

**Investigation of the Effect of Penicillin as a Green Corrosion Inhibitor
for Mild Steel Using Electrochemical Techniques**

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Received August 2013; Accepted November 2013

ABSTRACT

In this paper, the effect of penicillin G drug as a green corrosion inhibitor on mild steel in 1.0 M hydrochloric acid solution has been investigated using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) techniques. The inhibition efficiency was found to increase with increasing inhibitor concentration. Potentiodynamic polarization measurements indicated that penicillin G is a mixed type inhibitor. Furthermore, it has been demonstrated that the electrochemical noise (EN) technique under open circuit conditions as the only truly noninvasive electrochemical method can be employed for the quantitative evaluation of corrosion inhibition. This can be done using the standard deviation of partial signal (SDPS) for calculation of the amount of noise charges at the particular interval of frequency, thereby calculate the inhibition efficiency (IE) of an inhibitor. These IE values show a reasonable agreement with those obtained from potentiodynamic polarization and EIS measurements.

Keywords: Penicillin; Electrochemical noise; Wavelet analysis; Inhibition efficiency; Electrochemical impedance spectroscopy

INTRODUCTION

Corrosion inhibitors are substances that when they are added in small concentrations to corrosive media decrease or prevent the reaction of the metal with the media. However, the use of these compounds has been questioned lately, due to the several negative effects that they have caused in the environment. Thus, the development of the novel corrosion inhibitors from natural source and non-toxic type has been considered to be more important and desirable [1, 2]. Recently researchers have paid attention to the

development of drugs as inhibitors for metallic corrosion [2-5].

A very promising method for the investigation and monitoring of corrosion is the recording and analysis of the electrochemical noise (EN) data [6-17]. EN measurements can be performed in freely corroding systems without the external application of electrical signals, so that the natural evolution of corrosion processes is assured. EN is defined as the fluctuations of potential or current originating from the corrosion events in a

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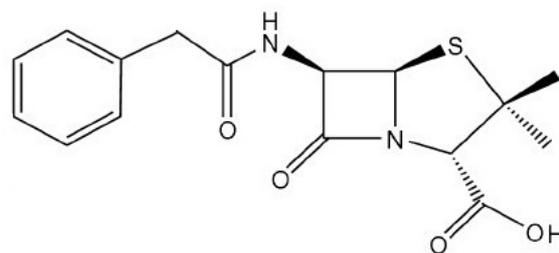
corrosion process. Two nominally identical working electrodes (WEs) are connected via a zero-resistance ammeter (ZRA) monitoring the coupling current between the electrodes.

While the EN measurement is simple, understanding of the information included in the EN signals, i.e. the EN analysis, remains difficult. Wavelet transform is a data analysis procedure without the precondition of stationarity or linearity and with a high distinguishing capacity in both time and frequency domain simultaneously [11-17].

Wavelet transform describes the EN signal at several timescales in so-called crystals. The inverse wavelet transform can produce partial signals of the original signal. Each partial signal is a signal which resembles the fluctuations of the original signal at a particular timescale. The standard deviation of partial signal (SDPS) can indicate the variations in the intensity of the partial signal about its mean, which can be an indication of the intensity of electrochemical activity on the surface of the electrodes within a particular interval of frequency [14, 16]. The plot of the SDPS versus corresponding crystal name is called SDPS plot. Such plot provides mechanistic information about physical processes: the position of the maximum in the SDPS plot indicates the dominant process in certain corrosion events and its change can reflect the behavior of the dominant corrosion process. For a more detailed discussion on wavelet transform and SDPS plot, please refer to an earlier paper [16].

The present paper describes study of the inhibition action of penicillin G (Scheme 1) on corrosion of mild steel in 1.0 M HCl solution using potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) techniques. The choice of this inhibitor as corrosion inhibitor is based

mainly on its nontoxic properties and high solubility in acidic media. Furthermore, this paper demonstrates that the electrochemical noise (EN) technique under open circuit conditions can be employed for the quantitative evaluation of corrosion inhibition using the SDPS from wavelet analysis of EN data.



Scheme 1. The molecular structure of penicillin G.

EXPERIMENTAL

Penicillin G was obtained from Sigma and used without any further purification. Scheme 1 shows the chemical structure of this antibacterial drug. The employed working electrodes were prepared from mild steel with the chemical composition (wt.%) of: C (0.15), Mn (0.73), Si (0.72) and Fe (98.4).

Potentiodynamic polarization, EIS and EN measurements have been used to study the corrosion behavior of mild steel in 1.0 M HCl solution without and with doping by penicillin at different concentrations. Before performing experiments, the specimens were connected to a copper wire at one end sealed using resin, with the other end that it exposed as the WEs surface. Then the working surface was polished by wet abrasive papers through 600-2500-grade, washed with distilled water, degreased with ethanol, finally dried in air.

Potentiodynamic polarization, EIS and EN experiments were conducted using Autolab 302N potentiostat with Nova 1.6 software. Potentiodynamic polarization and EIS measurements were conducted in

a conventional three-electrode cell. A platinum rod was used as the counter and a saturated (KCl) Ag/AgCl electrode as reference electrode. To obtain the stabilized open circuit potential (OCP), the samples were immersed 30 min in the solution before potentiodynamic polarization and EIS measurements. Polarization curves were recorded at a scan rate of 1 mV/s and Nova software was used for determination of corrosion current densities and polarization parameters. A sinusoidal potential perturbation of 10 mV versus OCP was used in the EIS measurements and a frequency range from 10 mHz to 100 kHz was employed and Nyquist plots from the impedance data were analyzed with Nova software.

Two WEs were facing each other vertically at a distance of about 2 cm in the EN experiments. The EN records were collected 45 min after immersion time and during 75 s. Two nominally identical WEs with surface areas of 100 mm² were used. The entire cell was placed inside a Faraday cage to limit external electromagnetic interference. The sampling frequency for the electrochemical noise data was 4 Hz. Noise data were analyzed with wavelet technique using the orthogonal Daubechies wavelets of the fourth order (db4). The necessary calculations for construction of the SDPS plots were performed using Matlab software.

The surfaces of alloy were observed in a CamScan MV2300 scanning electron microscope (SEM). SEM images were obtained from mild steel surface after specimen immersion in 1.0 M HCl solutions in the absence and presence of 10 mM inhibitor for 1 h at room temperature.

RESULTS AND DISCUSSION

Potentiodynamic polarization

Fig. 1 shows the potentiodynamic polarization curves of mild steel in 1.0 M

HCl solution in the absence and presence of various concentrations of inhibitor. The relevant parameter values are listed in Table 1 as corrosion current density (i_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (β_a , β_c). It is clear that corrosion current density decreases as the concentration of inhibitor goes up. Addition of inhibitor to acid media affects both cathodic and anodic branches of the potentiodynamic polarization curves; therefore, it behaves as mixed inhibitor. However, small potential shifts in the negative direction in the presence of penicillin indicate that the effect of inhibitor on the cathodic reaction is more observable than on the anodic reaction.

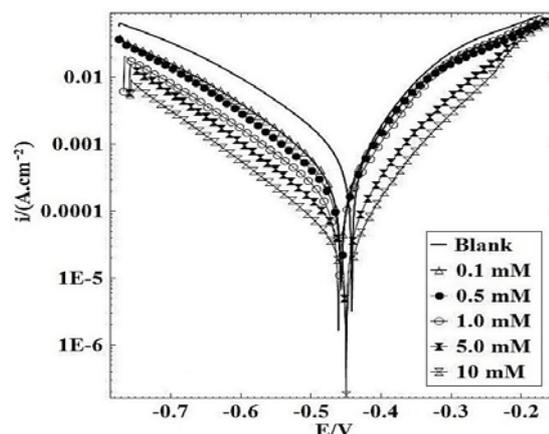


Fig. 1. Tafel polarization curves of mild steel in 1.0M HCl solution containing different concentrations of Penicillin.

Table 1 also presents values of the corrosion inhibition efficiency (IE) that the equation in this case is:

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

where i_{corr} and i'_{corr} are corrosion current densities in the uninhibited and inhibited cases, respectively. The IE_p values show that the inhibition is more pronounced with increasing inhibitor concentration. These results also show that this drug act as

effective corrosion inhibitor.

Table 1. Polarization parameters and the corresponding inhibition efficiencies for mild steel in 1.0 M HCl containing different concentrations of penicillin

C /mM	$i_{corr}/\mu A \cdot cm^{-2}$	$-E_{corr}/mV$	$\beta_a/mV \cdot decade^{-1}$	$\beta_c/mV \cdot decade^{-1}$	IE _R (%)
0	2370	442	226	142	-
0.1	854	457	195	108	64.0
0.5	611	458	169	114	74.2
1.0	281	461	164	85	88.1
5.0	129	451	147	96	94.6
10.0	39	450	125	78	98.4

To calculate the surface coverage, θ , it was assumed that the inhibition efficiency is due mainly to the blocking effect of the adsorbed species and hence $\theta = IE(\%)/100$ [18]. Here, an attempt was made to test the Langmuir, Temkin and Frumkin isotherms having the following relationships:

$$\frac{C}{\theta} = C + \frac{1}{K} \quad (\text{Langmuir}) \quad (2)$$

$$\ln C = -\ln K + a\theta \quad (\text{Temkin}) \quad (3)$$

$$\ln \frac{\theta}{C(1-\theta)} = \ln K + a\theta \quad (\text{Frumkin}) \quad (4)$$

where θ is the surface coverage, C is the inhibitor concentration, K is the adsorption equilibrium constant and a is the molecular interaction constant, a constant expressing the interaction between adsorbed and adsorbing molecules. The Langmuir adsorption isotherm was found to fit well with the experimental data (Fig. 2). Straight line were obtained when C/ θ were plotted against C (Fig. 2). The correlation coefficient is close to 1.0, confirming that the adsorption of penicillin obeys the Langmuir isotherm. This isotherm is based on the assumption that all the adsorption sites are equivalent and the particle binding occurs independently from the nearby sites being occupied or unoccupied.

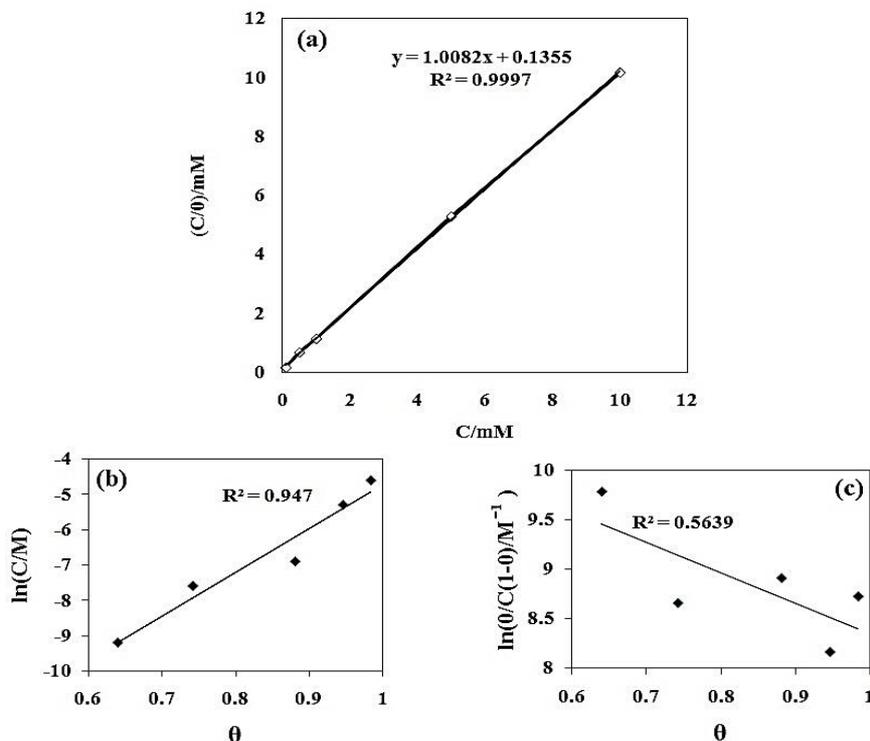


Fig. 2. Adsorption isotherms for mild steel in 1.0 M HCl solution at the presence of different concentrations of penicillin from polarization data (a) Langmuir (b) Temkin (c) Frumkin.

Electrochemical impedance spectroscopy

Nyquist presentations of EIS for mild steel in 1.0 M HCl in the absence and presence of various concentrations of penicillin are shown in Fig. 3. In these spectra, variation of impedance response from mild steel after addition of inhibitor to the acid media is remarkable. Increasing the concentration of antibacterial drug was caused the values of charge transfer resistance to shift to elevated amounts. Table 2 lists impedance parameters in the absence and presence of different concentrations of penicillin.

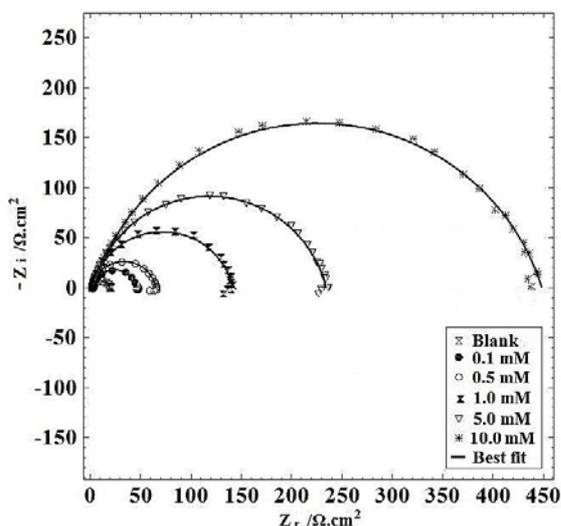
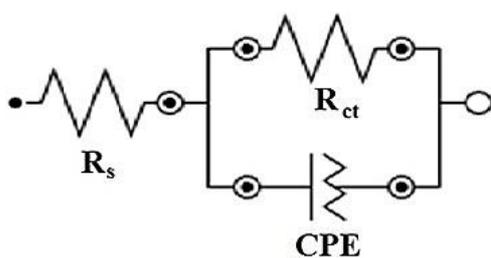


Fig. 3. Nyquist plots for mild steel in 1.0 M HCl solution in the presence of different concentrations of penicillin.



Scheme 2. The equivalent electrical circuit of the impedance spectra.

Scheme 2 shows the electrical equivalent circuit employed to analyze the impedance plots. In this scheme, 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 [19]:

$$Z_{CPE} = \frac{1}{Y_0(jw)^n} \quad (5)$$

where Y_0 is a proportional factor, j equals $\sqrt{-1}$, w is the angular frequency and n is the phase shift. For $n=0$, Z_{CPE} represents a resistance with $R=Y_0^{-1}$, for $n=1$ a capacitance with $C=Y_0$, for $n=0.5$ a Warburg element and for $n=-1$ an inductive with $L=Y_0^{-1}$ [20]. Because it was observed that n was closely near 1 (Table 2), the CPE obeys the capacitive behavior.

Table 2. Impedance parameters and the corresponding inhibition efficiency values for mild steel in 1.0 M HCl containing different concentrations of penicillin

C /mM	$R_s/\Omega.cm^2$	$R_{ct}/\Omega.cm^2$	n	$10^6 Y_0/\Omega^{-1}.cm^{-2}$	$C_{dl}/\mu F.cm^{-2}$	IE _{EIS} (%)
0	1.37	18.5	0.852	287	119.5	-
0.1	1.67	44.7	0.874	139	85.3	58.6
0.5	1.63	63	0.900	97.3	60.0	70.6
1.0	1.54	140	0.868	54.2	27.0	86.8
5.0	1.79	232	0.854	52.1	24.0	92.0
10.0	1.99	446	0.811	53.9	22.0	95.9

As it can be seen from Table 2, the R_{ct} values increase with the increasing the concentration of the inhibitor. On the other hand, the values of C_{dl} decrease with an increase in the inhibitor concentration. This situation is the result of an increase the surface coverage by the inhibitor. The thickness of the protective layer, d_{org} , was related to C_{dl} by the following equation [21]:

$$d_{org} = \epsilon_0 \epsilon_r / C_{dl} \quad (6)$$

where ϵ_0 is the vacuum dielectric constant and ϵ_r is the relative dielectric constant. Decrease in the C_{dl} , which can be resulted

from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggested that the inhibitor molecules act as the adsorption at the metal/solution interface. Thus, the change in C_{dl} values was caused by the gradual replacement of water molecules by the adsorption of the inhibitor molecules on the metal surface and thus decreasing the extent of the metal dissolution.

Inhibition efficiencies in Table 2 were calculated through the following expression:

$$IE_{EIS}(\%) = \frac{R'_{ct} - R_{ct}}{R'_{ct}} \times 100 \quad (7)$$

where R_{ct} and R'_{ct} represent the charge transfer resistance, before and after addition of the inhibitor to the corrosion media, respectively. Inhibition efficiencies increase with increasing inhibitor concentrations. Comparing the results with those in Table 1, one can conclude that satisfactory agreement is found with the inhibition efficiencies as obtained through potentiodynamic polarization measurements. The plots for each isotherm show that the EIS data agree with the Langmuir isotherm (Fig. 4).

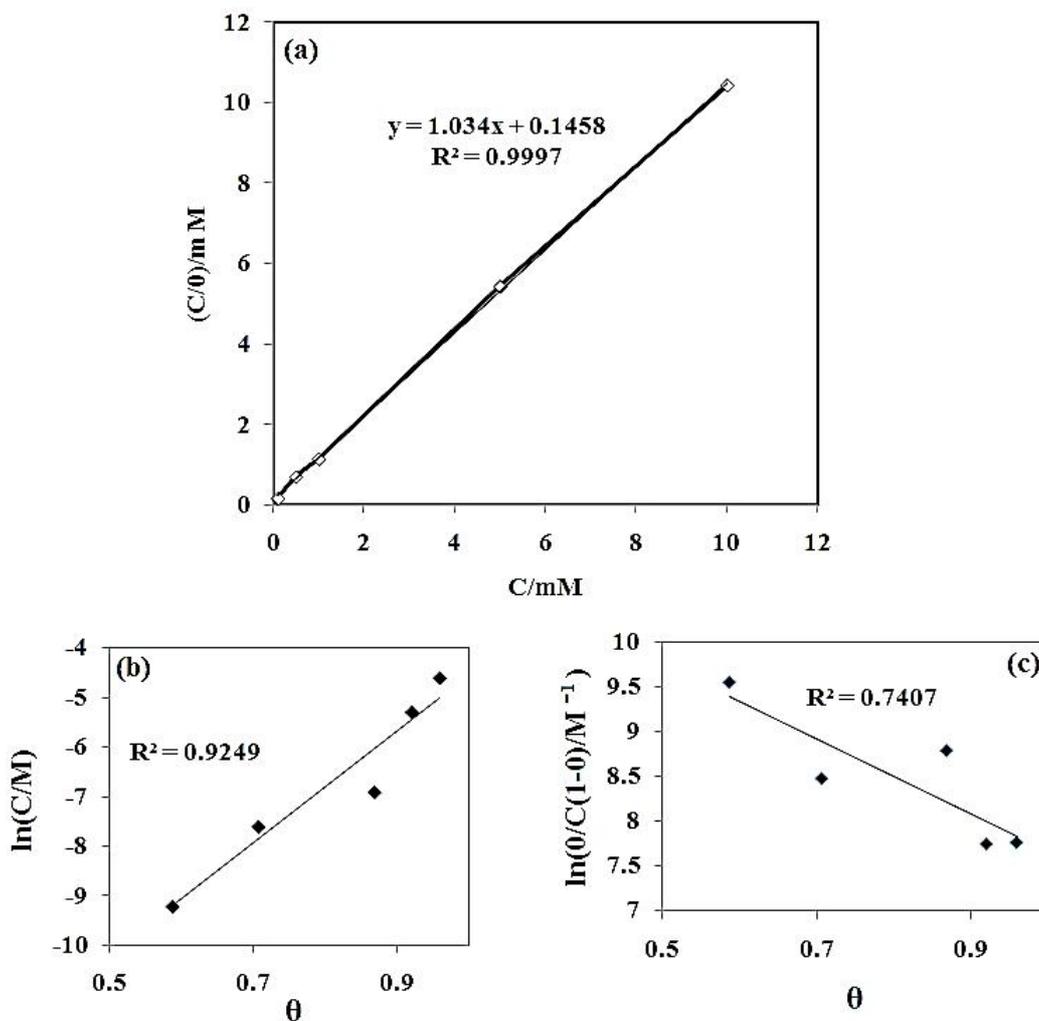


Fig. 4. Adsorption isotherms for mild steel in 1.0 M HCl solution at the presence of different concentrations of penicillin from impedance data (a) Langmuir (b) Temkin (c) Frumkin.

Electrochemical noise

The EN signals corresponding to two nominally identical WEs in the absence and presence of different penicillin concentrations have been measured during 75 s starting from 45 min after immersion time. Then wavelet transform was employed to decompose each set of data points and the SDPS plots of EN signals were obtained as shown in Fig. 5.

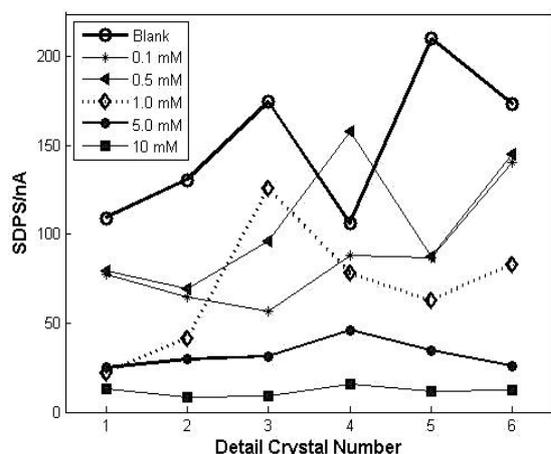


Fig. 5. SDPS plots of EN current records of mild steel in 1.0 M HCl solution in the absence and presence of different concentrations of penicillin.

A coulombs counting method, namely CoulCount has been developed earlier as a means of studying localized corrosion [8, 9]. The total amount of noise charges exchanged between two WEs in a given time interval is collected (counted). It takes two steps from the digital current noise signals to the calculation of the time-related amount of noise charges: 1) elimination of the DC part and 2) summation of the time-related current levels [8]. The DC part (the part of the signal with fluctuations <0.1 Hz) is eliminated with hardware filters. The total amount of noise charges $Q(t)$ at the time t is calculated according to the following equation [9]:

$$Q(t) = \sum_{i=0}^{t/\Delta t} |I_i| \Delta t \quad (8)$$

The reduction of data is achieved by averaging absolute current noise data, $|I_i|$ (e.g. 600 data points for 1 min) and corresponding adjustment of Δt (1 min).

Table 3. Noise parameters and the corresponding inhibition efficiency values for mild steel in 1.0 M HCl containing different concentrations of penicillin

C/mM	d_{\max}	$\Delta t/s$	SDPS/nA	Q/nCoul	$IE_{EN}(\%)$
0	d5	6	210	1260	-
0.1	d5	6	86	516	59.0
0.5	d4	3	158	474	62.4
1.0	d3	1.5	126	189	85.0
5.0	d4	3	46	138	89.0
10.0	d4	3	16	48	96.2

Instead of using the hardware filtered noise signal (with fluctuations >0.1 Hz), it is more convenient to use the partial signals resulted from wavelet analysis of EN current data to calculate the total amount of noise charges. As mentioned above in Section 1, each partial signal is a signal which resembles the fluctuations of the original signal at a particular interval of frequency. Therefore, it is suitable to use the standard deviation of partial signal (SDPS) for calculation of the amount of noise charges at the particular interval of frequency. The maximum peak in SDPS plots corresponds to predominant transients in the original EN signal [16]. The predominant transients can be attributed to metastable pits [11]. The development of a pit causes a quantity of electric charge to flow in the circuit which can be estimated by the following equation:

$$Q = i_{\max} \cdot \tau_{\max} \quad (9)$$

where i_{\max} is the SDPS value at the maximum peak crystal (d_{\max}) and τ_{\max} is the average time width of d_{\max} crystal.

Then it seems suitable to define the corrosion inhibition efficiency as follows:

$$IE_{EN}(\%) = \frac{Q - Q'}{Q} \times 100 \quad (10)$$

where Q and Q' are the noise charges in the uninhibited and inhibited cases, respectively.

It is evident from the SDPS plot of signal Blank (Fig. 5) that the maximum is located at d5 crystal with the SDPS value of 210 nA (i_{max}). The average time width of crystal d5 is equal to 6s. The values of

the parameters derived from all of the SDPS plots in Fig. 5 have been summarized in Table 3 (d_{max} , τ_{max} and i_{max}). Table 3 further presents values of Q and the inhibition efficiencies. Comparison with data in Tables 1 and 2 reveals that reasonable agreement is found with the IE values as obtained through potentiodynamic polarization and EIS measurements. Attempts were made to fit θ values to various isotherms and the Langmuir isotherm presents the best fit (Fig. 6).

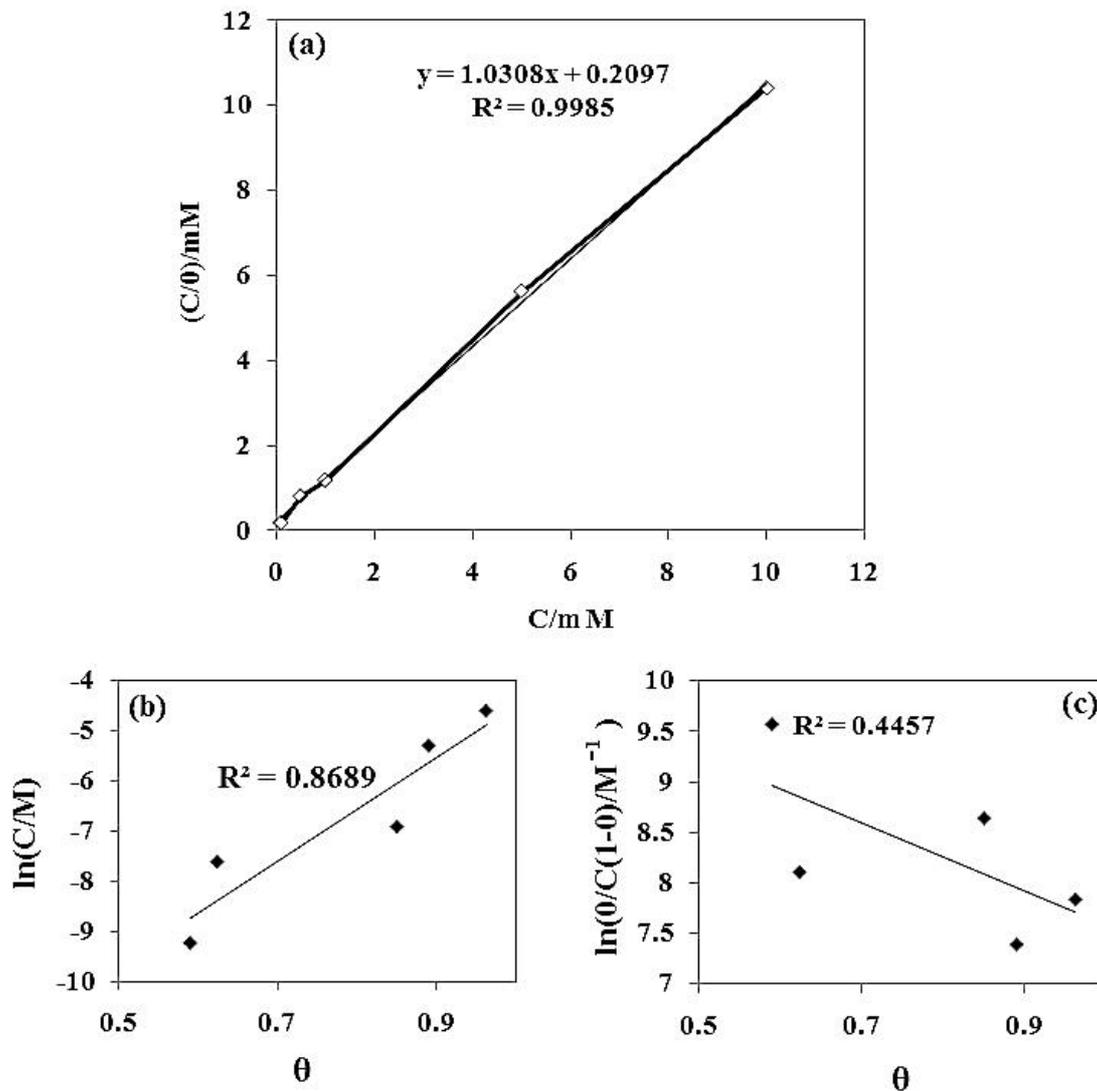


Fig. 6. Adsorption isotherms for mild steel in 1.0 M HCl solution at the presence of different concentrations of penicillin from EN data (a) Langmuir (b) Temkin (c) Frumkin.

Thermodynamic parameters

The value of adsorption equilibrium constant, K_{ads} , is calculated from the reciprocal of the intercept of Langmuir adsorption isotherm line. The free energy of the adsorption of inhibitor on mild steel surface can be evaluated with the following equation:

$$\Delta G_{ads} = -RT \ln(55.5 K_{ads}) \quad (11)$$

where 55.5 is the molar concentration of water in the solution expressed in M (mol.L^{-1}), R the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and T the absolute temperature (K). The values of K_{ads} and ΔG_{ads} are derived from Langmuir adsorption isotherms for the studied inhibitor (Figs. 2, 4 and 6). Table 4 summarizes K_{ads} and ΔG_{ads} values obtained through Tafel polarisation, electrochemical impedance and electrochemical noise measurements. Satisfactory agreement is found for ΔG_{ads} values between the different methods. Due to logarithmic relationship between K_{ads} and ΔG_{ads} values some difference in K_{ads} values obtained from different methods is observed.

Table 4. The values of K_{ads} and ΔG_{ads} corresponding to polarization, EIS and EN data in 1.0 M HCl solution

Tafel		EIS		EN	
K_{ads} (M^{-1})	ΔG_{ads} (kJ mol^{-1})	K_{ads} (M^{-1})	ΔG_{ads} (kJ mol^{-1})	K_{ads} (M^{-1})	ΔG_{ads} (kJ mol^{-1})
7353	-32.0	6849	-31.8	4769	-30.9

Generally, values of ΔG_{ads} around -20 kJ mol^{-1} or less negative are consistent with the electrostatic interaction between charged molecules and the charged metal surface (physisorption); values around -40 kJ mol^{-1} or more negative involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of metal bond (chemisorption) [22]. In the present work, the calculated ΔG_{ads} values are the intermediate case indicating that the adsorption of inhibitor molecules is not merely physisorption or chemisorption but obeying a comprehensive adsorption (physical and chemical adsorption).

Table 5 shows satisfactory agreement between IE% values acquired from three electrochemical methods.

Table 5. The values of IE% corresponding to polarization, EIS and EN data in 1.0 M HCl solution

C/mM	IE _p %	IE _{EIS} %	IE _{EN} %
0.1	64.0	58.6	59.0
0.5	74.2	70.6	62.4
1.0	88.1	86.8	85.0
5.0	94.6	92.0	89.0
10.0	98.4	95.9	96.2

SEM observations

The SEM images were taken and observed in order to support our findings. Fig. 7 shows the SEM photographs for mild steel after immersion for 1 h in 1.0 M HCl solution without and with 10 mM penicillin. There is pitting corrosion on the surface of two specimens. However, Fig. 7b shows an appreciable inhibiting ability to corrosion on mild steel surface compared with that of the surface immersed in 1.0 M HCl alone (Fig. 7a).

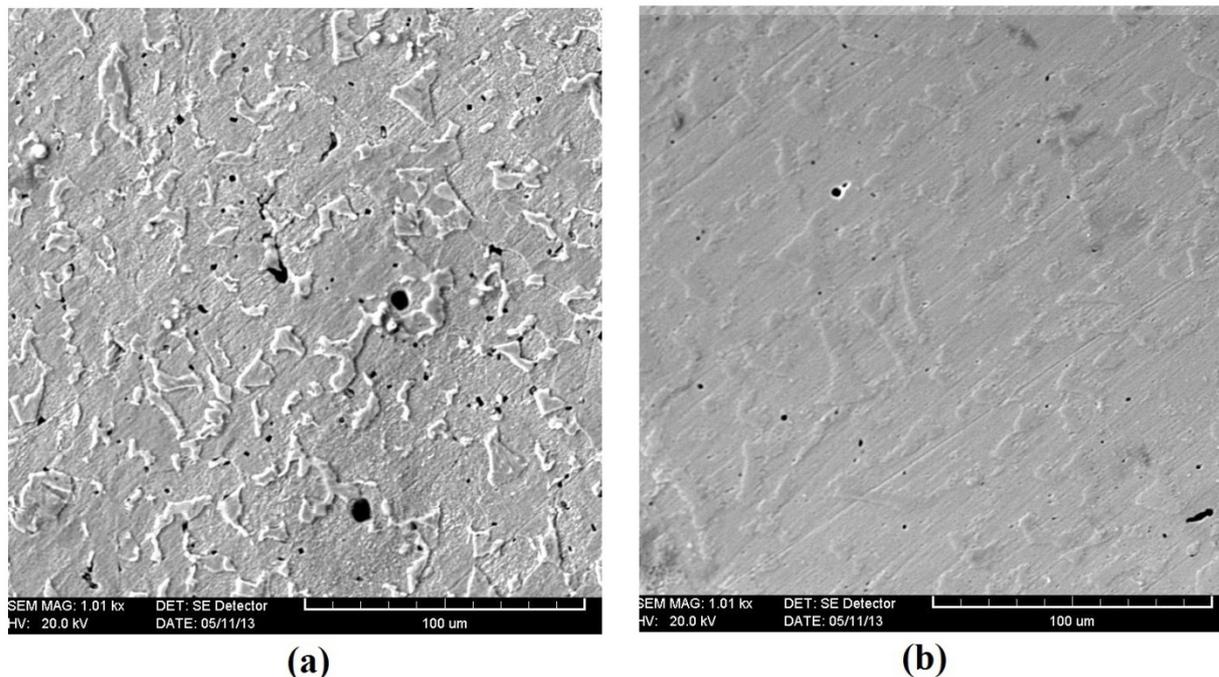


Fig. 7. SEM images of mild steel after immersion in 1.0 M HCl for 1 h (a) in the absence of inhibitor and (b) in the presence of 10 mM penicillin.

CONCLUSIONS

The adsorption and inhibition effect of antibacterial drug penicillin on the corrosion behavior of mild steel in 1.0 M HCl was studied using electrochemical techniques. Antibacterial drugs offer interesting possibilities for corrosion inhibition because of their nontoxic properties and high solubility in acidic media. Results obtained from potentiodynamic polarization, EIS and EN measurements demonstrated that the adsorption of penicillin on mild steel in 1.0 M HCl follows Langmuir isotherm. The calculated values of free energy indicated that both physical and chemical adsorption take place.

It seems that the EN method can apply as an alternative quantitative technique to study the corrosion behavior of inhibitors. According to calculation of the amount of noise charges using the standard deviation of partial signal (SDPS) at the particular interval of frequency it is possible to

obtain the inhibition efficiency of an inhibitor. The IE and ΔG_{ads} values obtained from EN data for penicillin show a reasonable agreement with those obtained from potentiodynamic polarization and EIS measurements.

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