

Research Article

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The anti-corrosion behaviour of *Satureja montana* L. extract on iron in NaCl solution

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Abstract: The effect of *Satureja montana* L. extract (SM) and phenolic fraction of *Satureja montana* L. (PF) on the corrosion behaviour of iron in 0.1 mol L⁻¹ sodium chloride solution was studied by electrochemical techniques, UV/Vis spectrophotometry and atomic absorption spectrometry. The results of all techniques showed that SM and PF contributed to iron corrosion inhibition. The calculated inhibition efficiency values were about 45% for SM and 55% for PF. Results indicate that the inhibitive action occurs via a precipitation of the Fe-complex onto the iron surface which resulting in a decrease of the passive current density. The atomic absorption spectrometry (AAS) method was applied to the quantitative determination of iron in solution. The obtained results demonstrated good agreement with results obtained by electrochemical techniques.

Keywords: iron; corrosion; *Satureja montana* L.; phenolic compounds; electrochemical methods.

1 Introduction

Many metals and alloys are an important category of materials due to the various industrial applications and economic importance but they are susceptible to different mechanisms of corrosion due to their exposure to different corrosive media [1-4]. The corrosion behaviour of these materials depends of the oxide layer on metal surface and a great number of corrosion investigations performed using different techniques: electrochemical [3,4], SERS [5,6], XANES [7,8] etc., have been focused on the surface

film. Because of the general aggressiveness of chloride-containing solution [9-10] corrosion control is an essential issue from application point of view. One of the important methods used to reduce the rate of metal corrosion is the addition of inhibitors [11-14]. Corrosion inhibitors are substances, which in small concentrations decrease or prevent the degradation of metal. The degree of inhibition depends on metal nature and type of the medium.

Unfortunately, many of the inhibitors used are compounds with toxic properties. However, an increasing awareness of health and ecological risks has drawn attention to finding nontoxic and environmental friendly corrosion inhibitors. Therefore, researchers are looking for eco-friendly natural inhibitors as an alternative [12-17]. Green inhibitors can be used in the form of extracts, essential oils or pure compounds. The natural compounds are biodegradable, easy available and non-toxic. Plants, which contain heterocyclic constituents (phenolic, aromatic compounds, etc.) can act as potential inhibitors. Protection efficiency of these inhibitors is attributed mainly to the presence of an active center for adsorption.

The possibility of corrosion inhibition of iron by natural antioxidants from *Satureja montana* L. was the focus of this study. In our earlier paper [18] the extract of the *Achillea millefolium* L. was investigated as corrosion inhibitor on a iron sample in an acid rain solution. The aim of the present work is to study the influence of *Satureja montana* L. extract on the corrosion behaviour of iron in NaCl solution.

Satureja montana L. is a plant with antimicrobial [19,20], cytotoxic [21], and antioxidant properties [22-25] and it is also used in ethno medicine against intestinal parasites and for the treatment of stomach disorders and cough. According to scientific papers [23-25] this activity of SM extract is attributed to presented phenolic compounds. Due to positive properties, *Satureja montana* L., was chosen as a potential environmentally friendly corrosion inhibitor.

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2 Experimental

The study was performed with spectroscopically pure iron (Fe). The sample of Fe cylinder was used as a working electrode. The lateral surface of the cylinder was coated with polymer material, exposing only the plane of the cylinder base with a 0.636 cm^2 surface area to the solution.

The surface of the electrode was polished with 1200 grade emery paper, degreased in ethanol in an ultrasonic bath and rinsed with ultrapure water produced by Millipore Simplicity UV Water Purification System.

A Pt plate and an Ag | AgCl | 3 mol L^{-1} KCl were used as the counter and reference electrodes, respectively. All potential values are reported vs. Ag | AgCl | 3 mol L^{-1} KCl. Measurements were carried out at room temperature in a standard three electrode arrangement using Autolab PGSTAT320N controlled by a personal computer using Nova 1.5 software.

The electrolyte was purified with argon. Prior to electrochemical measurements the electrode was held at the potential -1.40 V vs. Ag/AgCl for 30 seconds to remove spontaneously formed oxides.

Potentiodynamic polarization (PP) curves were recorded in the potential range from -400 mV to 400 mV near the open circuit potential (EOCP) and with the scan rate of 1.0 mV s^{-1} .

Cyclic voltammetry (CV) measurements were performed in the potential region from -1.40 V up to -0.20 V with a sweep rate of 40 mV s^{-1} .

Electrochemical impedance spectra (EIS) were performed at open circuit potential, EOCP in the frequency range $10 \text{ kHz} - 5 \text{ MHz}$ with a 10 mV rms amplitude. Prior to EIS measurements the electrode was immersed in the solution for 30 minutes to stabilize at the open circuit potential. All experiments were performed at least thrice to ensure the reproducibility of the data.

The content of dissolved iron during 1 hour-immersion of electrode in solution at EOCP were determined by atomic absorption spectrometry (AAS). This period of time was chosen to match the duration of EIS measurements.

The basic electrolyte was 0.1 mol L^{-1} sodium chloride solution. The pH value of solution was 7.0. pH value was adjusted by the addition of 0.2 mol L^{-1} NaOH and of 0.2 mol L^{-1} HCl. All chemicals used were of analytical grade and were obtained from Sigma Aldrich and all solutions were prepared with ultra pure water.

Experiments were performed in sodium chloride solution without and with the addition of *Satureja montana* L. extract (SM) and phenolic fraction of *Satureja montana* L. extract (PF). The aerial parts of *Satureja montana* L. were collected during summer 2017 in the wider area of Mostar,

Bosnia and Herzegovina and specimens were dried in air for three weeks. Extract of plant material was prepared after 6 h maceration in water at room temperature. The concentration of the *Satureja montana* L. extract was 2.0 g L^{-1} . 1 mL SM was added in 50 mL sodium chloride solution.

The neutral and acidic phenolic constituents of extract were separated using solid-phase extraction (SPE) on C18 Sep Pak cartridges (Waters Associates, Milford, MA, USA) according to the procedure outlined by Katalinić [26]. Briefly, 10 mL of extract was passed drop by drop through cartridges, previously conditioned with methanol and water. The acidic phenol fraction was eluted with 10 mL of water and the neutral phenolic fraction (PF) was eluted with 10 mL of ethyl acetate, evaporated under vacuum on a rotary evaporator at 30°C and the dry residue dissolved in 10 mL water. In this work the neutral phenolic fractions were used for investigation, 1 mL PF was added in 50 mL sodium chloride solution.

The total phenolic compounds of *Satureja montana* L. were extracted by 70% aqueous solutions of acetone [27,28]. Extraction was performed using 0.5 g of plant material and 25 mL solvent during 20 min in an ultrasonic bath at room temperature. The slurry was filtered. Then, extract was centrifuged at 3000 rpm for 10 min. at 4°C . The supernatant was recovered and used for the determination of total phenolic contents.

Total phenolics of *Satureja montana* L. extract were determined spectrophotometrically using Folin-Ciocalteu reagent [27-29]. Different concentrations of tannic acid ($20 - 120 \mu\text{g mL}^{-1}$) were used to plot a standard curve ($y = 0.0064 x + 0.0016$; $r^2 = 0.9952$). Aliquot ($100 \mu\text{L}$) of aqueous acetone extract was transferred into the test tube and was diluted with water to the final volume of 0.5 mL . To each tube, 0.25 mL of the Folin-Ciocalteu reagent and 1.25 mL of the Na_2CO_3 solution (20%) were added. After 40 min. at room temperature, the absorbance of all samples and standards was measured at 725 nm using a UV-Vis spectrophotometer (Shimadzu, 1240). The total phenolic contents were calculated according to the tannic acid and they were expressed as tannic acid equivalents per g dry sample.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results and Discussion

3.1 Potentiodynamic polarization

Figure 1 shows the potentiodynamic polarization curves for the Fe electrode in 0.1 mol L⁻¹ NaCl in the absence and presence of extract (SM) and phenolic fraction (PF) of *Satureja montana* L.

It is obvious from Figure 1 that the presence of SM and PF induces changes in the polarization behaviour of the iron and shifts cathodic curves to lower values of current densities compared with those in the pure 0.1 mol L⁻¹ NaCl solution. The addition of both extracts shifts the corrosion potential to more negative values and the anodic domain current density remains almost the same. This result suggests that the presence of both extracts reduces only the cathodic reaction of hydrogen evolution without affecting anodic dissolution of metal. Since the measurements were carried out in deaerated electrolyte solutions, the cathodic reaction was hydrogen evolution.

The corresponding electrochemical parameters such as corrosion potential, E_{corr} , corrosion current densities, j_{corr} , cathodic Tafel slope, b_c , anodic Tafel slope, b_a , along with the inhibition efficiency, η are listed in Table 1.

From Table 1 it is evident that by adding inhibitors b_a values do not change significantly with respect to the blank solution. However, b_c values change significantly so both extracts behave like cathodic inhibitors. An inhibitor can be referred as cathodic or anodic if the displacement in corrosion potential is more than 85 mV with respect to E_{corr} of the blank [17, 30]. In our study, the displacement in E_{corr} value was less than 85 mV and this indicates that both extracts can be classified as mixed-type inhibitor which is predominantly cathodic.

Inspection of Figure 1 reveals that the cathodic Tafel lines are parallel and it points to unchanged mechanism of cathodic reaction with extract addition to the solution [31].

The inhibition efficiency, η of SM extract and phenolic fraction determined through the corrosion current density is given by the following relation:

$$\eta(\%) = \frac{j_{\text{corr}}^0 - j_{\text{corr}}}{j_{\text{corr}}^0} \cdot 100$$

Where j_{corr}^0 and j_{corr} are corrosion current densities of the Fe in the absence and presence of SM or PF. Table 1 shows that the addition of both extracts has better corrosion inhibition effect and increases inhibition efficiency.

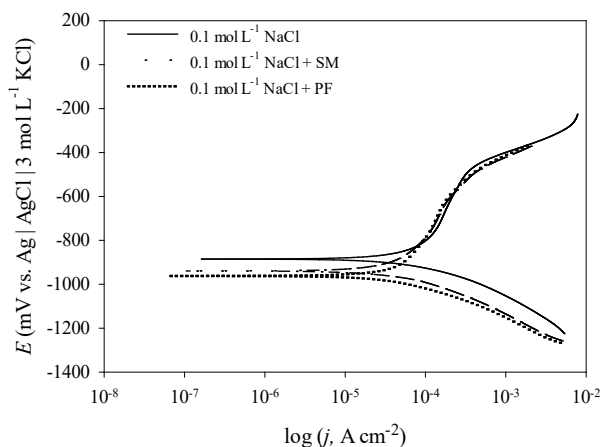


Figure 1: Potentiodynamic polarization curves for Fe electrode in 0.1 mol L⁻¹ NaCl containing SM extract and phenolic fraction (PF) of *Satureja montana* L. $v = 1 \text{ mV s}^{-1}$.

Table 1: Potentiodynamic polarization parameters for Fe electrode in 0.1 mol L⁻¹ NaCl containing SM extract and phenolic fraction (PF) of *Satureja montana* L.

solution	E_{corr} (V)	j_{corr} ($\mu\text{A cm}^{-2}$)	b_c V dec ⁻¹	b_a V dec ⁻¹	η (%)
NaCl	-0.887	54.21	0.325	0.130	-
NaCl + SM	-0.961	28.30	0.391	0.138	47.8
NaCl + PF	-0.966	23.29	0.369	0.141	57.0

3.2 Cyclic voltammetry

The cyclic voltammograms of iron in 0.1 mol L⁻¹ NaCl solution without and in the presence of extract (SM) and phenolic fraction (PF) of *Satureja montana* L. were recorded and are represented in Figure 2. The potential was started at -1.40 V and swept in the positive direction up to -0.20 V at a scanning rate of 40 mV s⁻¹.

Oxidation and reduction processes on the bare Fe electrode have already been discussed [4,18] and here will be only briefly covered. Two oxidation peaks can be observed in the anodic portion of cyclic voltammogram. The first oxidation peak, A_1 , at a potential -0.90 V, can be associated to the formation of a non-protective Fe(OH)₂ layer. Second peak, A_2 , in the anodic direction is observed at potential -0.52 V and this is associated with the oxidation of Fe(II) to Fe(III). It is followed by the region with the constant current density up to -0.20 V indicating a steady-state film growth in the

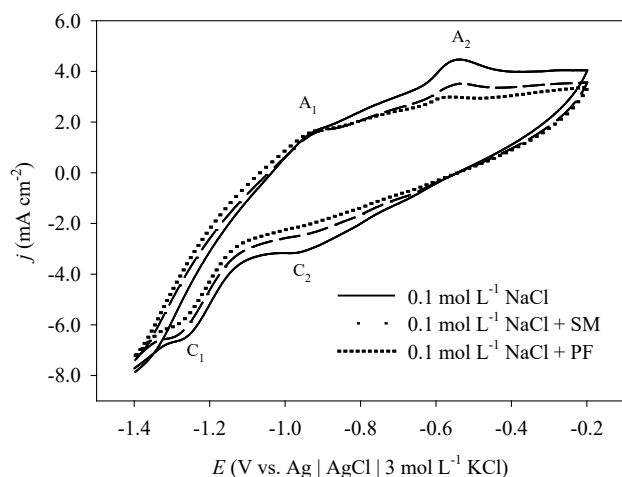


Figure 2: Cyclic voltammograms for Fe electrode in 0.1 mol L⁻¹ NaCl containing extract (SM) and phenolic fraction (PF) of *Satureja montana* L. $v = 40 \text{ mV s}^{-1}$.

passive region. In the reduction scan, two peaks (C_2 , C_1) are observed which are related to the reduction of Fe^{3+} to Fe^{2+} and Fe^{2+} to Fe, respectively. As shown in a previous investigation [4] the reduction of oxide layer is not complete. The CV spectra (Figure 2) showed that the addition of extract (SM) and phenolic fraction (PF) had no significant effect of the E/j profile in the potential region of peak A_1 while in the potential region of peak A_2 as well as the reduction processes in the potential region of peaks C_2 and C_1 , were inhibited.

The difference in current passivity plateau was also noticed. The results showed that the addition of both extracts contributed to the iron corrosion inhibition and their inhibitive action could be explained by an insoluble Fe(III) complex that precipitates onto the electrode surface and decreases in the passive current density.

According to the literature natural phenolic compounds are effective metal chelators, which easily form complexes with di- and trivalent metal cations [14,16,32].

Fe^{2+} and Fe^{3+} ions prefer octahedral geometry and can coordinate up to three polyphenol compounds. Polyphenols are so structurally varied and the complexes formed are pH dependent. In near-neutral solutions many polyphenols are easily deprotonated and form stable complexes with iron ions [32]. At oxidation peak, A_1 , the iron dissolution product, Fe^{2+} with the polyphenols does not form complex with protective properties [16,32] and in this area the current density does not change with addition of extracts (Figure 2). During anodic polarization at the potential of the second oxidation peak (A_2), polyphenols react with Fe^{3+} ions and form a protective ferric-complex.

Table 2: Anodic charge, Q_A and inhibition efficiency, η for Fe electrode in 0.1 mol L⁻¹ NaCl containing SM extract and phenolic fraction (PF) of *Satureja montana* L.

Solution	Q_A (mC cm ⁻²)	η (%)
NaCl	921.4	-
NaCl + SM	638.1	41.37
NaCl + PF	437.2	52.56

This process is facilitated by strong electron donating density of oxygen ligands of the polyphenols that stabilize higher oxidation iron state [32].

Our analysis of the *Satureja montana* L. by means of spectrophotometry using Folin-Ciocalteu reagent has revealed the presence of the natural phenolic compounds. The total phenolics were expressed as tannic acid equivalents and it was obtained 194 mg/g of plant material. It is well known that extraction solvents had significant effects on the quantity of phenolic compounds [23,25,33]. The high-performance liquid chromatography (HPLC) [25,34] analysis of composition of the *Satureja montana* L. has confirmed the presence of the phenolic compounds. Some authors [33] demonstrated good correlation between phenolic profiles and corrosion inhibition effect.

From the CV measurements, it is possible to determinate the total charges used for both processes (anodic, Q_A and cathodic, Q_C) occurring on the Fe electrode. The Q_A was estimated by integration of the anodic portion of cyclic voltammograms. Anodic charges determined after addition of *Satureja montana* L. extract (SM) and phenolic fraction (PF) are used to calculate the inhibition efficiency, h according to the equation:

$$\eta(\%) = \frac{Q_A^0 - Q_A}{Q_A^0} \cdot 100 \quad (2)$$

where Q_A^0 and Q_A represent anodic charges without and with extract (SM or PF). Inhibition efficiency is presented in Table 2 together with anodic charge values.

The calculated inhibition efficiencies obtained from the cyclic voltammetry method are close to the value determined from the potentiodynamic polarization measurements.

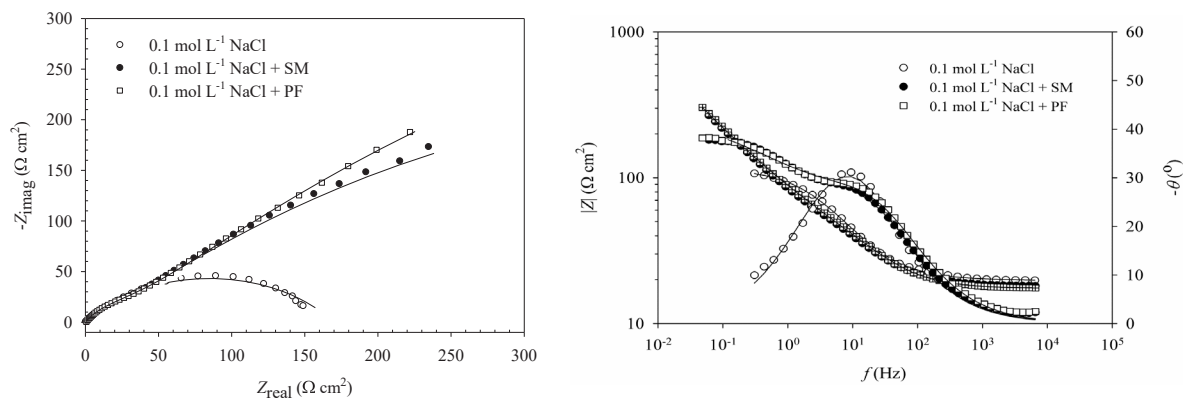


Figure 3: Nyquist and Bode plots of Fe electrode recorded at the E_{ocp} in 0.1 mol L⁻¹ NaCl solution, containing SM and PF of *Satureja montana* L.

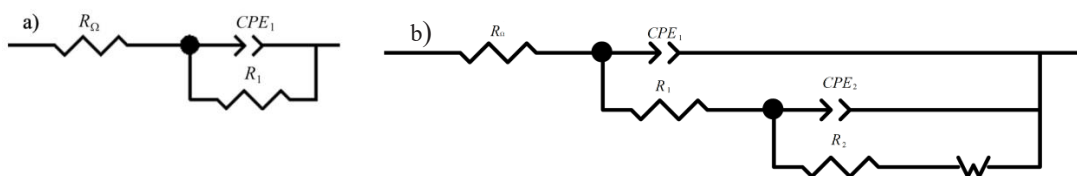


Figure 4: Electrical equivalent circuits used to fit the impedance spectra of Fe electrode (a) in the absence of extract and (b) in the presence of SM and PF.

3.3 Electrochemical impedance spectroscopy

The mechanism of the electrochemical processes included in the process of oxide film formation and how it is modified by the presence of a corrosion inhibitor has been investigated using impedance spectroscopy. Impedance spectra for Fe electrode without and with SM and PF extract in 0.1 mol L⁻¹ NaCl solution are presented in Figure 3 in the form of the Nyquist and Bode diagrams. The EIS diagrams were obtained at the open circuit potential.

The Nyquist plot obtained in the blank solution revealed one time constant; a single capacitive semi-circle, showing that the corrosion process is mainly charge transfer controlled [33,35]. As can be seen, in presence of inhibitor two time constants were observed in the Nyquist diagram: the capacitive loop at high frequencies and a straight line seen as Warburg impedance in the low frequency. The high frequency capacitive loops can be related to the charge transfer process. The second time constant, in the low frequency range, consists of surface layer resistance, R_2 , surface layer capacity, Q_2 and Warburg element that indicates a diffusion process through the surface layer.

The Bode plot obtained in the absence of the inhibitor shows three distinct regions (Figure 3).

In the higher frequency region ($f > 1$ kHz) the $\log|Z|$ values are low and phase angle values fall towards 0°, the data are dominated by electrolyte resistance. In the medium frequency region, the impedance of the system increases linearly with frequency decreases. In this area is appear the maximum phase angle ($\theta = -30^\circ$). This value differs considerably from those expected for an ideal capacitor, where $\theta = -90^\circ$. At the lowest frequencies the resistive behaviour of the system increases, but the area where $|Z|$ is independent on f is not completely reached.

Bode plots recorded in the presence of inhibitor showed that the Bode amplitude values over the entire frequency range increase with the addition of SM and PF. As further inspection in Figure 3, it can be seen that phase angles increased up to -40° at low frequency area in the presence of the SM and PF indicating a capacitive behaviour. These changes indicate improved corrosion resistance.

Equivalent circuit models shown in Figure 4 are used to simulate obtained impedance data from Figure 3. The standard criteria for evaluation of EEC best-fit were followed: the chi-square error was low ($\chi^2 \leq 10^{-4}$) and the acceptable errors of elements in fitting mode (5%). The numerical values of the EEC parameters are presented in Table 3.

Table 3: Impedance parameters for Fe electrode in 0.1 mol L⁻¹ NaCl solution in the absence and presence of SM and PF.

solution	$Q_1 \cdot 10^6$ (W ⁻¹ s ⁿ cm ⁻²)	n_1	R_1 (Ω cm ²)	$Q_2 \cdot 10^6$ (W ⁻¹ s ⁿ cm ⁻²)	R_2 (Ω cm ²)	$W \cdot 10^3$ (W ⁻¹ s ^{0.5} cm ⁻²)
NaCl	2004	0.65	118.3	-	-	-
NaCl + SM	1860	0.67	72.5	399	259.9	8.50
NaCl + PF	1524	0.76	85.7	385	285.6	7.91

Table 4: Amount of dissolved iron in 0.1 mol L⁻¹ NaCl solution at E_{ocp} containing SM and PF of *Satureja montana* L. obtained by the AAS technique.

Solution	The content of dissolved Fe (mg L ⁻¹ cm ⁻²)
NaCl	0.498
NaCl + SM	0.352
NaCl + PF	0.197

A constant phase element (CPE) was used in place of a capacitor to compensate for deviations from ideal dielectric behavior arising from the heterogeneities of the electrode surface [36]. The impedance of CPE is defined by the following equation: $Z_{\text{CPE}}(\omega) = [Q(j\omega)^n]^{-1}$, where Q is the frequency-independent constant, ω is the angular frequency, j is the imaginary constant and n is the CPE parameter which characterizes the deviation of the system from ideal capacitive behaviour. The value of n is between -1 and 1. For a perfect capacitor $n = 1$, for a perfect resistor, $n = 0$, and for an inductor $n = -1$ [37].

As can be seen from Table 3, the addition of SM and PF extracts leads to the increase in total resistance, $R_1 + R_2$ (from 118 to 332 and 371 W cm²) and decrease in double layer capacity, C_{dl} (from 2004 · 10⁻⁶ to 1860 · 10⁻⁶ and 1524 · 10⁻⁶ W⁻¹ s n cm⁻²). The decrease in C_{dl} , which can result from a decrease in local dielectric constant and/or an increase in the thickness of electrical double layer, suggests that the inhibitor molecules adsorbed at the metal/solution interface [33].

The total impedance of the Fe electrode/0.1 mol L⁻¹ NaCl interface without (3) and with SM and PF extract (4) is given by:

$$Z_{\text{tot}} = R_{\Omega} + \frac{R}{RQ(j\omega)^n + 1} \quad (3)$$

$$Z_{\text{tot}} = R_{\Omega} + \left[Q_1(j\omega)^{n_1} + \frac{1}{R_1 + (Q_2(j\omega)^{n_2} + \frac{1}{R_2 + W})^{-1}} \right]^{-1} \quad (4)$$

3.4 Atomic absorption spectrometry

Quantitative determination of iron ions concentration in 0.1 mol L⁻¹ NaCl solution obtained by atomic absorption spectrometry are presented in Table 2. Comparing these results, it can be observed that the quantities of released Fe ions are significantly reduced in the presence of both extracts.

It is obvious from Table 4 that the highest quantities of released Fe ions are in the pure NaCl solution (0.498 mg L⁻¹ cm²). An addition of phenolic compounds (SM and PF) in a NaCl solution reduces the amount of dissolved iron in the corrosive solution, especially in the presence of the PF extract. The results obtained from the AAS method are in accordance with the results recorded by electrochemical techniques. The inhibitive properties may be due to the presence of phenolic compounds in the extracts and formation of ferric complex.

4 Conclusions

The influence of *Satureja montana* L. extract and phenolic fraction of *Satureja montana* L. extract on the electrochemical behaviour of the iron in a 0.1 mol L⁻¹ NaCl was investigated using electrochemical techniques, atomic absorption spectrometry and UV/Vis spectrophotometry.

The presence of the total phenolic compounds in SM extract (194 mg/g; as tannic acid equivalents) was confirmed by UV/Vis spectrophotometry. Results of all techniques showed that the SM and PF contributed to the inhibition process. An inhibition activity is due to the precipitate of Fe-complex layer at the metal surface. According to the EIS results total resistance values were increased by adding SM and PF. The inhibition efficiency for SM extract was around 45% and for PF fraction was about 55%. The concentration of the metallic ions released into solution, measured by atomic absorption spectrometry, was in a good correlation with the results obtained from the electrochemical techniques.

Conflict of interest: Authors declare no conflict of interest.

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