

Antioxidant Capacity and Corrosion Inhibition Efficiency of *Sambucus nigra* L. Extract



This work is licensed under a Creative Commons Attribution 4.0 International License

I. Martinović,* G. Zlatić, Z. Pilić, M. Šušak, and F. Falak

Department of Chemistry, Faculty of Science and Education, University of Mostar, Matice Hrvatske bb, Mostar, Bosnia and Herzegovina

doi: <https://doi.org/10.15255/CABEQ.2023.2180>

Original scientific paper
Received: January 23, 2023
Accepted: April 4, 2023

The cyclic voltammogram recorded in the potential range between 0 V and 800 mV with scan rate of 100 mV s⁻¹ was used to determine the measure of antioxidants content (antioxidant capacity) present in *Sambucus nigra* L. extract. The antioxidant capacity of the extract was 4.06 mg GAE g⁻¹ fw (mg of gallic acid equivalents per gram of fresh weight of the extract). The corrosion inhibition efficiency of *Sambucus nigra* L. extract on aluminium, copper, and bronze in 3 % NaCl solution was studied by potentiodynamic polarization and electrochemical impedance spectroscopy. Polarization data showed that extract acted as a mixed-type inhibitor, that the corrosion inhibition process was spontaneous physical adsorption ($\Delta G \approx -16$ kJ mol⁻¹) of the extract molecules on metals surfaces and followed Freundlich isotherm. Impedance spectroscopy studies revealed that increasing the concentration of extract reduced the double-layer capacitance and increased the charge transfer resistance. The highest inhibition efficiencies (Cu: ~57 %, CuSn14: ~74 % and Al: ~58 %) were achieved for an extract concentration of 1.0 g L⁻¹.

Keywords

antioxidant capacity, corrosion, inhibition, *Sambucus nigra* L. extract

Introduction

Aromatic and medicinal plants contain a high amount of bioactive compounds allowing their use in different sectors (industry, buildings, and agriculture, pharmaceutical, cosmetic, and food industries). Over the last decades, due to increasing awareness of ecological and health risks associated with commercial inhibitors, plant extracts have been studied as a source of green corrosion inhibitors as they are easily biodegradable and readily available¹⁻⁷. Natural products are known for their ecological, antimicrobial, antioxidant, and anticorrosion properties, which are attributed to the presence of active compounds (phenols, flavonoids, tannins, etc.). Investigations have shown a relationship between antioxidant/free radical scavenging activity of the extracts and the anticorrosive properties⁸. While the antioxidant properties of plants cannot be the sole criterion for their anticorrosive properties, they can be used to evaluate and predict the applicability of natural products for such purposes.

In this work, we studied the antioxidant capacity of the extract of *Sambucus nigra* L. (elderberry), and the possibility of extract use as a green corrosion inhibitor. The black elder (*Sambucus nigra* L.) is widely distributed throughout Europe, and is a source of phytochemicals, such as flavonoids, phe-

nolic acids, different organic acids, lipids, flavonoids, terpenoids, alkaloids, major and trace elements (K, Ca, P, Mg, ...) and vitamins⁹. Due to their beneficial properties (antioxidant, anti-carcinogenic, immune-stimulating, anti-allergic, anti-viral and anti-bacterial properties), elderberries are used in the food industry (jams, yogurts, beverages) and in folk medicine^{9,10}. Since *Sambucus nigra* L. has a high antioxidant capacity due to the presence of high amounts of flavonols, phenolic acids, and anthocyanins, the primary objective this study was to investigate the antioxidant capacity of *Sambucus nigra* L. extract.

Previous studies have shown that plant extracts can be effective corrosion inhibitors for various metals in a corrosive medium. Extracts from *Treculia africana* leaves¹, *Linum usitatissimum* seeds⁶, rice straw⁷, *Alchemilla vulgaris* L.¹¹ and *Ocimum basilicum* seeds¹² effectively inhibited aluminium corrosion in chloride media, with inhibition efficiencies ranging from 70 % to 95 %.

Inhibition of copper corrosion in 0.5 M HCl solution showed efficiency of *Morinda tinctoria*¹³ and Jujube¹⁴ aqueous extracts of up to 83 % and 93 %, respectively. In 0.5 M NaCl, the inhibition efficiency of aqueous and hydrolysis acid extracts of olive leaf for copper corrosion was found between 81 % and 95 %¹⁵. *Aloe saponaria* extract showed an inhibition efficiency of 90 % for bronze B66 in 3 % NaCl¹⁶.

*Corresponding author: ivana.martinovic@fpmoz.sum.ba

Nonetheless, there is still a great interest for research on other plants that can be used as non-toxic, inexpensive, renewable, and readily available corrosion inhibitors.

The abundance of *Sambucus nigra* L. throughout Europe and no literature on its corrosion inhibiting properties makes it very interesting for studying as a corrosion inhibitor for metals. Therefore, the second objective was to investigate the corrosion inhibition of copper, bronze, and aluminium, with *Sambucus nigra* L. extract in a 3 % NaCl solution using electrochemical techniques. In a neutral NaCl medium, we attempted to simulate seawater due to the aggressiveness of chloride-containing environments in which surface oxide films break down and rapid corrosion occurs.

Materials and methods

Preparation of *Sambucus nigra* L. extract (SN)

The fresh flowers of the *Sambucus nigra* L. were collected in spring 2022, in Mostar, Bosnia and Herzegovina. The stock solution for determining the antioxidative capacity of SN was prepared by immersing 2.9000 ± 0.0001 g of *Sambucus nigra* L. flowers in 200 mL of sodium acetate buffer pH 3.6, 0.1 mol L^{-1} (SAB), and left for three-hour maceration. The sample was then filtered through a $0.45 \mu\text{m}$ filter paper, and diluted up to 200 mL.

The stock solution of SN for corrosion research was prepared by macerating 1.0 g of *Sambucus nigra* L. flowers in 1 L of 3 % NaCl at room temperature for 3 h. Extract solutions (0.05, 0.10, 0.50, and 1.00 g L^{-1}) were prepared by dilution of stock solution.

Electrochemical measurements

All measurements were performed with an Autolab PGSTAT320N controlled by a personal computer using Nova 1.5 software. The electrochemical measurements were performed in a standard three-electrode cell. The counter electrode was a platinum electrode, and the reference electrode, to which all measured potentials were referred, was an Ag | AgCl | 3 M KCl. The study was performed with aluminium (99.99 %), copper (99.97 %; Ag, Bi, Pb, Sb, As, Fe, Ni, Sn, Zn, S, Se, Te as trace elements), bronze CuSn14 (Cu, 85.2 %, Sn, 13.9 %, and Pb 0.9 %), and graphite as the working electrodes. The surface areas of the aluminium, copper, bronze CuSn14, and graphite exposed to the electrolyte were 0.636, 0.502, 0.785, and 0.283 cm^2 , respectively. Prior to each measurement, the elec-

trodes were polished with SiC paper (150 to 1000 grit), degreased in ethanol in an ultrasonic bath, and rinsed with distilled water. The graphite electrode was abraded using silicon carbide paper of 1200 grit. All measurements were performed in triplicate to ensure reproducibility.

Electrochemical determination of antioxidant capacity was investigated by cyclic voltammetry (CV) with a graphite electrode as a working electrode, where sodium acetate buffer pH 3.6 (our recent study showed that highest values of GAE were reached for the lowest pH¹⁷), 0.1 mol L^{-1} (SAB) solution served as electrolyte.

To examine the electrochemical behaviour of antioxidants present in an aqueous extract of SN, cyclic voltammograms were recorded for 50 mL of sample in the potential range between 0 V and 800 mV, and scan rate of 100 mV s^{-1} . Cyclic voltammograms were also recorded for the standard solution of gallic acid (GA) in the concentration range of $5.99\text{--}272.72 \text{ mg L}^{-1}$ to quantify the polyphenolic content of examined extract, where the final result of the antioxidant capacity of the tested sample was expressed in equivalents of GA per gram of fresh weight ($\text{mg GAE g}^{-1} \text{ fw}$). Gallic acid equivalent (GAE) for the tested sample was calculated from the anodic charge Q_A , determined from the peak area around the potential of 460 mV using a calibration curve ($y = 8 \cdot 10^{-8}x + 3 \cdot 10^{-7}$, $R^2 = 0.9929$) obtained by cyclic voltammograms of GA.

The corrosion behaviour of metals and inhibition efficiency of *Sambucus nigra* L. extract was investigated by potentiodynamic polarization (PP) and electrochemical impedance spectroscopy measurements (EIS) with aluminium, copper, and bronze CuSn14 as the working electrodes. The electrochemical measurements were conducted in a 3 % NaCl solution in the absence and presence of different *Sambucus nigra* L. extract concentrations. Before each PP and EIS measurement, working electrodes were immersed in the test solution for 30 minutes to reach a stable open circuit potential (E_{OCP}). The PP curves were obtained in the potential ranges of -200 to 200 mV with respect to open circuit potential at a scan rate of 1.0 mV s^{-1} . Electrochemical impedance spectroscopy was measured in the frequency range of 10 kHz to 5 mHz using $\pm 10 \text{ mV AC}$ perturbation (rms). EIS data were modelled with software NOVA1.5, which exploits a nonlinear least square regression to fit the data with the function from the equivalent circuit, using the Levenberg–Marquardt algorithm. The standard criteria for evaluation of EEC best fit were followed: chi-square error was low ($\chi^2 \leq 10^{-4}$), and the acceptable errors of elements in fitting mode (5 %).

Results and discussion

Electrochemical methods can be used to rapidly test the antioxidant activity of many compounds, including polyphenols. One of the most commonly used electrochemical techniques is cyclic voltammetry, which focuses on the correlation between chemical structure, oxidation potential, and antioxidant activity of individual compounds^{18–23}.

A cyclic voltammogram for SN extract in SAB recorded in the 0–800 mV potential range with scan rate of 100 mV s⁻¹ is given in Fig. 1. The figure shows an irreversible oxidation peak around 460 mV, which could be attributed to the oxidation of polyphenolic compounds with gallate or ortho-dihydroxy-phenol groups^{17,24–26}.

The chemical composition of *Sambucus nigra* L. was studied comprehensively, which led to the identification of many secondary metabolites. The most abundant polyphenolic compounds found were flavonoids, most of which were identified as anthocyanins and quercetins^{27–30}. These compounds contain atoms with free electron pairs through which they can be adsorbed on the metal surface, form a complex compound (with metal), and thus alter the structure of the metal or alloy's protective film^{31,31}.

The antioxidant capacity of the examined plant extract, calculated from the cyclic voltammogram of SN presented in Fig. 1, was 4.06 mg GAE g⁻¹ fw. This was in accordance with earlier studies, where the total content of polyphenols found in fresh elderberry flowers ranged from 364–582 mg GAE/100 g fw²⁷.

The extract was then subjected to further electrochemical tests to evaluate the adsorption mechanism of SN extract on the surface of copper, bronze CuSn14, and aluminium in a 3 % NaCl solution.

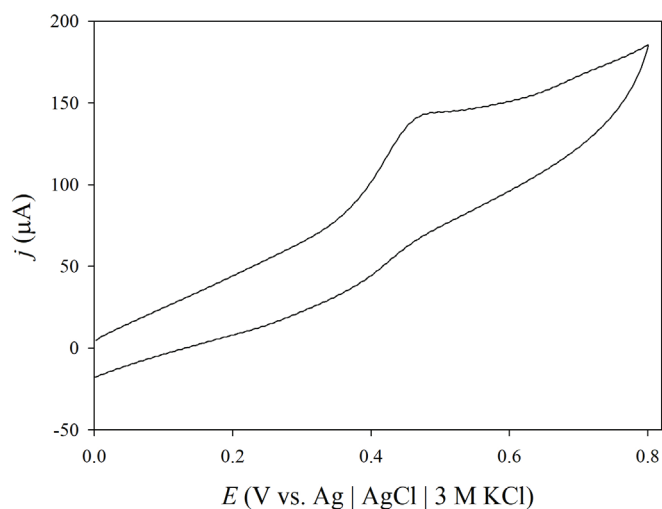


Fig. 1 – Cyclic voltammogram of *Sambucus nigra* L. extract in sodium acetate buffer solution, pH 3.6 recorded at scan rate of 100 mV s⁻¹

Potentiodynamic polarization

The potentiodynamic polarization curves obtained for copper, bronze CuSn14, and aluminium in 3 % NaCl with and without SN extract are shown in Fig. 2. The corrosion current density (j_{corr}) and corrosion potential (E_{corr}) obtained by extending the linear portion of the cathodic and anodic Tafel plots, surface coverage θ , and inhibition efficiency η , calculated using equations (1) and (2) are listed in Table 1.

$$\theta = \frac{j_{\text{corr}}^0 - j_{\text{corr}}}{j_{\text{corr}}^0} \quad (1)$$

$$\eta = \theta \cdot 100 \quad (2)$$

where j_{corr}^0 and j_{corr} represent the corrosion current densities of the metal electrode in the absence and presence of SN extract, respectively.

From the polarization curves, it can be seen that corrosion current density decreased with an increase in concentration of SN extract for all examined metals, indicating the formation of a film of the extract on the metal surface. With the reduction in corrosion current density with the addition of SN extract, there was an increase in inhibition efficiency, η and maximum values of 57.3, 73.5, and 58.4 % for Cu, CuSn14, and Al, respectively for the extract concentration of 1.0 g L⁻¹.

The presence of *Sambucus nigra* L. extract increased the corrosion resistance of metals due to blocking of active sites, although the inhibition efficiency was different for each metal.

Table 1 – Electrochemical parameters obtained from potentiodynamic polarization plots shown in Fig. 2, and calculated values of surface coverage, θ and inhibition efficiency, η

metal	$\gamma_{\text{SN extract}}$ (g L ⁻¹)	E_{corr} (V)	j_{corr} (A cm ⁻²)	θ	η (%)
Cu	Blank	-0.20	$3.82 \cdot 10^{-6}$	–	–
	0.05	-0.20	$3.29 \cdot 10^{-6}$	0.138	13.8
	0.10	-0.22	$2.81 \cdot 10^{-6}$	0.267	26.7
	0.50	-0.17	$2.26 \cdot 10^{-6}$	0.408	40.8
	1.00	-0.17	$1.63 \cdot 10^{-6}$	0.573	57.3
CuSn14	Blank	-0.23	$1.09 \cdot 10^{-5}$	–	–
	0.05	-0.22	$8.25 \cdot 10^{-6}$	0.243	24.3
	0.10	-0.22	$7.28 \cdot 10^{-6}$	0.332	33.2
	0.50	-0.18	$5.65 \cdot 10^{-6}$	0.482	48.2
	1.00	-0.19	$2.89 \cdot 10^{-6}$	0.735	73.5
Al	Blank	-0.82	$1.50 \cdot 10^{-6}$	–	–
	0.05	-0.80	$1.33 \cdot 10^{-6}$	0.113	11.3
	0.10	-0.76	$1.24 \cdot 10^{-6}$	0.173	17.3
	0.50	-0.77	$9.39 \cdot 10^{-7}$	0.441	44.1
	1.00	-0.79	$6.24 \cdot 10^{-7}$	0.584	58.4

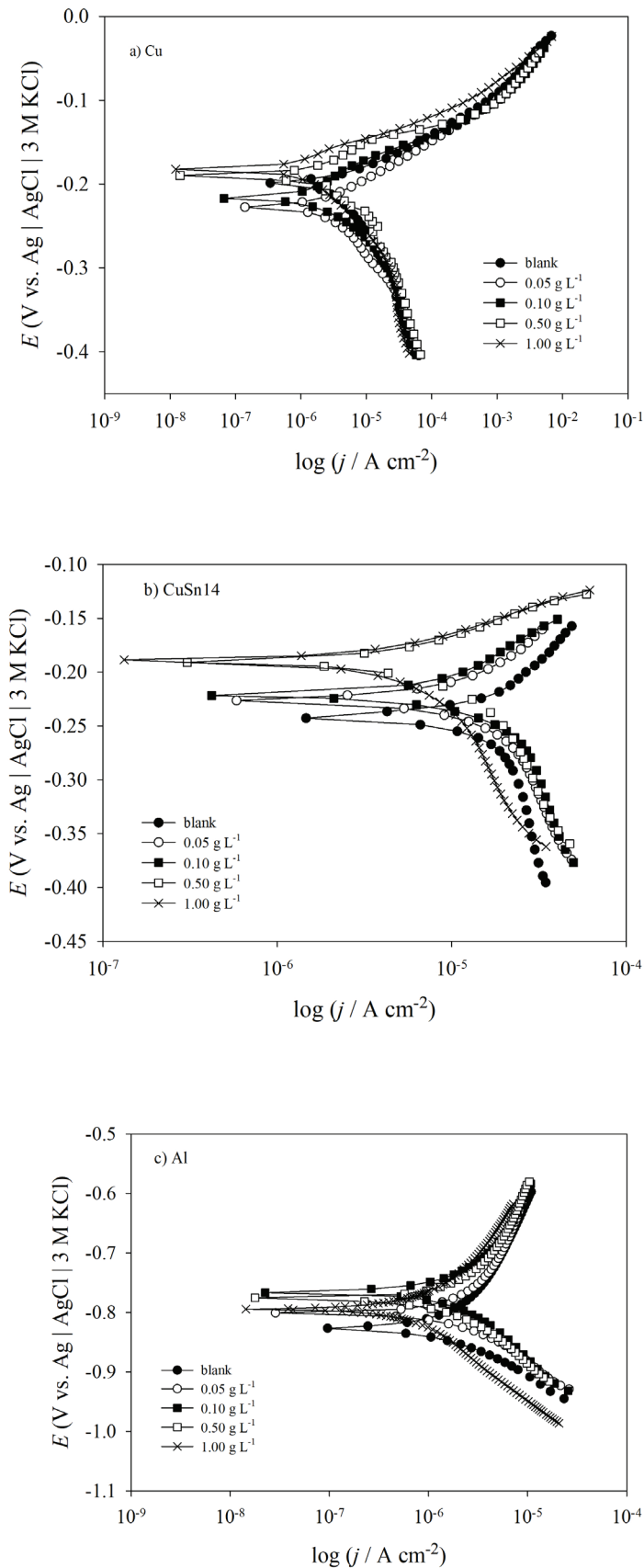


Fig. 2 – Potentiodynamic polarization curves for the Cu, CuSn14, and Al electrodes in 3 % NaCl, containing different concentrations of SN extract; $v = 1 \text{ mV s}^{-1}$

The inhibition efficiency depends on several factors, such as the components of the extract, the nature of the metal surface, and the chemical composition of the corrosive media. Adsorption of inhibitor molecules occurs as the interaction energy between molecule and metal surface is higher than that between water molecule and metal surface. According to the obtained results, the effectiveness of *Sambucus nigra* L. extract in corrosion inhibition was more pronounced for CuSn14 samples compared to those of Cu and Al. This can be related to the differences in the stability of surface layers of metals.

The surface bronze film is composed of a tin-rich internal region, a cuprous oxide layer, and an external porous region^{32,33} in highly corrosive environments, so dissolution rate is high, as may be seen from current density (Table 1). Due to low stability of surface bronze film, high concentration of dissolved metal ions induced greater effect of *Sambucus nigra* L. extract on bronze corrosion inhibition than on aluminium and copper corrosion inhibition.

Although the available literature data shows that some plant extracts do achieve higher inhibition efficiency in the same electrolyte^{1,6,7}, the preparation of extract, time of metal immersion in inhibitor solution, as well as the cost of extract preparation must be considered. *Sambucus nigra* L. extract is prepared by 3-hour maceration of its flowers in 1 L of 3 % NaCl aqueous solution, thereby avoiding the use of highly expensive toxic solvents that can adversely affect the surrounding environment and the economy of extract preparation³⁴. According to its distribution and shown inhibition properties, *Sambucus nigra* L. extract has great potential as a cheap, environmentally friendly corrosion inhibitor.

According to Table 1, variation in corrosion potential (E_{corr}) values is less than $\pm 85 \text{ mV}$ (40 mV for Cu, 30 mV for CuSn14, and 30 mV for Al with the highest inhibitor concentration of 1.0 g L^{-1}), indicating that the molecules of SN extract work as a mixed-type inhibitor^{3,7,35,36}. The parallel anodic and cathodic curves in the presence of various concentrations of SN extract can be explained by the fact that the corrosion process is caused by blocking the active sites on the metal surface, indicating that the presence of the extract does not change the dissolution mechanism^{7,37}.

Adsorption mechanism

From the potentiodynamic polarization data, the observed increase in corrosion inhibition efficiency results from the adsorption of the extract molecules on the metal surface. Adsorption isotherms are used to understand the interactions be-

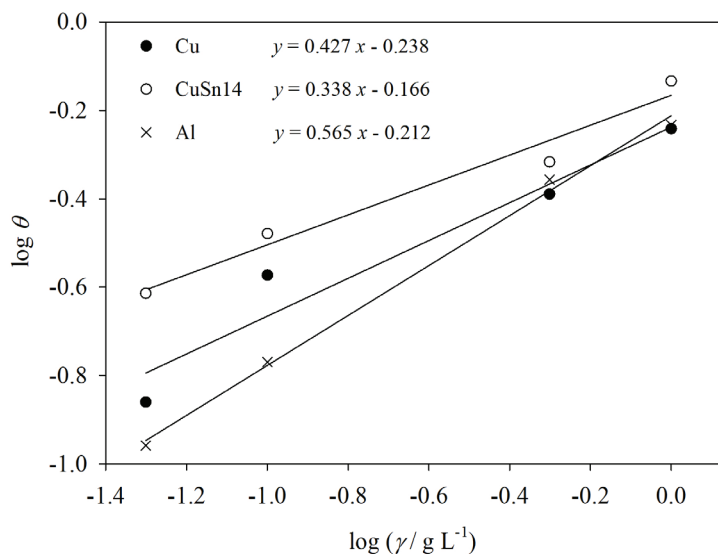


Fig. 3 – Freundlich adsorption plots for Cu, CuSn14, and Al in 3 % NaCl containing different concentrations of SN extract

tween extract molecules and metal surfaces. To describe the adsorption of SN extract on the metal surface, several adsorption isotherms were tested, but the best agreement was obtained using the Freundlich adsorption isotherm that is given by the following equation:

$$\log \theta = \log K + n \log \gamma \quad (3)$$

where K is the equilibrium adsorption constant, and n ($0 < n < 1$) is adsorption intensity. The linear plots of Freundlich isotherm for all electrodes are shown in Fig. 3. The equilibrium adsorption constants were determined from the intercepts of the straight lines from Fig. 3, and the equilibrium adsorption constant is also related to the free energy of adsorption (Gibbs energy), ΔG° ^{4,11}:

$$\Delta G^\circ = -RT \ln \left[1000 \left(\text{g L}^{-1} \right) \cdot K \left(\text{L g}^{-1} \right) \right] \quad (4)$$

where the value of 1000 is the mass concentration of water in the solution in g L^{-1} , R is the universal gas constant, and T is the absolute temperature. This multiplication was used to nullify the unit of K (L g^{-1}) with 1000 g of water per L of aqueous solution.

The equilibrium adsorption constant and the Gibbs free energy were determined from the Freundlich adsorption isotherm plots, as seen in Table 2.

Table 2 – Adsorption parameters obtained from Freundlich adsorption isotherms for Cu, CuSn14, and Al in 3 % NaCl containing SN extract

metal	K (L g^{-1})	ΔG° (kJ mol^{-1})
Cu	0.575	-15.74
CuSn14	0.681	-16.16
Al	0.613	-15.91

From the literature, negative values of ΔG up to -20 kJ mol^{-1} indicate physisorption, which results from the electrostatic interaction between charged inhibitor molecules and the charged metal. The negative values of ΔG -40 kJ mol^{-1} indicate chemisorption that involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate bond^{3,4}. The negative values of ΔG ($\sim 16 \text{ kJ mol}^{-1}$) indicate the spontaneous physisorption of SN extract on the metal surfaces and forming of a film that physically blocks attention of chloride ions from solution³⁸.

Electrochemical impedance spectroscopy

The corrosion behaviour of Cu, CuSn14, and Al electrodes in 3 % NaCl with and without SN extract was investigated using EIS. Nyquist plots for Cu, CuSn14, and Al electrodes in 3 % NaCl in the presence and absence of 1.0 g L^{-1} SN extract are shown in Fig. 4. Impedance parameters obtained from EIS measurements are given in Table 3. Impedance spectra are interpreted by means of electrical equivalent circuits (EEC) shown in detail in Fig. 4. In these circuits, a constant phase element (CPE) was used and its impedance can be defined as:

$Z_{\text{CPE}}(\omega) = [Q(j\omega)^n]^{-1}$, where Q is the constant, ω is the angular frequency, and n is the CPE power with values between 0.5 and 1. When $n = 1$, the CPE describes an ideal capacitor with Q equal to the capacitance (C). For $0.5 < n < 1$, the CPE describes a distribution of dielectric relaxation times in frequency space, and when $n = 0.5$, the CPE represents a Warburg impedance.

The Nyquist plots for copper in 3 % NaCl with and without SN extract comprise two-time constants. The first one at high frequency is attributed to the charge transfer process of copper dissolution reaction, and is described with a parallel combination of double-layer capacitance, C_{dl} (the CPE₁ with power n close to 1.0 describes a capacitor with $Q_1 = C_{\text{dl}}$), and the charge transfer resistance (R_1). The second time constant (R_2, Q_2) is related to the resistance and capacitance of the copper film, respectively in series with the Warburg impedance (W), which is due to the mass transfer of the species involved in the corrosion process. The Warburg impedance is clearly visible at low frequencies as a linear part of the EIS response (almost at 45°)³⁹.

In the case of the Cu electrode in 3 % NaCl with SN extract, the time constant in the high frequency range represents the capacitance (Q_1) and resistance (R_1) of the surface film (oxide + physisorbed SN extract layer), while the time constant in the medium/low frequency range (Q_2 and R_2) corresponds to the pseudocapacitance and resistance of defects within the surface film associated with ion/water movement and penetration through the film.

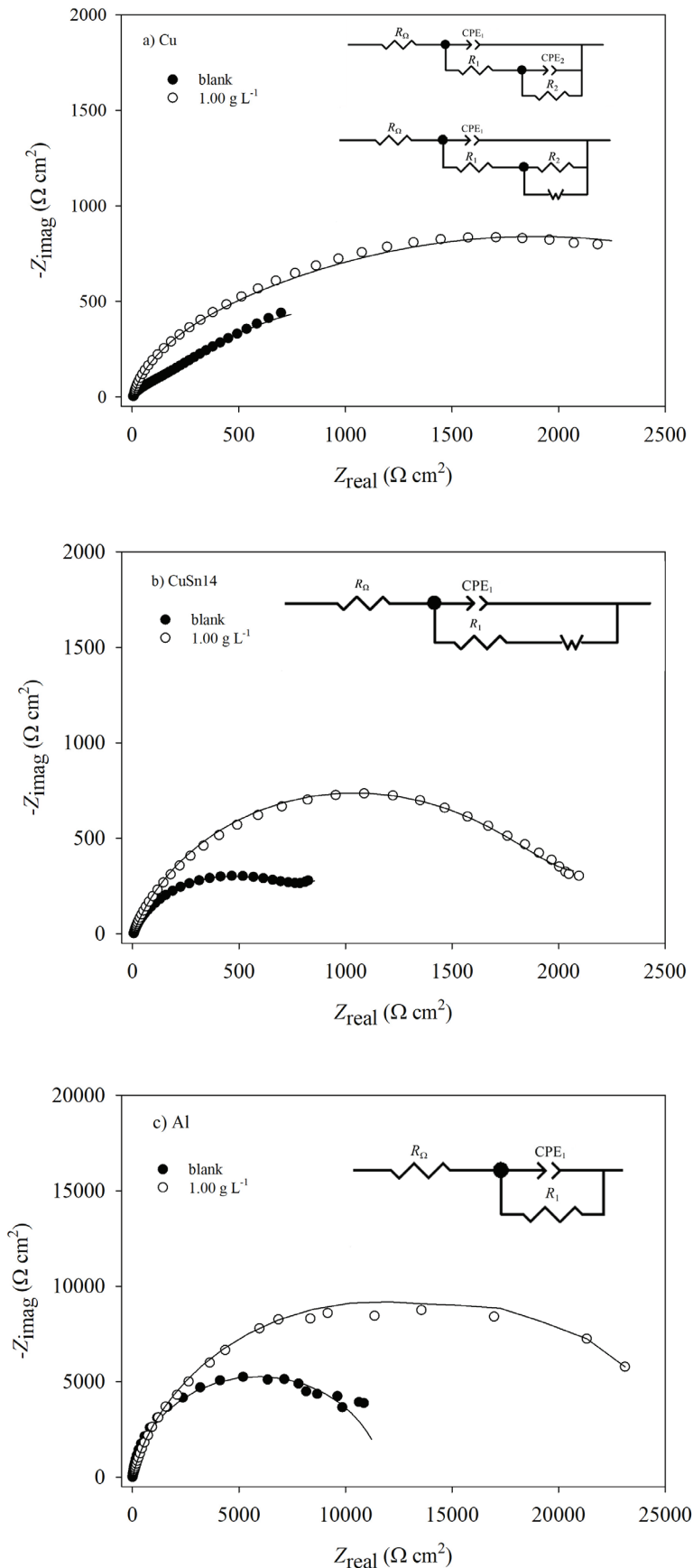


Fig. 4 – Nyquist plots for Cu, CuSn14, and Al electrodes in 3 % NaCl in the absence and presence of 1.00 g L⁻¹ SN extract

The polarization resistance R_p ($R_1 + R_2 + R_w$) is used to evaluate the overall corrosion resistance.

The Nyquist plots for bronze CuSn14 in 3 % NaCl with and without SN extract also include two-time constants. The first one, at high frequency, represents the charge transfer process at the electrolyte/metal interface, and is described as a combination of a double-layer capacitance ($Q_1 = C_{dl}$) and the charge transfer resistance (R_1).

The time constant in the low-frequency region ($Q_2(R_2W)$) results from mass transfer through the surface film of corrosion products (R_2 is the surface film resistance, Q_2 the capacitance of the surface film, and W is the Warburg diffusion element)³⁹.

For Cu and CuSn14, it can be seen that the presence of SN extract increased the total impedance of Cu in the 3 % NaCl solution; the charge transfer resistance (R_1) and the surface layer resistance (R_2) are increased, while the capacity of the double layer (Q_1), capacity of the surface layer (Q_2), and the Warburg diffusion element (W) are decreased, due to adsorption of extract.

The Nyquist plots for aluminium in 3 % NaCl with and without SN extract exhibit single capacitive loop (represented by double-layer capacitance and the charge transfer resistance), indicating a corrosion process mainly controlled by charge transfer resistance.

The increase in the diameter of the capacitive loops with the addition of SN extract indicates adsorption of extract molecules on the surfaces of examined metals and the formation of a protective film. When compared with 3 % NaCl solution, the shape of Nyquist plots obtained from the solutions containing SN extract, remain unchanged, indicating that the corrosion mechanisms of Cu, CuSn14, and Al are not affected by the addition of SN extract^{11,40}.

From the results in Table 3, there is a decrease in C_{dl} values with the addition of SN extract that can be explained by the Helmholtz model:

$$C_{dl} = \frac{\varepsilon^0 \varepsilon A}{d} \quad (5)$$

where ε^0 is the permittivity of the vacuum, ε is the dielectric constant of the solution, d is the thickness of the film, and A is the surface area of the electrode. Accordingly, a decrease in C_{dl} values with the addition of SN extract can be associated with a decrease in dielectric constant and/or increase in the thickness of the electrical double layer due to displacement of ions and water molecules originally adsorbed on the surface by extract molecules.

From Table 3, it can be observed that for Cu and CuSn14, polarization resistance increases (Cu: from 2.20 to 4.35 kΩ cm²; CuSn14: from 0.80 to

Table 3 – Impedance parameters and inhibition efficiency for Cu, CuSn14, and Al electrodes in 3 % NaCl, with and without SN extract

metal	$\gamma_{\text{SN extract}}$ (g L ⁻¹)	$Q_1 \cdot 10^5$ ($\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$)	n_1	R_1 (k $\Omega \text{ cm}^2$)	$Q_2 \cdot 10^4$ ($\Omega^{-1} \text{ s}^n \text{ cm}^{-2}$)	n_2	R_2 (k $\Omega \text{ cm}^2$)	$W \cdot 10^4$ ($\Omega^{-1} \text{ s}^{0.5} \text{ cm}^{-2}$)	η (%)
Cu	blank	14.15	0.71	0.15	10.39	0.65	1.75	33.25	–
	1.0	2.41	0.91	0.57	2.23	0.58	3.78	–	49.4
CuSn14	blank	13.75	0.79	0.006	1.79	0.80	0.72	137.93	–
	1.0	11.10	0.71	0.008	0.45	0.85	1.97	120.35	61.2
Al	blank	1.51	0.87	11.8	–	–	–	–	–
	1.0	1.45	0.89	24.1	–	–	–	–	51.2

2.06 k $\Omega \text{ cm}^2$), while for Al electrode, charge transfer resistance increases (from 11.8 to 24.1 k $\Omega \text{ cm}^2$) with the addition of SN extract as a result of adsorption of the extract molecules at the metal/solution interface^{7,41}. The increase in charge transfer resistance leads to an increase in inhibition efficiency.

The increase in charge transfer resistance value indicates that the adsorbed extract forms a protective film on the electrode surface, and consequently becomes a barrier to inhibit the mass and charge transfer, resulting in an increase in the inhibition efficiency, calculated according to the following equation for Cu and CuSn14 electrodes:

$$\eta = \frac{R_p - R_p^0}{R_p} \cdot 100 \% \quad (6)$$

where R_p^0 and R_p are the polarization resistances ($R_1 + R_2 + R_w$) of the metal in the absence and presence of SN extract.

For Al electrode, inhibition efficiency is calculated from the charge transfer resistance:

$$\eta = \frac{R_1 - R_1^0}{R_1} \cdot 100 \% \quad (7)$$

where R_1^0 and R_1 are the charge transfer resistances of the metal in the absence and presence of SN extract.

From EIS measurements, the obtained inhibition efficiencies were 49.4 %, 61.2 %, and 51.2 % for Cu, CuSn14, and Al corrosion, respectively. The values of inhibition efficiency are presented in Table 3, and it can be seen that PP and EIS data are in accordance.

Conclusions

The *Sambucus nigra* L. is widely used in the food industry and in folk medicine, but according to a literature survey, there have been no reports on the corrosion inhibition effects of *Sambucus nigra* L. on metals. In this work, antioxidant capacity and corrosion inhibition efficiency of *Sambucus nigra* L.

extract on three different metals, copper, bronze, and aluminium was tested.

Antioxidant capacity measured by cyclic voltammetry, using gallic acid as standard, proved good antioxidant properties of *Sambucus nigra* L. (4.06 mg GAE g⁻¹ fw), probably due to high content of polyphenolic compounds that contain either galate or ortho-, dihydroxy- phenol groups which may undergo an irreversible oxidation process at the studied potential range (0–800 mV).

Polarization measurements showed that by raising the concentration of SN extract, the inhibition efficiency increases due to its adsorption on the metal surface with maximum efficiency around 57.3 %, 73.5 %, and 58.4 % for Cu, CuSn14, and Al corrosion, respectively, at 1.0 g L⁻¹. The inhibition action is performed via the adsorption of the extract constituents on metal surfaces. The adsorption process is spontaneous and follows Freundlich isotherm, with a physisorption mechanism ($\Delta G \approx -16 \text{ kJ mol}^{-1}$). From polarization measurements, the small deviation of E_{corr} with respect to the corrosion potential in the blank indicated that SN extract was a mixed-type inhibitor that controls both anodic metal dissolution and cathodic hydrogen evolution reactions.

The impedance data showed that, with the addition of SN extract, resistance values increased and inhibition efficiencies of 49.4 %, 61.2 %, and 51.2 % were achieved for Cu, CuSn14, and Al corrosion, respectively. Considering the greater stability of Cu and Al surface film in a 3 % NaCl compared to bronze, it can be postulated that the lower concentration of dissolved metal ions was responsible for the lesser effect of *Sambucus nigra* L. extract on the inhibition of aluminium and copper corrosion.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support for this project received from the Federal Ministry of Education and Science of Bosnia and Herzegovina.

List of symbols

- CPE – constant phase element
 d – film thickness, nm
 E – potential, V
 f – frequency, Hz
 ΔG° – free energy of adsorption, kJ mol^{-1}
 j – current density, A cm^{-2}
 K – equilibrium adsorption constant
 n – characteristic parameter of CPE
 Q – coefficient reflecting combination of properties related to surface and electroactive species, $\Omega^{-1} \text{cm}^{-2} \text{s}^n$
 Q – charge density, C cm^{-2}
 R – resistance, Ωcm^2
 R – universal gas constant, $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
 T – absolute temperature, K
 W – Warburg impedance, $\Omega^{-1} \text{s}^{0.5} \text{cm}^{-2}$
 Z – impedance, Ωcm^2

Greek letters

- ϵ_0 – the permittivity of the vacuum, $8.854 \cdot 10^{-12} \text{ F m}^{-1}$
 ϵ – the dielectric constant of the solution
 γ – inhibitor concentration, g L^{-1}
 ν – scan rate, V s^{-1}
 ω – angular speed, rad s^{-1}
 θ – surface coverage
 η – inhibition efficiency, %

References

1. Udensi, S. C., Ekpe, O. E., Nnanna, L. A., Corrosion inhibition performance of low cost and eco-friendly *Treculia africana* leaves extract on aluminium alloy AA7075-T7351 in 2.86 % NaCl solutions, *Sci. Afr.* **12** (2021) e00791. doi: <https://doi.org/10.1016/j.sciaf.2021.e00791>
2. Raghavendra, N., Green compounds to attenuate aluminum corrosion in HCl activation: A necessity review, *Chem. Afr.* **3** (2020) 21. doi: <https://doi.org/10.1007/s42250-019-00114-6>
3. Pilić, Z., Martinović, I., Effect of *Helichrysum italicum* on the corrosion of copper in simulated acid rain solution, *Chem. Biochem. Eng. Q.* **33** (2019) 449. doi: <https://doi.org/10.15255/CABEQ.2019.1614>
4. Pilić, Z., Martinović, I., Pavlinović, M., Zlatić, G., Effect of *Helichrysum italicum* on the electrochemical corrosion behaviour of iron in simulated acid rain solution, *Croat. Chem. Acta* **92** (2019) 79. doi: <https://doi.org/10.5562/cca3451>
5. Nathiya, R. S., Perumal, S., Murugesan, V., Raj, V., Evaluation of extracts of *Borassus flabellifer* dust as green inhibitors for aluminium corrosion in acidic media, *Mater. Sci. Semicond. Process* **104** (2019) 104674. doi: <https://doi.org/10.1016/j.mssp.2019.104674>
6. Elgahawi, H., Gobara, M., Baraka, A., Elthalabawy, W., Eco-friendly corrosion inhibition of AA2024 in 3.5 % NaCl using the extract of *Linum usitatissimum* seeds, *J. Bio-Tribo-Corros.* **3** (2017) 55. doi: <https://doi.org/10.1007/s40735-017-0116-x>
7. Fouda, A. S., Gadow, H. S., Abd Elal, E. G., El-Tantawy, M. I., corrosion inhibition of aluminium by rice straw extract in 2 M hydrochloric acid solution, *J. Bio-Tribo-Corros.* **7** (2021) 102. doi: <https://doi.org/10.1007/s40735-021-00527-2>
8. Gust, J., Wawer, I., Relationship between radical scavenging effects and anticorrosive properties of polyphenols, *Corrosion* **51** (1995) 37. doi: <https://doi.org/10.5006/1.3293574>
9. Senica, M., Stampar, F., Veberic, R., Mikulic-Petkovsek, M., Processed elderberry (*Sambucus nigra* L.) products: A beneficial or harmful food alternative?, *LWT – Food Sci. Technol.* **72** (2016) 182. doi: <https://doi.org/10.1016/j.lwt.2016.04.056>
10. Dominguez, R., Zhang, L., Rocchetti, G., Lucini, L., Pateiro, M., Munekata, P. E. S., Lorenzo, J. M., Elderberry (*Sambucus nigra* L.) as potential source of antioxidants. Characterization, optimization of extraction parameters and bioactive properties, *Food Chem.* **330** (2020) 127266. doi: <https://doi.org/10.1016/j.foodchem.2020.127266>
11. Martinović, I., Pilić, Z., Zlatić, G., Barišić, M., Čelan, S., Corrosion inhibition of aluminium by *Alchemilla vulgaris* L. extract in 3 % NaCl solution, *Croat. Chem. Acta* **94** (2021) 103. doi: <https://doi.org/10.5562/cca3858>
12. Fernine, Y., Ech-chihbi, E., Arrousse, N., El Hajjaji, F., Bousraf, F., Ebn Touhami, M., Rais, Z., Taleb, M., *Ocimum basilicum* seeds extract as an environmentally friendly antioxidant and corrosion inhibitor for aluminium alloy 2024-T3 corrosion in 3 wt% NaCl medium, *Colloids Surf. A: Physicochem. Eng. Asp.* **627** (2021) 127232. doi: <https://doi.org/10.1016/j.colsurfa.2021.127232>
13. Krishnaveni, K., Ravichandran, J., Influence of aqueous extract of leaves of *Morinda tinctoria* on copper corrosion in HCl medium, *J. Electroanal. Chem.* **735** (2014) 24. doi: <https://doi.org/10.1016/j.jelechem.2014.09.032>
14. Jmiai, A., El Ibrahim, B., Tara, A., Chadili, M., El Issami, S., Jbara, O., Khallaayoun, M., Bazzi, L., Application of *Zizyphus Lotuse* – pulp of jujube extract as green and promising corrosion inhibitor for copper in acidic medium, *J. Mol. Liq.* **268** (2018) 102. doi: <https://doi.org/10.1016/j.molliq.2018.06.091>
15. Refait, P., Rahal, C., Masmoudi, M., Corrosion inhibition of copper in 0.5 M NaCl solutions by aqueous and hydrolysis acid extracts of olive leaf, *J. Electroanal. Chem.* **859** (2020) 113834. doi: <https://doi.org/10.1016/j.jelechem.2020.113834>
16. Benzidia, B., Barbouchi, M., Hsissou, R., Zouarhi, M., Erramli, H., Hajjaji, N., A combined experimental and theoretical study of green corrosion inhibition of bronze B66 in 3 % NaCl solution by *Aloe saponaria* (syn. *Aloe maculata*) tannin extract, *Curr. Res. Green Sustain. Chem.* **5** (2022) 100299. doi: <https://doi.org/10.1016/j.crgsc.2022.100299>
17. Zlatić, G., Arapović, A., Martinović, I., Martinović Bevranda, A., Bošković, P., Prkić, A., Paut, A., Vukušić, T., Antioxidant capacity of Herzegovinian wildflowers evaluated by UV–VIS and cyclic voltammetry analysis, *Molecules* **27** (2022) 5466. doi: <https://doi.org/10.3390/molecules27175466>

18. Yang, B., Kotani, A., Arai, K., Kusu, F., Estimation of the antioxidant activities of flavonoids from their oxidation potentials, *Anal. Sci.* **17** (2001) 599.
doi: <https://doi.org/10.2116/analsci.17.599>
19. Kilmartin, P. A., Zou, H. L., Waterhouse, A. L., A cyclic voltammetry method suitable for characterizing antioxidant properties of wine and wine phenolics, *J. Agric. Food Chem.* **49** (2001) 1957.
doi: <https://doi.org/10.1021/jf001044u>
20. Oliveira Brett, A. M., Ghica, M. E., Electrochemical oxidation of quercetin, *Electroanalysis* **15** (2003) 1745.
doi: <https://doi.org/10.1002/elan.200302800>
21. Ligonja, N. M., Stanković, D. M., Spasić, S. D., Roglič, G. M., Manojlović, D. D., Vričić, M. M., Comparative electrochemical determination of total antioxidant activity in infant formula with breast milk, *Food Anal. Methods* **7** (2014) 337.
doi: <https://doi.org/10.1007/s12161-013-9631-7>
22. Nikolić, M. D., Pavlović, A. N., Mitić, S. S., Tošić, S. B., Mitić, M. N., Kaličanin, B. M., Manojlović, D. D., Stanković, D. M., Use of cyclic voltammetry to determine the antioxidant capacity of berry fruits: Correlation with spectrophotometric assays, *Eur. J. Hortic. Sci.* **84** (2019) 152.
doi: <https://doi.org/10.17660/eJHS.2019/84.3.5>
23. Piljac-Žegarac, J., Valek, L., Stipčević, T., Martinez, S., Electrochemical determination of antioxidant capacity of fruit tea infusions, *Food Chem.* **121** (2010) 820.
doi: <https://doi.org/10.1016/j.foodchem.2009.12.090>
24. Rice-Evans, C., Miller, N., Paganga, G., Antioxidant properties of phenolic compounds, *Trends Plant Sci.* **2** (1997) 152.
doi: [https://doi.org/10.1016/S1360-1385\(97\)01018-2](https://doi.org/10.1016/S1360-1385(97)01018-2)
25. Benbougerra, N., Richard, T., Saucier, C., Garcia, F., Voltammetric behavior, flavanol and anthocyanin contents, and antioxidant capacity of grape skins and seeds during ripening (*Vitis vinifera* var. Merlot, Tannat, and Syrah), *Antioxidants* **9** (2020) 800.
doi: <https://doi.org/10.3390/antiox9090800>
26. Chiorcea-Paquim, A. M., Enache, T. A., De Souza Gil, E., Oliveira-Brett, A. M., Natural phenolic antioxidants electrochemistry: Towards a new food science methodology, *Compr. Rev. Food Sci. Food Saf.* **19** (2020) 1680.
doi: <https://doi.org/10.1111/1541-4337.12566>
27. Mlynarczyk, K., Walkowiak-Tomczak, D., Lysiak, G. P., Bioactive properties of *Sambucus nigra* L. as a functional ingredient for food and pharmaceutical industry, *J. Funct. Foods* **40** (2018) 377.
doi: <https://doi.org/10.1016/j.jff.2017.11.025>
28. Marisa Ribeiro, A., Estevinho, B. N., Rocha, F., Microencapsulation of polyphenols – the specific case of the microencapsulation of *Sambucus Nigra* L. extracts – A review, *Trends Food Sci. Technol.* **105** (2020) 454.
doi: <https://doi.org/10.1016/j.tifs.2019.03.011>
29. Ferreira, S. S., Silva, A. M., Nunes, F. M., *Sambucus nigra* L. fruits and flowers: Chemical composition and related bioactivities, *Food Rev. Int.* **38** (2022) 1237.
doi: <https://doi.org/10.1080/87559129.2020.1788578>
30. Veberic, R., Jakopic, J., Stampar, F., Schmitzer, V., European elderberry (*Sambucus nigra* L.) rich in sugars, organic acids, anthocyanins and selected polyphenols, *Food Chem.* **114** (2009) 511.
doi: <https://doi.org/10.1016/j.foodchem.2008.09.080>
31. Riccucci, G., Cazzola, M., Ferraris, S., Gobbo, V. A., Guaita, M., Spriano, S., Surface functionalization of Ti6Al4V with an extract of polyphenols from red grape pomace, *Mater. Des.* **206** (2021) 109776.
doi: <https://doi.org/10.1016/j.matdes.2021.109776>
32. Robbiola, L., Blengino, J. M., Fiaud, C., Morphology and mechanisms of formation of natural patinas on archaeological Cu–Sn alloys, *Corros. Sci.* **40** (1998) 2083.
doi: [https://doi.org/10.1016/S0010-938X\(98\)00096-1](https://doi.org/10.1016/S0010-938X(98)00096-1)
33. Martinović, I., Pilić, Z., Corrosion behavior of copper, tin, and bronze CuSn14 in acid rain solution, *Mater. Corros.* **72** (2021) 1635.
doi: <https://doi.org/10.1002/maco.202112470>
34. Alrefae, S. H., Rhee, K. Y., Verma, C., Quraishi, M. A., Eno, E., Ebenso, E. E., Challenges and advantages of using plant extract as inhibitors in modern corrosion inhibition systems: Recent advancements, *J. Mol. Liq.* **321** (2021) 114666.
doi: <https://doi.org/10.1016/j.molliq.2020.114666>
35. Salghi, R., Jodeh, S., Ebenso, E. E., Lgaz, H., Hmamou, D. B., Belkhaouda, M., Ali, T. H., Messali, M., Hammouti, B., Fattouch, S., Inhibition of C-steel corrosion by green tea extract in hydrochloric solution, *Int. J. Electrochem. Sci.* **12** (2017) 3283.
doi: <https://doi.org/10.20964/2017.04.46>
36. Eldesoky, A. M., Diab, M. A., El-Sonbati, A. Z., Salam, S. F., Anti-corrosive properties of new eco-friendly dimethylamino compounds on C- steel corrosion in 2 M HCl, *Int. J. Electrochem. Sci.* **12** (2017) 4215.
doi: <https://doi.org/10.20964/2017.05.73>
37. Lgaz, H., Saha, S. K., Chaouiki, C., Subrahmanya Bhat, K., Salghi, R., Shubhalaxmi, Banerjee, P., Ali, I. H., Khan, I. M., Chung, I.-M., Exploring the potential role of pyrazoline derivatives in corrosion inhibition of mild steel in hydrochloric acidsolution: Insights from experimental and computational studies, *Constr. Build. Mater.* **233** (2020) 117320.
doi: <https://doi.org/10.1016/j.arabjc.2018.08.004>
38. Grudić, V., Bošković, I., Gezović, A., Inhibition of copper corrosion in NaCl solution by propolis extract, *Chem. Biochem. Eng. Q.* **32** (2018) 299.
doi: <https://doi.org/10.15255/CABEQ.2018.1357>
39. Vrsalović, L., Gudić, S., Gracić, D., Smoljko, I., Ivanić, I., Kliškić, M., Oguzie, E. E., Corrosion protection of copper in sodium chloride solution using propolis, *Int. J. Electrochem. Sci.* **13** (2018) 2102.
doi: <https://doi.org/10.20964/2018.02.71>
40. Baran, E., Cakir, A., Yazici, B., Inhibitory effect of *Gentiana olivieri* extracts on the corrosion of mild steel in 0.5 M HCl: Electrochemical and phytochemical evaluation, *Arab. J. Chem.* **12** (2019) 4303.
doi: <https://doi.org/10.1016/j.arabjc.2016.06.008>
41. Kumari, P. P., Shetty, P., Rao, S. A., Electrochemical measurements for the corrosion inhibition of mild steel in 1 M hydrochloric acid by using an aromatic hydrazide derivative, *Arab. J. Chem.* **10** (2017) 653.
doi: <https://doi.org/10.1016/j.arabjc.2014.09.005>