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***Mentha spicata* L. Extract as a Green Corrosion Inhibitor for Carbon Steel in HCl Solution**

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The effect of *Mentha spicata* L. extract on the corrosion behaviour of carbon steel in 1.0 M HCl solution was investigated using polarization, electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) techniques. The solution containing 250 ppm of the ethanolic solution of extract showed the highest inhibition efficiency (*IE*). The effect of temperature on the rate of corrosion in the absence and presence of inhibitor was also studied. Adsorption of the extract on the carbon steel surface obeyed the Langmuir adsorption isotherm. Polarization measurements indicated that the inhibitor was of mixed type. The *IE* values from EN measurements showed a reasonable agreement with those obtained from polarization and EIS techniques. The EN method was applied as a complementary quantitative technique to study the corrosion behaviour of the inhibitor.

Keywords: Plant extract, Green inhibitor, Electrochemical impedance spectroscopy (EIS), Electrochemical noise (EN), Wavelet analysis

INTRODUCTION

Acid solutions play a very important role in the industry such as acid pickling, acid descaling and oil well acidizing. Among the methods of corrosion prevention and mitigation, the use of corrosion inhibitors is one of the most popular treatments [1-14]. Corrosion inhibitors are compounds that decrease the corrosion rate of metals or alloys when present at a sufficient concentration in a corrosive medium. Although many inhibitors demonstrate the high inhibition efficiencies, they are mostly toxic and harmful to the environment. Efforts have been made to employ natural products like plant extracts as green corrosion inhibitors for metals and alloys in acid solutions. In the plant extracts, a large number of chemical substances especially heterocyclic compounds, are involved in the corrosion inhibition. Plant extracts (dried stems, leaves and seeds) of *Chelidonium majus* and other plants were used in acid pickling baths in 1930. Most of plant extracts are nontoxic, biodegradable, readily available and renewable materials. In addition, they

can be extracted by simple procedures with low cost. Lawsonia, Gossypium hirsutum and Aloe Vera are some examples of natural source inhibitors with high corrosion inhibitive properties in acid and alkaline solutions [15-18].

This paper has been focused on the essential oil of spearmint (*Mentha spicata*). Mint is the common name of approximately 25 perennial species of the genus *Mentha* belonging to the *Lamiaceae* family [19]. The inhibition effect of *Mentha* extract has been studied by some researchers [20,21]. However, the concentration of mint in the oil varies considerably depending on the genetic and geographical origin [20].

Electrochemical noise (EN) is a relatively new technique which has been recently employed for corrosion analysis [22-30]. The EN technique assures the natural development of corrosion processes because it is usually performed without applying any external signal. EN is defined as the spontaneous fluctuations of current or potential arising from the localized corrosion processes. A zero-resistance ammeter (ZRA) is used to measure the current between two nominally identical working electrodes (WEs).

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Although the EN measurement is simple, the analysis of EN signals is often difficult. Wavelet transform is a data analysis procedure which may be regarded as a variant of Fourier transform. However, wavelet transform has some advantages over Fourier transform. Among them, the analysis of non-stationary signals without the requirement for pre-processing methods deserves mention. As another advantage, the wavelet transform can analyse signals in both time and frequency domains, simultaneously [26-30].

Wavelet transform analyzes each EN signal to produce several timescales, the so-called crystals, describing the EN signal. The frequency range and scale range of each crystal for the case in which $J = 6$ and $f_s = 4$ Hz are shown in Table 1.

The wavelet transform can analyse the raw signal to produce the partial signals. The intensity of electrochemical activity on the surface of the two working electrodes within a particular timescale range can be determined by the standard deviation of partial signals (SDPS). For a more detailed understanding of the wavelet transform as performed in this work and SDPS plot, the reader is referred to an earlier paper [29].

In the present paper, the inhibition action of *Mentha spicata L.* extract as a green inhibitor on corrosion of carbon steel in 1.0 M HCl solution is investigated using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and EN techniques. Additionally, the results are compared with those obtained from the similar work on the inhibitory effect of *Mentha spicata L.* [20].

EXPERIMENTAL

The aerial part of *Mentha spicata L.* was harvested in May 2015 in Kerman. Before the extraction, the aerial part of the plant was dried in the laboratory at room temperature and in the shade. The extraction of essential oil of the aerial part of the plant was conducted by hydrodistillation using a Clevenger-type apparatus.

Two nominally identical WEs of the equal surface area (1.0 cm² each) were made from carbon steel with the composition of (wt%): C (0.15), Mn (0.73), Si (0.72) and Fe (balance).

An ethanolic solution of *Mentha spicata L.* extract was prepared by dissolving it in ethanol as 30% (v/v) solution.

To prepare the desired concentrations of the extract (in the range of 50-750 ppm), a specific volume was taken from the ethanolic solution and added directly to 1.0 M HCl solution.

The measurements of EN, EIS and potentiodynamic polarization were used to study the corrosion behaviour of carbon steel in 1.0 M HCl solution without and with the addition of inhibitor at different concentrations. The specimens were connected to a copper wire at one end and then sealed using epoxy resin with the opposite end exposed as the surface of WE. Prior to experiments, the WE surface was abraded by wet abrasive papers (600-2500 grades) followed by washing with distilled water, ethanol and then dried in air.

The electrochemical experiments were performed by using a potentiostat/galvanostat Autolab 302N equipped with a frequency response analyser FRA-2 and Nova 1.9 software.

A platinum rod with the area of 100 mm² was used as the counter electrode (CE) and a saturated (KCl) Ag/AgCl electrode as the reference electrode. The electrochemical experiments were performed in the sequence of the EN, the EIS and the polarization measurements. Since the EIS and the polarization measurements needed a counter electrode during the test, the platinum electrode was immersed in the solution at the start of the sequence to avoid perturbations within the solution during the sequence. The four electrodes were arranged within the solution at the corners of a lozenge so that two WEs were facing each other vertically at a distance of 2 cm. The cell was placed in a Faraday cage in order to minimize the outside electromagnetic interference.

Before performing each sequence of the electrochemical experiments, the WEs were immersed in the test solution for 30 min to reach a stable open circuit potential (OCP). After that time, the EN signals were collected at a sampling frequency of 4 Hz during 30 min. The orthogonal Daubechies wavelets of order 4 (db4) were employed to analyse the EN data by the wavelet transform. The calculations were carried out by Matlab software using a method described in our earlier paper [29].

The EIS measurements were performed using a sinusoidal potential perturbation of 10 mV at the OCP in the 100-10 mHz frequency range. Polarization curves were recorded using a scan rate of 1 mV s⁻¹. Nova 1.9 software was used for determination of the impedance and

Table 1. Frequency and Scale Range for $J = 6$ and $f_s = 4$ Hz

Crystal name	Frequency range (Hz)	Scale range (s)
d1	4-2	0.25-0.5
d2	2-1	0.5-1
d3	1-0.5	1 -2
d4	0.5-0.25	2-4
d5	0.25-0.125	4-8
d6	0.125-0.0625	8-16

Table 2. Polarization Parameters and the Corresponding Inhibition Efficiencies for Carbon Steel in 1.0 M HCl Containing Different Concentrations of Inhibitor at 25 °C

C (ppm)	i_{corr} ($\mu\text{A cm}^{-2}$)	$-E_{corr}$ (mV)	β_a (mV decade ⁻¹)	β_c (mV decade ⁻¹)	IE (%)
0	2370	442	226	142	-
50	116	498	101	129	95
100	97	495	94	125	95.9
250	59	488	98	135	97.5
500	73	498	92	125	96.9
750	76	489	95	135	96.8

polarization parameters.

RESULTS AND DISCUSSION

Potentiodynamic Polarization

Figure 1 shows the potentiodynamic polarization curves of carbon steel in 1.0 M HCl solution in the absence and presence of various concentrations of the inhibitor. The relevant parameters are listed in Table 2 as corrosion current density (i_{corr}), corrosion potential (E_{corr}) and the anodic and cathodic Tafel slopes (β_a , β_c).

Both the anodic and cathodic Tafel slopes (β_a , β_c) varied

after the addition of inhibitor to the acid solution. The inhibitor is classified as anodic or cathodic type if the difference between the corrosion potential values in the absence and presence of the inhibitor is more than 85 mV; on the other hand, the inhibitor is called as mixed type if the difference between the E_{corr} values of the uninhibited and inhibited solutions is less than 85 mV [31]. In the present study, the maximum difference in E_{corr} values was 56 mV towards the cathodic side, indicating that the extract acts as a mixed type inhibitor. However, the effect of the inhibitor on the cathodic reaction is more significant than that on the anodic reaction.

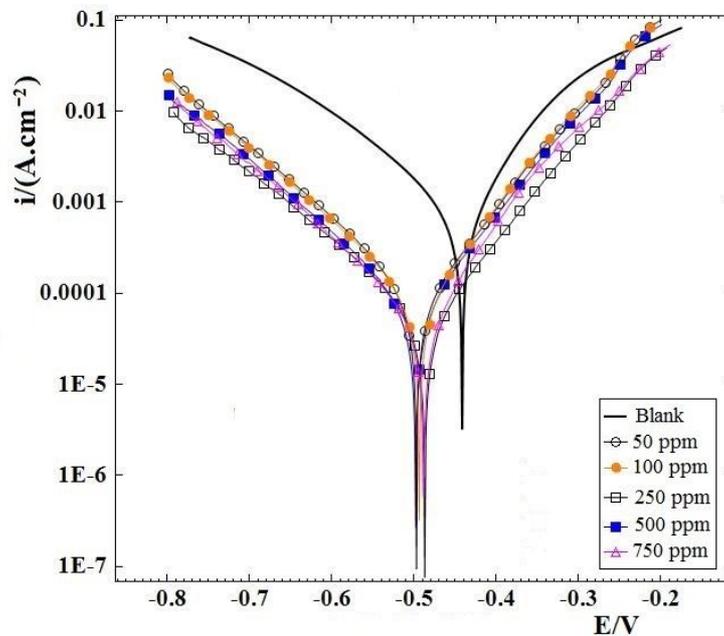


Fig. 1. Polarization curves for carbon steel in 1.0 M HCl solution in the absence and presence of different concentrations of extract at 25 °C.

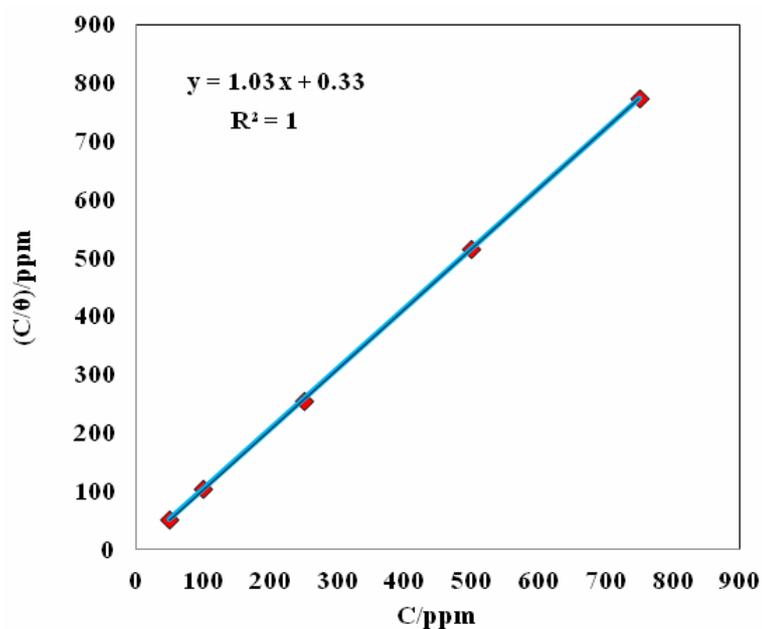


Fig. 2. Langmuir adsorption isotherm of the inhibitor using surface coverage values calculated by Tafel polarization results.

Table 2 also presents values of the corrosion inhibition efficiency (*IE*) for which the expression is:

$$IE(\%) = \frac{i_{corr} - i'_{corr}}{i_{corr}} \times 100 \quad (1)$$

where i_{corr} and i'_{corr} are corrosion current densities in the uninhibited and inhibited cases, respectively. From Table 2 it can be recognized that the inhibition efficiency is increased with inhibitor concentration up to 250 ppm, after which an additional increase of the inhibitor concentration up to 750 ppm leads to a reduction of the inhibition efficiency. This indicates that the solution containing the optimum concentration of extract (*i.e.* 250 ppm) gives the highest inhibition efficiency.

This extract as a native to Iran shows better corrosion protection in comparison with that collected from Errachidia oasis (Morocco) known as “Tazouka mint” [20]. The inhibition efficiency of Tazouka mint increases with concentration to attain 97% at 2.00 g l⁻¹. This concentration is about 27 times greater than the optimum concentration of the ethanolic solution of the extract in the present work.

Since the inhibition efficiency is due mainly to the blocking effect of the adsorbed species, the equation of $\theta = IE(\%)/100$ was used to calculate the surface coverage, θ .

In order to evaluate the adsorption of the inhibitor on the steel surface, an attempt was made to find a suitable adsorption isotherm by testing the Langmuir, Temkin and Frumkin isotherms. It was found that the adsorption of the inhibitor molecules is consistent with the Langmuir isotherm:

$$\theta = \frac{KC}{1 + KC} \quad (2)$$

or:

$$\frac{C}{\theta} = C + \frac{1}{K} \quad (3)$$

where θ is the surface coverage, C is the concentration of inhibitor and K is the adsorption equilibrium constant. As shown in Fig. 2, the plot of C/θ vs. C gives a straight line with the linear regression coefficient (R^2) almost equal to 1. Therefore, the adsorption of the inhibitor on the steel

surface obeys the Langmuir’s adsorption isotherm. Based on the assumptions of this isotherm, all the adsorption sites are equivalent and the adsorption of a molecule on a given site is independent of the occupation of the nearby sites [32].

Electrochemical Impedance Spectroscopy

Nyquist plots of EIS for carbon steel in 1.0 M HCl in the absence and presence of various concentrations of inhibitor are shown in Fig. 3. It is apparent from Fig. 3 that the impedance response of carbon steel in 1.0 M HCl solution changes with increasing the inhibitor concentration.

The electrical equivalent circuit shown in Fig. 4 was employed to analyse the impedance data. In this figure, R_s is the solution resistance and R_{ct} is the charge transfer resistance. The impedance of the constant phase element (CPE) is defined as follows [33,34]:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (4)$$

where Y_0 is the CPE constant (F cm⁻² sⁿ⁻¹ or sⁿ Ω⁻¹ cm⁻²), j equals $\sqrt{-1}$, ω is the angular frequency and n is the CPE exponent. Depending on n , CPE can represent resistance ($n = 0$, $Z_{CPE} = R$), capacitance ($n = 1$, $Z_{CPE} = C$), inductance ($n = -1$, $Z_{CPE} = L$) or Warburg impedance ($n = 0.5$). The double layer capacitance, C_{dl} , can be calculated from the CPE constant, Y_0 , by the following equation [35]:

$$C_{dl} = Y_0(\omega_{max})^{n-1} \quad (5)$$

where ω_{max} is the angular frequency at which the imaginary component of the impedance reaches its maximum magnitude. Table 3 lists impedance parameters in the absence and presence of different concentrations of inhibitor. From Table 3, it could be seen that the R_{ct} values increases with increasing the inhibitor concentration from 50 to 250 ppm and then decreases with further increasing the inhibitor concentration up to 750 ppm. Hence, the optimum concentration of the inhibitor was found to be 250 ppm. On the other hand, the values of C_{dl} decreased with increasing the inhibitor concentration. This situation was the result of increasing surface coverage by the inhibitor.

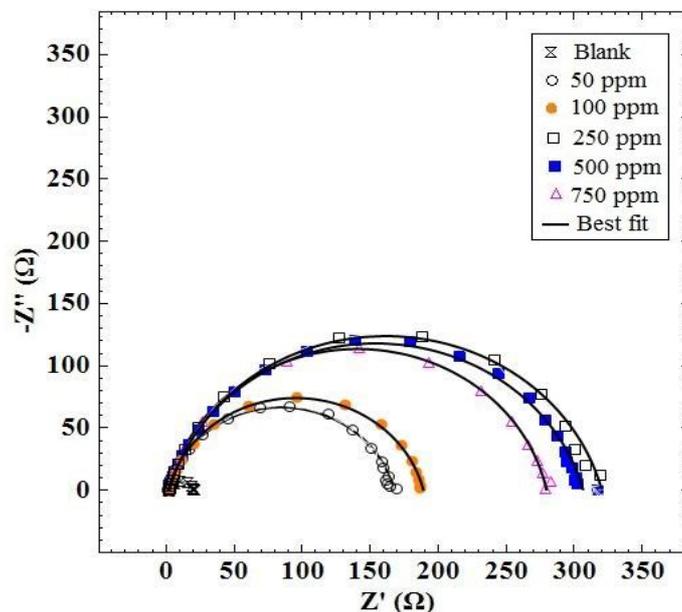


Fig. 3. Nyquist plots for carbon steel in 1.0 M HCl solution in the absence and presence of different concentrations of extract at 25 °C.

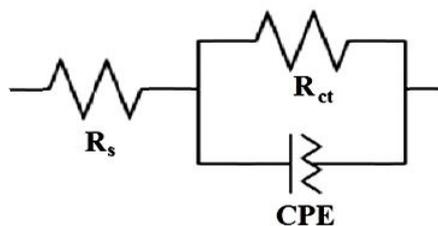


Fig. 4. The equivalent circuit used to fit the experimental data.

Table 3. Impedance Parameters and the Corresponding Inhibition Efficiencies for Carbon Steel in 1.0 M HCl Containing Different Concentrations of Inhibitor at 25 °C

<i>C</i> (ppm)	<i>R_s</i> (Ω cm ²)	<i>R_{ct}</i> (Ω cm ²)	<i>n</i>	10 ⁶ <i>Y</i> ₀ (F cm ⁻² s ⁿ⁻¹)	<i>C_{dl}</i> (μF cm ⁻²)	<i>IE</i> (%)
0	1.37	18.5	0.852	287	116.1	-
50	0.94	166	0.867	84.6	43.4	88.9
100	0.92	188	0.855	86	42.9	90.0
250	1.85	318	0.845	71.5	36.1	94.2
500	0.94	305	0.840	64.3	30.7	93.9
750	1.08	278	0.874	53.1	29.0	93.3

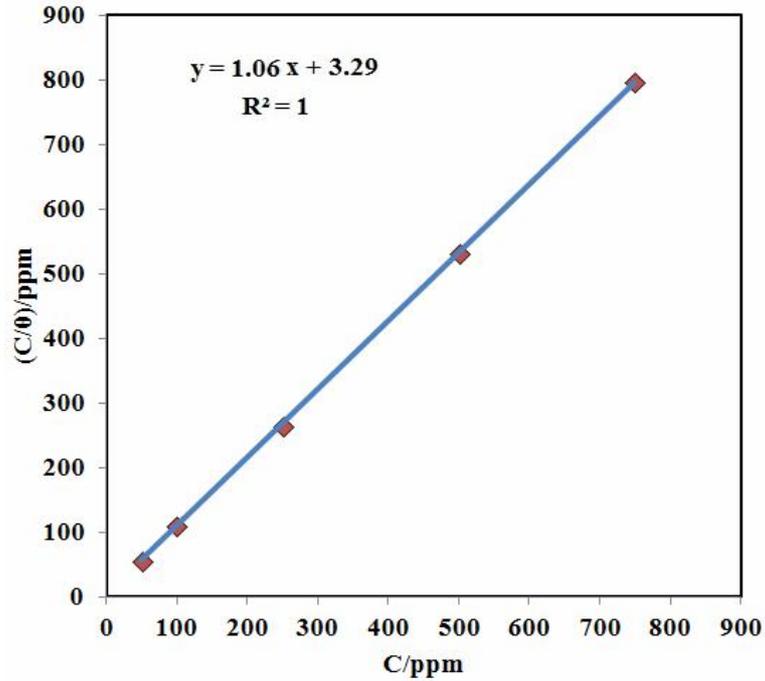


Fig. 5. Langmuir adsorption isotherm of the inhibitor using surface coverage values calculated by EIS results.

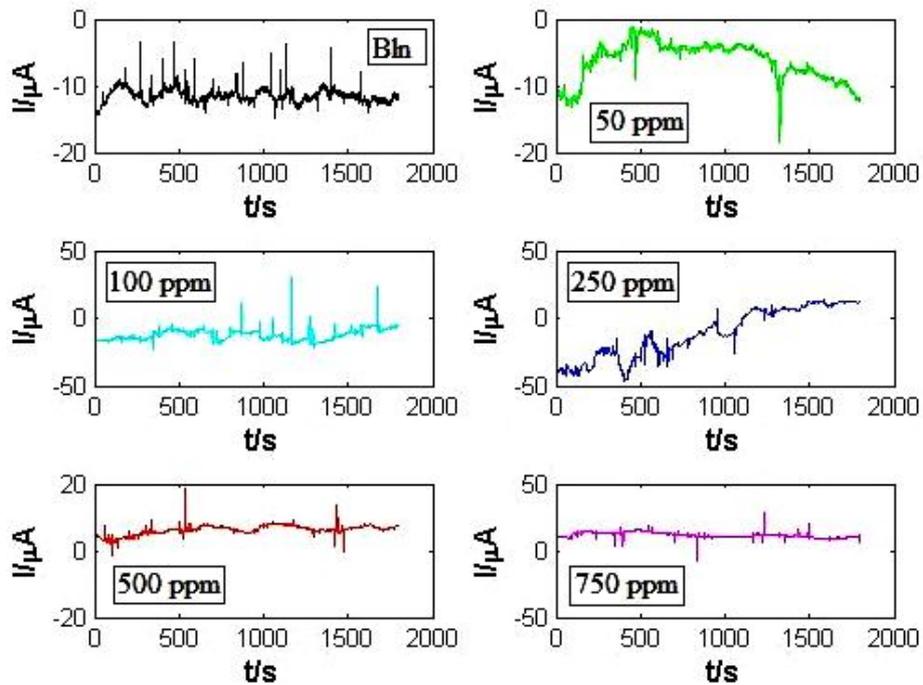


Fig. 6. EN current records of carbon steel in 1.0 M HCl solution in the absence and presence of different concentrations of extract during 30 min starting at 30 min after immersion time.

Inhibition efficiencies in Table 3 were calculated through the following expression:

$$IE(\%) = \frac{R'_{ct} - R_{ct}}{R'_{ct}} \times 100 \quad (6)$$

where R_{ct} and R'_{ct} represent the charge transfer resistance, before and after addition of the inhibitor to the corrosion media, respectively. Comparing the IE values reported in Tables 2 and 3 demonstrates a good agreement between the EIS and polarization data. It can be observed from Table 3 that the inhibition efficiency increases as the extract concentration increases until reaching a maximum value corresponding to 250 ppm concentration of the extract and then decreases. Thus, in agreement with the polarization results, the solution containing 250 ppm of extract gives the highest inhibition efficiency. Attempts were made to fit the EIS data to various isotherms including Langmuir, Temkin and Frumkin. As evident from Fig. 5, the relationship between C/θ and C is linear, confirming the Langmuir adsorption behaviour of the inhibitor. This suggests that the adsorbed molecules occupy only one site and there are no interactions between the adsorbed molecules.

Electrochemical Noise

The electrochemical noise measurements were performed on the two identical working electrodes made of carbon steel and immersed in the 1.0 M HCl solution. Figure 6 shows the EN signals in the absence and presence of different concentrations of extract measured during 30 min after an immersion time of 30 min.

The WT was employed to obtain the SDPS plots of each data set. The SDPS plots of the EN signals of Fig. 6 are shown in Fig. 7. The SDPS plots can be used to calculate the amount of noise charges at the particular interval of frequency. The predominant transients of the original EN signal appear as the maximum peak in the SDPS plot [29]. However, it should be verified using the original EN signal that this maximum peak arises from the single transients and not from the overlapped transients. When there is no obvious maximum in the SDPS plot, the scale of the predominant transients can be recognized by comparing the partial signals with the original signal [36]. The predominant transients can be attributed to metastable pits.

The quantity of electric charge arising from pit generation can be estimated by the following equation:

$$Q_{total} = \sum_{d_{max}-1}^{d_{max}+1} I_j \cdot \Delta t \quad (7)$$

where d_{max} is the maximum peak crystal, I_j is the SDPS value at j crystal and Δt is the average time width of j crystal. This equation is based on a coulomb counting method called CoulCount which has been developed earlier as a means of studying localized corrosion [23,24,37].

The corrosion inhibition efficiency can be defined as follows [37]:

$$IE(\%) = \frac{Q - Q'}{Q} \times 100 \quad (8)$$

where Q and Q' are the noise charges in the uninhibited and inhibited cases, respectively. It is clear from the SDPS plot of Signal Blank (Fig. 7) that the maximum is placed at d_6 crystal (d_{max}) with the SDPS value of 325 nA. The SDPS values corresponding to d_5 (*i.e.* $d_{max} - 1$) and d_7 (*i.e.* $d_{max} + 1$) crystals are 305 and 320 nA, respectively. The total quantity of electric charge (Q_{total}) is calculated as 13410 nC (Table 4). The values of the parameters derived from all the SDPS plots of Fig. 7 have been summarized in Table 4 (d_{max} , Δt and I_j).

Table 4 also presents IE values. These IE values are in good agreement with those obtained from polarization and EIS methods. According to Table 4, when the inhibitor concentration is increased from 50 to 250 ppm, the values of inhibition efficiency increases, while at concentrations more than 250 ppm the values of inhibition efficiency decreases. This indicates that the concentration of 250 ppm plays as the optimum concentration of the extract. The decrease of the inhibition efficiency with increasing the inhibitor concentration beyond the optimum value (*i.e.* 250 ppm) is consistent with the results obtained from polarization and EIS measurements and might be due to the saturation of the metallic surface with inhibitor molecules.

Attempts were made to fit θ values to various isotherms and the Langmuir isotherm presented the best fit as shown in Fig. 8.

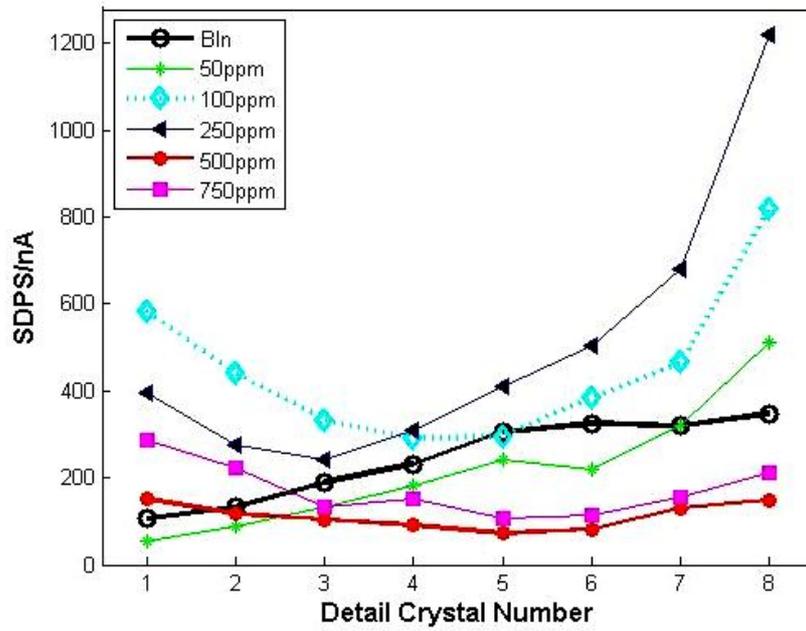


Fig. 7. SDPS plot of signals of Fig. 6.

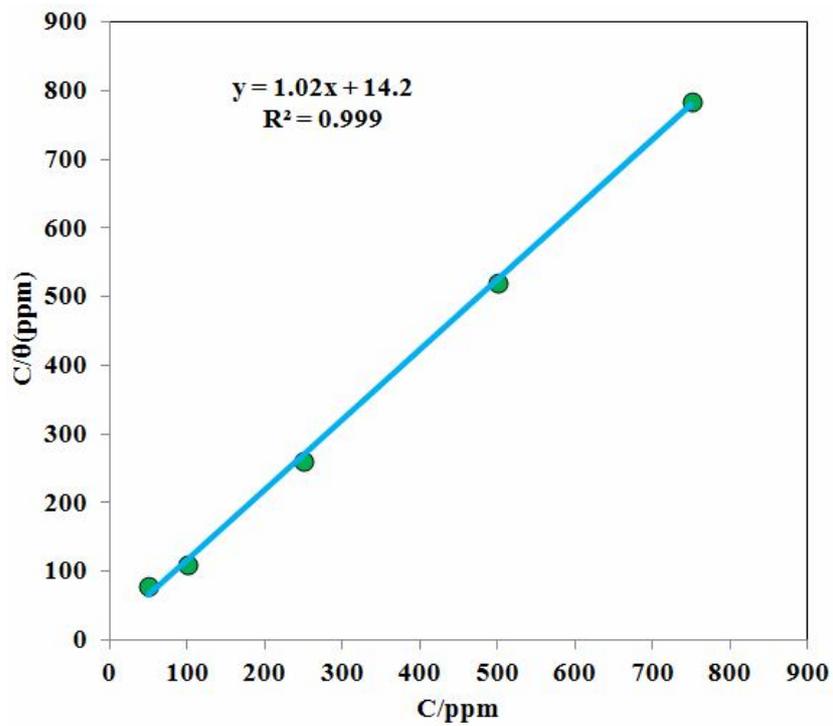


Fig. 8. Langmuir adsorption isotherm of the extract using surface coverage values calculated by EN results.

Table 4. Noise Parameters and the Corresponding Inhibition Efficiency Values for Carbon Steel in 1.0 M HCl Containing Different Concentrations of Inhibitor at 25 °C

<i>C</i> (ppm)	<i>d</i>	Δt (s)	I_j (nA)	<i>Q</i> (nC)	Q_{total} (nC)	<i>IE</i> (%)
0	d5	6	305	1830	13410	-
	d6	12	325	3900		
	d7	24	320	7680		
50	d4	3	182	546	4590	65.8
	d5	6	240	1440		
	d6	12	217	2604		
100	d1	0.375	585	219	1048.5	92.2
	d2	0.75	440	330		
	d3	1.5	333	499.5		
250	d1	0.375	394	148	354	97.4
	d2	0.75	275	206		
500	d2	0.75	116	87	514.5	94.8
	d3	1.5	103	154.5		
	d4	3	91	273		
	d1	0.375	287	107.6		
750	d2	0.75	222	166.5	473.6	96.5
	d3	1.5	133	199.5		

Table 5. Effect of Temperature on the Corrosion Current Density of Carbon Steel in 1.0 M HCl Solution in the Absence and Presence of 250 ppm Inhibitor

<i>C</i> (ppm)	<i>T</i> (°C)	i_{corr} ($\mu\text{A cm}^{-2}$)
0	25	2370
	35	5276
	45	8140
	55	14508
250	25	59
	35	99
	45	316
	55	628

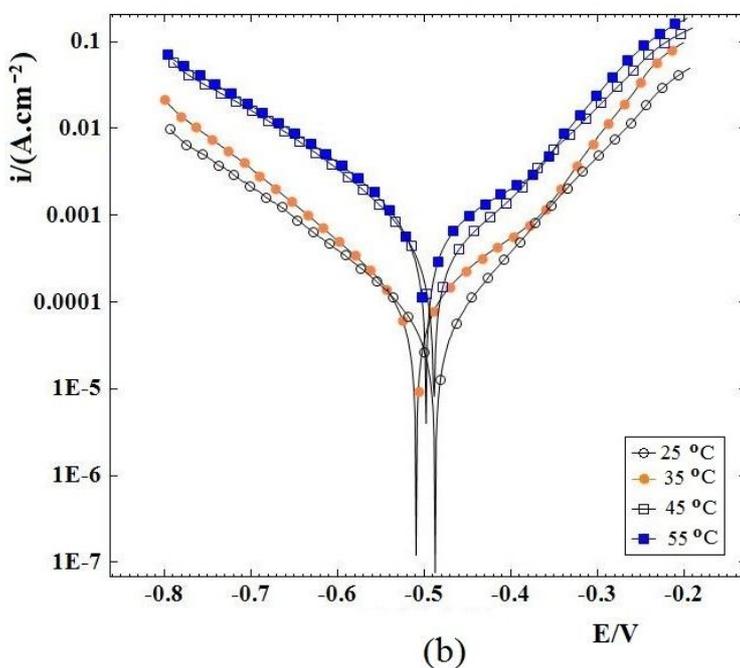
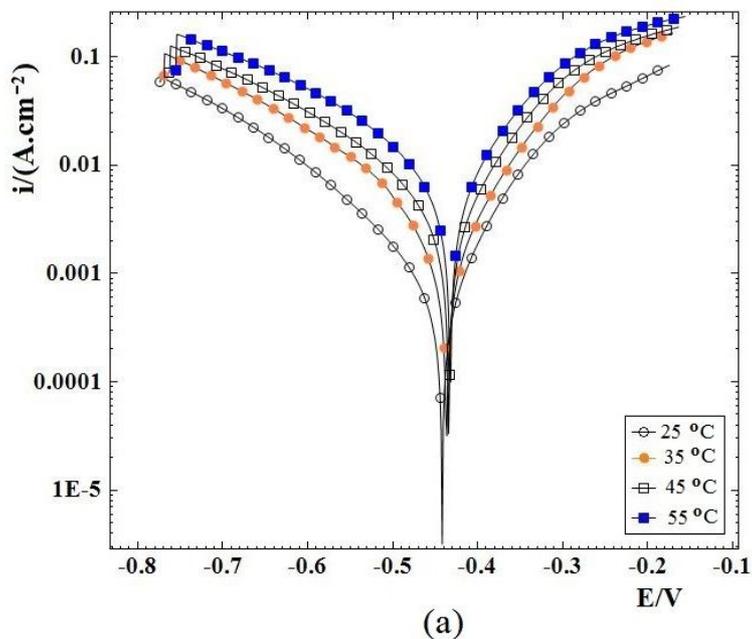


Fig. 9. Effect of temperature on the polarization curves in 1.0 M HCl solution (a) without inhibitor and (b) in the presence of 250 ppm of inhibitor.

Temperature Effect and Thermodynamic Parameters

Performing polarization tests in the temperature range of

25-55 °C in the absence and presence of the inhibitor is necessary to calculate the activation energy and thermodynamic parameters of the corrosion process. The

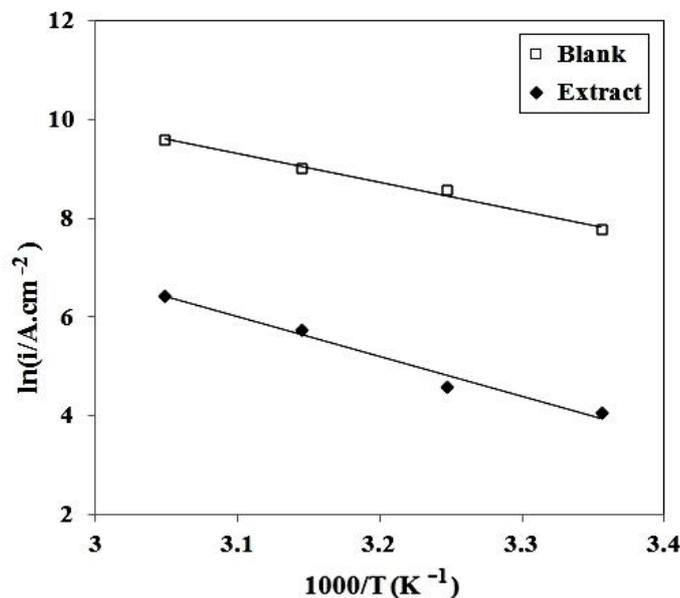


Fig. 10. Arrhenius plots for carbon steel in 1.0 M HCl solution in the absence and presence of 250 ppm inhibitor.

polarization curves in the absence and presence of 250 ppm extract are illustrated in Fig. 9. Table 5 lists the corrosion current density of carbon steel in the absence and presence of 250 ppm inhibitor concentration.

The dependence of corrosion rate on temperature can be expressed by the Arrhenius equation [38,39]:

$$i_{corr} = A \exp\left(\frac{-E_a}{RT}\right) \quad (9)$$

where i_{corr} is corrosion current, A is a constant, E_a is the activation energy of the alloy dissolution reaction, R is the gas constant and T is the absolute temperature. The E_a values were calculated from the slopes of Arrhenius plots [$\ln i_{corr}$ vs. $1/T$ (Fig. 10)]. The calculated activation energies for the corrosion process in the absence and presence of 250 ppm inhibitor are 48 and 67 kJ mol⁻¹, respectively. The E_a obtained in this work for the corrosion of carbon steel in HCl solution (48 kJ mol⁻¹) is in accordance with those obtained in other studies [2,4,38]. A decrease in the corrosion activation energy in the presence of 250 ppm inhibitor compared to its absence is interpreted as the formation of an adsorption film on the alloy surface.

The adsorption free energy of the inhibitor on carbon steel surface can be evaluated from the following equation;

$$\Delta G_{ads} = -RT \ln(55.5K) \quad (10)$$

where 55.5 is the molar concentration of water in the solution expressed in M. The value of the equilibrium constant, K , was calculated from the reciprocal of the intercept of Langmuir adsorption line (Fig. 2) as 3.0 l mg⁻¹. The unit of ΔG_{ads} is J mol⁻¹ and the unit of K is M⁻¹ in Eq. 10. Thus, the unit of the obtained K value (*i.e.* l mg⁻¹) should be changed into M⁻¹ to comply with the basic unit of SI. The molecular mass of the extract is not known, so, it is not possible to discuss the adsorption isotherm behaviour of extract in terms of thermodynamic parameters (such as the standard free energy of adsorption, ΔG_{ads} , the enthalpy of adsorption, ΔH_{ads} , and the entropy of adsorption, ΔS_{ads}) [40].

CONCLUSIONS

The adsorption and the inhibition effects of *Mentha spicata L.* extract on the corrosion behaviour of carbon steel in 1.0 M HCl were studied using electrochemical techniques. Natural products like plant extracts offer interesting possibilities for the corrosion inhibition because of their nontoxic properties. Results obtained from potentiodynamic polarization, EIS and EN measurements

demonstrated that the adsorption of the extract on carbon steel follows the Langmuir isotherm. The solution containing 250 ppm of extract showed the highest inhibition efficiency. The effect of temperature on the rate of corrosion in the absence and presence of inhibitor revealed an increase in the corrosion activation energy in the presence of inhibitor compared to its absence.

The electrochemical noise technique under open circuit conditions was employed for the quantitative evaluation of corrosion inhibition. In this way, the amount of noise charges at each interval of frequency and thereby the inhibition efficiency values were calculated from the SDPS plots. The inhibition efficiency values determined from noise technique showed a reasonable agreement with those obtained from polarization and EIS measurements.

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