The Use of Robinia Pseudoacacia L Fruit Extract as a Natural Corrosion Inhibitor in the Protection of Historical Bronze Objects

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Title Page:

The use of *Robinia pseudoacacia* L fruit extract as a natural corrosion inhibitor in the protection of historical bronze objects

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The Use of *Robinia pseudoacacia* L fruit extract as a natural corrosion inhibitor in the protection of historical bronze objects

Abstract

Background: The phenomenon of bronze disease is considered as the most important factor in the destruction of bronze objects. Different methods have been proposed to deal with it. The most important inhibitors used in this regard are BTA and AMT. While these inhibitors control the corrosion, they are toxic and cancerous. In ideal conditions, these inhibitors are able to slow down the activity of chlorine ion, but leave some side effects after a period of treatment. Today, plant extracts are used for this purpose. In this study, *Robinia pseudoacacia* L extract was selected for this purpose.

Material and methods: The acacia fruit extract (200ppm to 1800 ppm) was used to the prevention of corrosion inhibition of bronze alloy in corrosive sodium chloride solution 0.5 M. The Bronze alloy used in this research, was made based on the same percentage as the ancient alloys (Cu-10Sn). This alloy was used for the effect of corrosion inhibitors in the potentiostat device, the weight loss method. The experiment was conducted in split plot design in time based on the randomized complete design in four replications.

Results: Mean comparison showed that the highest rate of corrosion inhibition (93.5%) was obtained at a concentration of 1800 ppm and with increasing the concentration of the extract, corrosion inhibition also increased. EDX analysis of the control sample matrix showed that the amount of chlorine, which is the most important factor in the destruction of bronze disease, was 8.47%wt while in the presence of corrosive sodium chloride solution, after 4 weeks, the amount of chlorine detected was 3.20%wt. According to the morphology (needle and rhombus) of these corrosion products based on the SEM image, it can be said that they are of the type of atacamite and paratacamite that have caused bronze disease in historical bronze works. At higher concentrations of acacia extract, the presence and growth of fungi has been observed, which can cause poor performance of acacia extract in the long run.

Conclusion: the natural inhibitor of acacia fruit aqueous extract can play an effective role in inhibiting corrosion of bronze, but at higher concentrations, it became fungal, which can reduce the role of acacia fruit aqueous extract and even ineffective. Because natural inhibitors can play an effective role in preventing the corrosion of bronze works. But to get better performance of these inhibitors, more tests need to be done to improve and optimize.

Keywords: corrosion, bronze disease, natural inhibitors, acacia, potentiostat, SEM-EDX

Introduction

There are growing concerns about the use of corrosion inhibitors because some of these inhibitors are not only toxic to living organisms but also cause environmental damage although some may be helpful and non-toxic, they are probably less effective. When choosing an inhibitor, it is important to consider the cost of the inhibitor, access to the inhibitor (materials are often expensive if access is limited), and its environmental friendliness. Inhibitors are volatile, inactive (anodic), precipitated, cathodic, organic and inorganic compounds that prevent corrosion through adsorbing ions or molecules from the metal surface, increasing or decreasing anodic or cathodic reaction, reducing penetration rate of reactants on metal surface and electrical resistance of metal surface (Saeed et al. 2020; Verma et al. 2017; Yee 2004).

Inhibitors are generally substances which reduce the level of chemical reactions at appropriate concentrations. Corrosion inhibitors are active chemical species which help to slow down, delay or prevent corrosion, via different mechanisms, such as adsorption onto the metal surface that blocks active surface sites (Al-Moubaraki et al. 2017; Miralrio and Espinoza Vázquez 2020). These substances can inhibit the growth of biological agents and stop the physiological processes. The word “inhibitor” is rooted in the Latin word of “inhibere”, which means to prevent, protect or preserve. The inhibitor at low concentrations in corrosive medium delays the corrosion of metals (Barreto et al. 2017; Olajire 2017). These substances can be solid, liquid or gas, and used in closed, gaseous, and aqueous mediums (Groysman 2009; Ogawa et al. 2020).

Corrosion inhibitors reduce the rate of corrosion in several ways: (i) reduce the adsorption of ions/molecules on the metal surface; (ii) increase or decrease the anodic and/or cathodic reaction; to the metal surface, (iv) reduce the electrical resistance of the metal surface (Rani and Basu 2012).

Much attention has been paid to the use of corrosion inhibitors in protecting metal works (Keene and United Kingdom Inst. for Conservation 1985; Sushmitha and Rao 2019; Ye et al. 2020) [10-12]. Corrosion inhibitors in the form of non-soluble compounds on metal surfaces can provide better stability for metal corrosion. Using corrosion inhibitors is very common in protecting metal works. By forming a thin impermeable layer of the work, inhibitor compounds slow down the anodic and cathodic activities (Zucchi et al. 1996). This protection method can be used as the last and most common solution to fight bronze disease and get rid of this problem.

The inhibitory effect of BTA (Benzotriazole) and AMT (5-amino-2-mercapto-1, 3, 4-thiadiazole) on historical bronze art works has been proved previously (Artesani et al. 2020; Faltermeier 2013; Faltermeier and Archaeology 1992; Kumara et al. 2013). While these inhibitors have high efficiency, they have toxic and cancerous impacts on the environment. For this reason, natural inhibitors such as honey, fig juice (Pourzarghan et al. 2017), the extract of salvia (Vatankhah et al. 2011) and green tea extract (Vatankhah et al. 2013) have been examined and evaluated in recent years.

Most organic corrosion inhibitors have heteroatoms. P, O, N and S are known as active centers ($O < N < S < P$) for the adsorption process on the metal surface and have a higher electron density. These elements act as a corrosion inhibitor. The use of organic compounds containing oxygen, sulfur and especially nitrogen to reduce the corrosion attack on steel has been studied in detail. Most organic inhibitors have been shown to be adsorbed by displacing water molecules on the metal surface and forming a compact barrier. In addition, the availability of non-bonded electrons (single pair) and p in inhibitor molecules facilitates the transfer of electrons from the inhibitor to the metal (Rani and Basu 2012).

Corrosion control of metals is of technical, economic, environmental and aesthetic importance. The use of corrosion inhibitors is one of the best options for protecting metals and alloys. Organic corrosion inhibitors are somewhat toxic, so green corrosion inhibitors have been shown to be biodegradable because they are biodegradable and do not contain heavy metals or other toxic compounds. In addition to being environmentally friendly, plant products have acceptable environmental effects, are cheap, and are readily available and renewable. As a result, the corrosion inhibitory abilities of tannins, alkaloids, amino acids and organic dyes of plant origin are considered. Although significant research has been devoted to the inhibition of corrosion by plant extracts, reports on the exact mechanisms of the adsorption and identification process of the active substance are still scarce (Rani and Basu 2012).

Rosemary leaves were investigated as corrosion inhibitor for the Al + 2.5Mg alloy in a 3% NaCl solution at 25°C (Kliškić et al. 2000), and El-Etre studied natural honey as a corrosion inhibitor for copper (El-Etre 1998) and studied opuntia extract on aluminum (El-Etre 2003). The inhibitive influence of the extract of khillah (*Ammi visnaga*) seeds on the corrosion of SX 316 steel in HCl solution was determined utilizing weight loss amounts as well as the potentiostatic method. *Delonix regia* extracts inhibited the corrosion of aluminum in hydrochloric acid extracts (Abiola et al. 2007).

One of the most important causes of damage to historical monuments is bronze disease, one of the most important causes of this damage is chlorine ion (Scott 2011). Therefore, in the

present study, following various other researches, chloride medium has been used to study the corrosion process

The *Robinia pseudoacacia* L fruit extract was used for anti-corrosion effect on mild steel (Buchweishaija and Mhinzi 2008; Mohyaldinn et al. 2019; Nasab et al. 2019). In this experiment, *Robinia pseudoacacia* L fruit extract was used to evaluate the inhibitory effect on bronze alloy (Cu-10Sn).

The acacia plant, scientifically named *Robinia pseudoacacia* L from the *Papilionaceae* family, is one of the two-celled plants whose beautiful and ornamental flowers are cultivated by beekeepers to produce fragrant honey. The flowers also have a soothing, stomach tonic effect and astringent and biliary properties (Liu et al. 2020). The acacia plant (*robina psudoacacia*) is a fast growing tree. It has a broad crown with leaves consisting of 11-23 dark green oval leaflets. In the roots, bark, and seeds of the *Robinia pseudoacacia* L tree, there is a substance called Description Robin, and in the leaves and flowers, there is also a glucoside called Description Robinin. *Robinia pseudoacacia* L wood is hard and durable. For these reasons, it is of industrial and commercial importance and is used to build columns and scaffolding for mines, as well as to make sofas and chairs (Liu et al. 2020).

Mineral inhibitors such as chromate (hexavalent chromate, oxidizing) are stable in most systems but are known to be carcinogenic and have been implicated in bone, skin, kidneys and spleen and then they may even enter red blood cells in very small amounts (Engwa et al. 2019; Gray and Sterling 1950).

The phenomenon of bronze disease is considered to be the most important factor in the destruction of bronze objects. So far, various methods have been proposed to deal with it. The specific inhibitors used for this purpose are BTA and AMT. These inhibitors are toxic and carcinogenic during inhibitory control. Ideally, these inhibitors may be able to activate chlorine ions, but after treatment they may have some side effects (Monticelli et al. 2019; Pourzarghan et al. 2017).

Safety and environmental issues when using corrosion inhibitors in industry have always been a global concern. Because inhibitors are often toxic and carcinogenic. In addition, these toxic compounds are widely used in the protection of historical metal artifacts and some of them cause harmful effects on human health. These inhibitors may damage living tissue such as kidneys and liver. These toxic effects have led to the use of natural products (alternative corrosion inhibitors) as anti-corrosion agents, to reduce the dangerous effects on humans and the environment, which are environmentally friendly and range from rare earth elements to

organic compounds (Chugh et al. 2020; Finšgar and Jackson 2014; Izionworu et al. 2020; Xhanari et al. 2017).

Industrial and consumer interests in the development of green materials from abundant renewable resources have increased as they are readily available, are of low cost, and are nontoxic and biodegradable (Li et al. 2020; Vurro et al. 2019).

But one of the most important drawbacks of these inhibitors is that they are toxic. Although natural inhibitors have less inhibitory efficiency than organic inhibitors, their performance can also be optimized by re-treating these environmentally friendly inhibitors and making these inhibitors available.

The general compounds of The *Robinia pseudoacacia* L fruit extract contain the natural sugars of ramnoz, arabinose, and galactose, as well as gluconic acid, 4 methoxygluconic and rubinin (Karamalla et al. 1998; Mohamed et al. 2020; Raja and Sethuraman 2008).

Material and Methods

Preparation of plant and extract

Robinia pseudoacacia L fruit were obtained from the Agricultural and Natural Resources Research and Training Center of Isfahan (Fig. 1). *Robinia pseudoacacia* L fruit extract were obtained from the Art University of Isfahan in 2019.

Fruit samples collected were dried on a clean cloth and ground under appropriate conditions. 30 g of the resulting powder was soaked in 100 ml of double distilled water and shaken in a shaker for 24 hours at room temperature. The obtained liquid was then passed through sterile filter paper and finally the extract and powder were separated. The remaining particles in the extract were separated using a refrigerated centrifuge (2500 rpm) at 4 ° C for 20 minutes. The extract was dewatered using a vacuum rotary device. The obtained extract was turned into powder and stored in a dark glass at a temperature of 4 ° C. During the experiment, dilutions of 200 to 1800 ppm (Part per Million) were prepared from the extract (Fazeli-Nasab et al. 2017).

Experimental design

The acacia fruit extract (200, 400, 600, 800, 1000, 1200, 1400, 1600 and 1800 ppm) was used to the prevention of corrosion inhibition of bronze alloy in corrosive sodium chloride solution 0.5 M, for a period of four weeks consecutively. The experiment was conducted in split plot design in time based on the randomized complete design in four replications. Different concentrations of plant extracts were included in the main plots and the duration of application of the plant extract was in the sub-plots.

The Bronze alloy used in this research, was made based on the same percentage as the ancient alloys (Cu-10Sn)(The alloy used in the research, according to the ancient alloys, with 10% tin and 90% copper, was made by casting and finally analyzed to make electrodes and coupons). This alloy was used for the effect of corrosion inhibitors in the potentiostat device, the weight loss method.

Fig. 1 The characteristic of *Robinia pseudoacacia* L. plant

Preparation of solutions

Sodium chloride (0.5M) was used to make a control solution. This solution was poured into a special container at volume of 100 ml. After calibrating, the device begins to plot the polarization curve. In the polarization curve, the corrosion potential of the control solution (Sodium chloride M 0.5) was recorded -243 mV (Millivolts).

The acacia fruit extract was separately mixed and treated with a corrosive solution of sodium chloride 0.5 M with pH=5.5, so that its corrosion power could be examined by the potentiostat device(Table 1) (Pourzarghan et al. 2010). The corrosion potential of the control solution was obtained -243 mV. Based on the corrosion potential of the sample at the presence of the inhibitor solution, -222 mV indicates a shift in the direction of 21 mV to positive values, which

indicates that the type of inhibitor is combinatorial (mixed-type inhibitor (Some anodic and some cathodic)) (Fig. 2). In addition to change in potential of corrosion, a slight flow (Slight current drop) is also seen in the anodic branch.

If the potential increases continuously, the curve will be anodic polarization and also if the potential decreases continuously, the curve will be cathodic polarization. If polarization causes a slight change to positive or negative, the curve will be of the combined (mixed-type inhibitor) polarization type (Allen and Larry 2001; Li et al. 2017). It is related that Potentiodynamic if any compounds suppress has both the anodic and cathodic process, it behaves as mixed-type inhibitors (Wang et al. 2004).

Calculating the corrosion efficiency using potentiostat device calculations

$IE\%$ was used to obtain the inhibitory efficiency percentage (formula 1). In this formula, I_{corr} is density of the corrosion flow with inhibitory and I_0 is corrosion flow without inhibitory.

(1)

$$IE = \frac{I_0^{corr} - I_{corr}}{I_0^{corr}} \times 100$$

The corrosion current density (The corrosion current density is determined at a constant pH value of solution using no buffering additives and also it was calculated for the apparent specimen surface area)(Rybalka et al. 2016) can be calculated from the polarization resistance and the Stern-Geary constant and also R_p can be calculated from the resistance of polarization (equation 2) (Standard 2006).

(2)

$$R_p = \frac{B}{i_{corr}}$$

$$B = \frac{b_a * b_c}{2.303(b_a + b_c)}$$

b_a = slope of the anodic Tafel reaction, when plotted on base 10 logarithmic paper in V/decade,
 b_c = slope of the cathodic Tafel reaction when plotted on base 10 logarithmic paper in V/decade, and
 B = Stern-Geary constant, V.

In these experiments, corrosion flow density (formula 3), corrosion rate, and equivalent weight with the presence and absence of inhibitor were calculated by standard (ASTM (American Society for Testing and Materials), G 102-98) (Dean 1987; Tan et al. 2017).

(3)

$$i_{corr} = \frac{I_{corr}}{A}$$

i_{corr} : corrosion flow density ($\mu A/cm^2$)

I_{corr} : corrosion flow (μA)

A = contact surface (cm^2)

Corrosion rate is calculated based on the following equation

(4)

$$CR = K1 \frac{i_{corr}}{\rho} EW$$

CR = corrosion rate (mpy)

$K1=3.27 \times 10^{-3}$ (mm g/ μA cm yr)

ρ = density (g/cm^3)

Calculating the classic weight loss

Weight loss method is the simplest method for studying corrosion inhibitors due to the lack of need for device (except for using the digital scale). In this method, the weight variations of the metal sample are calculated before and after exposure to the corrosive medium (in the absence and presence of inhibitor). The time taken for this experiment is long, but as results of this method are more real than those of the electrochemical method, it is still used (Pourfarzad et al. 2020; Tang et al. 2006) [43, 44]. The classic weight loss can be calculated based on the IE formula (formula 5). In this formula, W_{corr} is the weight loss of the sample in the presence of the inhibitor and W_0 is the weight loss of the sample in the absence of the inhibitor.

(5)

$$IE = 1 - \frac{\Delta W_{inhibitor}}{\Delta W_{blank}} \times 100$$

In order to perform the experiment using the classic method, the prepared electrodes were cut with a percentage of (Cu-10Sn) as round coupons with a diameter of 0.73 cm and a thickness of 2 mm.

The coupons were polished using sandpaper with grades of 400, 800, and 2200. The coupons were degreased in alcohol and rinsed in distilled water. The rinsed samples were heated at 80 °C for one hour in an oven.

Then, coupons were placed in a desiccator for one hour. Finally, the coupons were weighed to be immersed in *Robinia pseudoacacia* L fruit extract. The inhibitory efficiency of the coupons were calculated each week for four week consecutively (formula 5). Hence, one of the coupons were removed from the control solution and *Robinia pseudoacacia* L fruit extract each week, after one month of immersion (From the first week to the end).

Determine the inhibitory efficiency of the *Robinia pseudoacacia* L fruit

In this paper, the potentiostat device, (SAMA 500 electro-analyzer system model (SAMA Research Center, Iran), was used to perform experiments to determine the inhibitory efficiency of the *Robinia pseudoacacia* L fruit. It included three electrodes, a platinum auxiliary electrode, a reference electrode of saturated chloride mercury (calomel) and a bar working electrode (Bard and Faulkner 2001; de Rooij 2003) with length of 7.5 cm and diameter of 0.73 cm with compound of Cu-10Sn). It was polished with sandpaper (grade from 400 to 2200). Each of these experiments was repeated four times. To calibrate the device, the LSV (Linear sweep voltammetry) Tafel plot technique was used. Additionally, the classical weight loss method, and finally, SEM-EDX (Scanning Electron Microscope-Energy Dispersive X-rays), manufactured by Philips Company of the Netherlands. The XL30 model were used to evaluate the surfaces of alloy as well as inhibitory efficiency of the *Robinia pseudoacacia* L fruit (Goyal et al. 2020; Pourzarghan et al. 2010).

Scanning Electron Microscope (SEM)

After preparing the coupons with a percentage of (Cu-10Sn), the coupons were completely polished using sandpaper with grades 400 to 2200 to create a completely smooth surface. Then, the coupons were rinsed with distilled water and degreased by alcohol. The samples were placed in an oven at 120 ° C for one hour. The coupons were immersed in *Robinia pseudoacacia* L with concentrations of 1000 ppm for 24 and 48 hours. After removing the coupons, they were dried at room temperature for one hour and photographed to examine the change in appearance

color on the coupon surfaces. To accelerate the corrosion, the samples were transferred to the humidity compartment. Coupons were placed in a relative humidity of 95 ± 2 and a temperature of 25 to 30 ° C. The samples underwent sodium chloride 0.5mM spray based on the standards of ASTM G85 and ISO 9227. Four weeks later, the samples were removed from the humidifier compartment and examined to evaluate the effect of the inhibitor on the coupon surfaces by using SEM-EDX device.

In order to determine the size and morphology of the nanoparticles produced using electron microscopy, the reaction mixture was centrifuged three times for 15 minutes at a speed of 12,000 rpm. Then a few drops of the resulting precipitate were dried on a piece of aluminum foil at room temperature and after drying, the electron microscope was photographed by Philips SEM machine (model CMC-300 KV, Netherlands).

Statistical analysis of data

After data collection, analysis of variance was performed by student statistic 9 software as well as comparison of means square using Duncan's multiple range test at one percent probability level.

Results

Polarization evaluation of Tafel acacia extracts

The Tafel polarization of *Robinia pseudoacacia* L fruit extract in 1200 ppm at the presence of a sodium chloride 0.5 M, was shown that the inhibitory corrosion potential is -216 mV. Based on the control solution, inhibitor chart has a shift of direction to positive values (Fig. 2). In addition to change in the corrosion potential, the flow in both the anodic and cathodic branches was decreased.

Fig. 2 Tafel polarization curve of *Robinia pseudoacacia* L fruit extract at 1200 ppm in the presence of a corrosive solution of sodium chloride 0.5 Mm

The Tafel polarization of *Robinia pseudoacacia* L fruit extract at 1400 ppm was shown showed that the inhibitory solution corrosion potential is -216 mV, which compared to control solution, it has a shift of direction to positive values (Fig. 3). The corrosion has also had slight drop (Slight current drop) in the anodic and cathodic branches.

Fig. 3 Tafel polarization curve of *Robinia pseudoacacia* L fruit extract at 1400 ppm in the presence of a corrosive solution of sodium chloride 0.5 Mm

The corrosion potential of the *Robinia pseudoacacia* L fruit extract was -213mV at 1600 ppm that it is showed displacement of 30mV, compared to the corrosion solution (Fig. 4). A slight drop (Slight current drop) is also observed in the anodic branch.

Fig. 4 Tafel polarization curve of *Robinia pseudoacacia* L fruit extract at 1600 ppm in the presence of a corrosive solution of sodium chloride 0.5 Mm

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The corrosion potential of the *Robinia pseudoacacia* L fruit extract was -213mV at 1800 ppm that it is showed displacement of 30mV, compared to the corrosion solution (Fig. 5). A slight drop (Slight current drop) is also observed in the anodic branch.

Fig. 5 Tafel polarization curve of *Robinia pseudoacacia* L fruit extract at 1800 ppm in the presence of a corrosive solution of sodium chloride 0.5 M

The inhibitory efficiency of *Robinia pseudoacacia* L fruit extract

The results of the analysis of variance showed that the main effects (different concentrations of aqueous acacia extract and duration of treatment) as well as the interaction of the extract and duration were effective on corrosion inhibition ($P < 0.01$) (Table 1). Mean comparison showed that the highest rate of corrosion inhibition (93.5%) was obtained at a concentration of 1800 ppm and with increasing the concentration of the extract, corrosion inhibition also increased, ie more bronze was prevented from burning (Fig. 6). Also, the highest corrosion inhibitory activity of acacia extract (79.66) was in the second week and with increasing duration, this effect has decreased (Fig. 7).

Table 1 Analysis of variance of the effect of aqueous extract of acacia fruit and duration of treatment on corrosion inhibition of bronze

Source	DF	SS	MS	F
Concentration of extract	8	33320.9	4165.11	134.50**

r	3	197.9	65.96	
Error r* Concentration of extract	24	743.2	30.97	
Week (period of time)	3	11575.7	3858.58	157.28**
Concentration of extract *week	24	16934.4	705.60	28.76**
Error r* Concentration of extract *week	81	1987.2	24.53	
Total	143	64759.3		
CV(r* concentration)			8.12	
CV(r* concentration *week)			7.23	

** is significant at one percent level

Fig. 6 the effect of mean square of different concentrations of aqueous extract of acacia fruit on preventing corrosion inhibition of bronze (Similar letters indicate no significant differences in the studied treatments)

Fig. 7 the effect of mean square of acacia fruit extract duration on bronze prevent corrosion inhibition (Similar letters indicate no significant differences in the studied treatments)

some traits like corrosion flow, corrosion potential, electrolyte resistance, flow density, cathodic and anodic slope coefficients, and corrosion rate of *Robinia pseudoacacia* L fruit was investigated by Potentiostat device (Table 2). As the result, the relationship between potential, current intensity and corrosion diagram was obtained based on the using of the anodic and cathodic hypertrophy, measuring the potential difference between this electrode and the reference electrode, as well as measuring the anodic and cathodic current intensity. Using the data derived from the Potentiostat device (Table 2), the Weight reduction rates of *Robinia pseudoacacia* L fruit extract was calculated.

The Weight-reduction rate method is the simplest in the study of corrosion inhibition due to the lack of need for a device. This experiment takes a long time, but because the results of this method are more realistic than the electrochemical method, it is still used.

The results of the analysis of variance showed that the effect of different concentrations of acacia aqueous extract on bronze weight reduction rate was significant ($P < 0.01$). In the study of the Weight reduction rates method, the results showed that the least Weight reduction rate occurred at a concentration of 1800 ppm of acacia extract (fig. 8), in general, the alloy weight loss was least with increasing the concentration of acacia extract (fig 9). These results are the same as results that were obtained by device

Table 2 Calculation of corrosion flow, corrosion potential, electrolyte resistance, flow density, cathodic and anodic slope coefficients*, and corrosion rate of *Robinia pseudoacacia* L fruit with a Potentiostat device

Concentration	$-E_{corr}$	R_p	B_a	B_c	I	$i_{corrosion}$	Corrosion
<i>Robinia pseudoacacia</i>	(mv)	(ohm)	(v/dec)	(v/dec)	corrosion	(A/cm ²)	rate (mpy)
L (W/V)					(A)		
blank	243	800.5	0.060	0.066	2.716*10 ⁻⁵	6.497*10 ⁻⁵	28.381
200 ppm	211	1244	0.061	0.084	1.748*10 ⁻⁵	4.181*10 ⁻⁵	18.264
400 ppm	228	1315	0.072	0.079	1.653*10 ⁻⁵	3.955*10 ⁻⁵	17.276
600 ppm	214	1268	0.061	0.068	1.714*10 ⁻⁵	4.102*10 ⁻⁵	17.091
800 ppm	219	1508	0.082	0.090	1.442*10 ⁻⁵	3.0449*10 ⁻⁵	15.066
1000 ppm	222	1765	0.059	0.072	1.232*10 ⁻⁵	2.947*10 ⁻⁵	12.873
1200 ppm	216	1573	0.067	0.095	1.382*10 ⁻⁵	3.306*10 ⁻⁵	14.441
1400 ppm	214	1734	0.077	0.108	1.254*10 ⁻⁵	2.99*10 ⁻⁵	13.100
1600 ppm	219	1218	0.076	0.104	1.785*10 ⁻⁵	4.27*10 ⁻⁵	18.652
1800 ppm	213	1029	0.121	0.117	2.113*10 ⁻⁵	5.054*10 ⁻⁵	22.077

* Anodic and cathodic slopes were plotted on the anodic and cathodic branches and finally the device automatically calculated these slopes.

Fig. 8 the Weight reduction rates based on 1800 ppm concentration of *Robinia pseudoacacia* L from one to four weeks floatation

Fig 9 the effect of mean square of different concentrations of aqueous extract of acacia fruit on the weight reduction rate of bronze(Similar letters indicate no significant differences in the studied treatments)

Use of SEM to evaluate the performance of acacia fruit extract on the surface of coupons

Aqueous extract of acacia fruit was able to prevent corrosion of bronze by increasing the concentration but to further confirm the role of the extract, electron microscopy was used. After removing the coupons from the control (no extract) and aqueous extracts of acacia fruit, the coupons were examined under a microscope to check the bronze level and corrosion. The examination of the surface of the control coupon revealed that it had green and localized corrosion products (Fig. 10). However, it was observed that the surface of the same coupons were covered after being placed in corrosive solution and acacia extract (Fig. 11), and no trace of corrosion products were observed on the surface of the alloy (Fig. 12).

Scanning electron microscopy was used to evaluate and accurately perform this inhibitor on the surface of these coupons. In the SEM images of the control coupon (Fig. 13), the corrosion products in the grain boundaries were identified and showed the high impact of the corrosive environment on this alloy. According to the morphology (needle and rhombus) of these corrosion products, it can be said that they are of the type of atacamite and paratacamite that

have caused bronze disease in historical bronze works. These corrosion products are mostly concentrated in the grain boundaries.

Although the aqueous extract of acacia fruit creates a uniform layer, which covers the surface of the alloy and prevents the formation of corrosion products on the surface of these coupons (Fig. 11) the SEM images showed that grain corrosion was induced in this alloy in the presence of acacia extract (Fig. 13). At higher concentrations of this extract, i.e. from 1000 to 1800 ppm, after immersion of the samples in the presence of acacia extract and 0.5 M sodium chloride solution, the presence and growth of fungi have been observed, which can cause poor performance of acacia extract in the long run.

EDX analysis of the control sample matrix showed that the amount of chlorine, which is the most important factor in the destruction of bronze disease, was 8.47wt (Fig. 14). Based on the EDX results on the sample containing acacia extract, it can be conclude that the amount of chlorine detected was 3.20wt in the presence of corrosive sodium chloride solution after four weeks. These results indicate that the amount of chlorine in the presence of inhibitor was least (Fig. 15).

In the present study, it was found that the natural inhibitor of acacia fruit aqueous extract can play an effective role in inhibiting corrosion of bronze, but at higher concentrations and by increasing the duration of treatment, the fungus has grown in the natural inhibitor. These fungal can reduce and even ineffective the role of acacia fruit aqueous extract. Natural inhibitors can play an effective role in preventing of corrosion. However to get better performance of these inhibitors, more tests need to be done to improve and optimize their performance.

Fig. 10 Coupons in a corrosive solution of sodium chloride 0.5 after 30 days of immersion. 60 x magnification (A); coupons in a corrosive solution of sodium chloride 0.5 after 30 days of immersion. 40 x magnification (B)

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Fig. 11 Coupon in the presence of *Robinia pseudoacacia* L inhibitor with a concentration of 1000 ppm after 30 days of immersion. 60x magnification (A); coupon in the presence of *Robinia pseudoacacia* L inhibitor with a concentration of 1800 ppm after 30 days of immersion. 40x magnification (B)

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Fig. 12 Coupon in the presence of *Robinia pseudoacacia* L inhibitor with a concentration of 1000 ppm after 30 days of immersion. 20x magnification (A); coupon in the presence of *Robinia pseudoacacia* L inhibitor with a concentration of 1800 ppm after 30 days of immersion. 20x magnification

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480

Fig. 13 SEM analysis of control sample versus Sodium chloride 0.5 M corrosive solution (A); SEM analysis of coupon surface containing inhibitor at the presence of Sodium chloride 0.5 M corrosive solution

Fig. 14 EDX analysis of control sample versus Sodium chloride 0.5 M corrosive solution

Fig. 15 EDX analysis of coupon surface containing inhibitor at the presence of Sodium chloride 0.5 M corrosive solution

Discussion

So far, different results have been reported regarding the use of the plants extract on the prevention of corrosion. The extract of *Salvia officinalis* and its efficiency in corrosion

inhibitory investigated in 0.5 M NaCl. The results indicated that the extract of *Salvia officinalis* acted as a cathodic inhibitor and the inhibitory efficiency increased with increasing sage extract concentration. The results of the weight loss test reported between 32 and 41% (Vatankhah et al. 2011).

In the present study, the Potentiostat device method and also the classic method of weight loss used to determine the efficiency of corrosion inhibitory. The results shown that this efficiency in the Potentiostat device method was 92% but in the classical method was equal to 55% that more has been mentioned than research (Vatankhah et al. 2011). Because acacia contained flavonoids and phenolic compounds with a complex structure and high molecular weight, it was expected to prevent corrosion, but it did not.

The inhibitory effect of two natural honeys (oak and acacia) with a mixture of black horseradish juice on corrosion of tin in aqueous media and sodium chloride solution by weight loss methods and polarization techniques has been studied. The results showed that the yield of acacia honey was lower than oak honey and by adding black horseradish juice to both honeys, their yield increased. The inhibition efficiency (IE) of all the inhibitors examined obtained by both methods used decrease in order: chestnut honey with black radish juice > acacia honey with black radish juice > chestnut honey > acacia honey (Radojčić et al. 2008). It has been found that acacia extract has less effect than black horseradish extract. In the present study, acacia extract had a positive effect at 1000 ppm, but with increasing acacia extract, the corrosion inhibitory effect decreased.

Natural honey has been studied as a corrosion inhibitor of carbon steel in high-salt environments. Inhibitory efficiency has been calculated through weight loss and static potential polarization technique and the results have introduced natural honey as a suitable inhibitor for corrosion of steel in high-salt environments. However, this beneficial effect has been limited to a certain level and after a while, due to the growth and development of fungi, its inhibitory efficiency has been reduced (El-Etre 1998). In the present study, acacia extract had a fungal growth of 1800 ppm, which over time reduced the inhibitory effect.

Inhibition of organic compounds such as honey and rosemary (*Salvia rosmarinus* L.) on four metals, aluminum, copper, iron and zinc in sodium chloride and sodium sulfate solution has been investigated. The results showed that the inhibitors had no effect on aluminum in sodium chloride and sodium sulfate solutions. The reason why honey is not inhibited is that honey may play a small cathodic inhibitory role on aluminum when placed in polarized sodium chloride solution (Yee 2004). Perhaps the reason for not increasing the inhibition of acacia extract by increasing the concentration of the extract to 1800 ppm and the inhibition oscillation between

cathode and anodic is also due to the fact that the role of cathodic and anodic inhibition after oscillation in polarized sodium chloride solution has decreased. However, it can have another reason, such as less absorption power on the bronze (Cu-10Sn).

The Corrosion inhibition of steel in hydrochloric acid conducted by betanin as a green inhibitor. The results obtained showed that betanin is a good “green” inhibitor for mild steel in 1 M HCl solution. Scanning electron microscopy observations of the steel surface confirmed the protective role of the inhibitor. The polarization curves showed that betanin behaves mainly as a mixed-type inhibitor (Ashassi-Sorkhabi and Es’haghi 2009). the Corrosion Inhibition by Beet Root (BR) Extract conducted and the results were shown that the BR extract with 50 ppm Zn^{2+} had about 98% inhibition efficiency to carbon steel immersed in well water(the results shown that a mixed-type effect existed between BR extract and Zn^{2+}) (Selvi et al. 2009). In the present study, the results indicate that the type of inhibitor is mixed-type inhibitor.

Conclusion

Given the investigations on *Robinia pseudoacacia* L fruit using potentiostat device, it was revealed that the data derived from this device showed that *Robinia pseudoacacia* L fruit inhibitory efficiency at 1800 ppm with a corrosion rate of 12.78% is 55% for bronze alloy with percentage of (Cu-10Sn) and has a mixed inhibitory effect. In the classic weight reduction rate, (in which the results are more real than those in electrochemical methods), the inhibitory efficiency of *Robinia pseudoacacia* L fruit was determined to be 92%. SEM images derived from the surface of coupons at the presence of *Robinia pseudoacacia* L and a corrosive solution of sodium chloride 0.5 M shown a kind of segregation on the surface of coupons in the presence of a corrosive solution. Based on the experiments performed, it is necessary to add other natural compounds to this inhibitor for better efficiency so that appropriate and optimal conditions for this type of inhibitor can be defined.

One of the points that should be considered during the restoration process is not to change the structure and appearance of the historical monument. Since corrosion in a metal monument, especially copper and bronze, has a special place and importance from a historical, structural and sometimes aesthetic point of view. As the result it seems necessary to pay more attention to the rate of color changes after the application of new materials.

Abbreviation

BTA: Benzotriazole

SEM-EDX: Scanning Electron Microscope-Energy Dispersive X-rays

560 LSV: Liner sweep voltammetry
561 ASTM: American Society for Testing and Materials
562 EDX: Energy Dispersive X-rays
563 PPM: Part Per Million
564 mV = Millivolts
565 AMT: 5-ami- no-2-mercapto-1,3,4-thiadiazole
566

567 **Conflict of interest**

568 All authors declare no conflict of interest exists.

569 **Ethics approval and consent to participate**

570 No human or animals were used in the present research.

571 **Consent for publications**

572 All authors read and approved the final manuscript for publication.

573 **Availability of data and material**

574 All the data is embedded in the manuscript.

575 **Authors' contributions**

576 V.P. and B.F.Z.N. designed the research and wrote the paper. All authors read and approved
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Figures

Figure 1

The characteristic of *Robinia pseudoacacia* L. plant

Figure 2

Tafel polarization curve of Robinia pseudoacacia L fruit extract at 1200 ppm in the presence of a corrosive solution of sodium chloride 0.5 Mm

Figure 3

Tafel polarization curve of Robinia pseudoacacia L fruit extract at 1400 ppm in the presence of a corrosive solution of sodium chloride 0.5 Mm

Figure 4

Tafel polarization curve of Robinia pseudoacacia L fruit extract at 1600 ppm in the presence of a corrosive solution of sodium chloride 0.5 Mm

Figure 5

Tafel polarization curve of *Robinia pseudoacacia* L fruit extract at 1800 ppm in the presence of a corrosive solution of sodium chloride 0.5 M

Figure 6

the effect of mean square of different concentrations of aqueous extract of acacia fruit on preventing corrosion inhibition of bronze (Similar letters indicate no significant differences in the studied treatments)

Figure 7

the effect of mean square of acacia fruit extract duration on bronze prevent corrosion inhibition (Similar letters indicate no significant differences in the studied treatments)

Figure 8

the Weight reduction rates based on 1800 ppm concentration of Robinia pseudoacacia L from one to four weeks floatation

Figure 9

the effect of mean square of different concentrations of aqueous extract of acacia fruit on the weight reduction rate of bronze(Similar letters indicate no significant differences in the studied treatments)

Figure 10

Coupons in a corrosive solution of sodium chloride 0.5 after 30 days of immersion. 60 x magnification (A); coupons in a corrosive solution of sodium chloride 0.5 after 30 days of immersion. 40 x magnification (B)

Figure 11

Coupon in the presence of *Robinia pseudoacacia* L inhibitor with a concentration of 1000 ppm after 30 days of immersion. 60x magnification (A); coupon in the presence of *Robinia pseudoacacia* L inhibitor with a concentration of 1800 ppm after 30 days of immersion. 40x magnification (B)

Figure 12

Coupon in the presence of *Robinia pseudoacacia* L inhibitor with a concentration of 1000 ppm after 30 days of immersion. 20x magnification (A); coupon in the presence of *Robinia pseudoacacia* L inhibitor with a concentration of 1800 ppm after 30 days of immersion. 20x magnification

Figure 13

SEM analysis of control sample versus Sodium chloride 0.5 M corrosive solution (A); SEM analysis of coupon surface containing inhibitor at the presence of Sodium chloride 0.5 M corrosive solution

Figure 14

EDX analysis of control sample versus Sodium chloride 0.5 M corrosive solution

Figure 15

EDX analysis of coupon surface containing inhibitor at the presence of Sodium chloride 0.5 M corrosive solution