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Black Pine (*Pinus nigra*) Essential Oil as a Green Corrosion Inhibitor for Carbon Steel

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Abstract: In this work, the essential oil of black pine (*Pinus nigra* J. F. Arnold) was used for the first time as a natural, ecological, and sustainable corrosion inhibitor for the acid cleaning of carbon steel. The essential oil was extracted by hydrodistillation using a Clevenger-type apparatus, and the oil was analyzed by gas chromatography–flame–ionization detection (GC–FID) and gas chromatography–mass spectrometry (GC–MS). The most abundant components in the essential oil were α-pinene, germacrene D, (*E*)-cariophyllene, and β-pinene. The inhibition efficiency was determined by electrochemical methods (electrochemical impedance spectroscopy and potentiodynamic polarization measurements). The results showed that the inhibitory efficiency of the black pine essential oil increases with time, reaching the highest values after 4 h of immersion for all inhibitor concentrations. It was also shown that black pine essential oil is a mixed-type inhibitor. The contact angle measurements confirmed that the black pine essential oil, as a new natural, environmentally safe inhibitor, is able to protect carbon steel from corrosion in a 1 M HCl solution.

Keywords: steel; corrosion; plants; essential oil

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1. Introduction

Due to its excellent mechanical and physical characteristics, carbon steel plays a very important role in engineering, construction, packaging, many types of machinery, and military applications [1,2]. Steel is very susceptible to corrosion, especially in acidic media [3–6]. Of all the acids, HCl is the most commonly used in industry from an economic standpoint in terms of wastewater recovery. However, the use of aggressive acids to remove surface contaminants and deposits on the metal leads to corrosion, which causes the greatest economic losses [7,8].

A major challenge for scientists working in this field of research is the study and development of materials as corrosion inhibitors. Corrosion inhibition is necessary from an economic point of view, but it is also dangerous for the environment, causing mutagenic damage to biological systems and cytotoxicity [9,10]. The use of chemicals that slow the corrosion of metals in the water phase endangers the ecosystem and living organisms, necessitating the search for environmentally friendly alternatives worldwide [11]. The use of most inorganic compounds, such as chromates, and some synthetic organic molecules that act as good corrosion inhibitors is banned or restricted in most applications due to their carcinogenic, toxic, and hazardous natures, as well as their costly and complex synthetic routes [12–15]. The evolution of green inhibitors of corrosion is significant and necessary for food quality and safety standards [9]. Considerable efforts are being made to find natural products that would not influence the environment and that could slow down the corrosion attack on metals as much as possible. According to previous investigations, natural corrosion inhibitors are readily available, cheap, biodegradable, and environmentally friendly [16–18].

Recently, more and more attention has been paid to plant oils and extracts, as they are a rich source of ecologically active molecules (plant-specific metabolites) and guarantee a high anticorrosive effect at a low price [19]. Constituents extracted from various parts of plants (leaves, flowers, fruits, stems, roots, etc.) have become one of the focal points of research in recent years [15,20]. Essential oils and extracts from various plants have been used as effective corrosion inhibitors for steel in HCl solutions: essential oil of *Cupressus arizonica* Greene [13], Ficus tikoua Bur. leaves' extract [1], *Cannabis sativa* L. seed oil [19], essential oil of *Dysphania ambrosioides* (L.) Mosyakin and Clemants [10], extract of ginkgo (*Ginkgo biloba* L.) leaves [21], extract of *Rollinia occidentalis* R.E.Fr. [22], leaves of *Platanus* × *acerifolia* (Aiton) Willd. [23], aqueous extract of borage flowers (*Borago officinalis* L.) [24], fruit shell extract of *Chinese gooseberry* (kiwifruit) (*Actinidia callosa* Lindl.) [25], extract of *Ammi visnaga* L. extract [26], extract from the peels of *Punica granatum* L. [27], extract of *Brassica oleracea* L. [28], extract from the seeds of *Ceratonia siliqua* L. [29], koiaz peels extract of *Akebia trifoliata* (Thunberg) Koidzumi [30], and biomass from *Ziziphus spina-christi* (L.) Desf. [31]. To test nutmeg oil as a corrosion inhibitor on carbon steel in a 1 M HCl solution, M. Abdallah and colleagues used electrochemical and computational methods [2]. They determined that this oil is a safe and effective corrosion inhibitor of steel, reaching an efficiency of 94.73% at a concentration of 500 ppm. It works by reducing the corrosion current density and anodic and cathodic reactions, which makes it a mixed inhibitor. This inhibitor is a mixture of different organic compounds, the most dominant of which are sabinene, α-pinene, β-pinene, and limonene. DFT calculations for individual molecules present in the oil showed that the ability to inhibit corrosion of steel in an acidic environment increases in the following direction: β-pinene<limonene<sabinene<α-pinene. Sara Cherrad et al. investigated *Cupressus arizonica* fruits' essential oil as a natural corrosion inhibitor [13]. Electrochemical measurements have shown that this oil can be successfully used to protect carbon steel from corrosion in an HCl environment. The oil acts as a mixed corrosion inhibitor with a greater influence on the reduction in the cathodic current density. It was determined that the investigated inhibitor is composed of the following chemicals: α-pinene (51.07%), myrcene (17.92%), and limonene (9.66%), which belong to monoterpenes. The authors also state that the higher content of α-pinene in the essential oil improves inhibitory efficiency. This green inhibitor showed the highest efficiency of 92% at a concentration of 0.5 g/L. Yujie Qiang et al. investigated ginkgo leaf extract as a potential corrosion inhibitor on X70 steel in a 1 M HCl solution [20]. The inhibition efficiency of this plant extract exceeded 90% at a concentration of 200 mg/L, which can be attributed to the synergistic action of the organic molecules present in it. The obtained results showed that this inhibitor could be classified as a mixed type. The main components found in this extract are isorhamnetin, 6-hydroxykynurenic acid, 4-O-methylpyridoxine, and sciadopitisin, and they protect the steel surface from aggressive chloride ions by adsorbing on the metal surface. Mohamed Damey et al. examined *Cannabis sativa* L. seed oil on steel in 1 M HCl [19]. Polarization measurements showed that the oil is a mixed-type inhibitor with a greater influence on the cathodic corrosion reaction. Impedance measurements showed that compounds from the green inhibitor are adsorbed on the steel surface. The results of gas chromatography showed that the most abundant components in this oil are fatty acids: linoleic acid (51.3%), oleic acid (20.3%), α-linolenic acid (15.7%), and palmitic acid (7.9%). The achieved efficiency of corrosion protection increased with the immersion time in the acidic medium and was greater than 92% at a concentration of 1 g/L. Borage flower extract contains a group of powerful, natural corrosion inhibitors, as shown by Ali Dehghani et al. [24]. Compounds that, among others, protected steel from corrosion in 1 M HCl solution are carotene, nicotinic acid, and lactic acid. The electrochemical results showed that the efficiency increased with the immersion time and that the highest one was achieved after 5 h at a concentration of 800 ppm (91%). This is a mixed type of inhibitor that increases the hydrophobicity of the surface, as proven by the contact angle measurement results. K. Dahmani et al. tested the essential oil of Myrtus Communis on copper in a 0.5 M H_2SO_4 solution [32]. The obtained experimental results showed that this

oil belongs to the group of mixed corrosion inhibitors. The highest efficiency of 93.5% was registered at a concentration of 2 g/L. Gas chromatography and mass spectrometry were used to identify the three most abundant active components in the inhibitor. The detected components belong to the group of monoterpenes: 1,8-cineole (35.6%), myrtenyl acetate (32.7%), and α-pinene (8.9%). Similarly, Walid Daoudi and colleagues show that essential oil from the leaves of *Dysphania ambrosioides* can protect mild steel from corrosion in 1 M HCl [10]. The best resistance to corrosion was shown at an oil concentration of 1.5 g/L. This essential oil belongs to the mixed family of corrosion inhibitors. Gas chromatography and mass spectroscopy determined that the composition of this natural inhibitor includes the following organic substances: acetate, thymol, ascaricum, (+)-4-carene, m-cymene, and 3-isopropényl-2-methylcyclohexyl.

Pinus nigra J. F. Arnold (European black pine, or black pine) has a discontinuous range and is naturally distributed in southern Europe, northwestern Africa, and Asia Minor. *P. nigra* belongs to the family Pinaceae (Pinales). This species grows as a tree to a height of 30–40 (−50) m, and its trunk is usually straight. The bark is dark gray to blackish [33]. Conifers are one of the most common renewable sources of essential oils [34].

The aim of our research is to evaluate the inhibitory effect of oil from *P. nigra* needles (PN) as an environmentally friendly replacement of harmful chromates and a number of synthetic organic molecules utilized as inhibitors against the corrosion of steel in 1 M HCl solution. The study of plant-based inhibitors as natural sources of organic substances promises to promote industrial production and has safety and socioeconomic implications. According to the available literature data and to the best of our knowledge, this is the first time that the essential oil of *P. nigra* has been tested as a potential eco-friendly corrosion inhibitor. The plant (needles) was collected in Serbia, and the essential oil was extracted by hydrodistillation using a Clevenger apparatus. The essential oil was analyzed by gas chromatography–flame–ionization detection (GC–FID) and chromatography–mass spectrometry (GC–MS). The presence of various organic components of the essential oil was demonstrated by attenuated total reflection spectroscopy (ATR). To evaluate the effect of inhibition, electrochemical measurements were performed: electrochemical impedance spectroscopy (EIS) and polarization measurements. Contact angle measurements were also performed.

2. Materials and Methods

2.1. Plant Material and Isolation of Essential Oil

A sample of needles from *P. nigra* was collected in March 2022 from Suvobor, Valjevske planine, Serbia. The voucher specimen was deposited at the Herbarium of the University of Belgrade, Faculty of Biology, Institute of Botany, and Botanical Garden "Jevremovac" (BEOU 17912). The essential oil was obtained from freshly crushed needles (500 g). Hydrodistillation of the plant substance placed in a flask with 2000 mL of distilled water was carried out for 3 h using the Clevenger apparatus by means of the process described in [35]. The oils obtained by this procedure were kept at 4 °C until further analysis.

2.2. GC-FID and GC/MS Analyses

The composition of the essential oil of *P. nigra* needles was performed by GC–FID and GC/MS, according to the procedure detailed in [35].

2.3. ATR Spectroscopy

Functional groups of organic molecules present in the oil were analyzed and confirmed using ATR spectroscopy. The eco-friendly inhibitor was characterized by a *Thermo Scientific Nicolet iS10* spectrometer over the range of 4000 to 400 cm^{-1}.

2.4. Electrode and Solutions' Preparation

Corrosion and inhibitor efficiency tests were performed on carbon steel plates. The chemical composition (wt%) of the working electrode is: Mn (0.276%), Cu (0.025%),

Cr (0.030%), Ni (0.012%), C (0.080%), and Fe rest. Before each experiment, impurities on the surface of the carbon steel specimens were carefully removed with 200–2000 grit sandpaper. The samples were then rinsed in deionized water and 99.7% ethyl alcohol and quickly dried with airflow. Commercial hydrochloric acid (37%) dissolved in deionized water was used to prepare the test solution. A solution of 1 M HCl was used as an aggressive corrosion medium. A stock solution of the essential oil of *P. nigra* was prepared by dissolving it in ethanol as a 30% (*v/v*) solution, which was used as an inhibitor [2,36]. The amount of ethyl alcohol in the solutions without inhibitor and in the solutions with inhibitor was the same to exclude its influence on the inhibition effect. Certain volumes of the inhibitor and HCl were added to deionized water to obtain 1 M HCl solutions with inhibitor concentrations of 50, 100, 200, and 300 ppm.

2.5. Electrochemical Methods

The instrument Gamry Reference 600 Potentiostat/Galvanostat/ZRA was used for electrochemical measurements. The tests were performed in an electrochemical cell with three electrodes: saturated calomel (SCE) as a reference, platinum as a counter electrode, and a carbon steel plate as a working electrode. To establish a stationary state, i.e., a stable open circuit potential, the steel plate was immersed in the tested solutions for 1 h prior to all electrochemical measurements. Impedance measurements were performed at open circuit potential in the frequency range from 0.01 Hz to 100 kHz with 10 points per decade using a 10 mV amplitude of sinusoidal voltage, and polarization measurements were performed in the potential range from -250 V to +250 V vs. E_{corr}. The obtained data were analyzed using the Gamry E-Chem Analyst software package.

2.6. The Contact Angle Measurements

The measurement of the contact angle with Milli-Q water was performed on the surface of the carbon steel samples after 1 h immersion in solutions of 1 M HCl and 50 ppm inhibitor, respectively, and after 4 h immersion in the inhibitor solution of the same concentration. After this testing period, samples were removed from the solution, washed with distilled water, and dried. Measurements were performed at room temperature by placing a drop of water on the dried steel samples. An optical microscope (Smart 5MP Pro, Delta Optical Instruments, Inc., North Little Rock, AR, USA) was used to take images of the contact angle with water. The angle was measured using Image-Pro Plus 4.0 image analysis software (Media Cybernetics Inc., Rockville, MD, USA).

3. Results

3.1. Composition of Essential Oil of Pinus nigra and ATR

Fifty-two compounds were detected in the essential oil of *P. nigra* needles, but only four of them represented more than 2% and accounted for 88.3% of the total oil composition. Table 1 lists the percentage of dominant compounds in essential oils. Figure 1 shows the molecular structural formulas of the components present in the oil. The essential oil is characterized by a high proportion of monoterpene hydrocarbons: *α*-pinene and *β*-pinene (66.5% and 2.1%, respectively). In addition, the sesquiterpene hydrocarbons *E*-caryophyllene and germacrene D (5.6% and 14.0%, respectively) were detected.

Table 1. Dominant compounds of the essential oil of *Pinus nigra* needles.

RI	Compound	Chemical Formula	Percentage (%)
931	*α*-Pinene	$C_{10}H_{16}$	66.5
975	*β*-Pinene	$C_{10}H_{16}$	2.10
1423	*E*-Caryophyllene	$C_{15}H_{24}$	5.67
1487	Germacrene D	$C_{15}H_{24}$	14.0
	Total	/	88.3

[a] Retention indices, RI, were determined experimentally using the standard method with retention times, tR, of n-alkanes injected under the same chromatographic conditions.

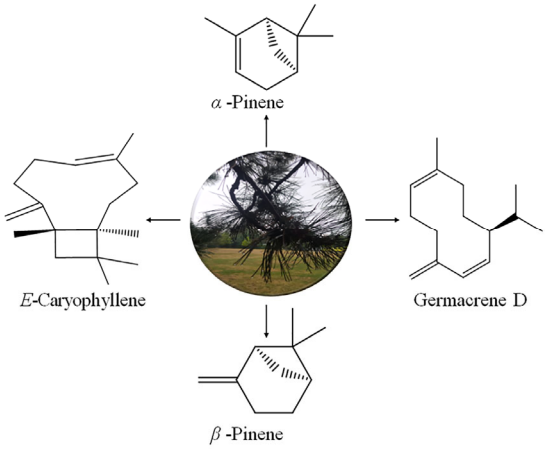

Figure 1. Molecular structures of the identified dominant components of the essential oil of *Pinus nigra* needles.

Owing to the important role that functional groups in inhibitor molecules play in their interaction with the carbon steel surface, active structures in PN essential oil were identified using ATR. As can be seen from the ATR spectrum (Figure 2), the stretching vibration of the C-H bond is detected at a wave number positioned around 2900 cm^{-1}, according to the literature data [10,11,24,32,37,38]. The peaks of the active functional groups -C=O- and -C=C- of the aromatic rings were observed at wave numbers of 1740.12 [24,32] and around 1600 [10,24,38,39], respectively. The absorption peak at 1446 cm^{-1} [10] and the peak at around 1380 cm^{-1} [38,39] are attributed to the -C-H vibration of the $-CH_3$ group. The peaks appearing at around 1200 cm^{-1} and 1000 cm^{-1} were associated with -C-O- vibrations [5,10,14,37,39]. The absorption peaks below 1000 cm^{-1} (between 600 and 900 cm^{-1}) were attributed to aromatic and aliphatic -C-H vibrations [10,11,38,39].

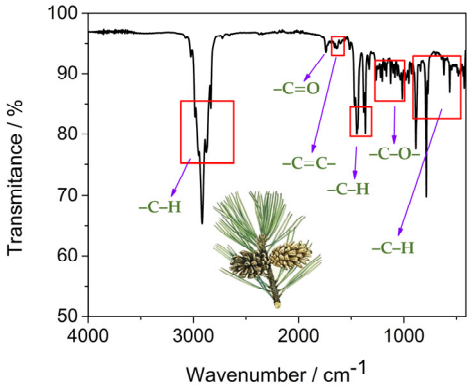

Figure 2. ATR spectrum of analyzed PN essential oil.

3.2. Electrochemical Measurements

3.2.1. Open Circuit Potential (OCP) Measurements Results

The OCP values (relative to SCE) as a function of immersion time (3600 s) for carbon steel samples immersed in 1 M HCl solution without or with 50, 100, 200, and 300 ppm *Pinus nigra* essential oil are shown in Figure 3. It can be seen from the diagram that, in the presence of all concentrations of PN inhibitors, potentials became stable after a certain period of time, that is, a stationary state was established. A stable corrosion potential is established almost immediately after the steel electrode is immersed in the corrosion medium. The tendency of the curve of the open-circuit potential at different concentrations of PN inhibitors to more negative values compared to the sample without inhibitor indicates the adsorption of substances from the oil on the metal surface, which changes the concentration of aggressive species at the steel/solution interface.

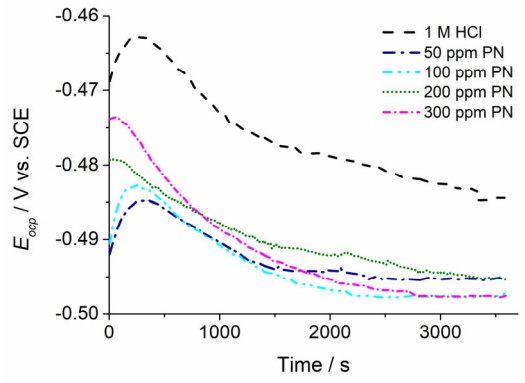

Figure 3. Open circuit potential curves of carbon steel without and with different concentrations of essential oil PN in 1 M HCl.

3.2.2. EIS Results

Electrochemical impedance tests for carbon steel in an aggressive acidic solution were performed to determine the inhibition mechanism of the essential oil of *Pinus nigra*. Figure 4a–d show Bode plots for steel in 1 M HCl medium at different immersion times (1 to 4 h) and with inhibitor concentrations of 50, 100, 200, and 300 ppm. The shape of the curves is unchanged compared to the sample without inhibitor, indicating that the organic molecules present in the essential oil adsorb on the steel surface through the charge transfer process without altering the mechanism of the corrosion process. There is only one peak in phase angle plots in the middle-frequency range, indicating the presence of only one time constant. The phase angle values became greater with the addition of inhibitors to the corrosion medium, indicating the presence of a protective layer on the steel surface [3].

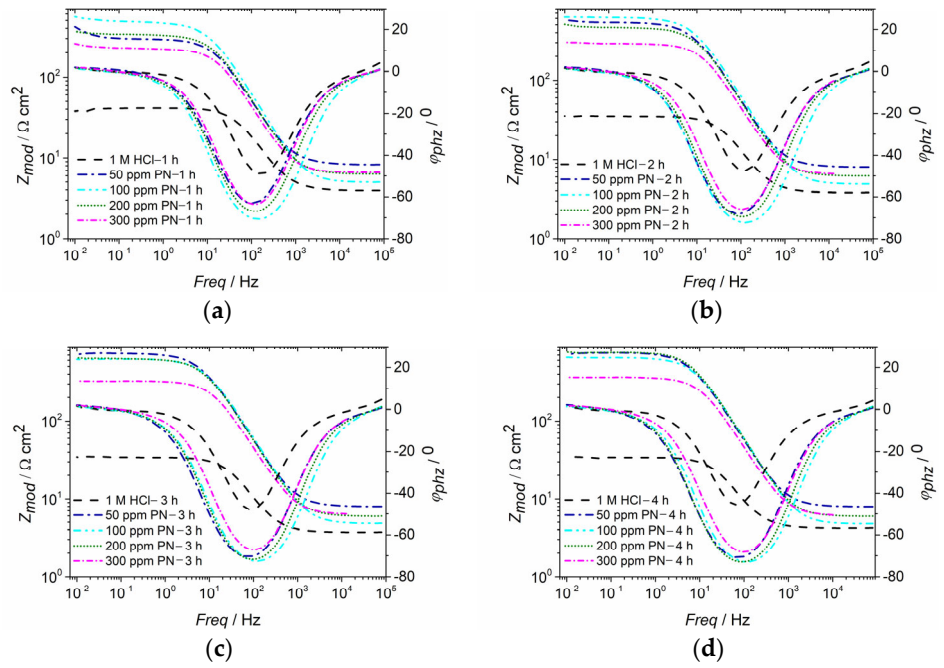

Figure 4. Bode diagrams for carbon steel in 1 M HCl solution in the absence and presence of PN inhibitor in different concentrations after: (**a**) 1 h; (**b**) 2 h; (**c**) 3 h; (**d**) 4 h immersion time.

Based on the shape of the Bode diagrams and taking into account the fact that the phase angles deviate from the value of −90° characteristic of an ideal capacitor, and according to the literature where the inhibitor test conditions are the same, the equivalent circuit shown in Figure 5 was used to fit the impedance spectrum [1,21,40].

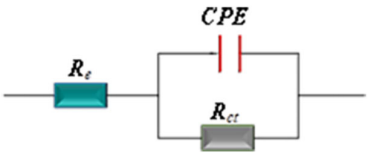

Figure 5. Model of the electrical equivalent circuit used to fit EIS data.

From the diagram, it can be seen that the phase angle has a value of about −70° when the inhibitor is added. This finding provides an opportunity to insert an element with a constant phase angle (CPE) into the equivalent circuit. The solution resistance R_e, the charge transfer resistance R_{ct}, the element with a constant phase angle CPE, and the inhibition effect η is determined and summarized in Table 2. The CPE is related to the double-layer capacitance C_{dl}. The non-ideal dielectric behavior of the inhomogeneous metal surface led to the use of the CPE instead of a pure capacitor. CPE describes various physical phenomena, such as the adsorption of inhibitors, the roughness of the electrode surface, and the formation of porous layers. The CPE impedance is defined by the following equation:

$$Z_{CPE} = Y_0^{-1}(j\omega)^{-n} \quad (1)$$

where Y_0 is the CPE magnitude, n is the deviation parameter, j represents the imaginary root, ω is the angular frequency, and f is the frequency at the maximum value of the imaginary part of the spectrum on the diagram.

Table 2. Impedance parameters for carbon steel after 1-4 h immersion in 1 M HCl in the presence and absence of inhibitors.

Solution	Time/h	R_s/Ω cm^2	R_{ct}/ Ω cm^2	CPE		η/%
				Y_0/10^{-6}/Ω^{-1} s^n cm^{-2}	n	
1 M HCl	1	3.94	37.5	156.2	0.906	/
	2	3.82	31.4	234.5	0.910	/
	3	3.72	30.6	297.0	0.918	/
	4	4.19	30.2	371.8	0.910	/
50 ppm PN	1	8.32	289.1	60.98	0.90	87.0
	2	8.08	528.5	54.97	0.903	94.0
	3	8.00	720.7	51.06	0.91	95.8
	4	7.96	733.5	51.25	0.911	95.9
100 ppm PN	1	4.92	481.7	47.27	0.906	92.0
	2	4.83	609.7	45.32	0.911	94.9
	3	4.77	612.1	46.04	0.914	95.0
	4	4.73	640.3	46.57	0.915	95.3
200 ppm PN	1	6.26	333.5	56.21	0.907	88.8
	2	6.15	456.9	52.78	0.912	93.0
	3	5.93	619.5	49.58	0.915	95.0
	4	5.93	749.2	45.97	0.92	96.0
300 ppm PN	1	6.55	223.7	67.72	0.91	83.0
	2	6.50	286.6	63.71	0.912	89.0
	3	6.30	320.6	62.36	0.914	90.0
	4	6.07	358.9	61.48	0.914	91.6

The following equation was used for the determination of the inhibition efficiency, η:

$$\eta(\%) = \frac{R_{ct} - R_{ct}^o}{R_{ct}} \cdot 100 \quad (2)$$

where R_{ct}^o and R_{ct} are the resistances in uninhibited and inhibited solutions, respectively.

The reduction in Y_0 in the solutions with the inhibitor compared to the solution without the inhibitor indicates that the water molecules were gradually replaced by molecules of organic compounds from the oil by the process of adsorption on the steel surface [21]. The figure shows an increase in the impedance value at low frequencies with the addition of an

inhibitor compared to a solution without an inhibitor. According to the figure, the Z_{mod} (10 mHz) values of carbon steel samples immersed in a solution containing PN essential oil are significantly higher than the values in 1 M HCl after an immersion time of 1 to 4 h. Moreover, the Z_{mod} (10 mHz) values for each inhibitor concentration increase with immersion time. The highest value of Z_{mod} (10 mHz) was obtained for a 200 ppm inhibitor after 4 h of immersion time, resulting in the highest efficiency (96%). However, as can be seen, further increasing the concentration of the inhibitor to 300 ppm leads to a decrease in the value of Z_{mod} (10 mHz), indicating that the ability to inhibit corrosion decreases when the concentration increases to a certain value. Small differences in the efficiency obtained for samples with PN at concentrations up to 300 ppm indicate the possibility of choosing the lowest inhibitor concentration, 50 ppm, to achieve corrosion protection.

3.2.3. Polarization Curves

The effect of *Pinus nigra* essential oil on corrosion reactions was studied by the polarization method in a 1 M HCl solution. Figure 6 shows the Tafel polarization curves for carbon steel at different inhibitor concentrations after a 4 h immersion in a 1 M HCl solution.

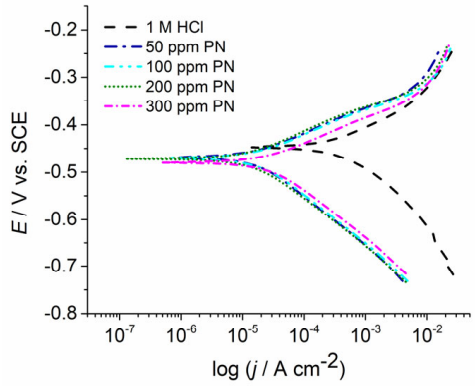

Figure 6. Carbon steel polarization curves in 1 M HCl containing different concentrations of PN inhibitor after 4 h immersion.

The relevant electrochemical parameters, including corrosion potential (E_{corr}) and corrosion current density (j_{corr}), were derived from the polarization curves, and are shown in Table 3.

Table 3. Fitted parameters of the polarization Tafel plots for cold-rolled steel after 4 h immersion in 1 M HCl.

Inhibitor	j_{corr}/μA cm^{-2}	E_{corr}/mV vs. SCE	η/%
Blank	173	−448	/
50 ppm PN	6.0	−469	96.5
100 ppm PN	6.5	−469	96.3
200 ppm PN	5.0	−472	97.0
300 ppm PN	10	−480	94.0

As can be seen from the chart, the addition of the inhibitor shifted both the anodic and cathodic parts of the Tafel curves to lower corrosion current densities at all concentrations tested after 4 h, resulting in a significant reduction in corrosion rate. From the Tafel curves, it can be observed that the shift of the cathodic branch was greater than that of the anodic branch, which may indicate that the cathodic reaction was largely suppressed. The results show that the addition of all inhibitor concentrations shifted E_{corr} to more negative values, but the shift was not significant. As shown in Figure 6 and Table 3, all changes in E_{corr} values were less than 85 mV. Therefore, PN essential oil can be considered a mixed-type inhibitor that exerts predominant control over the cathodic response at any inhibitor concentration after 4 h. The shape of the polarization curves is similar in the presence and absence of

the inhibitor. This indicates that the essential oil studied inhibits the corrosion of carbon steel by adsorbing the organic molecules it contains. These compounds block reaction sites while not modifying the mechanisms of cathodic and anodic corrosion reactions [13,21,24]. The addition of inhibitors at all concentrations contributed to a significant decrease in j_{corr} after 4 h of immersion in 1 M HCl, indicating the formation of an inhibition film of organic molecules of essential oil on the surface of carbon steel [3]. The table also shows the values of the inhibition effect, η, obtained by the equation:

$$\eta\ (\%) = \left(1 - \frac{j_{corr(i)}}{j_{corr(0)}}\right) \times 100 \quad (3)$$

where $j_{corr(o)}$ and $j_{corr(i)}$ are the corrosion current density in the absence and presence of the inhibitor, respectively. The environmentally acceptable inhibitor shows an efficiency greater than 90% after 4 h of immersion in a 1 M HCl solution at all concentrations tested. Based on the small differences in η determined for different inhibitor concentrations, a 50 ppm concentration could be considered the optimal one.

3.3. Contact Angle Measurements

The hydrophilic properties of inhibited and non-inhibited carbon steel samples were analyzed by the constant angle test according to ASTM standard [41]. Samples were immersed in 1 M HCl with or without inhibitor for 1 h or 4 h. After removing the samples from the solutions, they were rinsed with distilled water and dried. Contact angle was measured on samples prepared this way. Figure 7 shows the results of the contact angle measurements for carbon steel immersed in 1 M HCl for 1 h and for metal immersed in an inhibited environment for 1 and 4 h. The contact angle measured for the blank test was 33°. After 1 h of immersion in the inhibited solution, the contact angle was 42°, while for the metal sample immersed in the corrosion medium for 4 h, it was 48°. The increase in the contact angle of the inhibited sample compared to the non-inhibited one confirms that there is an organic barrier film of the inhibitor on the metal surface. The increase in the contact angle of the sample immersed in the solution with the inhibitor for 4 h compared to the sample immersed in the solution with the inhibitor for 1 h is in close agreement with the electrochemical results related to the increase in the effectiveness of the green inhibitor over time. The results obtained indicate an improvement in the hydrophobicity of the inhibited samples during the immersion period, i.e., that an inhibitor film is an effective barrier against aggressive media. It can be concluded that a hydrophobic film of inhibitors is formed on the metal surface, which leads to the prevention of corrosion attacks on the surface of carbon steel [6,24].

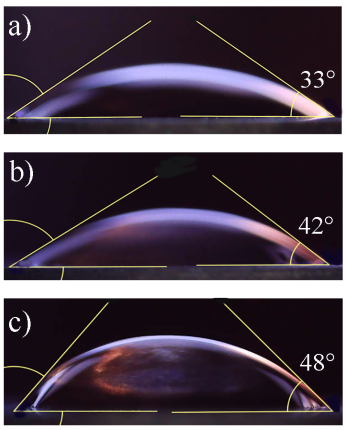

Figure 7. Contact angle measurements for carbon steel immersed in: (**a**) 1 M HCl for 1 h; (**b**) 1 M HCl with 50 ppm PN for 1 h; (**c**) 1 M HCl with 50 ppm PN for 4 h.

4. Conclusions

In this study, an environmentally friendly essential oil of *Pinus nigra* was investigated as a corrosion inhibitor for carbon steel in a 1 M HCl solution. The dominant components of the essential oil are α-pinene, germacrene D, (*E*)-cariophyllene, and β-pinene. EIS measurements showed that the charge transfer resistance R_{ct} increases with immersion time and that the CPE magnitude (Y_0) decreases in the presence of inhibitors at all concentrations compared to the non-inhibited sample, indicating that the process of adsorption of organic molecules from PN occurs at the steel surface. Polarization measurements showed that PN is a mixed-type inhibitor with greater influence on the inhibition of the cathodic reaction. The inhibition efficiency after 4 h was above 90% for all inhibitor concentrations, with the effect starting to decrease after a critical concentration of 200 ppm. This suggests that, from an economic point of view, it would be favorable to use a lower inhibitor concentration (50 ppm). Contact angle measurements confirmed that the inhibition effect increases with time.

Considering that black pine essential oil proved to be an effective inhibitor of corrosion on steel in an aggressive acid environment, this research will continue in the direction of a deeper examination of both the oil itself and its individual components. In this respect, some other techniques, such as weight loss measurements and scanning electron microscopy might be used to complement the future study.

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References

1. Wang, Q.; Tan, B.; Bao, H.; Xie, Y.; Mou, Y.; Li, P.; Chen, D.; Shi, Y.; Li, X.; Yang, W. Evaluation of Ficus tikoua leaves extract as an eco-friendly corrosion inhibitor for carbon steel in HCl media. *Bioelectrochemistry* **2019**, *128*, 49–55. [CrossRef] [PubMed]
2. Abdallah, M.; Altass, H.M.; Al-Gorair, A.S.; Al-Fahemi, J.H.; Jahdaly, B.A.A.L.; Soliman, K.A. Natural nutmeg oil as a green corrosion inhibitor for carbon steel in 1.0 M HCl solution: Chemical, electrochemical, and computational methods. *J. Mol. Liq.* **2021**, *323*, 115036. [CrossRef]
3. Fernandes, C.M.; Fagundes, T.d.S.F.; dos Santos, N.E.; Rocha, T.S.d.M.; Garrett, R.; Borges, R.M.; Muricy, G.; Valverde, A.L.; Ponzio, E.A. Ircinia strobilina crude extract as corrosion inhibitor for mild steel in acid medium. *Electrochim. Acta* **2019**, *312*, 137–148. [CrossRef]
4. Saxena, A.; Prasad, D.; Haldhar, R.; Singh, G.; Kumar, A. Use of Saraca ashoka extract as green corrosion inhibitor for mild steel in 0.5 M H_2SO_4. *J. Mol. Liq.* **2018**, *258*, 89–97. [CrossRef]
5. Saxena, A.; Prasad, D.; Haldhar, R.; Singh, G.; Kumar, A. Use of Sida cordifolia extract as green corrosion inhibitor for mild steel in 0.5 M H_2SO_4. *J. Environ. Chem. Eng.* **2018**, *6*, 694–700. [CrossRef]
6. Sedik, A.; Lerari, D.; Salci, A.; Athmani, S.; Bachari, K.; Gecibesler, H.; Solmaz, R. Dardagan Fruit extract as eco-friendly corrosion inhibitor for mild steel in 1 M HCl: Electrochemical and surface morphological studies. *J. Taiwan Inst. Chem. Eng.* **2020**, *107*, 189–200. [CrossRef]
7. Shahini, M.H.; Ramezanzadeh, M.; Ramezanzadeh, B.; Bahlakeh, G. The role of ethanolic extract of Stachys byzantina's leaves for effective decreasing the mild-steel (MS) degradation in the acidic solution; coupled theoretical/experimental assessments. *J. Mol. Liq.* **2021**, *329*, 115571. [CrossRef]

8. Lashgari, S.M.; Bahlakeh, G.; Ramezanzadeh, B. Detailed theoretical DFT computation/molecular simulation and electrochemical explorations of Thymus vulgaris leave extract for effective mild-steel corrosion retardation in HCl solution. *J. Mol. Liq.* **2021**, *335*, 115897. [CrossRef]
9. El Azzouzi, M.; Azzaoui, K.; Warad, I.; Hammouti, B.; Shityakov, S.; Sabbahi, R.; Saoiabi, S.; Youssoufi, M.H.; Akartasse, N.; Jodeh, S.; et al. Moroccan, Mauritania, and senegalese gum Arabic variants as green corrosion inhibitors for mild steel in HCl: Weight loss, electrochemical, AFM and XPS studies. *J. Mol. Liq.* **2022**, *347*, 118354. [CrossRef]
10. Daoudi, W.; El Aatiaoui, A.; Falil, N.; Azzouzi, M.; Berisha, A.; Olasunkanmi, L.O.; Dagdag, O.; Ebenso, E.E.; Koudad, M.; Aouinti, A.; et al. Essential oil of *Dysphania ambrosioides* as a green corrosion inhibitor for mild steel in HCl solution. *J. Mol. Liq.* **2022**, *363*, 119839. [CrossRef]
11. Molaeipour, P.; Ramezanzadeh, M.; Ramezanzadeh, B. Stachys byzantina extract: A green biocompatible molecules source for graphene skeletons generation on the carbon steel for superior corrosion mitigation. *Bioelectrochemistry* **2022**, *143*, 107970. [CrossRef] [PubMed]
12. He, J.; Yu, D.; Xu, Q.; Li, G.; Chen, G.; An, J.; Yang, J.; Li, W. Combining experimental and theoretical researches to insight into the anti-corrosion property of Morinda citrifolia Linn leaves extracts. *J. Mol. Liq.* **2021**, *325*, 115145. [CrossRef]
13. Cherrad, S.; Alrashdi, A.A.; Lee, H.S.; El Aoufir, Y.; Lgaz, H.; Satrani, B.; Ghanmi, M.; Aouane, E.M.; Chaouch, A. *Cupressus arizonica* fruit essential oil: A novel green inhibitor for acid corrosion of carbon steel. *Arab. J. Chem.* **2022**, *15*, 103849. [CrossRef]
14. Salmasifar, A.; Edraki, M.; Alibakhshi, E.; Ramezanzadeh, B.; Bahlakeh, G. Theoretical design coupled with experimental study of the effectiveness of the inhibitive molecules based on Cynara scolymus L extract toward chloride-induced corrosion of steel. *J. Mol. Liq.* **2021**, *332*, 115742. [CrossRef]
15. Zhang, X.; Li, W.; Zuo, X.; Tan, B.; Xu, C.; Zhang, S. Investigating the inhibitive effect of Davidia involucrata leaf extract as a biological eco-friendly inhibitor for copper in acidic medium. *J. Mol. Liq.* **2021**, *325*, 115214. [CrossRef]
16. Prasad, D.; Dagdag, O.; Safi, Z.; Wazzan, N.; Guo, L. Cinnamoum tamala leaves extract highly efficient corrosion bio-inhibitor for low carbon steel: Applying computational and experimental studies. *J. Mol. Liq.* **2022**, *347*, 118218. [CrossRef]
17. Parthipan, P.; Cheng, L.; Rajasekar, A. Glycyrrhiza glabra extract as an eco-friendly inhibitor for microbiologically influenced corrosion of API 5LX carbon steel in oil well produced water environments. *J. Mol. Liq.* **2021**, *333*, 115952. [CrossRef]
18. Narenkumar, J.; Ananthaselvam, A.; Alsalhi, M.S.; Devanesan, S.; Kadier, A.; Kannan, M.M.; Rajasekar, A. Effect of crude methanolic extract of Lawsonia inermis for anti-biofilm on mild steel 1010 and its effect on corrosion in a re-circulating wastewater system. *J. King Saud Univ.-Sci.* **2021**, *33*, 101611. [CrossRef]
19. Damej, M.; Skal, S.; Aslam, J.; Zouarhi, M.; Erramli, H.; Alrashdi, A.A.; Lee, H.S.; El Aoufir, Y.; Lgaz, H. An environmentally friendly formulation based on *Cannabis sativa* L. seed oil for corrosion inhibition of E24 steel in HCl medium: Experimental and theoretical study. *Colloids Surfaces A Physicochem. Eng. Asp.* **2022**, *643*, 128745. [CrossRef]
20. Abdelaziz, S.; Benamira, M.; Messaadia, L.; Boughoues, Y.; Lahmar, H.; Boudjerda, A. Green corrosion inhibition of mild steel in HCl medium using leaves extract of Arbutus unedo L. plant: An experimental and computational approach. *Colloids Surfaces A Physicochem. Eng. Asp.* **2021**, *619*, 126496. [CrossRef]
21. Qiang, Y.; Zhang, S.; Tan, B.; Chen, S. Evaluation of Ginkgo leaf extract as an eco-friendly corrosion inhibitor of X70 steel in HCl solution. *Corros. Sci.* **2018**, *133*, 6–16. [CrossRef]
22. Alvarez, P.E.; Fiori-Bimbi, M.V.; Neske, A.; Brandán, S.A.; Gervasi, C.A. *Rollinia occidentalis* extract as green corrosion inhibitor for carbon steel in HCl solution. *J. Ind. Eng. Chem.* **2018**, *58*, 92–99. [CrossRef]
23. Liu, Q.; Song, Z.; Han, H.; Donkor, S.; Jiang, L.; Wang, W.; Chu, H. A novel green reinforcement corrosion inhibitor extracted from waste *Platanus acerifolia* leaves. *Constr. Build. Mater.* **2020**, *260*, 119695. [CrossRef]
24. Dehghani, A.; Bahlakeh, G.; Ramezanzadeh, B.; Ramezanzadeh, M. Potential of Borage flower aqueous extract as an environmentally sustainable corrosion inhibitor for acid corrosion of mild steel: Electrochemical and theoretical studies. *J. Mol. Liq.* **2019**, *277*, 895–911. [CrossRef]
25. Dehghani, A.; Bahlakeh, G.; Ramezanzadeh, B. A detailed electrochemical/theoretical exploration of the aqueous *Chinese gooseberry* fruit shell extract as a green and cheap corrosion inhibitor for mild steel in acidic solution. *J. Mol. Liq.* **2019**, *282*, 366–384. [CrossRef]
26. Zaher, A.; Aslam, R.; Lee, H.S.; Khafouri, A.; Boufellous, M.; Alrashdi, A.A.; El Aoufir, Y.; Lgaz, H.; Ouhssine, M. A combined computational & electrochemical exploration of the *Ammi visnaga* L. extract as a green corrosion inhibitor for carbon steel in HCl solution. *Arab. J. Chem.* **2022**, *15*, 103573. [CrossRef]
27. Bhardwaj, N.; Sharma, P.; Guo, L.; Dagdag, O.; Kumar, V. Molecular dynamic simulation, quantum chemical calculation and electrochemical behaviour of *Punica granatum* peel extract as eco-friendly corrosion inhibitor for stainless steel (SS-410) in acidic medium. *J. Mol. Liq.* **2022**, *346*, 118237. [CrossRef]
28. Li, H.; Qiang, Y.; Zhao, W.; Zhang, S. A green *Brassica oleracea* L extract as a novel corrosion inhibitor for Q235 steel in two typical acid media. *Colloids Surfaces A Physicochem. Eng. Asp.* **2021**, *616*, 126077. [CrossRef]
29. Abbout, S.; Chebabe, D.; Zouarhi, M.; Rehioui, M.; Lakbaibi, Z.; Hajjaji, N. *Ceratonia siliqua* L seeds extract as eco-friendly corrosion inhibitor for carbon steel in 1 M HCl: Characterization, electrochemical, surface analysis, and theoretical studies. *J. Mol. Struct.* **2021**, *1240*, 130611. [CrossRef]

30. Zhang, M.; Guo, L.; Zhu, M.; Wang, K.; Zhang, R.; He, Z.; Lin, Y.; Leng, S.; Anadebe, V.C.; Zheng, X. Akebia trifoliate koiaz peels extract as environmentally benign corrosion inhibitor for mild steel in HCl solutions: Integrated experimental and theoretical investigations. *J. Ind. Eng. Chem.* **2021**, *101*, 227–236. [CrossRef]
31. Rajamohan, N.; Al Shibli, F.S.Z.S.; Rajasimman, M.; Vasseghian, Y. Eco-friendly biomass from Ziziphus spina-christi for protection of carbon steel in acidic conditions—Parameter effects and corrosion mechanism studies. *Chemosphere* **2022**, *291*, 132756. [CrossRef] [PubMed]
32. Dahmani, K.; Galai, M.; Ouakki, M.; Elgendy, A.; Ez-Zriouli, R.; Lachhab, R.; Briche, S.; Cherkaoui, M. Corrosion inhibition of copper in sulfuric acid via environmentally friendly inhibitor (Myrtus Communis): Combining experimental and theoretical methods. *J. Mol. Liq.* **2022**, *347*, 117982. [CrossRef]
33. Franjić, J.; Škvorc, Ž. *Croatian Forest Plants*, 1st ed.; University of Zagreb, Faculty of Forestry and Wood Technology: Zagreb, Croatia, 2021; pp. 82–83.
34. Sezik, E.; Üstün, O.; Demirci, B.; Başbr, K.H.C. Composition of the essential oils of *Pinus nigra* Arnold from Turkey. *Turkish J. Chem.* **2010**, *34*, 313–325. [CrossRef]
35. Radulović, M.; Rajčević, N.; Gavrilović, M.; Novaković, J.; Stešević, D.; Marin, P.; Janaćković, P. Five wild-growing Artemisia (Asteraceae) species from Serbia and Montenegro: Essential oil composition and its chemophenetic significance. *J. Serb. Chem. Soc.* **2021**, *86*, 1281–1290. [CrossRef]
36. Halambek, J.; Berković, K.; Vorkapić-Furač, J. The influence of Lavandula angustifolia L. oil on corrosion of Al-3Mg alloy. *Corros. Sci.* **2010**, *52*, 3978–3983. [CrossRef]
37. Alibakhshi, E.; Ramezanzadeh, M.; Haddadi, S.A.; Bahlakeh, G.; Ramezanzadeh, B.; Mahdavian, M. Persian Liquorice extract as a highly efficient sustainable corrosion inhibitor for mild steel in sodium chloride solution. *J. Clean. Prod.* **2019**, *210*, 660–672. [CrossRef]
38. Tan, B.; Xiang, B.; Zhang, S.; Qiang, Y.; Xu, L.; Chen, S.; He, J. Papaya leaves extract as a novel eco-friendly corrosion inhibitor for Cu in H_2SO_4 medium. *J. Colloid Interface Sci.* **2021**, *582*, 918–931. [CrossRef]
39. Deng, S.; Li, X. Inhibition by Ginkgo leaves extract of the corrosion of steel in HCl and H_2SO_4 solutions. *Corros. Sci.* **2012**, *55*, 407–415. [CrossRef]
40. Idouhli, R.; Oukhrib, A.; Khadiri, M.; Zakir, O.; Aityoub, A.; Abouelfida, A.; Benharref, A.; Benyaich, A. Understanding the corrosion inhibition effectiveness using Senecio anteuphorbium L. fraction for steel in acidic media. *J. Mol. Struct.* **2021**, *1228*, 129478. [CrossRef]
41. *ASTM D7490–13*; Standard Test Method for Measurement of the Surface Tension of Solid Coatings, Substrates and Pigments using Contact Angle Measurements. ASTM International: West Conshohocken, PA, USA, 2013.