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Effect of *Helichrysum italicum* on the Electrochemical Corrosion Behaviour of Iron in Simulated Acid Rain Solution

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Abstract: The aqueous extract of the *Helichrysum italicum* leaves (HI) is tested as a corrosion inhibitor of an iron in a simulated acid rain using potentiodynamic polarisation, cyclic voltammetry and electrochemical impedance spectroscopy. Results of all electrochemical methods indicate an increase of a corrosion inhibition efficiency of the iron with the HI extract concentration. Maximum inhibition efficiency (~ 50 %) is obtained at 2.0 g L^{-1} HI extract. The inhibitive action is assumed to occur via an adsorption of the HI extract on the iron surface. Results indicate that the adsorption process is spontaneous and follows the Freundlich adsorption isotherm. According to the calculated ΔG value (~ 15 kJ mol^{-1}), the corrosion inhibition of the iron occurs predominantly *via* a physisorption of the HI extract. The concentration of iron ions released into a solution, measured by atomic absorption spectrometry, is in accordance with the electrochemical results.

Keywords: iron, simulated acid rain, corrosion, *Helichrysum italicum*, electrochemical methods.

INTRODUCTION

IRON and stainless steel are among the most important materials because of their good properties and wide applications.[1–3] The main limitation for their applications is a corrosion attack.[4–7] The corrosion behaviour of metals and alloys primarily depends on the properties of the surface oxide layer. It is generally accepted that the passive film on the iron consists basically of a Fe(III) layer[4,6,7] and a good corrosion resistance of stainless steels lies in their ability to form a chromium-rich protective oxide layer, commonly called a passive film.[5,8] The stability of the oxide film depends on a large number of variables, such as temperature, chemical composition and pH of the electrolyte.[9–12]

Corrosion of metals and alloys particularly in an acidic media is an important industrial problem and primarily cause a breakdown of the oxide layer. In industrial environments the corrosion occurs quite rapidly due to highly corrosive nature of airborne pollutants (oxides of nitrogen, sulphur and carbon). These oxides in contact with water in the atmosphere cause a formation of an acid rain (sulphuric and nitric acids) and promote the corrosion.[13–17] A rainfall with pH < 5.6 is considered the acid rain. The importance of the protection against corrosion in acidic solutions is increased by the fact that iron and steel are more susceptible to be attacked in aggressive media. Because of general aggressiveness of the acidic media, inhibitors are commonly used to reduce the corrosion attack on metals and alloys which are in a contact with aggressive environments. In acid solution the corrosion inhibition of metals occurs through: electrostatic interaction of protonated molecules with already adsorbed ions, donor-acceptor interactions between π-electrons of aromatic ring and vacant *d* orbital of the surface iron atoms and interactions between unshared electron pairs of hetero atoms and vacant *d*-orbital of iron surface atoms.[9]

The use of plant extracts as corrosion inhibitors is justified by phytochemical compounds, which contain effective corrosion inhibition groups such as hydroxyl, carbonyl and aromatic. These groups adsorb on active metal surfaces and on that way they reduce the corrosion attack.[17–22] The anticorrosion activity of leaves extracts as *Achillea Millefolium* L.,[17] Mimosa tannin,[18,19] *Satureja* *montana* L.,[19] *Olea europaea* L.,[21] and *Helichrysum italicum*[22] was investigated.

The purpose of the present work is to evaluate the inhibitive effect of the *Helichrysum italicum* (Roth) G. Don as a green corrosion inhibitor of the iron in an acid rain. In our earlier paper[5] we studied an electrochemical behaviour of iron and AISI 304 stainless steel in an acid rain solution (pH 4.5). This study is a continuation of electrochemical investigations of the iron in an acid rain in the presence of the *Helichrysum italicum* (HI) as a potential corrosion inhibitor. The HI is a medicinal plant of a Mediterranean origin with outstanding antioxidant, antifungal and antibacterial activities.[23,24]

EXPERIMENTAL

A spectroscopically pure iron (Fe) was used as a working electrode. The surface area of the Fe exposed to the electrolyte was 0.636 cm^2. The electrode was mechanically abraded by 1200 grade emery paper, degreased with ethanol in an ultrasonic bath and rinsed with ultra pure water (18.2 MΩ cm, produced by Millipore Simplicity UV Water Purification System). Prior to each measurement the Fe electrode was polarized at –1.20 V *vs.* Ag|AgCl|3 M KCl electrode for 15 seconds to remove an air-formed surface oxide.

The electrochemical measurements were performed at a room temperature in a standard three electrode cell. The counter electrode was a platinum electrode and the reference electrode, to which all potentials in the paper are referred, was an Ag|AgCl|3M KCl.

The electrolyte was a simulated acid rain solution.[25] The pH value of solution was 4.5 and an electrical conductivity 1.306 mS cm^{-1}. pH value was adjusted by the addition of the appropriate amount of 0.5 mol L^{-1} H_2SO_4. All chemicals were of *p.a.* purity and obtained from Sigma Aldrich.

Experiments were performed in a simulated acid rain solution, pH 4.5, without and with an addition of a *Helichrysum italicum*. The aerial parts of the *Helichrysum italicum* were collected during summer 2017, in Čapljina, BiH. The HI specimens were dried in air for two weeks. An extract of plant materials was prepared after 3 h maceration at a room temperature. The concentrations of the *Helichrysum italicum* extract were 0.01, 0.10, 0.50, 1.00 and 2.00 g L^{-1}.

The formation and stability of an oxide film on the iron in a simulated acid rain solution were studied by the combination of electrochemical techniques, potentiodynamic polarisation measurement (PP), cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). All measurements were performed with an Autolab PGSTAT320N controlled by a personal computer using Nova 1.5 software.

The PP measurements were performed in the potential range from –0.20 V to 0.20 V near a corrosion potential with a scan rate of 1.0 mV s^{-1}. The CV measurements were carried out in the potential range between –1.20 V and –0.10 V.

The EIS measurements were carried out at open circuit potential in the frequency range between 10 kHz and 5 mHz with the ac amplitude ±10 mV.

Prior to each measurement the electrode was stabilized for 30 min at open circuit potentials. This procedure gave a good reproducibility of results.

The concentrations of metallic ions released into an acid rain solution after 60 minutes of specimens' immersion at the open circuit potential were obtained by atomic absorption spectrometry (AAS). Since the EIS measurements lasted approx. 60 minutes, the concentration of released ions was determined after this period of time.

RESULTS AND DISCUSSION

Potentiodynamic Polarisation

The potentiodynamic polarisation curves obtained for the Fe electrode in a simulated acid rain solution containing various concentrations of the *Helichrysum italicum* extract are shown in Figure 1. As can be seen from Figure 1 the presence of the HI extract induces changes in the polarisation behaviour of the iron compared with those in the pure acid rain solution. Observed results show that the HI extract addition decreases anodic and cathodic current densities, retards metallic deterioration and reduces the cathodic reaction of hydrogen evolution.

Table 1 shows the corresponding electrochemical polarisation parameters such as the corrosion potential

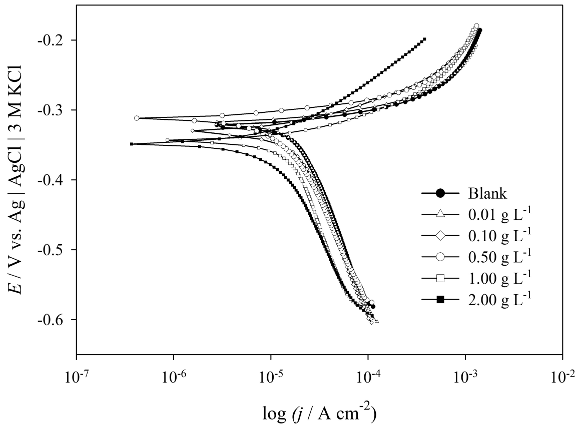

Figure 1. Potentiodynamic polarisation curves for the Fe electrode in a simulated acid rain solution, pH 4.5, containing different concentrations of the HI extract (shown in figure); v = 1 mV s^{-1}.

(E_{corr}) and corrosion current densities (j_{corr}) along with the inhibition efficiency (η). The inhibition efficiency was determined from corrosion current densities obtained by an intersection of cathodic and anodic Tafel lines, according to the equation:

$$\eta = \frac{j^0_{\mathrm{corr}} - j_{\mathrm{corr}}}{j^0_{\mathrm{corr}}} \cdot 100 \qquad (1)$$

where j^0_{corr} and j_{corr} represent the corrosion current densities of the Fe electrode in absence and presence of the HI extract, respectively. It can be seen from Table 1 that the addition of the HI extract decreases corrosion current density values and increases inhibition efficiencies. The decrease in the corrosion current density is most obvious at the maximal HI concentration.

The mode of the inhibition effect can be ascertained from a comparison of corrosion potentials and polarisation curves measured without and with an inhibitor.[26] When the corrosion potential changes noticeably with the inhibitor addition, the inhibition effect is due to the blocking of active sites on a metallic surface. Consequently, changes of activation energy barriers for anodic and cathodic reactions of the corrosion process occur.[26] On the other hand, if the E_{corr} negligible changes with the addition of an inhibitor, the inhibitory effect is by a geometric blocking effect. According to the results from Table 1, the corrosion inhibition of the HI extract is due to the blocking of active sites on the Fe surface.

Cyclic Voltammetry

The cyclic voltamograms of the iron recorded in a simulated acid rain solution in the absence and presence of the *Helichrysum italicum* extract are shown in Figure 2. The cyclic voltammograms were recorded within the narrow potential range (–1.20 to –0.10 V) where the initial film formation and its reduction occur. During the anodic sweep the current profile shows two anodic peaks. The first oxidation peak, A_1, at around –0.85 V, corresponds to the active-passive transition and can be ascribed to the formation of a non-protective $Fe(OH)_2$ layer.[27] The second anodic peak A_2, at around –0.45 V in the prepassive region, can be ascribed to the formation of a Fe(III) oxide. It was confirmed by XPS analysis under the similar experimental conditions.[28,29] At potentials more positive than –0.30 V, current profile reaches a steady-state value (j_{pl}) that remains constant up to –0.15 V. This is a passive region where a thickening of the oxide film with increasing anodic potentials occurs.[30] The reduction scan shows current peaks C_2 and C_1. They are related to the reduction of Fe(III) to Fe(II) and Fe(II) to Fe(0), respectively. Our previous research[5] showed that the reduction of anodically formed oxide layer is not complete.

Table 1. Electrochemical parameters (polarisation measurements) and calculated values of inhibition efficiency, η obtained from the data shown in Figure 1.

Solution, γ / g L^{-1}	E_{corr} / V	j_{corr} / A cm^{-2}	η / %
Blank	–0.321	$1.421 \cdot 10^{-5}$	–
0.01	–0.320	$1.244 \cdot 10^{-5}$	14.2
0.10	–0.327	$1.058 \cdot 10^{-5}$	25.5
0.50	–0.316	$9.440 \cdot 10^{-6}$	33.6
1.00	–0.344	$8.028 \cdot 10^{-6}$	43.5
2.00	–0.348	$6.530 \cdot 10^{-6}$	54.1

As can be seen from Figure 2, the addition of the HI extract had no significant effect on the oxidation process from Fe(0) to Fe(II) (peak A_1). The oxidation process from Fe(II) to Fe(III) (peak A_2) as well as the reduction processes from Fe(III) to Fe(II) and Fe(II) to Fe(0), peaks C_2 and C_1, were inhibited. The inhibitory action of the plant extract could be explained by the blocking of active sites on the iron surface by adsorbed organic molecules.

Adsorption Isotherm and Free Energy of Adsorption

The adsorption of organic compounds can be described by two main types of interactions, physical adsorption and chemisorption. These processes are influenced by the nature and charge of metal, the chemical structure of inhibitor and the type of electrolyte. It is widely acknowledged that adsorption isotherms provide an insight into the mechanism of corrosion inhibition.

From the CV experiments, it is possible to estimate the total charges used for anodic and cathodic processes

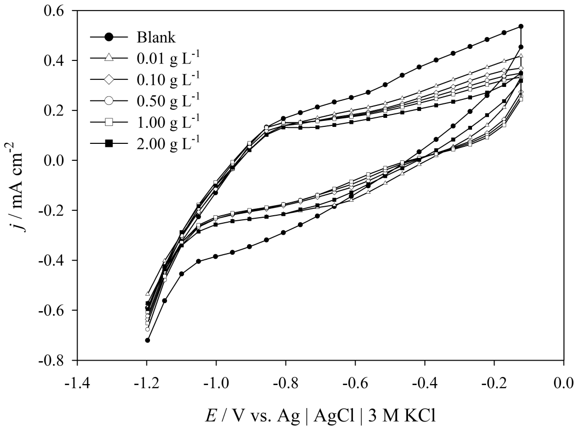

Figure 2. Cyclic voltammograms for the Fe electrode in a simulated acid rain solution, pH 4.5, containing different concentrations of the HI extract (shown in figure); v = 40 mV s^{-1}.

occurring on the Fe electrode. Integration of an anodic area of cyclic voltammograms (Figure 2.) gives the total charge of anodic processes, Q_A. Anodic charges determined without and with addition of the *Helichrysum italicum* extract are used to calculate the surface coverage, θ according to the equation:

$$\theta = \frac{Q_A^0 - Q_A}{Q_A^0} \tag{2}$$

where Q_A^0 and Q_A represent anodic charges in the absence and presence of the extract. Inhibition efficiency, η is calculated according to the Eq. (3) and presented in Table 2 together with surface coverage values.

$$\eta = \theta \cdot 100 \tag{3}$$

The values of inhibition efficiency follow the same trend as the values determined from the polarisation measurements.

Recently, we have investigated the corrosion inhibition of the iron in a simulated acid rain solution using the *Achillea Millefolium* L. extract. We have reported that in the presence of this extract an inhibition efficiency is very low around 26 % at concentration of 1.00 g L^{-1}.[17]

The degree of surface coverage values (θ) obtained from CV measurements using the Eq. (2) assuming a direct relationship between surface coverage and inhibition efficiency was tested graphically. The linear plot (Figure 3) obtained indicating that the experimental data fit the Freundlich adsorption isotherm.

The relationship between the surface coverage, θ, the equilibrium adsorption constant, K and the inhibitor concentration, γ is given by the following equations:

$$\theta = K\gamma^n \tag{4}$$

where $0 < n < 1$, or

Table 2. Anodic charge, surface coverage and inhibition efficiency calculated from the data shown in Figure 2.

Solution, γ / g L^{-1}	Q_A / mC cm^{-2}	θ	η / %
Blank	33.610	–	
0.01	28.720	0.146	14.6
0.10	25.329	0.246	24.6
0.50	21.605	0.357	35.7
1.00	20.934	0.377	37.7
2.00	16.151	0.519	51.9

$$\log\theta = \log K + n\log\gamma \tag{5}$$

The equilibrium adsorption constant is related to the free energy of adsorption $\Delta G°$:[17]

$$\Delta G° = -RT\ln\left[1000\ (\text{g L}^{-1})\cdot K\ (\text{L g}^{-1})\right] \tag{6}$$

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 calculated values of free energy of adsorption ($\Delta G° = -14.92$ kJ mol^{-1}) indicate a physical adsorption of organic compounds from the HI extract on the iron surface. The negative values of $\Delta G°$ ensure spontaneity of the adsorption process and stability of the adsorbed surface layer. Generally, values of the free energy of adsorption up to -20 kJ mol^{-1} are consistent with electrostatic interactions between organic molecules and charged metal surface and point to a physical adsorption.

Electrochemical Impedance Spectroscopy

Impedance measurements on the iron electrode in a simulated acid rain, pH 4.5, in the absence and presence (0.01, 0.10, 0.50, 1.00 and 2.00 g L^{-1}) of the *Helichrysum italicum* extract were performed at the open circuit potential. Impedance spectra are presented as Nyquist plots (Figure 4).

The impedance experimental data of the Fe electrode in pure acid rain solution and in the presence of the HI extracts were analysed by a fitting to the electric equivalent circuit (EEC) shown in detail of Figure 4, and

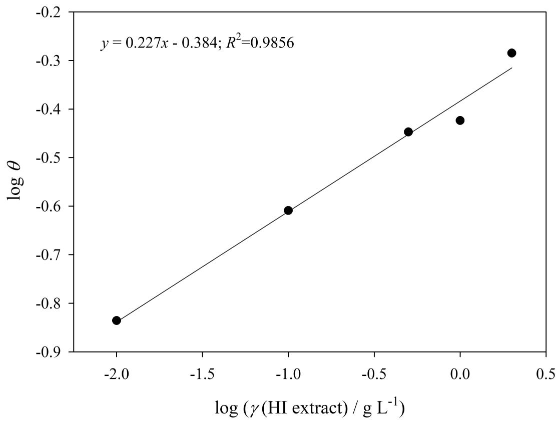

Figure 3. The Freundlich adsorption isotherm for the HI extract.

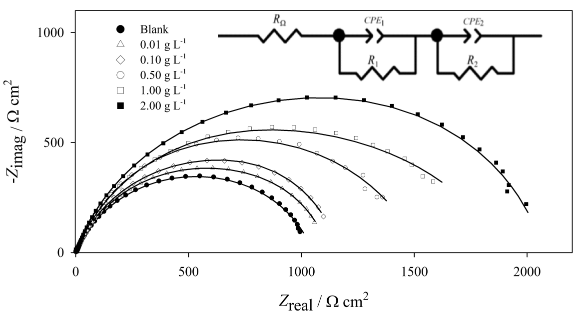

Figure 4. Impedance spectra (Nyquist plot) of the Fe electrode recorded at the E_{OCP} in a simulated acid rain solution, pH 4.5, containing different concentrations of the HI extract (shown in figure).

resultant values of EEC elements are given in Table 3. The usual criteria for the selection of best-fit electric equivalent circuits (EEC) are minimum number of circuit elements employed, the χ^2 error suitably low ($\chi^2 \leq 10^{-4}$), and errors associated with each element up to 5 %.

EEC consists of an electrolyte resistance (R_Ω = 50 Ω cm^2) connected with two time constant.

The first time constant, in the medium frequency range, is a result of a fast charge transfer process in the iron dissolution reaction in acid rain. R_1 is the charge transfer resistance corresponding to the corrosion reaction at the iron/solution interface. R_2 represents the resistance of the film formed on the iron surface.

CPE_1 and CPE_2 are constant phase elements, representing a modified double-layer capacitance and film capacitance.[31]

The CPE is introduced instead of a capacitor to compensate for deviations from ideal dielectric behaviour arising from roughness and inhomogeneous of the electrode surface.[32] Its impedance may be defined: $Z_{CPE}(\omega) = \left[Q(j\omega)^n\right]^{-1}$, where Q is a 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. 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 total impedance of the Fe electrode/acid rain interface in the absence and presence of the HI extract, recorded at the open circuit potential, is given by:

$$Z_{\text{tot}} = R_\Omega + \frac{R_1}{1+R_1Q_2(j\omega)^{n_1}} + \frac{R_2}{1+R_2Q_2(j\omega)^{n_2}} \tag{7}$$

As can be seen from Table 3, the increase in HI concentration leads to the increase of the charge transfer resistance (R_1) and the film resistance (R_2) while the capacity of the double-layer (Q_1) and capacity of film (Q_2) decrease.

From the Table 3 it can be seen that, when the HI extracts concentration increases from 0.01 to 2.00 g L^{-1}, the impedance of the system increases from 1.13 to 2.08 kΩ cm^2.

Observed behaviour is attributed to a decrease in a local dielectric constant and/or an increase in the thickness of the double layer due to the adsorption of the HI extract constituents.[33,34]

The inhibition efficiency, η can be calculated from charge transfer resistance values according to the following equation:[35]

$$\eta = \frac{R_{\text{ct}} - R_{\text{ct}}^0}{R_{\text{ct}}} \cdot 100 \tag{8}$$

where R_{ct}^0 and R_{ct} are the charge transfer resistance of the Fe in the absence and presence of HI extract. The values of the inhibition efficiency are presented in Table 3 and follow the same trend as the values determined from polarisation measurements and cyclic voltammetry.

Corrosion rate of iron was determined by impedance spectroscopy measurements using polarisation resistance, R_p (R_p is the sum of R_1 and R_2). Corrosion current densities,

Table 3. Impedance parameters for Fe electrode in a simulated acid rain solution, pH 4.5, in the absence and presence of HI extracts.

γ / g L^{-1}	$10^6\ Q_1$ / Ω^{-1} s^n cm^{-2}	n_1	R_1 / Ω cm^2	$10^6\ Q_2$ / Ω^{-1} s^n cm^{-2}	n_2	R_2 / Ω cm^2	η / %
blank	4161.6	0.886	156	338.7	0.747	895	–
0.01	6393.6	0.796	185	340.5	0.766	941	15.6
0.10	3498.5	0.871	210	310.1	0.779	958	25.7
0.50	1349.4	0.89	239	462.1	0.747	1162	34.7
1.00	1374.1	0.697	288	416.7	0.803	1507	45.8
2.00	1043.4	0.853	341	346.5	0.783	1734	54.3

Table 4. Corrosion parameters for the Fe electrode in a simulated acid rain solution, pH 4.5, in the absence and presence of HI extract.

γ / g L^{-1}	j_{corr} / A cm^{-2}	r / mm year^{-1}
Blank	8.14	0.063
0.01	7.60	0.059
0.10	7.33	0.057
0.50	6.11	0.047
1.00	4.77	0.037
2.00	4.12	0.032

j_{corr} and corrosion rates, r were calculated using Eq. (9)[36] and Eq. (10)[37] and are presented in Table 4.

$$j_{\mathrm{corr}} = \frac{RT}{zF}\frac{1}{R_{\mathrm{p}}} \tag{9}$$

$$r = \frac{0.00327\,M\,j_{\mathrm{corr}}}{z\rho} \tag{10}$$

where T is the temperature, R is the gas constant, F is the Faraday's constant, z is the number of electrons, R_{p} is the polarization resistance, M is atomic weight of iron and ρ is density of iron (7.874 g cm^{-3}).

From Table 4 it is clear that the increase of the HI concentration markedly decreases corrosion current density and corrosion rate of the iron in a simulated acid rain.

Iron Concentration in Acid Rain Solution

The quantities of Fe ions dissolved during 1 hour-immersion of the Fe specimen in an acid rain solution at E_{OCP} with and without the HI extract were determined by using the AAS technique. Generally, a metal dissolution is dependent on metal/alloy itself and pH of solutions. The results obtained in static immersion tests are listed in Table 5.

As can be seen from Table 5, the quantity of the Fe released originates from the iron immersed in the pure acid rain solution amounts to 214.22 μg L^{-1} cm^{-2}. An addition of the *Helichrysum italicum* extract in higher concentrations reduces the quantity of Fe ions released in the solution. These results are in a good agreement with the results obtained by electrochemical techniques and confirm the adsorption of organic compounds from the HI extract on the iron surface. The adsorption layer acts as an effective barrier between the Fe surface and an aggressive electrolyte.

CONCLUSION

The inhibition effectiveness of the *Helichrysum italicum* extract against the iron corrosion in a simulated acid rain was studied using electrochemical techniques. The aqueous extract of the *Helichrysum italicum* leaves was showed inhibitive properties for the iron corrosion in an investigated electrolyte. The protection efficiency of the HI extract was increased with increasing its concentration, showing maximal efficiency around 50 % at 2 g L^{-1}. The adsorption behaviour of the extract followed the Freundlich adsorption model. A physical adsorption between the HI extract and the iron surface was confirmed by the Gibbs energy value (–15 kJ mol^{-1}). The polarisation measurements revealed that the HI extract decreases anodic and cathodic current densities of the Fe, so the HI could be classified as an inhibitor of a mixed effect.

The results showed that the HI extract contributes to the iron corrosion inhibition by blocking active sites on the Fe surface. The adsorbed HI molecules act as a physical barrier preventing the electrolyte from contacting the iron surface. According to the impedance results, polarization resistance values increase (from 1.13 to 2.08 kΩ cm^2), and double layer capacitance values decrease (from $41.6\cdot10^{-4}$ to $10.4\cdot10^{-4}$ Ω^{-1} s^{n} cm^{-2}), which can be ascribed to an increase of the electrical double layer thickness. Atomic absorption spectrometry results showed that an addition of the HI extract reduces the quantity of Fe ions released in the solution (from 214.22 to 78.61 μg L^{-1} cm^{-2}).

Table 5. The quantities of Fe ions dissolved during 1 hour-immersion of the Fe specimen in an acid rain solution at E_{OCP} containing of the *Helichrysum italicum* extract obtained from the AAS technique.

Solution γ / g L^{-1}	Quantity of released Fe / μg L^{-1} cm^{-2}
Blank	214.22
0.50	147.23
2.00	78.61

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