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The Use of *Rheum Ribes* (Işgın) Extracts for Copper Protection in Acidic Media

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Abstract: The extracts of different parts of ışgın such as flower (RRF), leaf (RRL), and root (RRR) were prepared and their protective effects on copper corrosion in an acidic media were investigated in this study. Other components that are not currently in use will thus be able to be transformed into benefits. Extracts from various parts of the plant were dissolved in a 1 M HCl solution at a concentration of 1000 ppm for this purpose. The time variation of open circuit potential (Eocp-t), linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization (PP) techniques were used to investigate the electrochemical behaviour of copper metal in these solutions. The surface of copper was examined after corrosive medium treatment using a scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDX), and contact angle measurements. The results revealed that the effects of extracts obtained from different parts of the RR on the behavior of copper in an acidic medium varied. The best protection was provided by the RRF extract. Despite this, RRR extract failed to protect Cu from corrosive ions in 1 M HCl solution. According to surface analyses, the plant extracts formed an adherent and compact organic film on the Cu surface.

Rheum Ribes (Işgın) Özütlerinin Asidik Ortamda Bakırın Korunması için Kullanılması

Anahtar Kelimeler
Rheum Ribes (Işgın),
Bakır,
Doğal bitki özütleri,
Korozyon inhibitörü

Öz: Bu çalışmada, ışgının çiçek (RRF), yaprak (RRL) ve kök (RRR) gibi farklı bölgelerinin ayrı ayrı özütleri hazırlanarak asidik ortamda bakırın korozyonuna koruma etkileri incelenmiştir. Böylelikle ışgının kullanılmayan diğer kısımlarının da faydaya dönüştürülmesi mümkün olabilecektir. Bu amaçla, RR özütlerinin 1 M HCl çözeltisinde 1000 ppm çözeltileri hazırlanmıştır. Bakır metalinin bu çözeltilerdeki elektrokimyasal davranışları açık devre potansiyelinin zamanla değişimi (Eocp-t), elektrokimyasal impedans spektroskopisi (EIS), lineer polarizasyon direnci (LPR) ve potansiyodinamik polarizasyon (PP) teknikleri ile incelenmiştir. Bakırın korozif ortam ile muamelesi sonrasında yüzeyi taramalı elektron mikroskopu (SEM), enerji dağılımlı X-ışını spektroskopisi (EDX) ve temas açısı ölçümleri ile incelenmiştir. Elde edilen bulgular, RR'nin farklı bölgelerinden elde edilen özütlerin bakırın asidik ortamdaki davranışına etkilerinin farklı olduğunu göstermiştir. En iyi koruma RRF özütünde elde edilmiştir. RRR özütü ise bakırı 1 M HCl çözeltisinde korozyona karşı koruyamamaktadır. Yüzey analizleri bitki özütlerinin metal yüzeyinde koruyucu bir film oluşturduğunu göstermiştir.

1. INTRODUCTION

In 2016, the Council of Higher Education designated Bingöl University as a pilot university under the Regional Development-Oriented Mission Differentiation and Specialization Program of Universities. In terms of flora, Bingöl province is one of our country's most important regions. In this context, one of the primary goals of this work is to identify and introduce new plants with high economic value into the economy. This is critical for the development of the region. In this context, this study was planned to determine the new usage areas of the RR plant, which is well-known in the region.

Copper metal, on the other hand, is one of the most frequently used metals in the industry due to important properties such as high electrical and thermal conductivity [1-3]. Nevertheless, in corrosive environments such as acidic, basic, chloride, humidity, and air, this metal incredibly quickly loses its metallic conductivity [4]. When copper metal corrodes, most of its properties and consequently its industrial use properties are lost [3, 5]. As a result, protecting this metal from corrosion is critical from a strategic standpoint. The use of corrosion inhibitors is the most common and effective method of protecting metals from corrosion. Corrosion inhibitors are classified as either inorganic or organic. Inorganic corrosion inhibitors work by corrosion of metals and forming a protective oxide film on the metal surface or a poorly soluble salt of the metal. However, because of their oxidizing properties, their concentrations in the corrosive environment must be constantly monitored. The majority of them have toxic qualities, which make them extremely harmful to both humans and the environment. Some metal salts, such as those in the lanthanide group, are quite costly.

Organic compounds, which are used as corrosion inhibitors are generally adsorbed on the metal surface and form a barrier between the metal and corrosive media. According to the literature, molecules containing P, N, S, and O atoms, as well as molecules with double or triple bonds, are better adsorbed on the metal surface and thus more effective inhibitors [6-8]. Studies on the use of environmentally friendly molecules are being conducted in this field because the majority of organic inhibitors used are toxic and have negative effects on people and the environment [9-12]. Natural plant extracts have become popular for this purpose in recent years [13-20]. Natural plant extracts or active ingredients are natural and have no adverse effects on humans or the environment. It is natural and its prices are lower than synthetic corrosion inhibitors. For this reason, it is extremely important to concentrate studies on these plants. Natural products are both healthy and economical, and for this purpose, the most important use potential for the future is chemicals [21-22].

Işgın (RR) is found in some countries as well as our country's Eastern Anatolia (Ağrı, Bingöl, Elazığ, Hakkari, Kars, Van, and Sivas) region [23]. Mountainous and flinty terrain is ideal for its flourishing. It is quite common for people to consume the plant fresh. This plant has a sour taste, strengthens the stomach, prevents vomiting, and is constipating [24]. Aside from using the underground parts to treat hemorrhoids and diabetes, this plant is also used to aid digestion in various parts of the country [25]. Due to its low pH value, RR is eaten by peeling and has a sour taste [3,56]. The young roots and stems of RR are used as a preventative against measles and smallpox, as well as an anti-gall agent. In addition to curing diabetes, ulcers, and stomach ailments, its roots have anti-inflammatory properties [25, 26]. Anthraquinones in RR are spotlighted as having antibacterial properties [27, 28]. In terms of vitamin C, this plant is extremely abundant. The RR plant has the following compositional characteristics: 5.59% dry matter, 0.63% total ash, 1.3% protein, 3.75 g/g iron, 1.13 g/g zinc, 0.5 g/g copper, 0.423 g/g manganese, 0.255 g/g vitamin A, 0.614 g/g vitamin E, and 98.6 g/g selenium [29, 30]. RR is a safe and natural plant that can be used to protect metals, as was already mentioned.

Plant-based anticorrosive secondary metabolites may be used to overcome corrosive deformations due to material quality, oxidation reactions, acidic and basic environment exposure. Effective anticorrosive compounds can be isolated and identified from leaves, flowers or roots of plants of natural origin. In some studies, it has been reported that especially the flower parts of the plants are rich in total phenolics, flavonoid alkaloids, terpenoids and glycosides [31, 32]. Therefore, extracts from different parts of plants, which have such a rich variety of secondary metabolites that are economical, environmentally friendly and easily available, could be used for anticorrosive purposes.

The inhibitory effects of the extracts from various RR parts on copper corrosion in 1 M HCl solution were investigated. Several electrochemical techniques were used to accomplish this. Following exposure to corrosive RR extracts, the metal's surface was examined with the help of SEM, EDX, and contact angle measurements. Based on the information gathered, it was determined which area of this plant would best protect the copper. The top extract will be the focus of the next stage of research, and its protective properties will be improved by adjusting a few parameters.

2. MATERIAL AND METHOD

2.1. Preparation of Electrodes

The working electrode was made of Cu with a purity of 99.98-99.99%. The cylindrical copper rods were prepared by embedding them in polyester and leaving out only the lower end of the measurement. The electrode's total surface area in contact with the solution was 0.0707 cm2. The Cu electrodes were cleaned with sandpaper, the last of which was a 2000 grid, using a sanding machine before the measurements. After washing with pure water and absolute ethanol, they were immersed in absolute ethanol in an ultrasonic bath for a set amount of time before being immersed in the test solutions without waiting. Pt sheet with a total surface area of 2 cm2 was utilized as an auxiliary electrode. The reference electrode was Ag/AgCl (3 M KCl).

2.2. Preparation of RR Extracts

This study made use of RR from Bingöl region. The extraction procedure has previously been described in detail [33]. After collecting the RR taxon grown in its natural habitats, the leaf, flower, and root parts were separated and dried on unprinted papers in a sunny place. The dried plant parts were ground to 30 mesh particle size by grinding with a laboratory type mill. Each of the ground plant organs was weighed 100 g and extracted with 2 L methanol. As a result of the extraction process, it was filtered and separated from the extract pulp part. The remaining pulp was extracted two more times with the same amount of methanol. The methanol in the extract solution obtained as a result of the extraction process was removed with the help of a rotary evaporator at temperatures not exceeding 40°C under low pressure. The dry extract obtained as a result of the evaporation process was taken into an amber colored bottle and stored in the refrigerator at +4 °C.

2.3. Test Solutions

The corrosion tests were performed in 1 M HCl and 1000 ppm extracts containing 1 M HCl solutions. Dilution of 1 M HCl solution produced an analytical grade HCl solution (37%). 1000 mg dried RR extracts were dissolved in pure water and diluted to 1 L in a 1 L flask with distilled water. The temperature of corrosive solutions was kept at 298 K in a water bath during the tests. The experimental set-up was opened to the atmosphere and the solutions were not stirred during the experiments.

2.4. Electrochemical Measurements

Electrochemical behavior of Cu was investigated using computer-controlled CHI 660D and CHI6096 A.C. Electrochemical Analyzers. Pt and Ag/AgCl electrodes were used as counter and reference electrodes. Initially, the working electrodes were immersed in 1 M HCl in the absence and presence of the extracts for 1 hour, and the change in E_{ocp} was plotted against the immersion time. Regarding this exposure time, EIS data were collected in the frequency range from 100 kHz to 0.003 Hz. The amplitude was 10 mV from peak to peak. Upon completion of these tests, LPR experiments were carried out at 0.001 V s^{-1}, ranging from -10 mV more negatively to +10 mV more positively versus E_{ocp}, and an *i*-*E* plots were obtained. Polarization resistance was discovered in the formation of these lines. Finally, polarization plots from E_{ocp} to anodic potentials were obtained in the same system at a scan rate of 1 mV s^{-1}.

2.5. Characterization of the Metal Surface

Cu was left in the 1 M HCl solution for 1 hour without and with each extract added. The metal was then removed, cleaned thoroughly with purified water, dried, and stored in a desiccator until measurements were taken. A Jeol model (JEOL 6510) SEM was used to examine their surface structure and appearance. EDX measurements were used to determine the chemical composition of the surface. To determine surface hydrophobic or hydrophilic characters and the guest the orientation of the molecules at the surface contact angle measurements were taken [34, 35]. The sessile water drop theory was used in these experiments.

3. RESULTS AND DISCUSSION

3.1. The Change of Open Circuit Potential with Exposure Time

Changes at the metal/solution interface, as well as the initiation and continuation of copper corrosion, could all cause E_{ocp-t} variation. These lines could also reveal details about the reaction mechanism or the dominance of anodic or cathodic processes. Before conducting electrochemical measurements, a constant steady-state open circuit condition is also required. As a result, the change in E_{ocp} of Cu during test solution exposure was initially recorded for 1 h. Figure 1 shows a graphical representation of this information.

Figure 1 shows that the potential of Cu sharply shifts to more negative potentials during the first 80 seconds. This behavior is responsible for copper dissolution. After about a half-hour, the potential shifts to the positive side and nearly remains constant. Copper passivation is caused by $CuCl_{(k)}$ and other copper corrosion products [36]. The addition of the extracts causes the metal's E_{ocp} to abruptly shift into passive regions. This result shows that the molecules of extracts form a surface-protective film that serves as a fundamental physical barrier and prevents the corrosion of Cu by mainly influencing the anodic mechanism. After the addition of the extracts E_{ocp} of the metal shifts to passive regions sharply [37]. The potential changes depending on the type of extract, with RRF having the most passive and stable potential. These differences could be explained by the difference in the chemical composition of each part of the plant. In all cases, the potential approaches steady-state conditions, making electrochemical measurements possible.

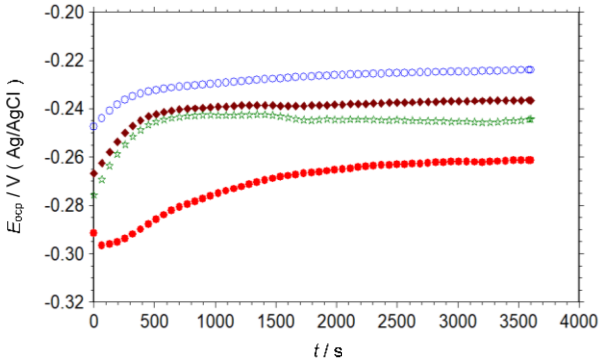


Figure 1. The change of open circuit potential of Cu with immersion time in 1 M HCl (●) and containing 1000 ppm RRF (○), RRL (♦), and RRR (☆) solutions

3.2. Electrochemical Impedance Spectroscopy

EIS is one of the most effective electrochemical methods available today for studying the behavior of metal/solution interfaces because it allows for resistance measurement without polarizing the surface. In order to examine the behavior of the film-modified metal surface/solution interface, the EIS technique was employed. Figure 2 shows related Nyquist and Bode plots of Cu obtained in acidic solutions containing RRF, RRL, and RRR extract. Even though the Nyquist plots (Figure 2a) only define two loops, the Bode plots (Figures 2b and c) show that three time constants appeared. When the plots obtained in uninhibited HCI solution were examined, the high-frequency loop that appeared at high frequencies could be attributed to charge transfer resistance and double layer resistance [38]. The resistance of copper chloride species formed on the surface could be assigned to the second middle-frequency one. At low frequencies, a straight line appeared, which is generally defined as Warburg impedance [39], This is due to the diffusion resistance of corrosive ions such as $CuCl_2^-$ at the metal/solution interface.

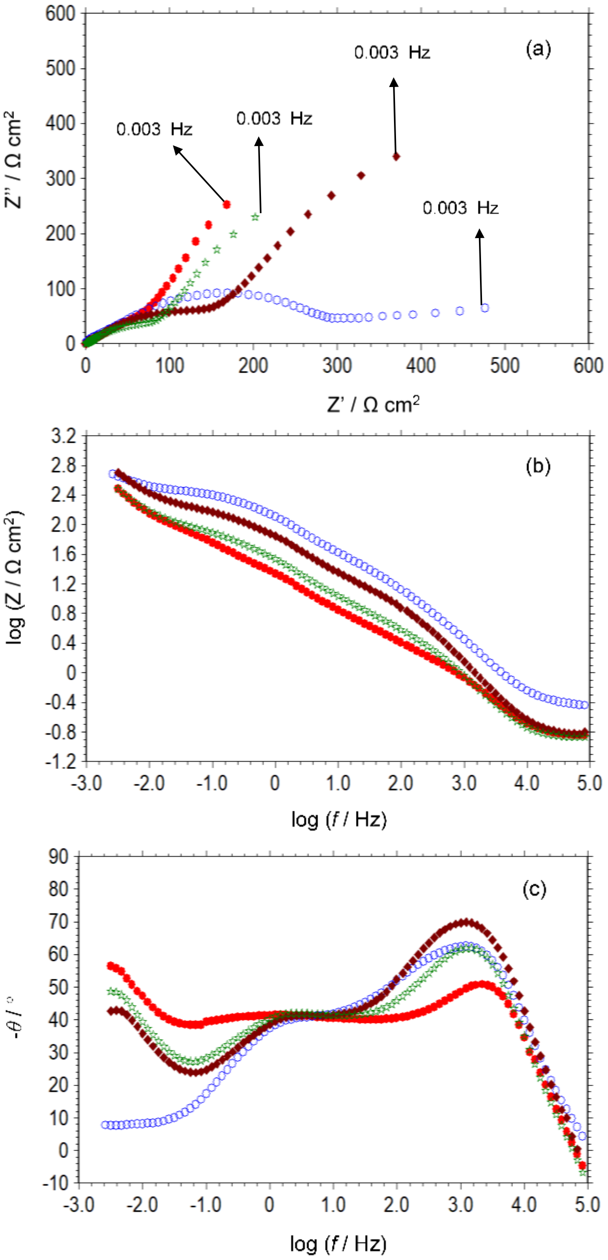


Figure 2. The Nyquist (a), log Z-log f (b), and phase angle-log f (c) (Bode) plots of Cu obtained in 1 M HCl solution without (●) and with the addition of 1000 ppm RRF (○), RRL (♦) and RRR (☆) solutions after 1-hour exposure

The general behavior of Cu did not change when the RR extracts were added to 1 M HCl solution, indicating that the extracts inhibit Cu corrosion without changing the mechanism [37]. However, the total number of high and middle-frequency loops increased in the order RRF > RRL > RRR. The increased charge transfer resistance and film resistance suggest that the extract molecules form a protective organic film over the Cu surface [39] and protect Cu from acidic corrosion. High and low frequencies are explained in the same way as 1 M HCl. The middle time constant, which corresponds to film resistance, could be assigned to the formation of film at the surface as well as copper products under the film or film pores. In the presence of the extracts, the angle of the low-frequency line related to the Warburg impedance decreases, reaching its lowest value in the case of RRF. This could be attributed to the formation of a compact and adherent film at the surface, which prevents corrosive ions from diffusing [39]. Polarization resistance was defined as the total resistance of charge transfer resistance, double layer resistance, film resistance, and resistance to corrosive species accumulation at the surface (R_p). Figure 2 shows that the extracts of RRF and RRL inhibit the corrosion rate of Cu and protect it from corrosion. However, the RRR extract was unable to adequately protect the metal in this acidic solution. Therefore, it cannot be advised to use this extract for this purpose. Further research, on the other hand, is required to improve the protection efficiency of RRF or RRL. In the next stage, we intend to improve the protection efficiency by incorporating a suitable organic molecule or KI to create a synergy between the extract molecules and the additive. The extracts' protection ability will also be tested in H_2SO_4 solution because the surface is cleaner in this acid and more molecules are expected to be adsorbed over the surface and perform better protection. The data presented here are preliminary data from this project, and additional studies such as the effect of extract concentration, exposure time, corrosive media type, and synergistic effect of KI to increase protection efficiency, as well as data analyses by a licensed fitting program, are ongoing and will be reported in another study.

3.3. Linear Polarization Resistance

The LPR technique was also used to investigate the extracts' corrosion resistance. Current-potential curves were obtained in 1 M HCl solution in the absence and presence of 1000 ppm of each plant extracts for this purpose. Table 1 shows the R_p values and inhibition efficiencies (η) that were used to generate the data.

The slopes of the *E-i* curves were used to calculate R_p values, while the following equation was used to calculate η values:

$$\eta = \left(\frac{R'_p - R_p}{R'_p}\right) \times 100 \qquad (1)$$

In this equation, R'_p and R_p are the polarisation resistances of Cu in 1 M HCl solution with and without RR extracts, respectively. The LPR results are in excellent accordance with the EIS data, as shown in Table 1. Although RRF and RRL could protect the Cu in 1 M HCl solution, RRR almost does not change the corrosion rate of the metal in these conditions and thus cannot be used as a corrosion inhibitor. RRF provides the best protection capability. The best inhibitor (RRF), whose protection ability will be increased by more than 90% in the following section, will be the subject of additional research, as was previously stated.

Table 1. Electrochemical parameters obtained from LPR measurements in 1 M HCl solution in the absence and presence of 1000 ppm RRF, RRL, and RRR at 298 K

Inhibitor	R_p (Ω cm^2)	η %
1 M HCl	107	
RRF	270	60.3
RRL	195	45.1
RRR	112	4.7

The ability of RRF and RRL to protect the metal surface could be attributed to the formation of a protective film of extract molecules on the metal surface. Further research into the adsorbed molecules and protection mechanism is ongoing and will be reported later.

3.4. Potentiodynamic Polarization

Semi-logarithmic anodic current potential curves of Cu obtained in 1 M HCl in the absence and presence of the extracts are shown in Figure 3.

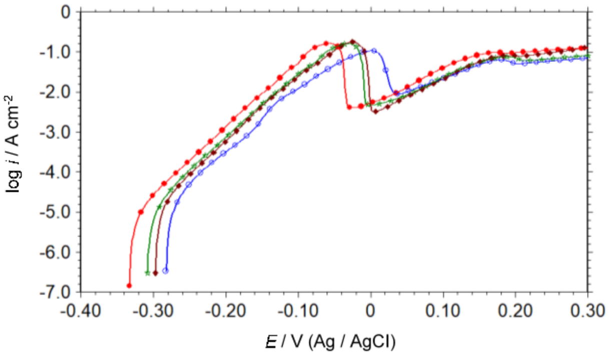


Figure 3. Polarization curves of Cu were obtained in 1 M HCl solution without (●) and with the addition of 1000 ppm RRF (○), RRL (♦), and RRR (☆) solutions after 1-hour exposure

As is seen in Figure 3, E_{ocp} of Cu in 1 M HCl without the extracts was -0.333 V. When the potential of the metal increases in these conditions the current density increases sharply due to the dissolution of Cu [38, 39].

$$Cu \rightarrow Cu^+ + e^- \qquad (2)$$

$$Cu^+ + Cl^- \rightarrow CuCl_{(s)} \qquad (3)$$

$CuCl_{(s)}$ deposits on the surface and diminishes the dissolution rate when the concentration of copper ions on the surface reaches its resolution constant. A passivation peak appears around -0.056 V as a result of $CuCl_{(s)}$ formation on the surface[38, 39]. Around -0.03 V, full passivation occurs. Because the $CuCl_{(s)}$ is not stable at the surface, the current density remains high. By increasing the potential scan to more positive potentials, the current density increases again, resulting in the formation of soluble cuprous complex $CuCl_2^-$ [39-41]:

$$CuCl_{(s)} + Cl^- \rightarrow CuCl_2^-{}_{(aq)} \qquad (4)$$

The E_{ocp} of Cu shifts toward more positive regions when the RR extracts are added to the corrosive media, and the current densities decrease, which is greater at the RRF. These findings are consistent with the $E_{ocp\text{-}t}$ measurements. Thus, polarization measurements show that the extracts are mixed-type corrosion inhibitor with a predominantly anodic action [37]. The lines are almost parallel around the Tafel region, indicating that the extracts inhibit corrosion without affecting the dissolution mechanism and that the dissolution reaction is controlled by activation. However, as described in the EIS studies, the overall reaction mechanism is diffusion controlled. Surface extract films work by simply blocking [37].

Table 2. Electrochemical data derived from polarization measurements obtained in 1 M HCl solution in the absence and presence of 1000 ppm RRF, RRL, and RRR at 298 K

Inhibitor	E_{ocp} (V)	$i_{-0.2\ V}$ (μA cm^{-2})
1 M HCl	-0.333	1348
RRF	-0.283	318
RRL	-0.297	592
RRR	-0.308	736

Table 2 contains some electrochemical data derived from these curves (More details will be given in the next studies). The polarization data in Figure 3 and Table 2 also show that RRF provides better corrosion protection. However, RRR's protection ability is very low, making it unsuitable for practical applications. On the other hand, RRF's protection ability needs to be improved for practical applications, and we will conduct additional studies as described above in the following studies.

3.5. Surface Characterization Studies

SEM images of Cu exposed to the extract containing HCl solution for 1 h are shown in Figure 4. Adsorption of the extract molecules results in the formation of compact and adherent organic films over the copper in the presence of the extract. These films act as a physical barrier between the corrosive solution and the metal surface. In the case of RRF, the best film is formed, which could explain the higher corrosion protection efficiency.

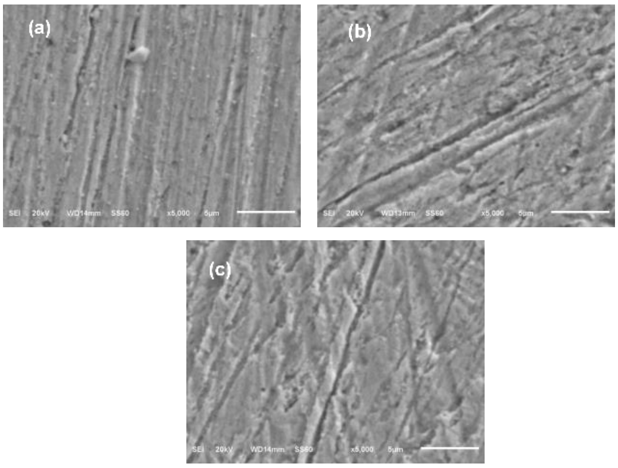
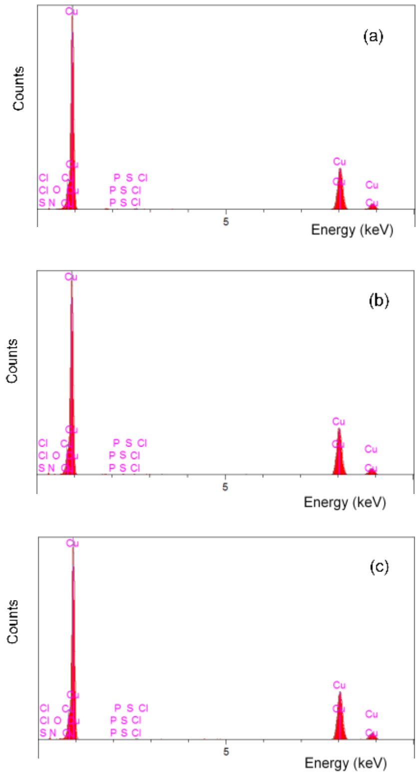


Figure 4. SEM images of Cu surface after exposure to 1 M HCl solution in the presence of 1000 ppm RRF (b), RRL (b), and RRR (c)

EDX measurements were used to examine the chemical composition of the same surfaces. Figure 5 depicts the obtained data. Because Cu does not contain C, O, S, N, or P, these metals are derived from the surface film formed by the molecules of plant extract. The presence of Cl- indicates the formation of $CuCl_x$ species on the bare metal regions under the film or in the film pores. There is no linear relationship between an element's composition and inhibition efficiency, which may be due to differences in the chemical composition of different parts of the plant.



Elt.	Conc
C	1.730
N	0.013
O	0.835
P	0.083
S	0.109
Cl	0.460
Cu	96.77

Elt.	Conc
C	1.012
N	0.061
O	0.352
P	0.084
S	0.260
Cl	0.269
Cu	97.963

Elt.	Conc
C	2.172
N	0.044
O	0.503
P	0.065
S	0.027
Cl	0.312
Cu	96.876

Figure 5. EDX spectrums and elemental composition of Cu surface after exposure to 1 M HCl solution in the presence of 1000 ppm RRF (b), RRL (b), and RRR (c)

Contact angle measurements were used to investigate the hydrophilic or hydrophobic properties of the RRF film formed on the surface, which performed better in terms of protection. The measurements of the other extract films were not performed even though future studies will only be performed on this extract to improve its protection efficiency. Figure 6 demonstrates the obtained data. Since having to add RRF to the corrosive solution, the surface's contact angle increases. The whole observation implies that the extract molecules are oriented and adsorbed to the surface along with more electronegative sites, and the surface's hydrophobic character tends to increase.

Figure 6. Contact angles of Cu surface after exposing to 1 M HCl solution in the absence and presence of 1000 ppm RRF

4. CONCLUSIONS

The extracts of different parts of ışgın such as flower (RRF), leaf (RRL), and root (RRR) were prepared and their protective effects on copper corrosion in 1 M HCl solution were investigated by electrochemical techniques. The surface of the metal after exposure to the test solutions was investigated by SEM, EDX, and contact angle measurements. The following major points could be concluded:

1) The effects of extracts obtained from various parts of the RR on copper behavior in an acidic environment differed.
2) The extracts adsorb on the Cu surface and form a compact and adherent film, which prevents the corrosion of Cu.
3) The RRF extract provided the best corrosion protection.
4) RRR extract was ineffective at protecting Cu from corrosion in 1 M HCl.
5) The extracts contained anodic and mixed-type corrosion inhibitors.
6) The addition of RRF to the corrosive solution increases the surface's hydrophobicity.
7) RRF has a corrosion protection efficiency of more than 60%, but the inhibition efficiency could be better.

More research, on the other hand, is required to improve RRF's protection effectiveness so that it can be used in real-world applications without risk. This study identified the plant part that best protects copper. We intend to improve the protection effectiveness in the following phase by adjusting factors such as extract concentration, exposure time, corrosive media type, and KI's synergistic effects. A licensed fitting program is currently kinetically analyzing data, and the results will be reported in another study.

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