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The Effect of the Oğuzlar Walnut Extract as a Green Corrosion Inhibitor on AISI 1010 Mild Steel

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ABSTRACT

Mild steel is primarily used in reinforced concrete structures because it has a low corrosion rate due to the formation of a passive oxide film in an alkaline environment. However, when exposed to acidic and atmospheric environments or aqueous environments containing dissolved salts such as seawater, the protective film deteriorates and corrosion occurs due to contamination caused by chloride and carbonation. It is possible to obtain corrosion inhibitors by extraction of bioactive compounds from plants. Thus, inexpensive and environmentally friendly new effective inhibitors are obtained as an alternative to environmentally harmful inhibitors. In this context, the subject of the study was determined as the investigation of the inhibition efficiency of the vanillin phenolic compound in the Çorum Oğuzlar walnut shell extract, which is a local product, on the corrosion of AISI 1010 mild steel in acidic, alkaline, and salty environments. The walnut shells, which were cleaned, ground and pre-sieved with a certain grain size, were extracted in seven different solvents. In order to find the appropriate solvent, the total phenolic content (TPC) in the extracts was determined by both the Folin Ciocalteu method and the liquid chromatography-mass spectrometry/mass spectrometry (LC-MS/MS) system. Cyclic voltammetry (CV) and Tafel polarization methods were applied to determine the effect of the extract on the electrochemical behavior of AISI 1010 and its corrosion rate. LC-MS/MS analysis showed the presence of compounds containing p electrons, N and O heteroatoms responsible for the corrosion inhibition. The best inhibition effectiveness was obtained as 86.1% with the acetone-water mixture in an acidic environment (0.2 M HCl).

Keywords:
Corrosion; Green inhibitor; Oğuzlar walnut; AISI 1010; Vanillin

INTRODUCTION

Metallic materials, which are very sensitive to chemical and electrochemical reactions, interact with the components in their environment and corrode. This situation causes great economic losses, loss of life, and safety hazards [1]. Many methods can be applied to protect metal structures from corrosion. Among these methods coating of plastic, polymer, inorganic or organic compounds on the metal surface [2,3], anodic and cathodic protection [4,5], and inhibitors [6] are widely used. The use of inhibitors stands out among other methods because it is a practical method that can be used to protect metals in contact with aqueous solutions from corrosion and has become one of the most researched subjects in the field of corrosion protection [7]. However, concerning the development of corrosion inhibitors, technical requirements, as well as function, environmental impact, economic cost, and capacity, should be considered [8,9]. At this point, organic green corrosion inhibitors obtained from plants stand out as an important alternative. These materials are biodegradable, environmentally compatible, relatively inexpensive, and have harmless properties, which is why they have proven to be one of the most excellent approaches to combating corrosion [9]. Plant extracts used as corrosion inhibitors can be obtained from various parts of plants, generally including leaves [10,11], stem, root bark [12], fruits [13], fruit peel [14,15], seeds [16,17], flowers, and nuts [18-20]. Plant compounds and plant-based extracts used as organic green corrosion inhibitors generally contain heteroatoms such as N, O, S, P and/or conjugated double or triple bonds that allow them to be attached to the metal surface [1,9,21]. While investigating the inhibitory activity of some plant extracts, many studies focused on the TPC in the compounds. Indeed, studies in the literature show that the inhibitory activity of extracts increases with TPC [21]. Nuts such as walnuts are plants containing many phenolic compounds with important biological properties [22]. One of these compounds is vanillin, a non-toxic phenolic aldehyde. In the literature, studies have been conducted in which vanillin and its derivatives have been investigated as green corrosion inhibitors on various metals due to their advantages such as safe use and high solubility in water [23-28]. It has been reported in the literature that in protecting mild steel from corrosion, phenolic compound types in walnut such as vanillic acid are adsorbed on the surface of steel due to their negative charges. For example, Satpati et al. investigated the inhibition efficiency of the synthesized vanillin-based Schiff base for mild steel in 1 M HCl. They reported that it was adsorbed on the metal surface by chemical adsorption via the vanillin moiety and the imine group [28-30]. Currently, there is no generally accepted method for the recovery of all or a particular group of phenolic compounds in the five main groups called phenolic acids, flavonoids, tannins, phenolic ligands, and stilbene derivatives due to the complex structure of plants. However, to extract phenolic compounds from plants, unconventional extraction methods consisting of the use of ultrasound, microwave, and pressurized/supercritical fluids and combinations of these methods are widely used with organic solvents that are considered safe [22,31-33].

In the literature, the extraction of biologically active compounds from plants has been widely studied by using solvent extraction. However, this study differs from others on the extracts obtained from the shells of the Çorum Oğuzlar walnut, which is a local product, by ultrasound assisted extraction (UAE) technique. To the best of our knowledge, although there are many studies of synthetically obtained vanillin and its derivatives as corrosion inhibitors, there has been no study in the literature on the examination of vanillin extracted from walnut shells as a corrosion inhibitor.

For these reasons, in this study, the effect of the vanillin phenolic compound in the Oğuzlar walnut extract as a green inhibitor for AISI 1010 mild steel was investigated in three different environments as acidic, alkaline, and salty. The presence of phenolic compounds, especially vanillin, in extracts obtained from walnut shells was determined by TPC determination/analysis (Folin-Ciocalteu method and LS MS/MS analysis), and the extract structure was clarified by FTIR. The corrosion behavior of AISI 1010 was investigated using CV and Tafel polarization methods.

MATERIAL AND METHODS

Materials and Chemicals

Walnuts were obtained from a local grower in the Oğuzlar district of Çorum and were used after the shells were cleaned, dried, milled, and brought to a certain grain size. Ethanol (C_2H_5OH, anhydrous) from Carlo Erba; hydrochloric acid (HCl, 37%), acetone (C_3H_6O, for analysis), and methanol (CH_3OH, for analysis) from Merck; Folin-Ciocalteu reagent, gallic acid, sodium carbonate (Na_2CO_3, ≥ 99.5%), sodium hydroxide (NaOH, > 98-105%) from Sigma-Aldrich; sodium chloride (NaCl, ≥ 99.5%) was purchased from Tekkim companies and used without further purification.

Characterization

Attenuated total reflection-Fourier transform infrared spectrophotometer (ATR-FTIR) was used to characterize the chemical structure of extracts obtained from walnut shells. The TPC of the extracts was analyzed by LC-MS/MS device as well as the Folin-Ciocalteu method.

To examine the corrosion behavior of AISI 1010 in a corrosive environment with and without extract, an electrochemical workstation consisting of a CHI 660E model potentiostat and a 680C model amplifier booster was used to obtain CV and Tafel polarization curves. A three-neck electrolysis cell with a volume of 500 mL was used in the experiments. The working electrode used in the electrochemical cell was AISI 1010, the reference electrode was a saturated calomel electrode and the counter electrode was a graphite rod. The working electrode was placed in a cylindrical mold and covered with polyester resin except for the 0.2 cm^2 active surface area. The active surface of the working electrode was polished underwater with 4000-grit sandpaper before each experiment. Then, it was cleaned with water and acetone to remove any impurities. CVs were obtained with a scanning rate of 200 mV s^{-1} between -1.5 V to -0.2 V in 0.2 M NaOH and 5% NaCl, while the potentials changed from -1.0 V to 0.0 V for 0.2 M HCl. Tafel polarization curves were obtained with a scanning rate of 5 mV s^{-1} between -1.5 V to -0.5 V in 0.2 M NaOH, -1.3 V to -0.6 V in 5% NaCl, and -0.75 to -0.4 V in 0.2 M HCl.

The inhibition efficiency (%) of the inhibitors was calculated from Equation 1 using the corrosion rates determined by the Tafel polarization method.

$$\text{Inhibition efficiency (\%)} = \frac{I_0 - I_{inh}}{I_0} \times 100 \qquad (1)$$

where I_0 and I_{inh} are corrosion rates in a corrosive environment without and with inhibitor, respectively.

Extraction of Walnut Shells

The shells of the walnuts obtained from the local grower were cleaned, cut into small pieces with the help of a blade crusher, and dried under suitable conditions to remove the moisture inside. It was then ground into a fine powder with the help of an electric grinder. Samples with a particle size of less than 0.35 mm obtained after sieving using a 45 mesh sieve were collected for use in extraction.

Acetone, ethanol, methanol, water, and the mixture of these three organic solvents with water were studied as solvents. In the extraction process, 25 mL of the solvent was mixed with 2.5 g of a powdered walnut shell. Solvent mixtures were prepared using 3 parts of organic solvent and 1 part of water by volume. The mixture was placed in an ultrasonic bath operating at 50°C and a frequency of 53 kHz, and UAE was performed for 30 minutes. The extract was separated from its solid by centrifugation at 7500 rpm for 15 minutes. Lastly, the obtained extracts were stored in a vial and kept in the fridge until analysis. These solutions were directly used as an inhibitor in corrosion studies.

Determination of TPC by Folin-Ciocalteu Method

For the extracts obtained using seven different solvents, TPC was determined spectrophotometrically by the Folin-Ciocalteu method [29,30]. First, 100 μL of the extract was diluted 10 times and 2.5 mL of Folin solution (0.2 N) were mixed and left for 3 minutes. After that, 2 mL of Na_2CO_3 solution (7.5%) was added to this solution and mixed again. This mixture was kept at dark and room temperature for 1 hour. Then, absorbance values were determined for each of the blue-colored solutions at a wavelength of 760 nm using the Genesys 10S UV-Visible (Thermo Scientific, USA) spectrophotometer (n=3). In addition, the blank sample was prepared with distilled water. For the numerical determination of TPC in the extracts, a standard calibration line was obtained using gallic acid (R^2=0.9977). Results were given in milligram gallic acid equivalents per kilogram dry weight (mg GAE/kg).

RESULTS

TPC Analysis and Determination of Individual Phenolic Compounds in Walnut Extract

The TPC values of the extracts obtained using seven different solvents are given in Fig. 1. When the results were examined, the highest TPC value was achieved with the methanol-water mixture. However, it was observed that the amount of phenolic content obtained with the acetone-water mixture was very close to that obtained in the methanol-water mixture.

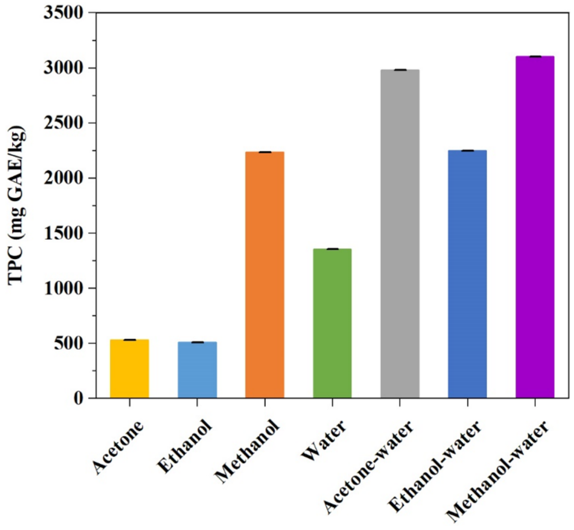

Figure 1. TPC values of walnut extracts obtained by UAE using different solvents.

The chemical structure of the walnut extract was investigated by FTIR analysis. The FTIR spectra of the extracts in acetone-water and methanol-water, which have the highest phenolic compound content according to the Folin-Ciocalteu method, are given in Fig. 2. O-H stretching bands are observed around 3326 cm^{-1} for the extract in methanol-water and around 3406 cm^{-1} for the extract in acetone-water. It has been reported in the literature that the O-H group in walnuts may originate from the phenolic groups of ferulic acid, juglone, and myricetin [34,35]. The peaks at 1404 and 1361 cm^{-1}, and 2950 and 3001 cm^{-1} for extracts in methanol-water and acetone-water can be attributed to the aromatic rings and the C-H stretching vibration, respectively. The absorption peaks observed at 1656 cm^{-1} for the methanol-water extract and 1705 cm^{-1} for the acetone-water extract indicate the presence of a C=C bond or N-H bending vibration of the amine group, which may be caused by all possible phenolic compounds. In addition, the peak seen at 1227 cm^{-1} for the acetone-water extract indicated the presence of a C-H bond from the $-CH_3$ group. The stretching peak observed at 1019 cm^{-1} for the extract in methanol-water belongs to the C-O group. The wide absorption band observed in the range of 640-650 cm^{-1} for both extracts indicated the presence of aromatic C-H groups. These outcomes are compatible with the properties of traditional corrosion inhibitors and con-

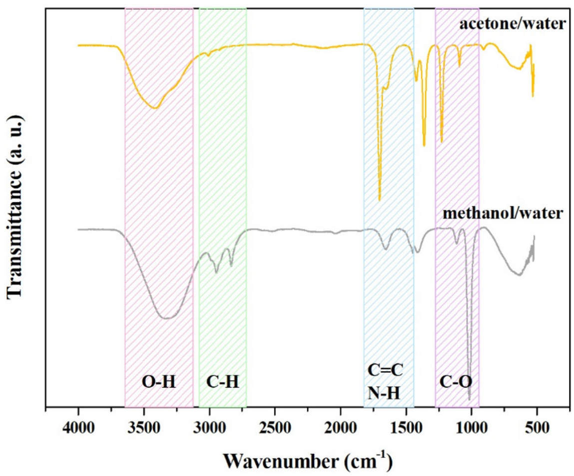

Figure 2. FTIR spectrum of walnut extracts obtained by UAE using different solvents.

firmed the presence of O, N, and aromatic rings belonging to the functional groups of Oğuzlar walnut extracts [35-37].

The quantitative analysis results for the determination of the types and, amounts of phenolic compounds contained in the extracts obtained in the extraction process using acetone-water and methanol-water mixtures are given in Table 1. More vanillin phenolic compound was obtained when acetone-water mixture was used as the extraction solvent. Therefore, this extract was chosen for electrochemical processes.

Table 1. Phenolic compound contents obtained by LC-MS/MS analysis of walnut extracts obtained with different solvents.

Phenolic compound	*mg phenolic/L solvent*	
	Acetone-water extract	*Methanol-water extract*
Gallic acid	1.941	1.477
Protocatechuic acid	3.311	2.574
Protocatechuic aldehyde	0.616	0.604
Sesamol	0.795	0.618
Catechin	2.876	1.911
Vanillin	4.568	3.750
Taxifolin	1.949	1.303
Oleuropein	1.987	5.141
Ellagic acid	1.727	0.777

Electrochemical Behavior of AISI 1010 in Inhibitor-Free Environment

In order to determine the inhibition efficiency of the walnut shell extract, the electrochemical behavior of AISI 1010 in different corrosive environments was determined by the CV (Fig. 3) and the corrosion rate measurements were determined by the Tafel polarization method (Fig. 4).

In Fig. 3, it is seen that the AISI 1010 was passivated in 0.2 M NaOH, passivation up to about -0.15 V in a 5% NaCl, and never passivated in 0.2 M HCl. In 0.2 M HCl, very large cathodic and anodic currents passed through the steel surface compared to other environments. An anodic current at about 100 mA passed at -0.2 V in 0.2 M HCl, while an anodic current at about 12 mA in 5% NaCl and less than 0.8 mA in 0.2 M NaOH. These results showed that the AISI 1010 was very endurable, partially durable and durable in acidic, salty, and alkaline environments, respectively.

In order to determine the corrosion rate of AISI 1010 in these environments, the polarization curves obtained by the Tafel polarization method are given in Fig. 4. In the Tafel polarization curves, while there was no passivation in the anodic branch in 0.2 M HCl, passivation was observed in the anodic branch of salty and alkaline environments, supporting the voltammograms in Fig. 3.

By overlapping the slopes of the anodic and cathodic polarization curves obtained by the Tafel polarization method, the corrosion rate, the linear polarization resistance, and the corrosion potential in HCl were determined as 1.014 mm/year, 182.4 ohms and -0.582 V, respectively. The corrosion rates in 0.2 M NaOH and 5% NaCl were 0.062 and 0.126 mm/year; and polarization resistances were measured as 1760 and 2387 ohms, respectively.

Electrochemical Behavior of AISI 1010 in Different Corrosive Environments with Inhibitor

The electrochemical behavior of AISI 1010 in different corrosive environments with walnut extract added at 500, 1000, and 2000 ppm concentrations was investigated by CV (Figs. 5-7). As can see in Fig. 5, because walnut extract prevented the oxidation steps of steel, the anodic peak at approximately -0.60 V, observed in the CV obtained without the inhibitor, gradually decreased while the concentration of the extract increased and this peak completely disappeared at 2000 ppm.

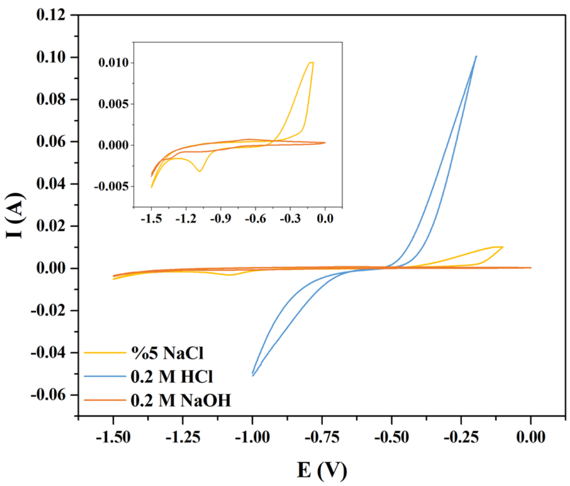

Figure 3. CVs of AISI 1010 obtained in different corrosive environments without inhibitor.

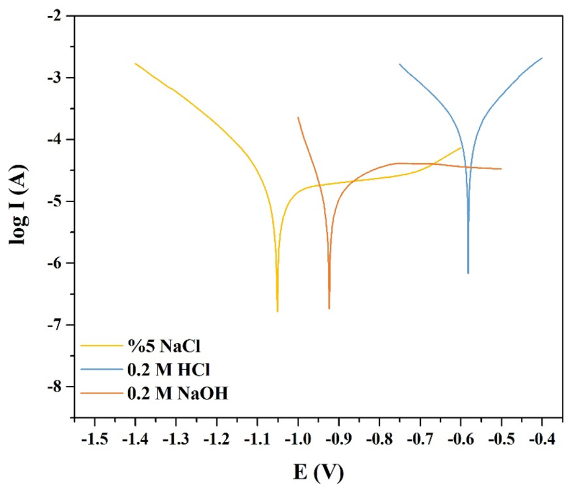

Figure 4. Tafel polarization curves of AISI 1010 obtained in different corrosive environments without inhibitor.

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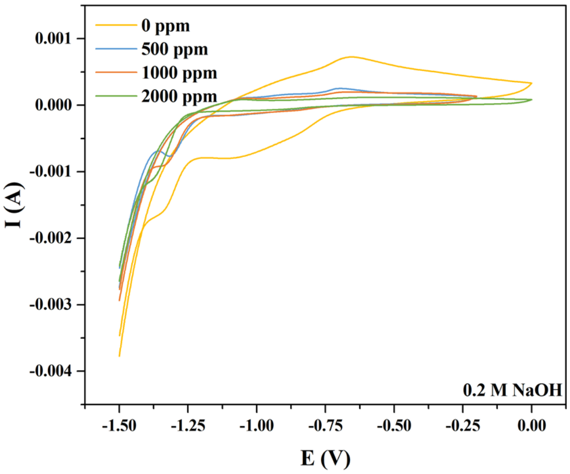

Figure 5. CVs of AISI 1010 in 0.2 M NaOH containing walnut extract at various concentrations.

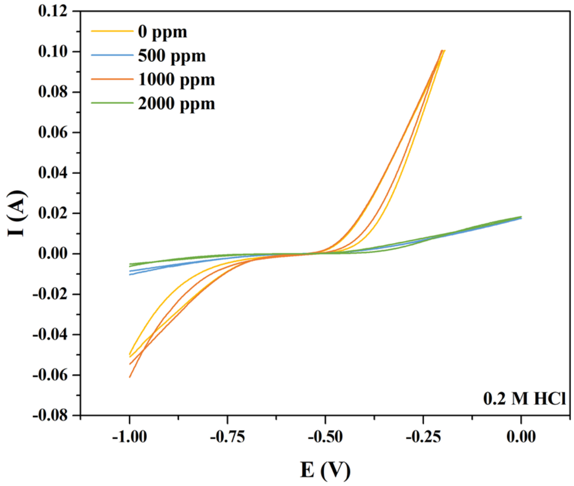

Figure 6. CVs of AISI 1010 in 0.2 M HCl containing walnut extract at various concentrations.

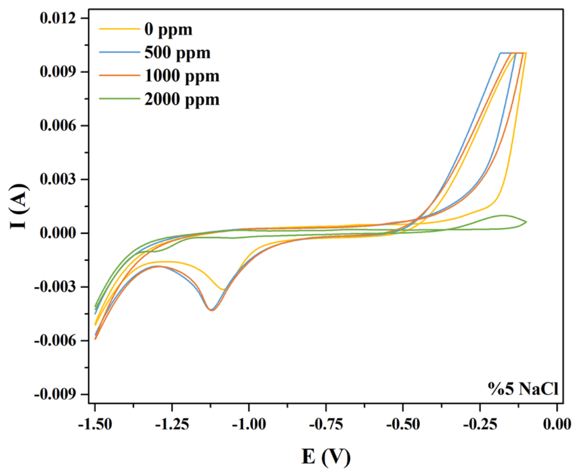

Figure 7. CVs of AISI 1010 in 5% NaCl containing walnut extract at various concentrations.

In Fig. 6, it is observed that AISI 1010 did not passivate in an acidic environment, but with the addition of walnut extract, both anodic and cathodic currents decreased.

In Fig. 7, it is seen that the anodic peak, which was obtained in the 0.2 M NaOH without extract, at about -1.0 V in the anodic branch, did not observe in the 5% NaCl. In addition, there was an increase in anodic and cathodic currents compared to the alkaline environment. This can be attributed to the lower pH and the effect of chloride ions in the environment. Chloride ions destroy the steel passivity. Moreover, the fact that the forward anodic current was smaller than that of the backward anodic current in all curves has indicated the pitting corrosion [38]. Passivity increased to higher potentials with the increase of walnut extract concentration. Passivity continued up to -0.2 V when 2000 ppm walnut extract was used.

Tafel Polarization Curves of AISI 1010 in Different Corrosive Environments with Inhibitor

Tafel polarization curves obtained in different corrosive environments with walnut extract added at concentrations of 0, 500, 1000, and 2000 ppm are shown in Figs. 8-10. In addition, the corrosion potential, polarization resistance, corrosion rate, and inhibition efficiency of the AISI 1010 obtained by the Tafel polarization method are given in Table 2.

Tafel polarization curves obtained in 0.2 M NaOH containing walnut extract at various concentrations are shown in Fig. 8. Although the anodic and cathodic regions of all curves were similar, it is seen that the corrosion potential shifted to more positive values with a rise in the concentration of inhibitor. The shift of the corrosion potential to the positive region and the decrease in the anodic current with the increase in inhibitor concentration signified that the anodic reaction was slowed down by walnut extract. Moreover, the polarization resistance decreased as the inhibitor concentration raised. These results showed that walnut extract was effective as an anodic inhibitor in an alkaline environment.

Tafel polarization scans acquired in 0.2 M HCl with walnut extract at various concentrations are shown in Fig. 9. With the increase in walnut extract concentration, the corrosion potential shifted to the more positive region and the corrosion rate decreased. This result pointed out that walnut extract acted as an anodic inhibitor. The rising in polarization resistance with the increase in concentration supported these results. The extract did not provide much inhibition of the AISI 1010 corrosion in a salty environment.

In Fig. 10, Tafel polarization scans are given which were obtained in 5% NaCl with walnut extract at various

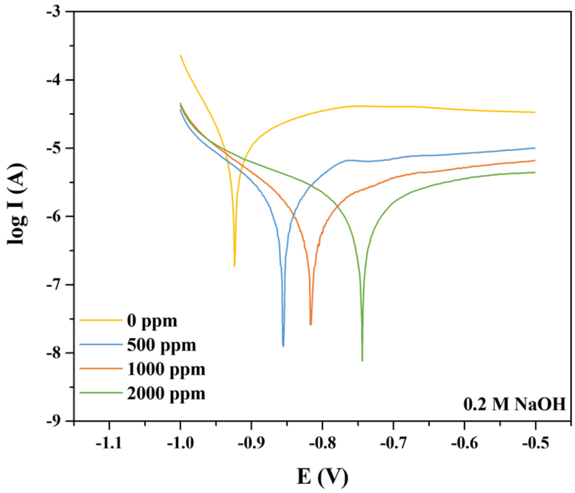

Figure 8. Tafel polarization curves of AISI 1010 in 0.2 M NaOH with and without inhibitor.

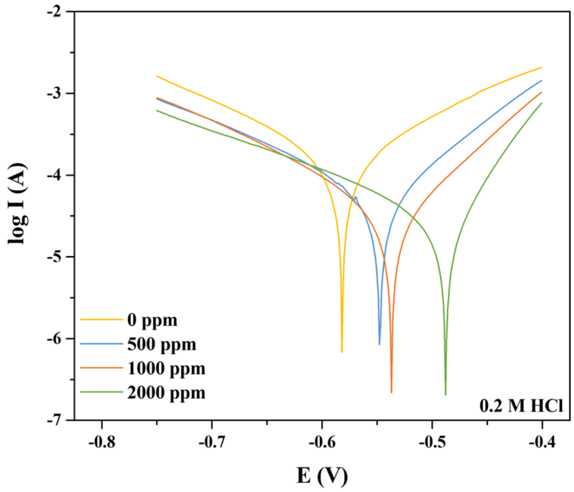

Figure 9. Tafel polarization curves of AISI 1010 in 0.2 M HCl with and without inhibitor.

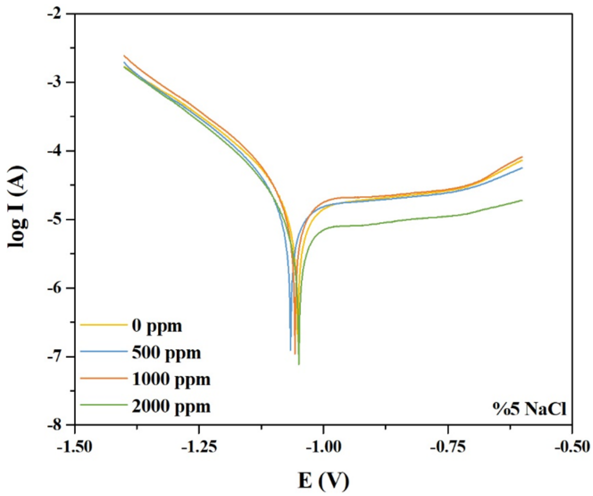

Figure 10. Tafel polarization curves of AISI 1010 in 5% NaCl with and without inhibitor.

Table 2. Corrosion parameters of AISI 1010 in three different corrosive environment with and without walnut extract as an inhibitor [39].

	Extract concentration (ppm)	*Corrosion potential E_{corr} (Volt)*	*Polarization resistance R_p (ohms)*	*Corrosion rate (mm/year)*	*Inhibition efficiency (%)*
0.2 M NaOH	*0*	*-0. 924*	*1760.1*	*0.062*	*-*
	500	*-0.855*	*14074.9*	*0.018*	*71.0*
	1000	*-0.817*	*24606.4*	*0.013*	*79.0*
	2000	*-0.744*	*26020.2*	*0.012*	*80.6*
0.2 M HCl	*0*	*-0.582*	*182.4*	*1.014*	*-*
	500	*-0.548*	*420.4*	*0.352*	*65.2*
	1000	*-0.537*	*693.7*	*0.185*	*81.8*
	2000	*-0.488*	*733.3*	*0.141*	*86.1*
5% NaCl	*0*	*-1.051*	*2387.1*	*0.126*	*-*
	500	*-1.066*	*2340.2*	*0.118*	*6.3*
	1000	*-1.057*	*2028.6*	*0.091*	*27.8*
	2000	*-1.049*	*4230.8*	*0.066*	*47.6*

concentrations. Although the anodic and cathodic branches of all curves were similar, there was no significant change in corrosion potential with increasing the inhibitor concentration. There was a decrease in corrosion current with inhibitor concentration, but no significant change was observed in the cathodic branch. However, a significant fall was observed in the anodic branch only at 2000 ppm [39].

DISCUSSION

Plants are the source of numerous biologically active compounds, but these compounds are found in small amounts in plants. The extraction is a technique that can obtain these biological components (extracts) with high yield and the least alteration in their functionalities. Research on this subject shows that there are differences in the bioactivity of extracts obtained by using diverse techniques. For this reason, it is needed to choose the convenient extraction method as well as the solvent according to the sample matrix properties, the chemical properties of the analytes, the matrix-analyte interaction, the efficiency, and other properties. Heat is transferred from the surface by convection and conduction in conventional extraction. Here, the extracting ability of solvents is mainly based on the solubility of the constituent in the solvent, the mass transfer kinetics of the product, the heat and mass diffusion, and the strength of the solute/matrix interaction. UAE is a technique that utilized high intensity/frequency sound waves and solvents to extract targeted compounds from different matrices. Ultrasound disrupts the cell walls of the plant; make easier the release of extractable components and increasing the mass transfer of the solvent from the continuous phase to the plant cells. Therefore, UAE is more advantageous than other extraction types in terms of yield, extraction time, and consumption of solvent [40].

The shell extract of the walnut investigated in this study was obtained by UAE. Acetone-water mixture at a ratio of

3/1 was chosen as the most suitable solvent for UAE, since it allowed the extraction of a high amount of vanillin. The extract was separated from its solid by centrifugation and this solution was stored to be used directly as an inhibitor in corrosion studies.

Extracts from plants are a widely studied topic in corrosion science in recent years as corrosion inhibitors, and they have advantages such as being cheap, soluble in water and biodegradable. Extracts of plants are mixtures of different organic materials and they commonly contain oxygen, nitrogen, sulfur or double bond, triple bond, or conjugated system. In this respect, they resemble common organic inhibitors and are considered a promising group of highly effective inhibitors [36]. According to the analysis of FTIR and determination of phenolic components after the extraction process, it has been determined that there were functional groups containing the above mentioned bonds and atoms in the structure of the components in the walnut shell extract. Therefore, it was predicted that the walnut shell extract will have a positive effect on decreasing the corrosion rate of AISI 1010 mild steel as an inhibitor.

Mild steel (<0.15% carbon), also known as low carbon steel, is widely used in construction, manufacturing, and other industries due to its low cost, easy availability, malleability, high ductility, and mechanical resistance. The main problem encountered in the use of mild steel is its increased tendency to corrosion when exposed to acidic, alkaline, or salty environments. Especially in industries where aggressive acids such as hydrochloric acid are used, corrosion leads to the destruction of this material and ultimately shortens the expected life of steel. As it is well known a small amount of inhibitor is sufficient to prevent corrosion [41]. Herein, first of all, CVs and Tafel polarization curves of AISI 1010 were obtained for three inhibitor-free corrosive environments. According to Tafel polarization curves, the corrosion rates of AISI 1010 for 0.2 M NaOH, 0.2 M HCl, and 5% NaCl were measured at 0.062, 1.014, and 0.126 mm/year, respectively. The most corrosive environment was found to be 0.2 M HCl, as expected. It was determined that the least corrosive environment was 0.2 M NaOH due to the passivation of AISI 1010 in an alkaline environment. It has been determined that 5% NaCl is more corrosive than that of an alkaline environment due to the chloride ions disrupting the passivity of the AISI 1010. When the extract was added, these three corrosive environments at 500, 1000, and 2000 ppm, it is understood that the Oğuzlar walnut shell extract is an effective inhibitor for AISI 1010 steel in all corrosive environments owing to its phenolic components, especially vanillin. The inhibition efficiency of this extract was measured 47.6% in 5% NaCl, 80.6% in 0.2 M NaOH, and 86.1% in 0.2 M HCl.

There are studies in the literature examining the inhibition efficiency of vanillin on various metals. In a study examining the inhibition efficiency of vanillin on an aluminum alloy (AA6061) in seawater, it was reported by Rosliza et al. that the efficiency increased with the vanillin concentration changing from 200 to 1000 ppm [23]. Tawfik et al. investigated the effect of non-ionic surfactants containing vanillin derivatives on the corrosion of carbon steel in 0.5 M HCl. They reported that the inhibition efficiency varied between 84-96% according to the length of the ethylene oxide chain contained in the inhibitor [25]. Fernandes et al. reported that the efficiencies of three vanillin derived Schift bases for mild steel in 1 M HCl were 82.2%, 83.1%, and 93.1% [26]. Lotto et al. reported that the rosemary extract (Rosmarinus officinalis) with added vanillin exhibited 95.63% inhibition efficiency for mild steel in 1 M HCl [27]. Haddadi et al. investigated the corrosion behavior of mild steel exposed to seawater when a walnut green shell (Juglans regia) containing vanillic acid in its structure was used as an inhibitor. They reported that approximately 94% efficiency was achieved at an extract concentration of 1000 ppm [42]. As can be seen, this study with a corrosion efficiency of 86.1% for mild steel in an acidic environment is comparable to its counterparts in the literature. Moreover, even though the inhibitor yields are relatively higher than the value obtained in this study; when the ones based on the synthesis of vanillin compound and its derivatives are considered, it is thought that it is more practical to obtain vanillin via UAE, which is a simple, fast and effective approach, rather than the organic synthesis of any chemical.

CONCLUSION

Walnut is a popular nut that has more than twenty types all over the world and it has consumed quite a lot in our country. In this study, the Çorum Oğuzlar walnut extract was investigated as a candidate for an environmentally friendly inhibitor. It was determined that this extract, which was found to contain various phenolic groups mainly vanillin in its structure from FTIR and LC-MS/MS analyses, could effectively prevent corrosion for AISI 1010 mild steel in an acidic and salty environments. It is believed that this study will provide a valuable reference for the development and practical applications of green inhibitors.

CONFLICT OF INTEREST

Authors approve that to the best of their knowledge, there is not any conflict of interest or common interest with an institution/organization or a person that may affect the review process of the paper.

AUTHOR CONTRIBUTION

Merve Okutan: Conceptualization, Investigation, Methodology, Resources, Supervision, Visualization, Writing-Original Draft, Writing-Review&Editing;
Abdurrahman Asan: Conceptualization, Methodology, Resources, Supervision, Writing-Review&Editing;
Hacer Ebru Singer: Investigation, Experimental studies

REFERENCES

1. Verma C, Verma DK, Ebenso EE, Quraishi MA. Sulfur and phosphorus heteroatom-containing compunds as corrosion inhibitors: An overview. Heteroatom Chemistry 29(4) (2018) e21437. https://doi.org/10.1002/hc.21437
2. Sounthari P, Kiruthika A, Saranya J, Parameswari K, Chitra S. Corrosion inhibition property of polyester-groundnut shell biodegradable composite. Ecotoxicology and Environmental Safety 134 (2016) 319-326. https://doi.org/10.1016/j.ecoenv.2015.08.014
3. Tran M, Mohammedi D, Fiaud C, Sutter EMM. Corrosion behaviour of steel in the presence of Y(III) salts: Kinetic and mechanistic studies. Corrosion Science 48(12) (2006) 4257-4273. https://doi.org/10.1016/j.corsci.2006.03.015
4. Covelo A, Rodil S, Nóvoa XR, Hernández M. Development and characterization of sealed anodizing as a corrosion protection for AA2024-T3 in saline media. Materials Today Communications 31(November 2021) (2022) 103468. https://doi.org/10.1016/j.mtcomm.2022.103468
5. Loto CA, Loto RT, Popoola AP. Performance evaluation of zinc anodes for cathodic protection of mild steel corrosion in HCl. Chemical Data Collections 24 (2019) 100280. https://doi.org/10.1016/j.cdc.2019.100280
6. Cevallos-Morillo C, Cisneros-Pérez P, Llive R, Ricaurte M, Reinoso C, Meneses MA, Guamán MDC, Palma-Cando A. Croton lechleri extracts as green corrosion inhibitors of admiralty brass in hydrochloric acid. Molecules 26 (2021) 7417. https://doi.org/10.3390/molecules26247417
7. Alibakhshi E, Ramezanzadeh M, Bahlakeh G, Ramezanzadeh B, Mahdavian M, Motamedi M. Glycyrrhiza glabra leaves extract as a green corrosion inhibitor for mild steel in 1 M hydrochloric acid solution: Experimental, molecular dynamics, Monte Carlo and quantum mechanics study. Journal of Molecular Liquids 255 (2018) 185-198. https://doi.org/10.1016/j.molliq.2018.01.144
8. Ma IAW, Ammar S, Kumar SSA, Ramesh K, Ramesh S. A concise review on corrosion inhibitors: Types, mechanisms and electrochemical evaluation studies. Journal of Coatings Technology and Research 19(1) (2022) 241-268. https://doi.org/10.1007/s11998-021-00547-0
9. Popoola LT. Organic green corrosion inhibitors (OGCIs): a critical review. Corrosion Reviews 37(2) (2019) 71-102. https://doi.org/10.1515/corrrev-2018-0058
10. Anh HT, Vu NSH, Huyen LT, Tran NQ, Thu HT, Bach LX, Trinh QT, Prabhakar Vattikuti SV, Nam ND. Ficus racemosa leaf extract for inhibiting steel corrosion in a hydrochloric acid medium. Alexandria Engineering Journal 59(6) (2020) 4449-4462. https://doi.org/10.1016/j.aej.2020.07.051
11. Silva MVLD, Policarpi EDB, Spinelli A. Syzygium cumini leaf extract as an eco-friendly corrosion inhibitor for carbon steel in acidic medium. Journal of the Taiwan Institute of Chemical Engineers 129 (2021) 342-349. https://doi.org/10.1016/j.jtice.2021.09.026
12. Feng Y, He J, Zhan Y, Feng Y, He J, Zhan Y, An J, Tan B. Insight into the anti-corrosion mechanism Veratrum root extract as a green corrosion inhibitor. Journal of Molecular Liquids 334 (2021) 116110. https://doi.org/10.1016/j.molliq.2021.116110
13. Cherrad S, Alrashdi AA, Lee HS, Cherrad S, Alrashdi AA, Lee HS, El aoufir Y, Lgaz H, Satrani B, Ghanmi M, Aouane EM, Chaouch A. Cupressus arizonica fruit essential oil: A novel green inhibitor for acid corrosion of carbon steel. Arabian Journal of Chemistry 15(6) (2022) 103849. https://doi.org/10.1016/j.arabjc.2022.103849
14. Bhardwaj N, Sharma P, Guo L, Dagdag O, Kumar V. Molecular dynamic simulation and Quantum chemical calculation of phytochemicals present in Beta vulgaris and electrochemical behaviour of Beta vulgaris peel extract as green corrosion inhibitor for stainless steel (SS-410) in acidic medium. Colloids and Surfaces A: Physicochemical and Engineering Aspects 632(October 2021) (2022) 127707. https://doi.org/10.1016/j.colsurfa.2021.127707
15. Wu Y, Zhang Y, Jiang Y, Qian Y, Guo X, Wang L, Zhang J. Orange peel extracts as biodegradable corrosion inhibitor for magnesium alloy in NaCl solution: Experimental and theoretical studies. Journal of the Taiwan Institute of Chemical Engineers 115 (2020) 35-46. https://doi.org/10.1016/j.jtice.2020.10.010
16. Radi M, Melian R, Galai M, Dkhirche N, Makha M, Verma C, Fernandez C, EbnTouhami M. Pumpkin seeds as an eco-friendly corrosion inhibitor for 7075-T6 alloy in 3.5% NaCl solution: Electrochemical, surface and computational studies. Journal of Molecular Liquids 337 (2021) 116547. https://doi.org/10.1016/j.molliq.2021.116547
17. Sadik K, El hamdani N, Byadi S, Hachim ME, El harafi H, Aboulmouhajir A. Quantum and dynamic investigations of complex iron-alkaloid-extract cytisine derivatives of retama monosperma (L.) boiss. seeds as eco-friendly inhibitors for mild steel corrosion in 1M HCl. Journal of Molecular Structure 1244 (2021) 130921. https://doi.org/10.1016/j.molstruc.2021.130921
18. Furtado LB, Nascimento RC, Seidl PR, Guimarães MJOC, Costa LM, Rocha JC, Ponciano JAC. Eco-friendly corrosion inhibitors based on Cashew nut shell liquid (CNSL) for acidizing fluids. Journal of Molecular Liquids 284 (2019) 393-404. https://doi.org/10.1016/j.molliq.2019.02.083
19. Shahini MH, Keramatinia M, Ramezanzadeh M, Ramezanzadeh B, Bahlakeh G. Combined atomic-scale/DFT-theoretical simulations & electrochemical assessments of the chamomile flower extract as a green corrosion inhibitor for mild steel in HCl solution. Journal of Molecular Liquids 342 (2021) 117570. https://doi.org/10.1016/j.molliq.2021.117570
20. Zaher A, Aslam R, Lee HS, Khafouri A, Boufellous M, Alrashdi AA, 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. Arabian Journal of Chemistry 15(2) (2022) 103573. https://doi.org/10.1016/j.arabjc.2021.103573
21. Xhanari K, Finšgar M, Knez Hrnčič M, Maver U, Knez Ž, Seiti B. Green corrosion inhibitors for aluminium and its alloys: A review. RSC Advances 7(44) (2017) 27299-27330. https://doi.org/10.1039/c7ra03944a
22. Bodoira R, Maestri D. Phenolic compounds from nuts: Extraction, chemical profiles, and bioactivity. Journal of Agricultural and Food Chemistry 68(4) (2020) 927-942. https://doi.org/10.1021/acs.jafc.9b07160
23. Rosliza R, Nora'aini A, Wan Nik WB. Study on the effect of vanillin on the corrosion inhibition of aluminum alloy. Journal of Applied

Electrochemistry 40(4) (2010) 833-840. https://doi.org/10.1007/s10800-009-0066-1
24. Quraishi MA, Ansari KR, Chauhan DS, Umoren SA, Mazumder MAJ. Vanillin modified chitosan as a new bio-inspired corrosion inhibitor for carbon steel in oil-well acidizing relevant to petroleum industry. Cellulose 27(11) (2020) 6425-6443. https://doi.org/10.1007/s10570-020-03239-x
25. Tawfik SM, Negm NA. Vanillin-derived non-ionic surfactants as green corrosion inhibitors for carbon steel in acidic environments. Research on Chemical Intermediates 42(4) (2016) 3579-3607. https://doi.org/10.1007/s11164-015-2233-9
26. Fernandes CM, Pina VGSS, Alfaro CG, Sampaio MTG, Massante FF, Alvarez LX, Barrios AM, Silva JCM, Alves OC, Briganti M, Totti F, Ponzio EA. Innovative characterization of original green vanillin-derived Schiff bases as corrosion inhibitors by a synergic approach based on electrochemistry, microstructure, and computational analyses. Colloids and Surfaces A: Physicochemical and Engineering Aspects 641(January) (2022) 128540. https://doi.org/10.1016/j.colsurfa.2022.128540
27. Loto RT, Loto CA. Data on the comparative evaluation of the corrosion inhibition of vanillin and vanillin admixed with rosmarinus officinalis on mild steel in dilute acid media. Chemical Data Collections 24 (2019) 100290. https://doi.org/10.1016/j.cdc.2019.100290
28. Satpati S, Saha SK, Suhasaria A, Banerjee P, Sukul D. Adsorption and anti-corrosion characteristics of vanillin Schiff bases on mild steel in 1 M HCl: experimental and theoretical study. RSC Advances 10(16) (2020) 9258-9273. https://doi.org/10.1039/C9RA07982C
29. Güzel N, Kahraman O, Feng H. Solid–liquid extraction by manothermosonication: recapturing the value of pomegranate peels and nanocomplexation of extracts with pea protein. ACS Sustainable Chemistry & Engineering 8(44) (2020) 16671-16679. https://doi.org/10.1021/acssuschemeng.0c06316
30. Singleton VL, Orthofer R, Lamuela-Raventós RM. Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagent, in: Lester P (Ed.). Methods in Enzymology. Academic Press, pp 152-178, 1999.
31. Alara OR, Abdurahman NH, Ukaegbu CI. Extraction of phenolic compounds: A review. Current Research in Food Science 4(February) (2021) 200-214. https://doi.org/10.1016/j.crfs.2021.03.011
32. El Ibrahimi B, Jmiai A, Bazzi L, El Issami S. Amino acids and their derivatives as corrosion inhibitors for metals and alloys. Arabian Journal of Chemistry 13(1) (2020) 740-771. https://doi.org/10.1016/j.arabjc.2017.07.013
33. Fazal BR, Becker T, Kinsella B, Lepkova K. A review of plant extracts as green corrosion inhibitors for CO2 corrosion of carbon steel. Nature partner journals Materials Degradation 6(1) (2022) 5. https://doi.org/10.1038/s41529-021-00201-5
34. Cosmulescu S, Trandafir I. Variation of phenols content in walnut (Juglans regia L.). South-Western Journal of Horticulture Biology and Environment 2(1) (2011) 25-33.
35. Wu Y, Zhang Y, Jiang Y, Li N, Zhang Y, Wang L, Zhang J. Exploration of walnut green husk extract as a renewable biomass source to develop highly effective corrosion inhibitors for magnesium alloys in sodium chloride solution: Integrated experimental and theoretical studies. Colloids and Surfaces A: Physicochemical and Engineering Aspects 626(April) (2021) 126969. https://doi.org/10.1016/j.colsurfa.2021.126969
36. Wang Q, Zhang Q, Liu L, Zheng H, Wu X, Li Z, Gao P, Sun Y, Yan Z, Li X. Experimental, DFT and MD evaluation of Nandina domestica thunb. extract as green inhibitor for carbon steel corrosion in acidic medium. Journal of Molecular Structure 1265 (2022) 133367. https://doi.org/10.1016/j.molstruc.2022.133367
37. Zhu H, Xu JL. Authentication and provenance of walnut combining Fourier transform mid-infrared spectroscopy with machine learning algorithms. Molecules 25(21) (2020) 4987. https://doi.org/10.3390/molecules25214987
38. Liu C, Gong M, Zheng X. Pitting corrosion of 2205 duplex stainless steel at high concentrations of NaCl solution. International Journal of Electrochemical Science 13(8) (2018) 7432-7441. https://doi.org/10.20964/2018.08.41
39. Singer HE. Yumuşak çeliğin korozyonuna bazı kuruyemiş özütlerinin inhibitör etkisinin araştırılması. Master's Thesis, Hitit University (2022).
40. Dhanani T, Shah S, Gajbhiye NA, Kumar S. Effect of extraction methods on yield, phytochemical constituents and antioxidant activity of Withania somnifera. Arabian Journal of Chemistry 10 (2017) S1193-S1199. https://doi.org/10.1016/j.arabjc.2013.02.015
41. Baskar P, Rathinapriya P, Prabakaran M. Use of trochodendron aralioides extract as green corrosion inhibitor for mild steel in 1M HCl solutions. Processes 10(8) (2022) 1480. https://doi.org/10.3390/pr10081480
42. Haddadi SA, 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. Journal of Molecular Liquids 284 (2019) 682-699.