Journal of Physical Chemistry and Electrochemistry

Journal homepage: http://journals.miau.ac.ir/jpe

Islamic Azad University
Marvdasht Branch

Electrochemical Investigation of the Effect of Penicillin G Benzathine as a Green Corrosion Inhibitor for Mild Steel

*M.R. Gholamhosseinzadeh** [a], *R. Farrehi Moghaddam* [b]

[a]Young Researchers and Elite Club, Kerman Branch, Islamic Azad University Kerman, Iran
[b]Department of Chemistry, Shahid Bahonar University of Kerman, Kerman, Iran

Abstract

In this paper, the effect of penicillin G benzathine (PGB) drug as a green corrosion inhibitor on mild steel in 1.0 M hydrochloric acid solution has been investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The inhibition efficiency (IE) was found to increase with increasing inhibitor concentration. Potentiodynamic polarization measurements indicated that PGB is a mixed type inhibitor. The results of potentiodynamic polarization and EIS measurements demonstrated that the adsorption of PGB 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. The IE values obtained from EIS measurements show a reasonable agreement with those obtained from potentiodynamic polarization method.

Keywords: Penicillin G benzathine; Inhibition Efficiency; Potentiodynamic Polarization; Electrochemical Impedance Spectroscopy.

1. 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. Although many organic inhibitors demonstrate the high inhibition efficiencies, they are mostly toxic and harmful to the environment. Saleh reported that hexadecyl pyridinium bromide (HDPB) as a cationic surfactant shows high inhibition efficiency for the corrosion of low carbon steel [1]. However, cationic surfactants are known of its toxicity and carcinogenicity in addition to their high cost. Recently researchers have paid attention to the development of drugs as inhibitors for metallic corrosion [2-7]. The inhibition of mild steel in acid solutions by different types of organic inhibitors has been extensively studied [8-12].

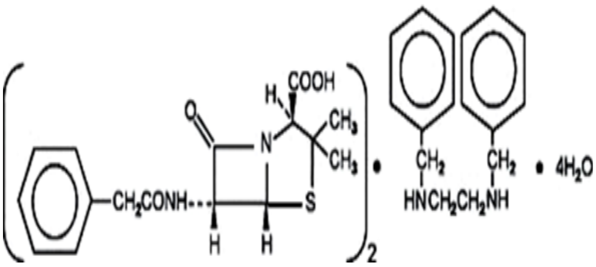
The present paper describes study of the inhibition action of penicillin G benzathine (PGB) (Scheme 1) on corrosion of mild steel in 1.0 M HCl solution using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The choice of this inhibitor as corrosion inhibitor is based mainly on its nontoxic properties and high solubility in acidic media.

2. Materials and Methods

Penicillin G benzathine was obtained from Sigma and used without any further purification. Scheme 1 shows the chemical

*Corresponding Author
E-mail address: mrgholamhosseinzadeh@gmail.com

structure of this antibacterial drug. The employed working electrodes (WEs) were prepared from mild steel with the chemical composition (wt.%) of: C (0.15), Mn (0.73), Si (0.72) and Fe (98.4).



Scheme 1. The molecular structure of penicillin G benzathine

Potentiodynamic polarization and EIS measurements have been used to study the corrosion behavior of mild steel in 1.0 M HCl solution without and with doping by PGB 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 and EIS experiments were conducted using Autolab 302N potentiostat with Nova 1.6 software. The 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 1.9 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 1.9 Nova software.

3. Results and discussion

3.1. Potentiodynamic polarization

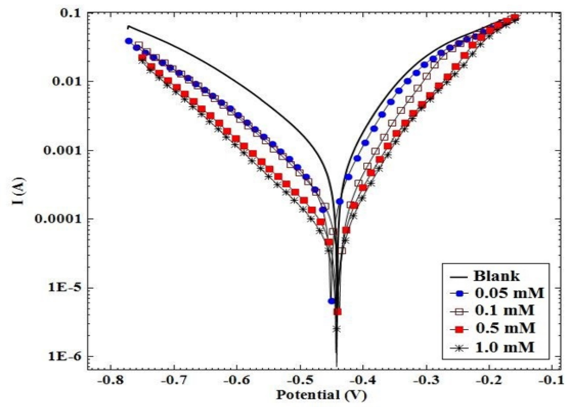


Fig. 1. Tafel polarization curves of mild steel in 1.0M HCl solution containing different concentrations of Penicillin G benzathine.

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

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

C /mM	i_{corr}/μA.cm^{-2}	-E_{corr}/mV	β_a/mV.dacade^{-1}	β_c/mV.dacade^{-1}	IE_p(%)
0	2370	442	142	226	-
0.05	505	452	103	158	79
0.1	371	439	96	157	84
0.5	120	442	93	131	95
1.0	90	443	94	122	96

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

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

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.

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 θ=IE(%)/100 [13]. Here, an attempt was made to test the Langmuir, Temkin and Frumkin isotherms having the following relationships:

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

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

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

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. 2a). The correlation coefficient is close to 1.0, confirming that the adsorption of PGB 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.

3.2. Electrochemical impedance spectroscopy

Nyquist plots of EIS for mild steel in 1.0 M HCl in the absence and presence of various concentrations of PGB are shown in Fig. 3. In these spectra, variation of impedance response from mild steel after addition of inhibitor to

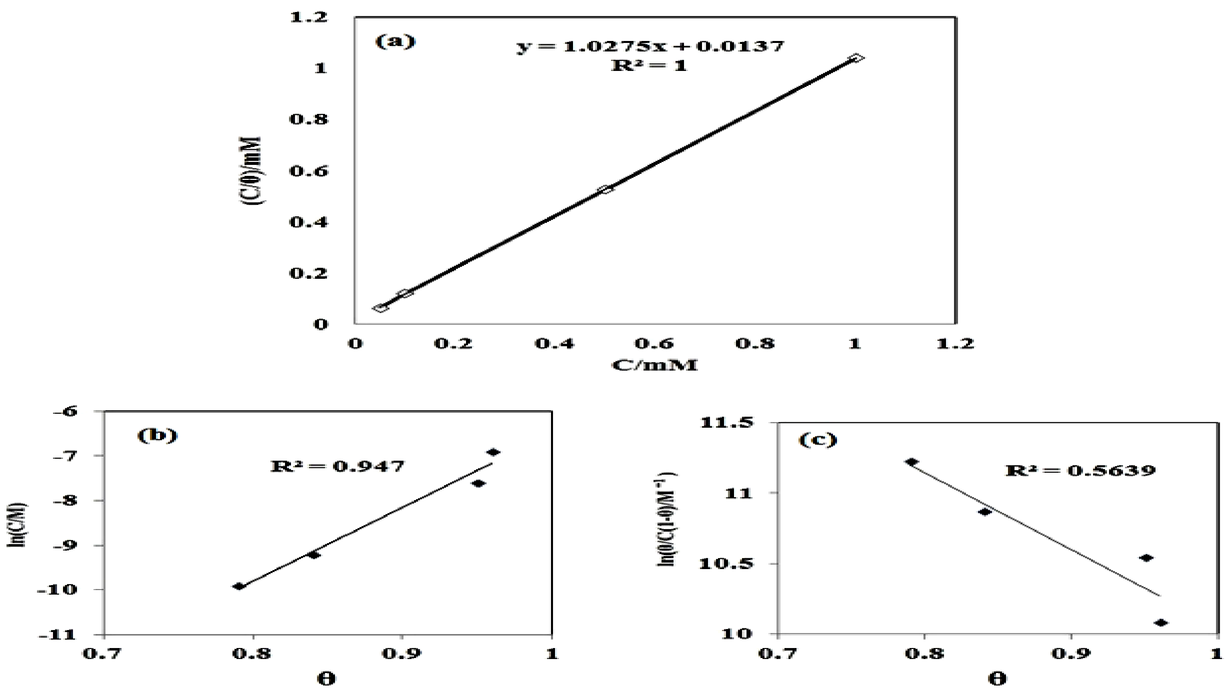


Fig. 2. Adsorption isotherms for mild steel in 1.0 M HCl solution at the presence of different concentrations of penicillin G benzathine from polarization data (a) Langmuir (b) Temkin (c) Frumkin.

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 G benzathine.

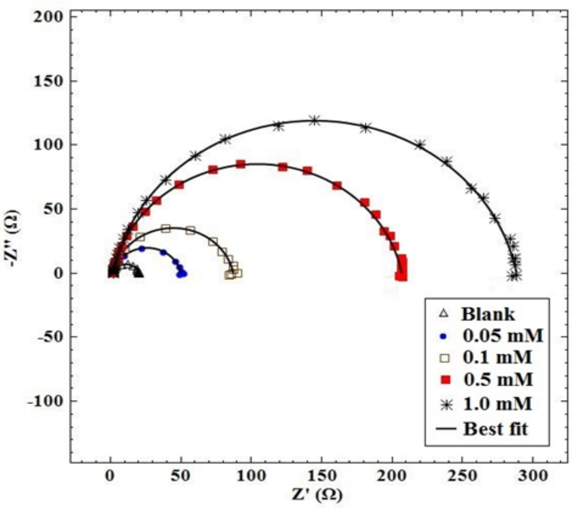


Fig. 3. Nyquist plots for mild steel in 1.0 M HCl solution in the presence of different concentrations of penicillin G benzathine.

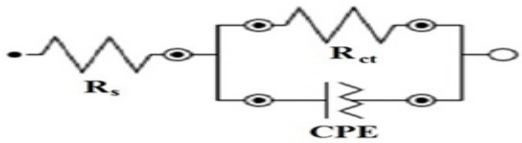
Table 2. Impedance parameters and the corresponding inhibition efficiency values for mild steel in 1.0 M HCl containing different concentrations of penicillin G benzathine.

C /mM	R_s/Ω.cm^2	R_{ct}/Ω.cm^2	n	C_{dl}/μF.cm^{-2}	IE_{EIS}(%)
0	1.4	18.5	0.852	152	-
0.05	1.6	48	0.888	85	62
0.1	1.5	85	0.885	55	78
0.5	1.3	205	0.885	35	91
1.0	1.4	287	0.884	30	94

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 [14]:

$$Z_{CPE} = \frac{1}{Y_0 (j\,w)^n} \qquad (5)$$

where Y_0 is a proportional factor, j equals √-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 $L=Y_0^{-1}$ [15]. Because it was observed that n was closely near 1 (Table 2), the CPE obeys the capacitive behavior.



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

It is clear from Table 2 that 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 [16]:

$$d_{org} = \varepsilon_0 \varepsilon_r / C_{dl} \qquad (6)$$

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:

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

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).

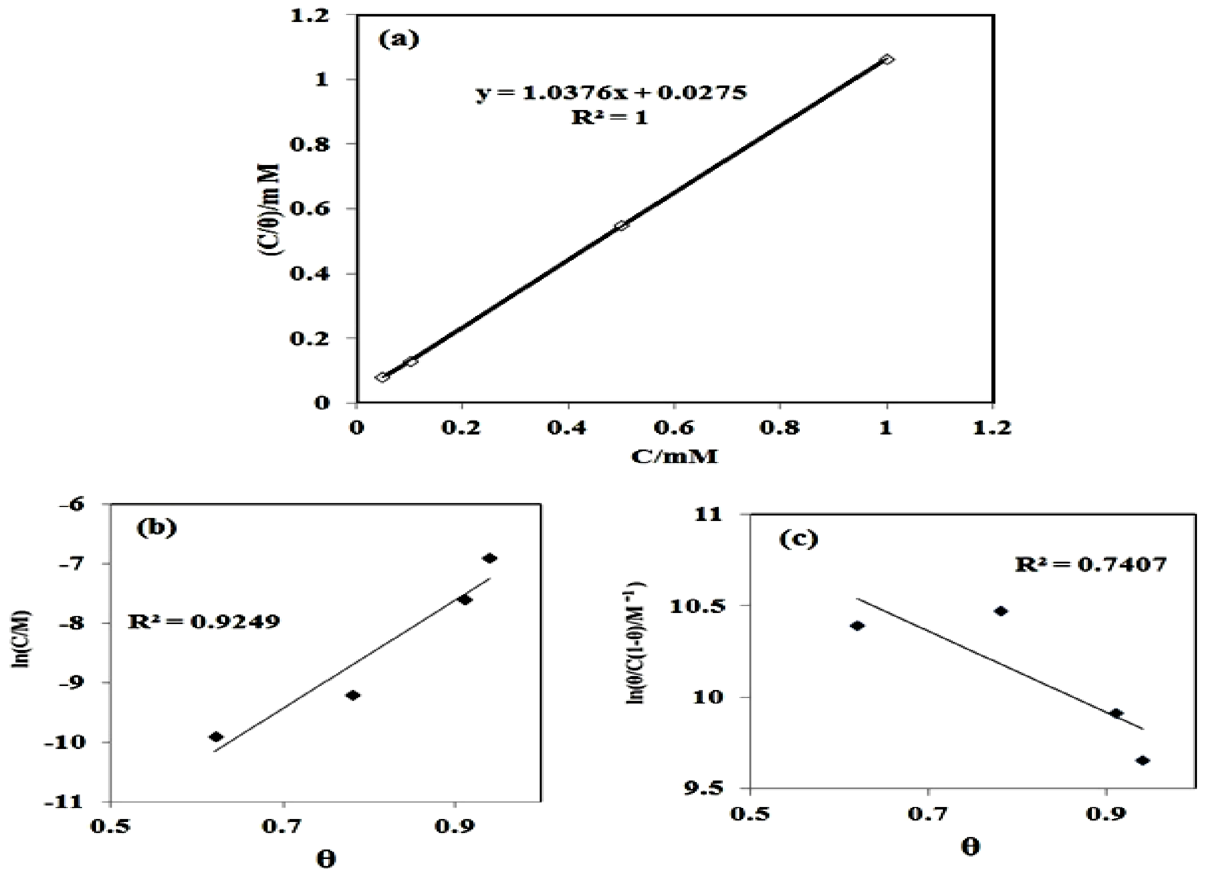


Fig. 4. Adsorption isotherms for mild steel in 1.0 M HCl solution at the presence of different concentrations of penicillin G benzathine from impedance data (a) Langmuir (b) Temkin (c) Frumkin

3.3. 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;

$$\Delta G_{ads} = -RT\,ln(55.5K_{ads}) \quad (8)$$

where 55.5 is the molar concentration of water in the solution expressed in M (mol.L^{-1}), R the gas constant (8.314 J K^{-1}.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 and 4). Table 3 summarizes K_{ads} and ΔG_{ads} values obtained through Tafel polarisation and electrochemical impedance 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 3. The values of K_{ads} and ΔG_{ads} corresponding to polarization and EIS data in 1.0 M HCl solution.

Tafel		EIS	
K_{ads} (M^{-1})	ΔG_{ads} (kJ.mol^{-1})	K_{ads} (M^{-1})	ΔG_{ads} (kJ.mol^{-1})
72993	-37.7	36363	-36.0

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) [17]. 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 4 shows satisfactory agreement between IE% values acquired from two electrochemical methods.

Table 4. The values of IE% corresponding to polarization and EIS data in 1.0 M HCl solution.

C/mM	IE_p%	IE_{EIS}%
0.05	79	62
0.1	84	78
0.5	95	91
1.0	96	94

The IE_p values of some different inhibitors corresponding to mild steel in 1.0 M HCl solution are gathered in Table 5 for comparison purpose. These values prove that the drug of PGB worked as an efficient inhibitor for mild steel in HCl solution.

4. Conclusions

The adsorption and inhibition effect of antibacterial drug PGB on the corrosion behavior of mild steel in 1.0 M HCl was studied using electrochemical techniques. Antibacterial drug offers interesting possibilities for corrosion inhibition because of its nontoxic properties and high solubility in acidic media. Results obtained from potentiodynamic polarization and EIS measurements demonstrated that the adsorption of PGB 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.

The IE and ΔG_{ads} values obtained from EIS data for PGB show a reasonable agreement with those obtained from potentiodynamic polarization measurements.

Acknowledgements

The authors are grateful to Islamic Azad University, Kerman Branch, for financial assistance of this work.

References

[1] M.M. Saleh, Inhibition of mild steel corrosion by hexadecylpyridinium bromide in 0.5 MH 2 SO 4, Materials chemistry and physics, 98 (2006) 83-89.
[2] I. Ahamad, M.A. Quraishi, Mebendazole: New and efficient corrosion inhibitor for mild steel in acid medium, Corros. Sci., 52 (2010) 651-656.
[3] A.S. Fouda, H.M. El-Abbasy, Inhibitive Action of Ampicillin and Benzyl Penicillin Drugs for Corrosion of Type 304 Stainless Steel in 1.0 M HCl Solution, Corrosion, 68 (2012) 1-9.
[4] G. Gece, Review, Drugs: A review of promising novel corrosion inhibitors, Corros. Sci., 53 (2011) 3873-3898.
[5] Y. Liang, C. Wang, J. Li, L. Wang, J. Fu, The Penicillin Derivatives as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution: Experimental and Theoretical Studies, Int. J. Electrochem. Sci., 10 (2015) 8072-8086.
[6] G. Golestani, M. Shahidi, D. Ghazanfari, Electrochemical evaluation of antibacterial drugs as environment-friendly inhibitors for corrosion of carbon steel in HCl solution, Appl. Surf. Sci., 308 (2014) 347-362.
[7] M. Srivastava, P. Tiwari, S.K. Srivastava, R. Prakash, G. Ji, Electrochemical investigation of Irbesartan drug molecules as an inhibitor of mild steel corrosion in 1 M HCl and 0.5 M H2SO4 solutions, Journal of Molecular Liquids, 236 (2017) 184-197.
[8] A. Mohammadi, S.M.A. Hosseini, M.J. Bahrami,

Table 5. The values of IE_p% of different inhibitors corresponding to mild steel in 1.0 M HCl solution.

Inhibitor	0.05 mM	0.1 mM	0.5mM	1.0mM	Ref.
Penicillin	-	64.0	74.2	88.1	[6]
Oxacillin	82.1	93.1	-	93.2	[5]
Ampicillin	-	46.9	62.4	84.5	[6]
Irbesartan	-	71	92	-	[7]
PGB	79	84	95	96	This work

M. Shahidi, Corrosion Inhibition of Mild Steel in Acidic Solution by Apricot Gum as a Green Inhibitor, Prog. Color Colorants Coat., 9 (2016) 117-134.

[9] G. Karthik, M. Sundaravadivelu, Studies on the inhibition of mild steel corrosion in hydrochloric acid solution by atenolol drug, Egyptian Journal of Petroleum, DOI (2015).

[10] P. Roy, P. Karfa, U. Adhikari, D. Sukul, Corrosion inhibition of mild steel in acidic medium by polyacrylamide grafted Guar gum with various grafting percentage: Effect of intramolecular synergism, Corros. Sci., 88 (2014) 246-253.

[11] P.B. Matad, P.B. Mokshanatha, N. Hebbar, V.T. Venkatesha, H.C. Tandon, Ketosulfone Drug as a Green Corrosion Inhibitor for Mild Steel in Acidic Medium, Industrial & Engineering Chemistry Research, 53 (2014) 8436-8444.

[12] I.B. Obot, E.E. Ebenso, M.M. Kabanda, Metronidazole as environmentally safe corrosion inhibitor for mild steel in 0.5 M HCl: Experimental and theoretical investigation, J. Environ. Chem. Eng., 1 (2013) 431-439.

[13] G. Achary, Y.A. Naik, S.V. Kumar, T.V. Venkatesha, B.S. Sherigara, An electroactive co-polymer as corrosion inhibitor for steel in sulphuric acid medium, Appl. Surf. Sci., 254 (2008) 5569-5573.

[14] M.G. Hosseini, M. Ehteshamzadeh, T. Shahrabi, Protection of mild steel corrosion with Schiff bases in 0.5M H_2SO_4 solution, Electrochim. Acta, 52 (2007) 3680-3685.

[15] D.A. Lopez, S.N. Simison, S.R.d. Sanchez, The influence of steel microstructure on CO_2 corrosion. EIS studies on the inhibition efficiency of benzimidazole, Electrochim. Acta, 48 (2003) 845-854.

[16] F. Bentiss, M. Lebrini, M. Lagrenee, Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in mild steel/ 2,5-bis(n-thienyl)-1,3,4-thiadiazoles/hydrochloric acid system, Corros. Sci., 47 (2005) 2915-2931.

[17] E.A. Noor, A.H. Al-Moubaraki, Thermodynamic study of metal corrosion and inhibitor adsorption processes in mild steel/1-methyl-4[4 (-X)-styryl pyridinium iodides/hydrochloric acid systems, Mater. Chem. Phys., 110 (2008) 145-154.