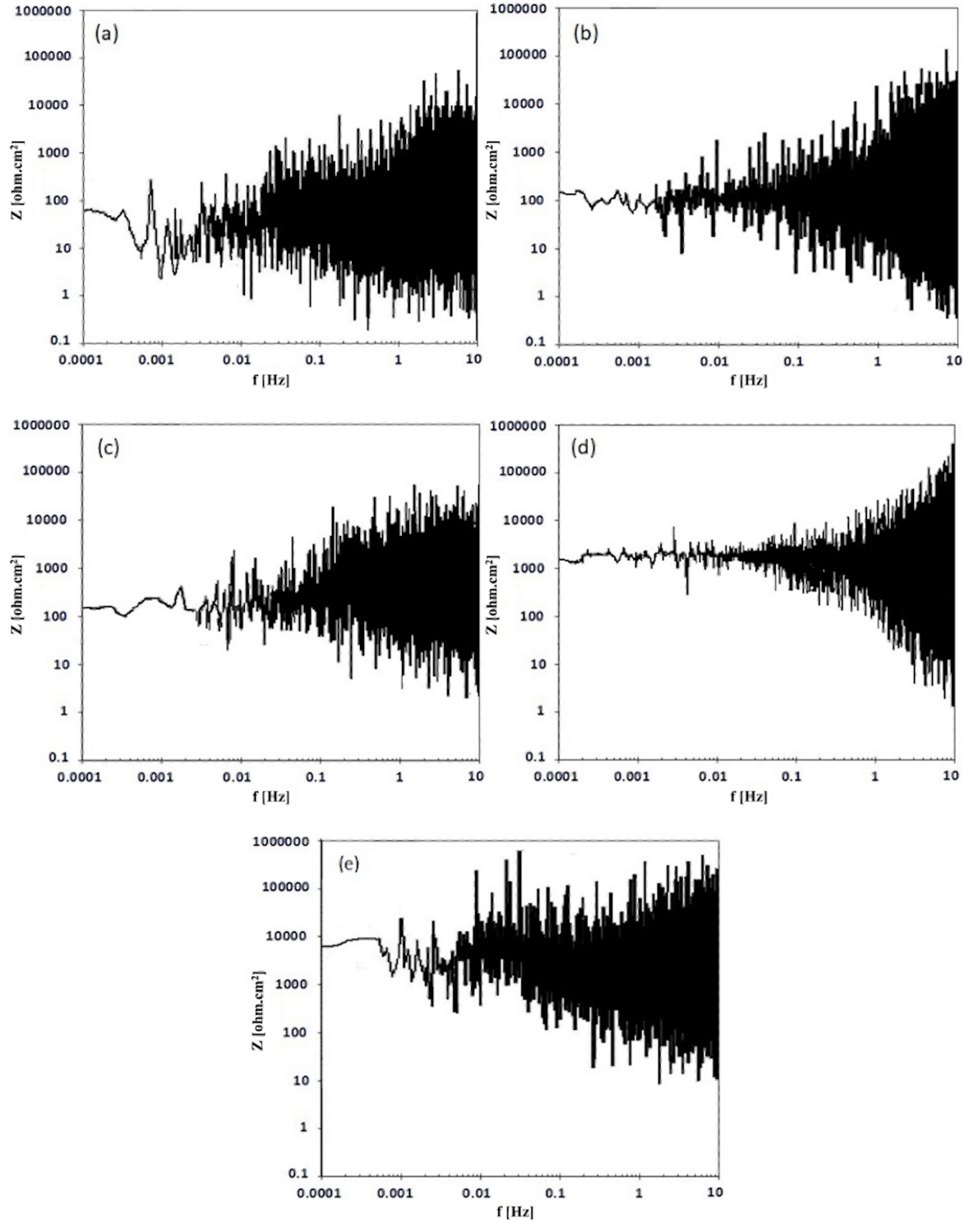


Fig. 6. PSD spectral noise resistance of AISI 304 stainless steel samples for the (a) inhibitor-free, (b) 2.5 wt.% inhibitor, (c) 5 wt.% inhibitor, (d) 7.5 wt.% inhibitor, and (e) 10 wt.% inhibitor

in the low-frequency range [56] on the y-axis at a specific frequency. It also shows that PSD plots had lower noise magnitude in the lower frequency range and diverged at higher frequencies. So, the low-frequency region provided more useful information about the inhibitor efficiency. The basis of the impedance technique is the measurement of current response as an outcome of small potential perturbation over a frequency range [57]. Then, when comparing spectral noise resistance visually with low-frequency impedance value, it can be noticed that the spectral noise resistance increased by increasing the quantity of frankincense inhibitor to ferric chloride solution (Fig. 6). The increase in spectral noise resistance may be attributed to an enhanced pitting resistance, which agrees with the findings of M.G. Pujar et al. [58] and Xiaolan Liu et al. [56]. M.G. Pujar et al. [58] applied the EN technique to investigate the effect of sulfate ions on the pitting corrosion of AISI 316 SS. They found that the increase in noise resistance and spectral noise resistance was attributed to the enhanced passivation against the pitting corrosion attack. Xiaolan Liu et al. [56] investigated the formation of a coating on magnesium alloy using EN technique and found that the spectral noise resistance increased with time during the coat-formation process.

The reduced pitting susceptibility with frankincense addition was supported by optical microscope images shown in Figure 7 and ImageJ's analysis of the formed pits, as shown in Figure 8. The scratches resulting from the grinding process are evident in the optical microscope images presented in Figure 7. Most of the pits exhibit a circular shape, while others display irregular shapes, and all are in varying sizes. Additionally, a change in the color of the 304 SS surface is noticeable upon the introduction of frankincense, particularly when comparing Figures 7b and 7f. This may suggest the potential formation of an adsorbent protective layer on the surface of the 304 SS, leading to a reduction in both the number and size of pits on the sample surface with a 10% frankincense addition, as shown in Figure 7f. Nevertheless, further investigation is required concerning the impact of frankincense addition on

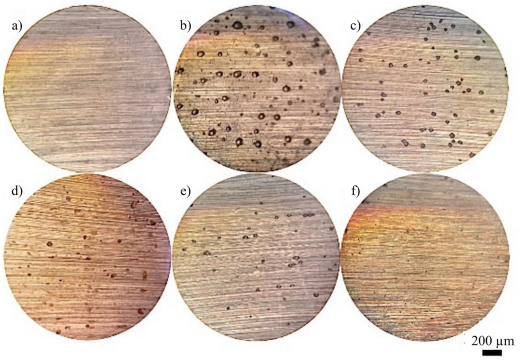


Fig. 7. Optical microscope images for the a) as-received AISI 304 SS and for the AISI 304 SS samples tested in 0.5 M ferric fluoride with b) frankincense-free, c) 2.5 wt.%, d) 5 wt.%, e) 7.5 wt.%, and f) 10 wt.% of frankincense addition

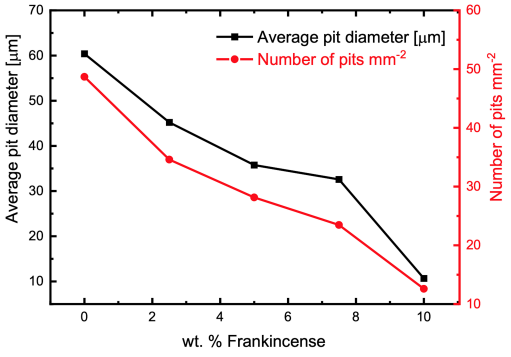


Fig. 8. The effect of frankincense addition on the number of pits mm^{-2} and the size of pits

the color change of the 304 SS surface and its role in pit formation. This aspect will be explored in future research endeavors. Figures 7 and 8 reveal a decrease in both the pit size and pit density (pits mm^{-2}) with increasing wt.% of the added frankincense. The reduction was most significant after the 7.5 wt.% of frankincense addition. This may further support the above finding that the 7.5 wt.% of the frankincense addition is the threshold value and also supports the effective inhibition of pitting corrosion by frankincense addition.

Figure 9a shows the potentiodynamic polarization curves for the AISI 304 SS in the ferric chloride solution and in the solution with different percentages of frankincense additions. The corrosion currents and the corrosion potentials

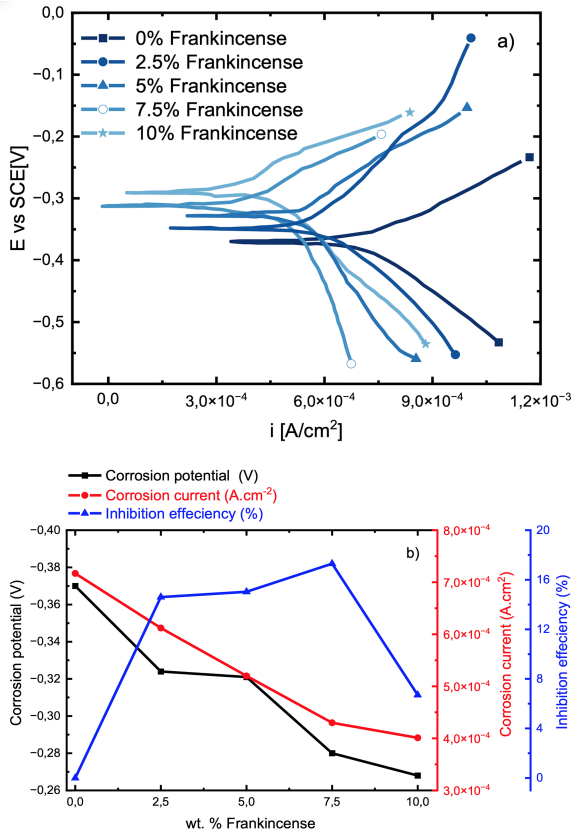


Fig. 9. Potentiodynamic polarization curves for AISI 304 SS in a) 0.5 M $FeCl_3$ solution and in the solution with different percentages of frankincense addition and b) the change in corrosion current, corrosion potential, and inhibition efficiency with frankincense addition

were found from the polarization curves by taking tangents to the anodic and cathodic portions of the polarization curves. The corrosion potential and the corrosion currents were read from the (Y) and (X) axes, respectively, at the intersection of the taken tangents. Figure 9b and Table 3 show that the corrosion current decreased with frankincense addition and the corrosion potential shifted to more positive values. These changes in the corrosion current and corrosion potential agree with the results obtained above – that the frankincense addition improved corrosion resistance. The inhibition efficiency was also calculated according to Equation (2) below [53]:

$$Inhibition\ effeciency\ (EI) = \frac{I_{0\%} - I_{x\%}}{I_{0\%}}, \quad (2)$$

Table 3. Polarization parameters of 304 SS in 0.5 M $FeCl_3$ with various percentages of frankincense additions

% of frankincense addition	$I_{corr.}$ **(A.cm^{-2})**	$E_{corr.}$ **(V)**	**EI (%)**
0	7.17×10^{-04}	−0.370	0
2.5	6.12×10^{-04}	−0.324	14.62
5	5.20×10^{-04}	−0.321	15.03
7.5	4.30×10^{-04}	−0.280	17.31
10	4.01×10^{-04}	−0.268	6.70

$I_{corr.}$: corrosion current, $E_{corr.}$: corrosion potential.

Where $I_{0\%}$ is the corrosion current of the frankincense-free solution and the $I_{x\%}$ is the corrosion current of the ferric chloride solution with a specific percentage of frankincense addition. The frankincense addition resulted in improved inhibition efficiency compared to the frankincense-free solution. However, a lower efficiency was obtained at the 10% addition compared to the 7.5% addition, which may suggest that the 7.5% addition is the critical value of frankincense. Though this critical value agrees with the electrochemical noise measurement finding, the reason for the reduced inhibition by increasing the frankincense to 10% is still unknown and needs further investigation.

4. Conclusion

The electrochemical noise technique was utilized to study the effect of frankincense addition, in different concentrations, on the pitting inhibition of AISI 304 SS in 0.5M ferric chloride solution. A change in current and potential noises was noticed for all frankincense-added solutions. However, the largest changes were observed when adding 10 wt.% frankincense, where the current noise decreased from 6.052×10^{-02}A for the frankincense-free solution to 7.897×10^{-04}. Also, the 10 wt.% frankincense addition shifted the potential noise to a more positive value, from -3.827×10^{-03} V for the frankincense-free solution to 1.343×10^{-02} V. Additionally, the fluctuations in current noise reduced in amplitude with frankincense addition. Furthermore, the spectral noise resistance and noise resistance were

increased with frankincense additions. Moreover, the pits decreased in number per area and size when frankincense was added to the ferric chloride solution. The potentiodynamic polarization test showed that the corrosion current decreased and the corrosion potential shifted to more positive values with frankincense addition. The inhibition efficiency was also found to increase with frankincense addition relative to the frankincense-free solution. However, the efficiency dropped at the 10% frankincense addition compared to the 7.5% addition for a reason that needs further investigation. All of the abovementioned changes with frankincense addition indicated reduced susceptibility to pitting corrosion. The Inhibition effect was attributed to the adsorption of inhibitor on the stainless steel surface to form a protective film, preventing chloride ions from reaching the metal surface. The film may be formed from new ions produced during the dissolution of frankincense. Also, frankincense addition may have decreased the active surface area and, accordingly, reduced the susceptibility to pitting when exposed to chloride ions. The reduction in pitting susceptibility can be significantly influenced by the inhibitor adsorption on the surface of AISI 304 SS. However, the nature of the solution formed by frankincense addition still needs further investigation.

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Data and code

Some or all data used are available from the corresponding author by request.

Conflict of interest

The authors declare that they have no conflict of interest.

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