

## CARBON STEEL CORROSION INHIBITION BY PLANT EXTRACT BASED GREEN INHIBITORS

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**ABSTRACT.** The inhibition effect of several plant extracts on the corrosion of carbon steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> has been investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). One has attempted to determine the corrosion characteristics in the absence and in the presence of natural plant extracts obtained from *Allium Sativum* and *Juglans Regia* using VoltaLab 40 potentiostat.

Potentiodynamic polarization curves were plotted at a scan rate of 20 mV/min. The EIS investigations have measured the response of the electrochemical system using a 10 mV a.c. potential excitation within a frequency zone ranging from 100 kHz to 50 mHz. Equivalent circuit model was proposed based on fitting the impedance data and hence the main parameters of the corrosion system were obtained.

The potentiodynamic polarization curves were employed to represent the Tafel lines and to evaluate the corrosion potential  $E_{\text{corr}}$  and the kinetic parameters namely the corrosion current density  $i_{\text{corr}}$  and the anodic,  $b_a$  and cathodic  $b_c$  Tafel slopes. The corrosion current densities have lower values in the presence of plant extracts. The inhibition efficiency calculated from the potentiodynamic polarization parameters and from EIS measurements were in agreement, the best results were obtained for the mixtures containing 400 ppm AS for all AS/JR concentration ratios.

**Keywords:** Inhibitors, Electrochemical impedance spectroscopy, Corrosion, Sulphuric acid, Steel

### INTRODUCTION

Nowadays intensive researches are accomplished to find new natural environmental friendly products, the so-called "green products". These may be able to substitute, up to a certain limit, the synthetic products, considered harmful for the environment, and no longer acceptable taking into account the environmental impact and also the true cost of using the synthetic products with serious side effects. Natural plant extracts may show inhibiting effects,

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these products presenting the advantage of biodegradability, being able to replace synthetic inhibitors phased out due to increased enforced stringent environmental legislation.

The cost of corrosion is very high for any country. Corrosion never stops but its damages can be decreased. The use of inhibitors is one of the best-known methods of corrosion protection [1, 2]. The importance of inhibitive protection in acidic solutions is increased by the facts that steels, that are more susceptible to be attacked in aggressive media, are the commonly exposed metals in industrial environments. Numerous works have been dedicated to corrosion inhibiting effects of different plant extracts in acidic aqueous solutions on metallic materials [3-6]. Their choice is based on their low-cost and stability as corrosion inhibitors for metallic materials in acidic media and because these compounds are environmental friendly.

Among other methods of corrosion investigation, the application of electrochemical impedance spectroscopy technique (EIS) as a new tool for the study of corrosion research has resulted in information concerning the methods of corrosion protection [7], which were difficult to study with traditional dc techniques; EIS has provided useful information concerning corrosion protection by anodic films and by inhibitors [8-13]. In addition to specification of the physical properties of the system, the technique leads to important mechanistic and kinetic information [14-16]. Some advantages of ac impedance techniques are the use of only very small signals which do not disturb the electrode properties to be measured, the possibility of studying corrosion reactions and measuring corrosion rates in media where traditional dc methods fail, and the fact that polarization resistance as well as double layer capacitance data can be obtained in the same measurements.

The authors have previously investigated [17] the effect of the addition of single plant extract as inhibitor for steel corrosion in sulphuric acid. This paper shows the results obtained on the corrosion inhibition of steel in 0.5 M sulphuric acid by combining the studied plant extracts at different ratios. It was analyzed the interaction between the plant extracts by calculating the synergism parameter, and also the authors have proposed an electrical equivalent circuit model by using EIS results.

## RESULTS AND DISCUSSION

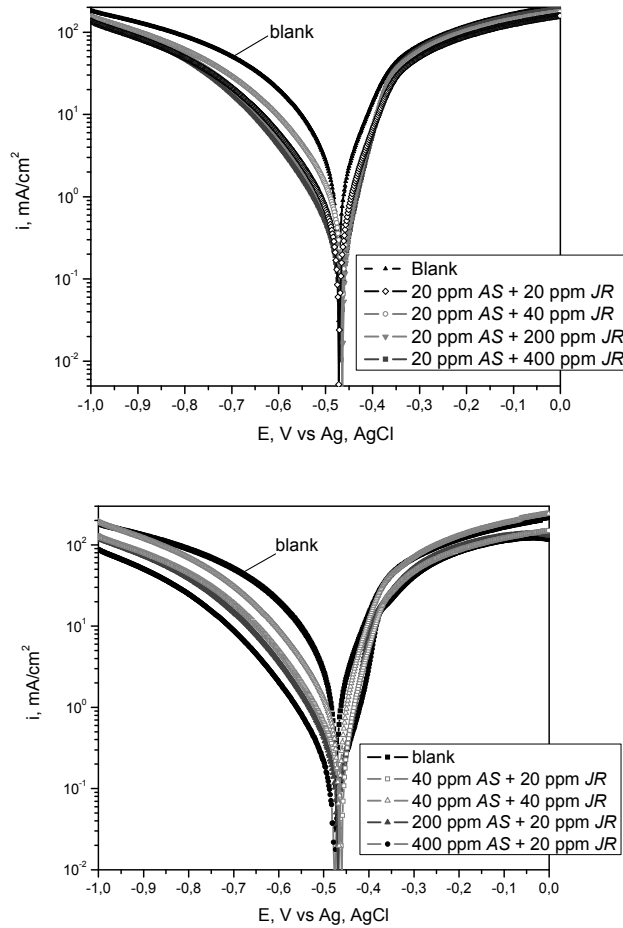
### Polarization measurements

The potentiodynamic curves were recorded in the absence (blank test solution) and in the presence of various plants extract concentration. Figure 1 shows some of the potentiodynamic polarization curves carried out at 25<sup>o</sup> after 30 minutes of immersion time in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence and absence of *Allium Sativum* (AS) and *Juglans Regia* (JR). By using the

experimental data important parameters were extracted: corrosion current density,  $i_{\text{corr}}$ , corrosion potential,  $E_{\text{corr}}$ , anodic  $b_a$  and cathodic  $b_c$  Tafel slopes, which are listed in Table1. These values were calculated from the intersection of the anodic and cathodic Tafel lines of the polarization curve at  $E_{\text{corr}}$ . The inhibition efficiencies were calculated by the following expression:

$$IE = \left( 1 - \frac{i_{\text{corr}}}{i_{\text{corr}}^0} \right) \times 100, \% \quad (1)$$

where  $i_{\text{corr}}^0$  and  $i_{\text{corr}}$  are respectively, the corrosion current densities without and with addition of plant extracts in 0.5 M  $\text{H}_2\text{SO}_4$  solution.



**Figure 1.** Polarization curves for steel in 0.5 M  $\text{H}_2\text{SO}_4$  with mixtures of different concentrations of *Allium Sativum* and *Juglans Regia*

Although the addition of *AS* and *JR* does not affect the general shape of the curves, it can be seen (Figure 1) that both cathodic and anodic curves are affected by the inhibitor presence. The results presented in Table 1 indicate that the presence of *AS* and *JR* inhibit the corrosion process by reducing the corrosion current densities to lower values.

Tafel plots in 0.5 M H<sub>2</sub>SO<sub>4</sub> revealed that the presence of the plant extracts generally shifted the corrosion potential towards positive values with reference to the blank 0.5 M H<sub>2</sub>SO<sub>4</sub>. This signifies that the addition of *AS* and *JR* has an inhibitor effect on the corrosion process. The presence of plant extracts lead to a decrease of anodic Tafel slopes, indicating that the inhibitor acts mainly on the anodic reaction. Based on these results *AS* and *JR* are considered as mixed-type inhibitor, meaning that it reduces the anodic dissolution of steel and also retards the cathodic reaction.

**Table 1.** Tafel polarization parameters for steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence of different concentrations of *Allium Sativum* and/or *Juglans Regia*

AS conc. (ppm)	JR conc. (ppm)	$i_{\text{corr}}$ (mA/cm <sup>2</sup> )	$E_{\text{corr}}$ (mV)	$b_c$ (mV/dec)	$b_a$ (mV/dec)	IE%
0	0	0,738	-483	110	74	-
0	20	0.611	-470	115	69	17.22
20	0	0.424	-465	111	53	42.58
20	20	0.387	-477	111	58	47.62
40	20	0.331	-463	114	50	55.09
200	20	0.265	-470	109	46	64.09
400	20	0.158	-478	103	51	78.60
40	0	0.549	-480	107	54	25.69
0	40	0.500	-463	120	59	32.22
20	40	0.651	-469	98	63	11.87
40	40	0.625	-471	99	50	15.39
200	40	0.268	-469	109	43	63.66
400	40	0.114	-472	113	44	84.63
200	0	0,211	-462	115	47	71.42
0	200	0.376	-457	119	54	49.03
20	200	0.369	-466	113	51	50.02
40	200	0.587	-465	115	57	20.49
200	200	0.301	-469	115	40	59.30
400	200	0.177	-477	104	53	76.01
400	0	0.216	-459	101	45	70.79
0	400	0.438	-452	119	57	40.69
20	400	0.300	-469	110	51	59.33
40	400	0.617	-465	116	55	16.47
200	400	0.207	-473	111	44	72.02
400	400	0.134	-486	109	51	81.90

The inhibition efficiencies from Table 1 are calculated with equation (1), and show highest values for 400 ppm AS, the highest efficiency value being obtained for the mixture 400 ppm AS + 40 ppm JR. For the same concentration of JR the inhibition efficiency is generally increasing with the increase of AS concentration.

### Electrochemical Impedance Spectroscopy

The impedance diagrams are given in the Nyquist (Figure 2) and Bode (Figure 3) representations.

The data processing was based on a non-linear least squares fitting procedure. In this case inhibition efficiencies IE% were calculated through the following expression:

$$IE = \left( 1 - \frac{R_p^0}{R_p} \right) \times 100, \% \quad (2)$$

where  $R_p^0$  and  $R_p$  are the polarization resistance values observed in absence and presence of inhibitor, respectively.

The polarization resistance ( $R_p$ ) values are calculated from the difference in impedance at lower and higher frequencies [12].

To obtain the double layer capacitance ( $C_{dl}$ ) one must find the frequency at which the imaginary component of the impedance is maximum ( $Z_{max}$ ) and the capacitance is represented by the equation

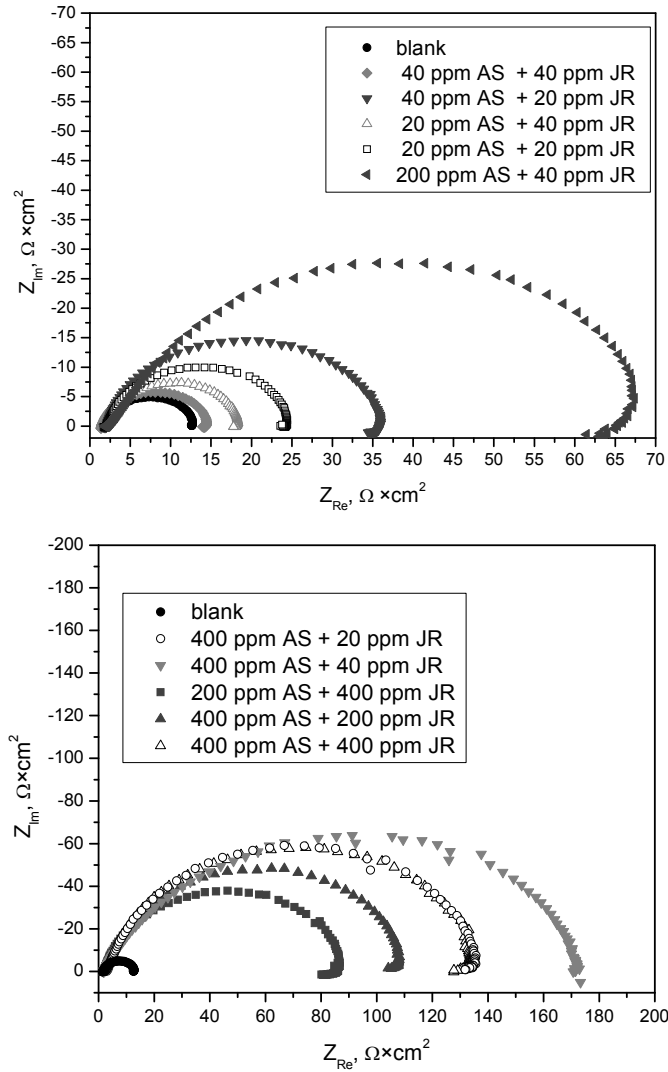
$$C_{dl} = \frac{1}{\omega \cdot R_p} \quad (3)$$

where  $\omega = 2 \cdot \pi \cdot f_{max}$ , is the angular frequency.

All Nyquist diagrams of steel exposed for 30 min at free corrosion potential in inhibited and uninhibited acidic solution containing different concentrations of AS and JR plant extracts consist of a depressed capacitive semicircle at high frequencies and a small inductive one at low frequencies (Figure 2). The low frequency inductive loop may be attributed to the relaxation process of the adsorbed species.

The intersection of the capacitive loop with the real axes at the highest values of frequencies gives the value for the resistance of the solution ( $R_s$ ) enclosed between the working electrode and the counter electrode. The point of intersection between the inductive loop and the real axis represents the sum ( $R_s + R_p$ ) where  $R_p$  is the polarization resistance defined as the dc limit of the impedance.

The highest values of polarization resistances were generally obtained for the mixtures containing 200 and 400 ppm AS.



**Figure 2.** Nyquist plots for steel corrosion in 0.5 M  $H_2SO_4$  with different concentrations of *Allium Sativum* and *Juglans Regia*

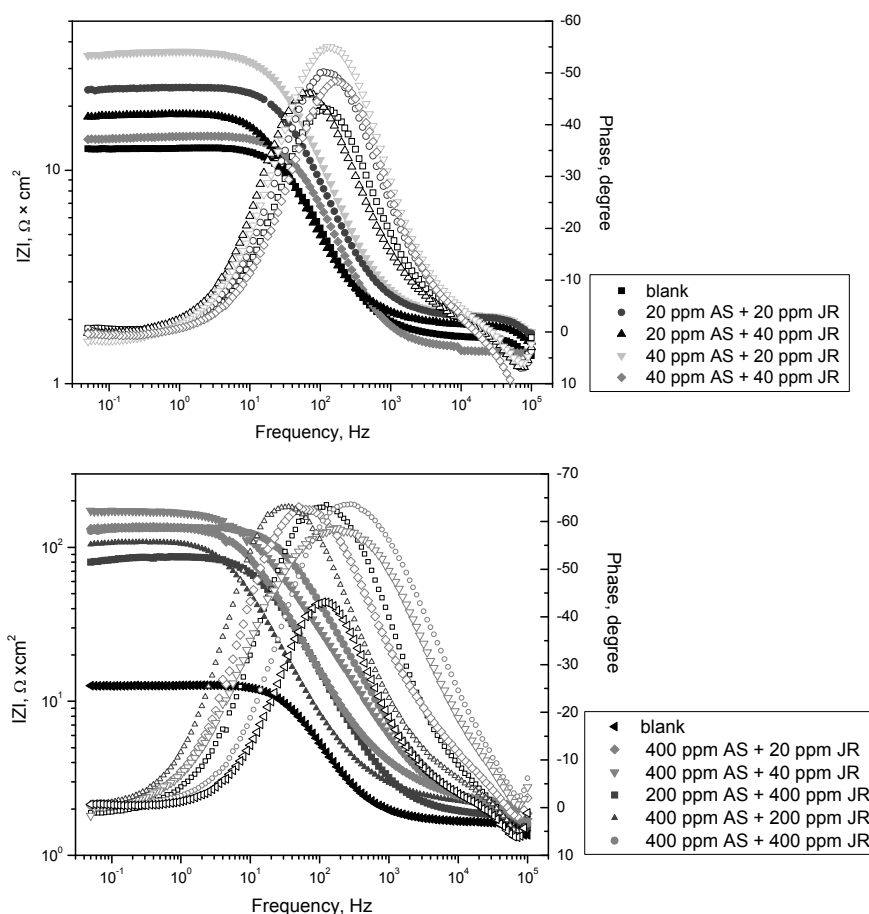
It is essential to develop the appropriate model for the impedance, which then can be used to fit the experimental data and to evaluate the parameters that characterize the corrosion process.

The Nyquist plots in Figure 2 are not perfect semicircles, and in the Bode plots, in Figure 3, the slopes of the  $\log |Z|$  against  $\log f$  curves are lower than -1. This kind of deviations can be attributed to the non-homogeneity of the electrode surface arising from surface roughness or interfacial phenomena.

The impedance parameters obtained from electrochemical spectroscopy investigations are mentioned in Table 2.

The presence of AS and JR compounds (Table 2) enhances the value of  $R_p$  in acidic solution indicating that a charge transfer process is mainly controlling the corrosion of steel, also the increase of  $R_p$  is generally interpreted by the adsorption of inhibitor molecules [18].

The decrease of the double layer capacitance  $C_{dl}$  is due to the adsorption of plant extract on the metal surface leading to the formation of film from acidic solution [19]. More the inhibitor is adsorbed, more the thickness of the deposited film is increased according to the expression of the layer capacitance presented in the Helmholtz model [20].



**Figure 3.** Bode plots of impedance spectra for steel in 0.5 M  $H_2SO_4$  at 25°C with various concentrations of *Allium Sativum* and *Juglans Regia*

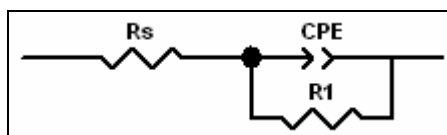
**Table 2.** Electrochemical parameters of impedance for the corrosion of steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> in the presence of different concentrations of *Allium Sativum* and/or *Juglans Regia*

AS conc. (ppm)	JR conc. (ppm)	R <sub>p</sub> , Ω×cm <sup>2</sup>	C <sub>dl</sub> , μF×cm <sup>-2</sup>	Φ <sub>max</sub> , degree	IE%
0	0	11.35	350.4	-43	-
0	20	27.82	326.1	-47	59.20
20	0	31.76	220.0	-55	64.26
20	20	22,80	195.4	-50	50.22
40	20	34.13	165.9	-55	66.74
200	20	66.86	266.5	-62	83.02
400	20	134.10	149.4	-63	91.54
0	40	60.23	797.7	-55	81.15
40	0	44.75	157.3	-54	74.64
20	40	16.22	490.5	-46	30.02
40	40	13.12	242.5	-48	13.49
200	40	64.55	345.1	-53	82.42
400	40	172.70	92.1	-59	93.43
0	200	25.28	588.8	-55	55.10
200	0	90.11	228.2	-62	87.40
20	200	20.66	308.1	-52	45.06
40	200	20.19	441.2	-52	43.78
200	200	57.56	221.1	-60	80.28
400	200	107.00	296.6	-63	89.41
0	400	23.68	521.8	-53	52.07
400	0	71.46	291.9	-62	84.12
20	400	25.92	245.6	-54	56.21
40	400	13.82	230.2	-48	17.87
200	400	86.70	130.6	-64	86.91
400	400	136.90	36.7	-64	91.71

Figure 3 shows the influence of concentrations on modulus spectra of steel and on phase angle in absence and presence of the inhibitor. In all cases the figures show that the IZI against  $f$  logarithmic curves exhibit three distinctive segments. In the higher frequency region, the IZI tends to become 1 with the phase angle values falling rapidly towards 0 with increasing frequency. This is a typical response of resistive behavior and corresponds to the solution resistance [21]. In the medium frequency region, a linear relationship between IZI against  $f$ , with a slope lower than -1 and the phase angle being in the range -43 in blank acidic solution to -64 degree in the presence of plant extracts, can be observed (Table 2). This response is characteristic for a capacitive behavior. An ideal capacitive response would result in a slope of -1 and a phase angle of -90 degree. In the low-frequency region, the resistive behavior of the electrode increases.

The phase angle for the double layer in the presence of *AS* and *JR* inhibitors were shifted toward higher degrees comparing to the case of acidic solution, because these extracts may have effects on the frequency dispersion of the double layer capacitance.

The equivalent circuit used to fit the experimental data, in the absence and in the presence of inhibitor, is shown in Fig. 4. The components of the circuit are  $R_s$ , the electrolyte resistance ( $\Omega \times \text{cm}^2$ ),  $R_p$ , the polarization resistance ( $\Omega \times \text{cm}^2$ ) and CPE, a constant phase element. As mentioned before, the presence of CPE in the electrical circuit instead of a capacitance is due to the non-homogeneity of the electrode surface.



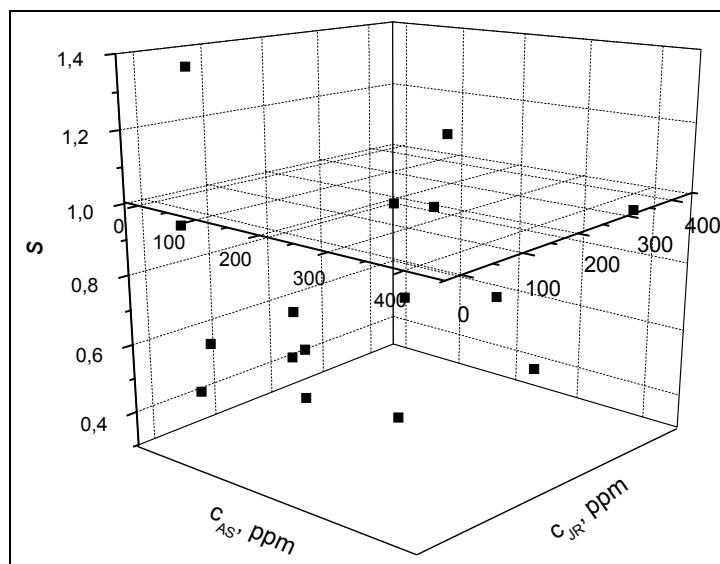
**Figure 4.** The equivalent electrical circuit of the impedance spectra obtained for steel in the absence and presence of the investigated mixtures of inhibitor

With this proposed model a very good fit was obtained with our experimental data, the fitted data matching the experimental, with an average error of about 2.5%.

For studying the joint effect of *Allium Sativum* and *Juglans Regia*, the synergism parameter,  $s$  was calculated, as proposed by Hosseini et al [22] which is describing the combined inhibition behavior of the studied extracts. Generally, for the interaction of two inhibitors A and B, the synergism parameter is defined as [23]:

$$s = \left( \frac{1 - IE_A - IE_B + IE_A \times IE_B}{1 - IE_{AB}} \right) \quad (4)$$

where  $IE_A$  and  $IE_B$  are the inhibition efficiencies evaluated for compound A and B respectively acting alone, and  $IE_{AB}$  is the experimentally observed inhibition efficiency for the mixture AB, the concentration of the compounds A and B in the mixture being the same as in the corresponding separate situations. The expression compares the theoretically expected corrosion rate based on the condition where either A or B are present or on the condition that they do not interact, with the experimentally observed rate in the presence of the inhibitor mixtures [23]. In the case where inhibitors A and B have no effect on each other and adsorb at the metal/solution interface independently,  $s = 1$  as in that case the predicted behavior is experimentally confirmed. Alternatively, the effect would be synergistic if  $s > 1$  or antagonistic if  $s < 1$ .



**Figure 5.** Synergism parameter  $s$  for the combined effect of AS and JR on the corrosion of steel in 0.5 M  $H_2SO_4$

In Figure 5 the values of synergism parameter,  $s$ , for the investigated concentrations of AS and JR are presented. This 3D graph shows that antagonism occurs in many of the studied mixtures. It can be observed that the mixture 200 ppm AS + 20 ppm JR is characterized by a very moderate synergism ( $1 < s < 1.2$ ) whereas for the mixtures 40 ppm AS + 20 ppm JR and 200 ppm AS + 40 ppm JR a more pronounced synergistic effect is found.

The antagonistic and synergetic effects observed can be due to the electrostatic interaction between the oppositely charged ions that prevents their co-adsorption on the metal surface. The forces involved in that case enable interfacial adsorption to occur at a higher extent (resulting in a higher value of surface adsorption for the same concentration) than in the case if only one inhibitor is present.

## CONCLUSIONS

Tafel polarization and EIS measurements were accomplished in the present study to increase the possibility of using plant extracts as green type inhibitors for the corrosion of steel in 0.5 M  $H_2SO_4$ . The inhibitive and the combining effect of *Allium Sativum* (AS) and *Juglans Regia* (JR) were studied.

Tafel measurements showed that the presence of AS and JR mixtures lowered the corrosion current densities and shifted the corrosion potential towards positive values. This fact signifies that the addition of AS and JR

inhibitive mixture has an inhibitor effect on the corrosion of steel in 0.5 M sulphuric acid solution. The anodic Tafel slopes decrease in the presence of plant extracts and the cathodic Tafel slopes has a generally increasing tendency.

The electrochemical impedance spectroscopy studies have shown that the impedance response consists of large capacitive depressed semicircles for high frequencies values and small inductive loops for the low frequency values. The presence of *AS* and *JR* compounds increases the polarization resistance values indicating that a charge transfer process is mainly controlling the corrosion of steel. The decrease of the double layer capacitance is due to the adsorption of plant extracts on the metal surface. A Randles type equivalent circuit was proposed for the studied system and the fitting data matched the experiment with an average error of about 2.5%.

The best inhibition efficiencies were obtained for the mixtures containing 400 ppm *AS* and also for the mixture 200 ppm *AS* + 400 ppm *JR*.

For studying the joint effect of *Allium Sativum* and *Juglans Regia*, the synergism parameter,  $s$  was calculated, and the mixture 200 ppm *AS* + 20 ppm *JR* was found to be characterized by a weak synergism ( $1 < s < 1.2$ ) whereas the mixtures 40 ppm *AS* + 20 ppm *JR* and 200 ppm *AS* + 40 ppm *JR* has a more pronounced synergistic effect. For the other studied mixtures the data showed that antagonism occurs.

The study showed that *Allium Sativum* and *Juglans Regia* can act as corrosion inhibitor for steel in sulphuric acid media.

## EXPERIMENTAL SECTION

Working electrodes consist of steel sheets with the following chemical composition, wt.%, C: 0.21, Mn: 2.5, S: 0.04, P: 0.04, Si: 0.35, Fe: to balance.  $H_2SO_4$  reagent used was of analytical grade without previous purification. Double distilled water was used for solution preparations. The plant extracts are commercially available, being purchased from different manufacturers: *Allium Sativum* (*AS*) supplied by HOFIGAL S.A. Romania (50% vol in ethylic alcohol), reference no. 93 GMP and *Juglans Regia* (*JR*) supplied by PlantExtract®, Romania (50% vol in ethylic alcohol), reference no. 05170807A. For the experiments containing plant extracts, the appropriate quantity was added to blank solutions to reach final concentrations of 20, 40, 200 and 400 ppm.

The methodologies used to investigate steel corrosion inhibition of *Allium Sativum* and *Juglans Regia* in aerated 0.5 M  $H_2SO_4$  included potentiodynamic polarization (Tafel polarization) and electrochemical impedance spectroscopy techniques. Thermostated double-walled (50 mL) Metrohm glass cell was used for all the electrochemical tests.

Prior to all measurements, the steel samples were polished with different emery paper grades up to 1000, washed with bidistilled water and dried. The base solution (0.5 M  $H_2SO_4$ ) was prepared by dilution of analytical grade (Merck) 98%  $H_2SO_4$ , used without further purification, with bidistilled water.

Impedance spectroscopy measurements were carried out in the same three electrodes glass cell, with a square steel sheet with the exposed area  $0.5 \text{ cm}^2$  as the working electrode. A silver/silver chloride immersed directly into the solution and a platinum disc with the surface of  $1.13 \text{ cm}^2$  Radiometer Analytical electrodes are used, as reference and auxiliary electrodes, respectively. All potentials in the text are referred to this reference electrode (Ag, AgCl). The temperature was thermostatically controlled and set up at  $25 \pm 1^\circ\text{C}$  and the electrolyte solutions were in equilibrium with the atmosphere (i.e., aerated solutions).

All the measurements were carried out using a Voltalab 40, Radiometer Analytical potentiostat/galvanostat interfaced with a computer using VoltaMaster 4.0 software. Experiments were performed in duplicate; data reported are the average.

Before polarization and EIS measurements, the working electrode was introduced in the test solution and left for 30 min to attain the open circuit potential. Polarization curve measurements were made at a scan rate of  $20 \text{ mV/min}$  starting from cathodic potential towards anodic direction. Electrochemical impedance spectroscopy was carried out at the open-circuit potentials in the frequency range  $100 \text{ kHz} - 50 \text{ mHz}$  with a sinusoidal potential perturbation of  $10 \text{ mV}$  amplitude. The data of impedance spectra results were fitted on equivalent circuits, a Randles type circuit, using ZView software.

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## REFERENCES

1. R. Javaherdashti, *Anti-Corrosion Methods and Materials*, **2000**, *47*, 30.
2. M. Elachouri, M.R. Infante, F. Izquierdo, S. Kertit, H.M. Goudaya, B. Nciri, *Corrosion Science*, **2001**, *43*, 19.
3. K. Anuradha, R. Vimala, B. Narayanasamy, J. Arockia Selvi, Susai Rajendran, *Chemical Engineering Communication*, **2008**, *195*, 3, 352.
4. Y. Abboud, A. Abourriche, T. Ainane, M. Charrouf, A. Bennamara, O. Tanane, B. Hammouti, *Chemical Engineering Communication*, **2009**, *196*, 7, 788.
5. H. Ashassi-Sorkhabi, E. Asghari, *Electrochimica Acta*, **2008**, *54*, 162.

6. P.C. Okafor, U.J. Ekpe, E.E. Ebenso, E.M. Umoren, K.E. Leizou, *Bulletin of Electrochemistry*, 21, 8, **2005**, 347.
7. S.S. Abdel Rehim, H.H. Hassaan, M.A. Amin, *Materials Chemistry and Physics*, **2001**, 70, 64.
8. F. Mansfeld, M.W. Kendig, *Journal of Electrochemical Society*, **1988**, 135, 828.
9. K.F. Khaled, *Electrochimica Acta*, **2003**, 48, 2493.
10. S.W. Donne, J.H. Kennedy, *Journal of Applied Electrochemistry*, **2004**, 34, 159.
11. F. Bentiss, M. Traisnel, H. Vezin, H.F. Hildebrand, M. Lagrenée, *Corrosion Science*, **2004**, 46, 278.1.
12. M. Bouklah, A. Attayibat, B. Hammouti, A. Ramdani, S. Radi, M. Benkaddour, *Applied Surface Science*, **2005**, 240, 341.
13. B. El Mehdi, B. Mernari, M. Traisnel, F. Bentiss, M. Lagrenée, *Materials Chemistry and Physics*, **2002**, 77, 489.
14. F. Mansfeld, M.W. Kendig, W. Lorenz, *Journal of Electrochemical Society*, **1985**, 132, 290.
15. D.D. Macdonald, *Electrochimica Acta*, **1990**, 35, 1509.
16. F. Mansfeld, S. Lin, S. Kim, H. Shin, *Corrosion Science*, **1987**, 27, 997.
17. A. Cojocaru, I. Major, D.I. Vaireanu, I. Lingvay, C. Lingvay, S. Caprarescu, *Revista de Chimie*, **2009**, *in press*.
18. A. Yurt, A. Balaban, S. Üstün Kandemir, G. Bereket, B. Erk, *Materials Chemistry and Physics*, **2004**, 85, 420.
19. F. Bentiss, M. Lagrenée, M. Traisnel, J.C. Hornez, *Corrosion Science*, **1999**, 41, 789.
20. M. Kissi, M. Bouklah, B. Hammouti, M. Benkaddour, *Applied Surface Science*, **2006**, 252, 4190.
21. Z. Zhang, S. Chen., Y. Li, S. Li, L. Wang, *Corrosion Science*, **2009**, 51, 291.
22. M. Hosseini, S.F.L. Mertens, M.R. Arshadi, *Corrosion Science*, **2003**, 45, 1473.
23. L. Larabi, Y. Harek, M. Traisnel, A. Mansri, *Journal of Applied Electrochemistry*, **2004**, 34: 833.