Estimation of Inhibition Efficiency for Carbon Steel Corrosion in Acid Media by Using Natural Plant Extracts

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The inhibitive effect of Allium Sativum (AS), Juglans Regia (JR) and Pogostemon Cablin (PC) plant extracts on the corrosion of steel in aqueous solution of 1N sulphuric acid was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Potentiodynamic polarization curves indicated that all the studied plant extracts act as mixed-type inhibitors. EIS measurements showed that the corrosion process is under activation control. The values of inhibition efficiency of the extract obtained from both impedance and polarization measurements were in agreement and in most cases were found to increase with increasing concentration of the extract with the exception of JR extract. The obtained results showed that the AS extract could serve as an effective inhibitor for the corrosion of steel in acid media.

Keywords: corrosion, steel, Allium Sativum, Juglans Regia and Pogostemon Cablin, potentiodynamic polarization, electrochemical impedance spectroscopy

Carbon steel corrosion is a very important phenomenon studied from both theoretical and applicative point of view especially in acidic medium [1, 2]. This interest is due to the development of industrial use of acidic solutions among which the most important fields are acid descaling, industrial cleaning, acid pickling of steel and ferrous alloys or petrochemical processes [1-3].

Different corrosion inhibitors are used to control and reduce corrosion of metals in corrosive media. Due to toxicity of most inorganic corrosion inhibitors, such as chromates and nitrites, and also because of restrictive environmental regulations, these inhibitors are being replaced by new environment-friendly compounds [4-10]. The search of new classes of compounds completely soluble in aqueous media with high inhibition efficiency but with low environmental pollution risk is a goal of many researchers in the last years [11-40].

Steel corrosion in different solutions has been effectively controlled using organic inhibitors containing nitrogen, oxygen or sulphur [11-20]. Amino acids are non-toxic, relatively cheap and easy to be produced with purities higher than 99% and have been used in corrosion inhibition of different metals such as nickel [21], iron and steel [22-24], aluminium [25, 26] and Pb–Sb–Se–As alloy [27] in H_2SO_4 and HCl solutions.Corrosion inhibition and adsorption behavior of methionine on mild steel in H_2SO_4 solution and synergistic effect of iodide ion in static conditions were studied [28]. The study showed that methionine acts as a corrosion inhibitor for mild steel in acid solution and its performances are improved in the presence of iodide ion.

The rich source of naturally synthesized chemical compounds in plants that can be extracted by simple procedures at a low cost has motivated the use of these natural products.

The aim of this paper is to study the possibility of using Allium Sativum (AS), Juglans Regia (JR) and Pogostemon Cablin (PC) of various concentrations as safe inhibitors for steel corrosion in aerated 1 N H₂SO₄ solutions. From our knowledge there are no studies regarding these plant extracts tested as corrosion inhibitors. Measurements were

carried out using various corrosion monitoring techniques: open circuit potential, potentiodynamic polarization (Tafel polarization) and impedance techniques at $25 \pm 1^{\circ}$ C.

Experimental part

Working electrodes consisted in carbon steel sheets with the chemical composition, wt.%, C: 0.21, Mn: 2.5, S: 0.04, P: 0.04, Si: 0.35, Fe: to balance. H₂SO₄ reagent was of analytical grade chemical reagent used without previous purification. Distilled water was used for solution preparations. The plant extracts are commercially available, being purchased from various manufacturers: Allium Sativum (AS) supplied by HOFIGAL s.a. Romania (50% vol in ethylic alcool), reference no. 93 GMP, Juglans Regia (JR) supplied by PlantExtract®, Romania (50% vol in ethylic alcool), reference no. 05170807A and Pogostemon Cablin (PC) supplied by TchiboGmbH Germany, reference no.256305 (oily extract). For the experiments containing plant extracts, the appropriate quantity was added to blank solutions to reach final concentrations for all of the plant extracts of 0.1, 0.2, 1 and 2% volume. All experiments were carried out at room temperature and no deaeration procedure was applied.

A double-walled glass three-electrode standard electrochemical cell of 50 mL was used to carry out the corrosion tests. The steel working electrode had the geometric area of 0.50 cm². Prior to each polarization experiment, the electrode surface was polished with emery paper, rinsed with distilled water and dried. The auxiliary electrode was a Radiometer Analytical platinum electrode with the surface of 1.13 cm² and the reference electrode was a Radiometer Analytical saturated silver/silver chloride electrode immersed directly into the solution. All potentials in the text are referred to this reference electrode.

The electrochemical measurements, including Electrochemical Impedance Spectroscopy, were carried out using a Voltalab 40, Radiometer Analytical potentiostat/ galvanostat interfaced with a computer using VoltaMaster 4.0 software for data acquisition and data processing. The test solutions were thermostated during all the experiments.

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Before polarisation and EIS measurements, the working electrode was introduced in the test solution and left for 10 min to attain the open circuit potential at which the system had been stabilized. Polarization curve measurements were obtained at a scan rate of 20 mV/min starting from cathodic potential going to anodic direction.

The open-circuit potential (OCP) versus time and potentiodynamic polarization curves were recorded. The OCP was measured for 10 min before starting the potentiodynamic polarization experiments. The initial potential sweep was always negative to the OCP previously measured, while the final potential was near 0V.

Electrochemical impedance spectroscopy (EIS) was carried out at the open-circuit potentials in the frequency range 100 kHz– 100 mHz with a sinusoidal potential perturbation of 10mV amplitude. The data of impedance spectra results were fitted on equivalent circuits, a Randles type circuit, using ZView software.

Results and discussions

Open-circuit potential evolution in time

Although open-circuit potentials (OCP) values do not provide any direct information on the corrosion kinetics, they provide qualitative thermodynamic information. Measuring the variation versus time of the OCP of the working electrode is important in defining of the corrosion domains, partial and complete inhibition processes and in determining the appropriate inhibition concentrations [29]. The variation of OCP as a function of time in aerated nonstirred 1N H_2SO_4 solutions in the absence and in the presence of various concentrations of PC, AS and JR plant extracts at 25°C was recorded. The results are presented in figure 1.





Fig. 1 Variation of open-circuit potential as function of time recorded for a carbon steel electrode in 1N H₂SO₄ solutions without and with various concentrations of plant extracts AS (a), JR (b) and PC (c) at 25°C; the extract concentrations (vol %) in acid solution was shown in each figure

As it can be seen in figure 1, the presence of plant extracts influences the OCP value in all the cases, shifting the OCP towards more electropositive values. These results suggest that the addition of the tested plant extracts may provide an inhibition effect for carbon steel in sulphuric acid medium. The variation of OCP in time towards more electropositive values indicates the coverage of the metal surface with products or with some compounds from the inhibitor, that decrease the corrosion rate. In some cases OCP shifted first to more electronegative values and after a certain period of time the potential shifts towards more electropositive values. The first process may be attributed to an initial dissolution process and the second process to the formation of a protective adsorbed layer on the electrode surface.

Polarization measurements

The polarization curves for the steel electrode in 1N H_2SO_4 solution, in the absence and in the presence of various plant extracts are given in figure 2. Electrochemical parameters obtained from the polarization curves are listed in table 1. These include the corrosion potential (E_{corr}) and the corrosion current density (i_{corr}), both determined by extrapolation of the Tafel lines [30], as well as anodic Tafel slope (b_a) and cathodic Tafel slope for hydrogen evolution (b_b); the inhibition efficiency IE (%) was calculated as follows [31]:

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

where i⁰ and i corr represent the corrosion current densities of steel electrodes in 1 N H₂SO₄ without and with different amounts of plant extracts, respectively.

One may see that the addition of plant extracts shifts the anodic and the cathodic parts of the polarization curves to more electropositive values indicating that all the studied extracts could be classified as mixed-type inhibitors [32, 33].

The above data show that the extract concentration decreases the corrosion current density (i_{corr}). The presence of plant extracts has the beneficial effect of shifting the corrosion potential towards more electropositive values in comparison with the result





Fig. 2 Tafel plots of steel electrode in 1N H₂SO₄ containing various concentrations of plant extracts at 25°C; AS (a), JR (b) and PC (c)

Table 1ELECTROCHEMICAL PARAMETERS CALCULATED FROM POLARIZATION MEASUREMENTS
ON STEEL ELECTRODE IN 1N $H_3SO_4 + x \%$ VOL INHIBITORS AT 25°C

Acid	Plant							
solution	extract	i _{corr} .	Ecorr,	R _p ,	b.,	b _a ,	IE, %	
(1N	conc.,	mAcm ⁻²	mV/ECS	$\Omega \times cm^2$	mV/dec	mV/dec		
H ₂ SO ₄)	vol.%							
-	0	0.7383	-483	44.66	109.74	74	-	
AS	0.1	0.5159	-454	34.27	117.9	54,4	30,12	
	0.2	0.5159	-454	34.27	117.9	54.4	30.12	
	1	0.2222	-445	63.81	108.4	47.1	69.90	
	2	0.2166	-439	63.78	99.8	42.4	70.66	
JR	0.1	0.5629	-456	26.64	134.3	61	23.76	
	0.2	0.6838	-438	29.49	117.6	63.1	7.38	
	1	0.3683	-454	49.4	127.8	54	50.12	
	2	0.4746	-438	41.61	120.4	60.3	35.72	
PC	0.1	0.5044	-451	32.7	121.6	53.8	31.68	
	0.2	0.5249	-461	19.93	78.6	47.6	28.90	
	1	0.2488	-461	38.84	118.1	58.1	66.30	
	2	0.2465	-464	46.96	85.2	47	66.61	

obtained in the absence of the inhibitor. In some cases both anodic and cathodic Tafel slopes (b_a and b_c) are significantly changed indicating that the inhibition mechanism occurred by blocking the available cathodic and anodic active sites on the metal surface. The results of the inhibition efficiencies revealed a fairly good inhibition action of PC at high concentrations, the best inhibition

efficiencies being found in the case of AS plant extract at higher values of the extract concentration, while the lowest inhibition efficiencies can be found in the case of JR extract. The anodic Tafel slope, b always decreases for inhibiting solutions, indicating some changes in corrosion mechanism of steel.



Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy was also used for the characterization of electrode behaviour in 1 N H_2SO_4 solution without and with the addition of plant extracts. Figure 3 shows the Nyquist plots of AS, JR and PC at various plant extract concentrations (0.1, 0.2, 1 and 2 vol%).

It can be seen that the addition of plant extracts in the acid medium did not change the general shape of the curves, that are in all cases semicircles of capacitive type. However, with increasing PC concentration their diameters increased, whereas in the cases of AS and JR this increase in the resistance values is not regularly for some particular concentrations of plant extracts, suggesting that supplementary study should be performed for AS and JR with increasing amounts of extracts.

Also, it may be observed that the loops in almost all cases are depressed semicircles. This may be attributed to the porosity effect of the electrode surface [34]. The intercept of the loops with horizontal axis, as well as the diameter of the capacitive loop, represents the polarization resistance (R_p) for corrosion process. A large R_p value indicates a strong resistance against corrosion.

The impedance of the circuit can be expressed as follows [33]:

$$Z = Z_{Re} - jZ_{Im}$$
(2)

$$Z_{Re} = \mathbf{R}_{s} + \frac{\mathbf{R}_{p}}{1 + \omega^{2} \mathbf{C}_{dl}^{2} \mathbf{R}_{p}^{2}}$$
(3)

$$Z_{\rm Im} = \frac{\omega C_{\rm dl} R_{\rm p}^2}{1 + \omega^2 C_{\rm dl}^2 R_{\rm p}^2}$$
(4)



Fig. 3 Nyquist plots of the steel electrode after immersion in 1 N H_2SO_4 containing different concentrations of plant extracts: AS (a), JR (b) and PC (c) at 25°C

where Z_{Re} and Z_{Im} are the real and imaginary components of the impedance, R_p and R_s are the polarization resistance and the solution resistance respectively, C_{dl} is the interfacial double layer capacitance and ω is the angular frequency of the applied ac potential, $\omega = 2\pi f$ and f is the frequency.

Also on Bode plots (not presented here) it can be seen the differences between the maximum phase angle for acid medium without plant extracts (-50°) and solutions containing the studied extracts; so, for AS this angle (in degree) is -61°, in the presence of JR the maximum phase angle is -55° and for PC the maximum phase angle is the highest -65°. All the values for the maximum phase angle are shown in table 2.

The inhibition efficiency is calculated from the electrochemical impedance spectroscopy data using the following equation [34]:

$$IE = \frac{R_{p} - R_{p}^{\circ}}{R_{p}} \times 100, \ \%$$
 (5)

where R_p and R_p^0 represent the polarization resistance of the electrode in the presence of plant extracts and in the absence, respectively.

From EIS results regarding JR plant extract action for studied concentrations over 0.1 vol. % seems to have an accelerator effect instead of inhibiting role, similar to AS extract for 0.1 vol. % concentration. This corrosion acceleration has not been observed in potentiodynamic polarization experiments. Generally, R value has a tendency to increase for PC and AS extracts with the increase of plant extract concentration.

In order to determine the impedance parameters of the studied systems, the obtained impedance data were analyzed and an equivalent circuit subjected to only one

Acid solution (1N H ₂ SO ₄)	Plant extract conc., vol.%	$R_{ct},$ $\Omega \times cm^2$	C _{dl} , mF×cm ⁻²	Maximum phase angle q _{max} , degree	IE, %
-	0	24.76	130.6	-50	-
AS	0.1	23.73	120	-52	-4.34
	0.2	73.39	117.1	-61	66.26
	1	43.61	272.3	-59	43.22
	2	48.17	285.1	-60	48.60
JR	0.1	38.06	80.34	-52	34.94
	0.2	15.05	1488	-50	-64.52
	1	23.43	884.1	-55	-5.68
	2	18.45	889.5	-51	-34.20
РС	0.1	31.73	150.9	-58	21.97
	0.2	36.95	115.6	-59	32.99
	1	73.71	67.51	-65	66.41
	2	83.62	74.74	-64	70.39

Table 2EIS PARAMETERS AND CORRESPONDING IERect (%) FOR STEEL CORROSION IN 1N H2SO4 IN ABSENCE ANDIN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF PC, JR AND AS PLANT EXTRACTS

time constant hypothesis was proposed, according to [34]. The parameters calculated from best fitting the impedance data using the equivalent circuit shown in figure 4 are listed in table 3.



Fig. 4. Electric circuit model used in fitting experimental data for steel in 1N H₂SO₄ solution in absence and presence of various plant extract concentrations

The associated values of R_s and R_p represent the resistance of solution between the working electrode and the reference electrode and the polarization resistance corresponding to the process at metal substrate/solution interface, respectively. The double-layer capacitance usually behaves as a constant phase element (CPE) that has general characteristics of a typical double layer capacitor with significant porosities. The R_p value is a measure of the electron transfer across the surface and is inversely proportional to the corrosion rate.

The impedance of a constant phase element is defined by two parameters, Q and n [34] as expressed below:

Acid	Inhib.				
solution	Concentration	$R_s, \Omega \times cm^2$	Q, μ F×cm ⁻²	n	$R_{ct}, \Omega \times cm^2$
$(1N H_2 SO_4)$	vol %				
	0	2.42	244.2	0.89	27.2
AS	0.1	1.63	425.7	0.85	26.0
	0.2	1.75	252.5	0.84	76.7
	1	1.72	644.4	0.86	45.6
	2	1.63	459.7	0.88	48.5
JR	0.1	1.74	229.4	0.82	41.1
	0.2	1.77	2140	0.91	17.1
	1	1.99	2543	0.92	25.9
	2	1.59	1475	0.87	20.5
РС	0.1	1.5	264.1	0.89	32.8
	0.2	1.63	201.4	0.89	38.4
	1	1.59	113.1	0.90	74.3
	2	1.66	143.9	0.88	83.7

$$Z_{CPE} = \frac{1}{Q(j\omega)^n}, \quad j = \sqrt{-1}$$
(6)

Table 3VALUES OF THE FITTED ELEMENTS OFEQUIVALENT CIRCUIT FOR STEEL IN1N H2SO4 SOLUTIONSIN ABSENCE AND PRESENCE OFVARIOUS PLANTS EXTRACTCONCENTRATIONS

where Q is the capacitance, and n has the meaning of the phase shift, its value being considered as a measure of the surface inhomogenity. For a non-homogeneous system, n values ranges from 0.5 to 1.

Increasing the PC extract concentration leads to a decrease in the none-ideal double layer capacitance (Q introduced instead of C_{dl}). This decrease could be attributed to the adsorption of the chemical constituents of PC extract over the metal surface. As it has been reported that the adsorption process on the metal surface is characterized by a decrease in C_{d} [35]. The lowest concentration of JR plant extract has the highest value of R_{p} and with the increase of concentration the polarization resistance decreases. For AS extract the highest polarization resistance is for 0.2% plant extract addition, for the other more concentrated solutions R_b being lower.

It can be observed that the general tendency regarding increase of plant extract concentration was to increase the inhibition efficiency, except of JR extract. The better results in terms of efficiency were recorded for PC and AS plant extract.

The polarization and impedance measurements indicate that the studied extracts inhibit the corrosion processes probably by blocking both available cathodic and anodic sites of the metal surface by adsorption of the extract chemical constituents on the metal/solution interface. This phenomenon could take place via electrostatic attraction between the positively charged groups from the plant extracts and negatively charged sites of steel surface that act as cathodic sites.

Conclusions

Potentiodynamic polarization and electrochemical impedance spectroscopy results indicate that all the studied plant extracts Allium Sativum, Juglans Regia and Pogostemon Cablin acted in appropriate concentrations as corrosion inhibitors in $1N H_3SO_4$ for steel, the best performance being obtained in the case of Allium Sativum and Pogostemon Čablin extract.

The OCP measurements show that the addition of plant extracts shifted the open circuit potential towards more electropositive values, suggesting that these extracts may provide inhibition effect.

In the case of the potentiodynamic polarization studies, one noticed that the presence of all plant extracts tested has the effect of shifting the corrosion potential towards more electropositive values in comparison with the result obtained in the absence of the inhibitor. The values for both anodic and cathodic Tafel slopes are also changed by the addition of plant extracts indicating that the inhibitors are mixed-type and the inhibition efficiency, reached to 66-70% values with increasing the inhibitor concentration.

The inhibition efficiency values for the studied extracts were in the order Allium Sativum > Pogostemon Cablin > Juglans Regia, the best results being obtained in the case of Allium Sativum for 1 and 2% and for Pogostemon Cablin for the same concentrations.

Almost the same inhibiting behavior was found out in impedance measurements, where AS and PC show quite equal high efficiencies whereas JR exhibits a negatively effect (*i.e.* an accelerating corrosion effect).

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