

Synthesis and Evaluation of Benzhydrylidene-(2, 5-dimethyl-phenyl)-amine for Anti-corrosive Activity on Mild Steel in Acidic Medium

Akshay Kumar

*Department of Chemistry,
University of Delhi, Delhi-110007*

Abstract

A newly synthesised Schiff base Benzhydrylidene-(2, 5-dimethyl-phenyl)-amine (BHDPA), characterised by ^1H NMR Spectroscopy, was evaluated as corrosion inhibitor of mild steel in 0.5 M H_2SO_4 using electrochemical technique potentiodynamic polarization for various concentrations. Polarisation curves indicate that BHDPA acts as a mixed type of inhibitor. Finally it is concluded from electrochemical studies that inhibition efficiency increases with increase in BHDPA concentration. The number of water molecules (X) replaced by a molecule of BHDPA adsorbate was determined from the langmuir isotherms applied to the data obtained from the gravimetric experiments performed on mild steel specimen in 0.5 M H_2SO_4 solution at 298. The kinetic and adsorption parameters for mild steel in the presence and absence of BHTPA were evaluated. The negative value of ΔG shows that adsorption is spontaneous.

1. INTRODUCTION:

Mild steel is widely used in down-hole tubing, flow lines and transmission pipelines despite being availability of other corrosion resistant materials [1]. Imp role is played throughout world by mild steel pipelines in transporting liquids and gases [2]. Acid solutions are most frequently used for pickling, industrial acid cleaning and oil-well acidifying processes [3-7]. The acid induces serious corrosive effect on tubes, pipelines and other equipments [8-10]. A huge cost is invested to control corrosion in oil and gas industry, usually corrosion inhibitors are used to inhibit corrosion. Corrosion inhibitors are organic compounds having polar groups including nitrogen, sulphur and/or oxygen atoms and heterocyclic compounds with polar functional groups and conjugated double bonds [11-13]. Inhibition appears as a result of

adsorption of molecules and ions on the metal surface [14]. Several Schiff bases have been reported as effective corrosion inhibitors for different metals and alloys in acidic media [15-18]. The higher adsorption ability and corrosion inhibition efficiency of Schiff bases is due to the presence of $-C=N-$ group [19-20]. The present investigation reports the anticorrosive behaviour of Benzhydrylidene-(2, 5-dimethyl-phenyl)-amine for mild steel in 0.5 M H_2SO_4 .

2. Experimental details

2.1 Materials

Mild steel (C = 0.15%, Si = 0.08%, S = 0.025%, P = 0.025% and Mn = 1.02%) encapsulated in a Teflon holder with the exposed area of 0.1 cm^2 was used as the working electrode (WE). The surface was abraded successively by emery papers of different grades, i.e. 150, 320, 400 and 600 and finely polished with a 4/0 polishing paper to obtain uniform mirror like finish, degreased with acetone and washed with distilled water before experiment. Platinum wire and dip type saturated calomel electrodes were used as counter and reference electrodes, respectively. BHDPA solutions of concentration 10^{-1}M , 10^{-2}M , 10^{-3}M , 10^{-4}M were prepared in analytical-grade chemical reagents 0.5 M H_2SO_4 using distilled water. For each experiment, a freshly prepared solution was used.

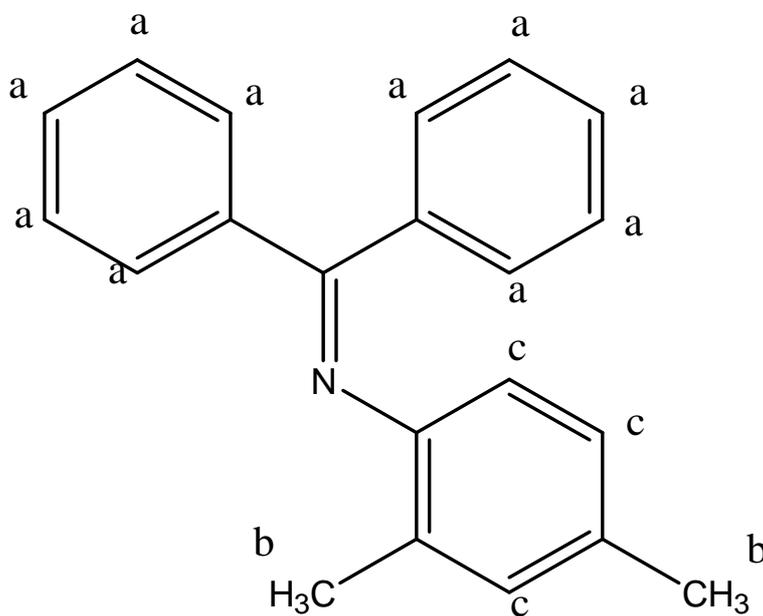


Fig. 1. The chemical structure of Schiff base prepared.

2.2. Synthesis of Schiff base.

3, 5-Dimethyl-phenylamine was refluxed with Diphenyl-methanone in ethanol at 65°C for 4 hours to form Benzhydrylidene-(2, 5-dimethyl-phenyl)-amine. The product,

“an symmetric Schiff’s base” BHDPA (the structure of which is shown in Fig. 1), was separated by vacuum distillation and purified by vaccum distillation in hexane and ethyl acetate medium. The ethanol solution of the product obtained was distilled to remove the unreacted reactants.

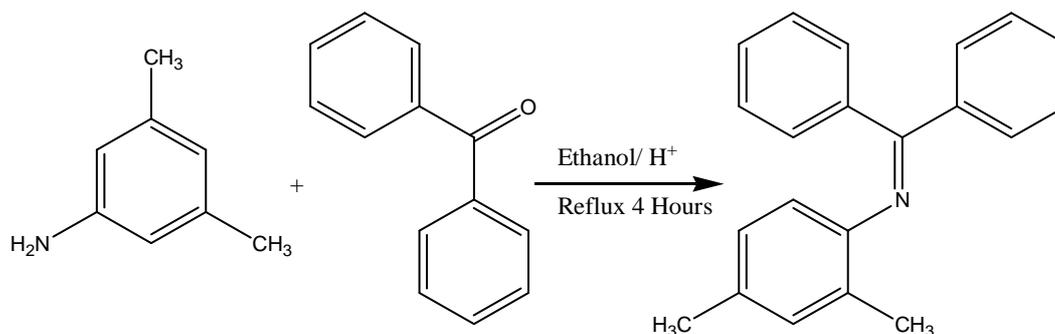


Fig.2. Scheme of synthesis.

The structures of the compounds were confirmed by ¹H nuclear magnetic resonance spectroscopy (¹H NMR).

¹H NMR data of BHDPA (in DMSO):7.5-7.8ppm (10 H, m), 6.7-6.9ppm (3H, dd), 2.1-2.2ppm (6H, m)

The multiplet peak at 7.5 to 7.8ppm is for 10 H of two phenyl rings numbered as a in fig 1. The multiplet peak at 2.1-2.2ppm is for 6 hydrogens of Two CH₃ groups numbered as b in fig 1. The double doublet at 6.7-6.9 is for three H numbered as c in fig 1.

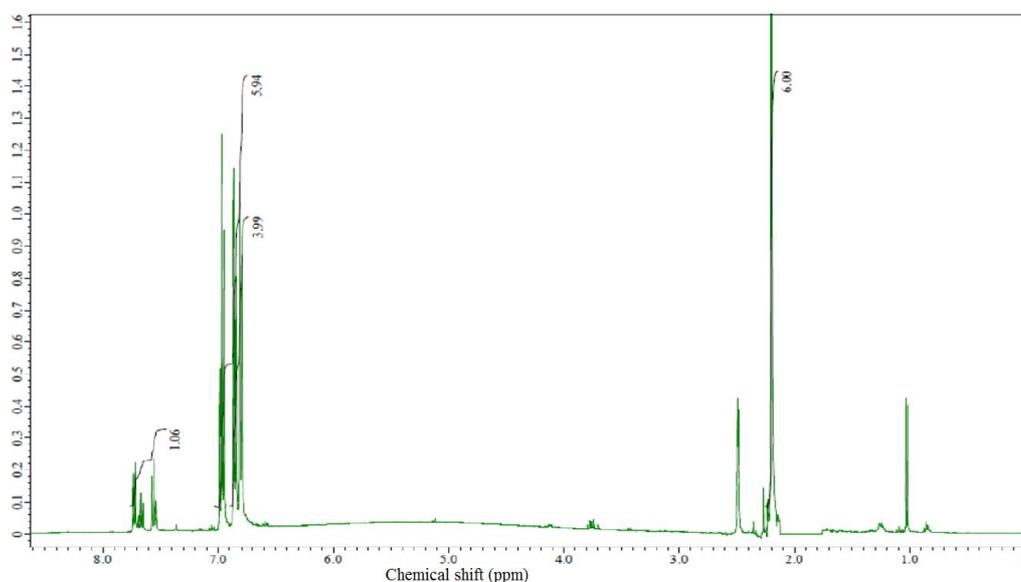


Fig.3. The ¹H NMR spectra of BHDPA.

The data of ^1H NMR spectrum confirmed the expected hydrogen proton distribution in the synthesized Schiff base.

2.3. Electrochemical measurements

The electrochemical measurements were carried out in CHI 760C electrochemical work station (CH Instruments, Austin, USA) at 25°C . The cell consists of three electrodes, the working electrode (steel), counter electrode (platinum), and reference electrode (SCE). Before each electrochemical measurement, the working electrode was allowed to stand for 3 hours in test solution to allow stabilization of open circuit potential (OCP). All reported potentials were with respect to SCE. For Tafel measurements, the potential-current curves were recorded at a scan rate of 0.001 V s^{-1} in the potential range obtained by adding -0.2 and $+0.2$ V to open circuit potential (OCP) value. The corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}) cathodic Tafel slope (bc), and anodic Tafel slope (ba) were obtained from the instrument.

3. Results and discussion

Galvanostatic studies

Cathodic and anodic Tafel polarization curves for mild steel in $0.5\text{M H}_2\text{SO}_4$ solutions in the absence and presence of various concentrations of BHDPA were obtained and are shown in Fig. 4. From the polarisation curves at various concentrations and temperatures, corrosion parameters, e.g. open circuit potential (OCP), corrosion current (I_{corr}), cathodic and anodic Tafel slope values, inhibition efficiencies (IE%) and surface coverage (θ) of acid corrosion of mild steel in the presence of BHDPA were obtained and are given in Table 1. Inhibition Efficiency (IE %) was calculated using the relationship(1)

$$IE \% = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}} \times 100 \quad (1)$$

Where I_{corr} and $I_{\text{corr(inh)}}$ represent the corrosion current density values without and with inhibitor, respectively.

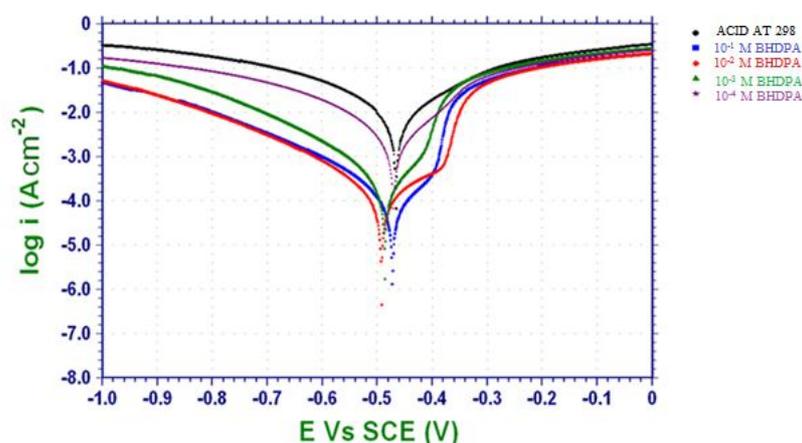


Fig.4. Tafel polarisation curves for mild steel in 0.5M H₂SO₄ solution in the presence and in the absence of the BHDPA at various concentrations.

Surface coverage (θ) was calculated using:

$$\theta = 1 - (I_{\text{corr}}/I_0) \quad (2)$$

Galvanostatic polarisation studies on mild steel in 0.5M sulphuric acid solution containing various concentrations and temperatures reveal that BHDPA influences the corrosion parameters (table 1). This inhibitor has produced a noticeable decrease in the corrosion current density at all the concentrations. The inhibitive action is better expressed by inhibition efficiency which increases with BHDPA concentration (Table 1). The inhibitor efficiency attains the maximum value of 99.60% at 10⁻¹ M BHDPA.

The irregular trends of b_a and b_c values indicates the involvement of more than one type of species adsorbed on the metal surface. Therefore, the adsorption of the π -electron system of BHDPA possibly overlaps with the vacant d-orbitals of the surface of iron resulting in a strong $d\pi$ - $p\pi$ interaction. This electrostatic interaction probably leads to a stronger adsorption of the inhibitor and formation of a barrier between the metal surface and reactive sites. At lower concentration (10⁻⁵ M) surface coverage drops considerably because of the inability of BHDPA to block the active sites, hydrogen permeation onto the metal surface.

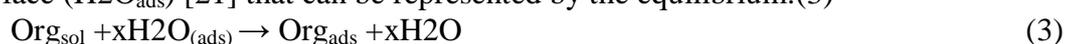
There is no remarkable change in the OCP of inhibited solutions from that of uninhibited solution (fig.4). This indicates that BHDPA is a mixed type of inhibitor and influences both the cathodic and anodic partial processes to almost an equal extent.

Table.1. Electrochemical parameters for the corrosion of mild steel in 1.0 M HCl solution with and without different concentrations of inhibitors at 25 °C.

Temp	Conc (M)	I _{corr} (mA/cm ²)	-E _{corr} Vs SCE(mV)	b _a (mV/dec)	b _c (mV/dec)	I.E. %	Q
298	Blank	8.805	465	70.59	60.89	-	-
	10 ⁻⁴	0.386	470	114.79	68.55	95.61	0.9561
	10 ⁻³	0.198	486	296.79	76.31	97.74	0.9774
	10 ⁻²	0.119	492	76.82	77.29	98.64	0.9864
	10 ⁻¹	0.035	472	389.47	75.01	99.60	0.9960

Adsorption isotherm

The corrosion inhibitive action of the Schiff's base molecules in the acid media on mild steel is due to its adsorption at the metal–solution interface. This adsorption can be regarded as a substitution adsorption process between an organic compound (org_{sol}) in the aqueous media and the water molecules associated with the metallic surface (H₂O_{ads}) [21] that can be represented by the equilibrium:(3)



where 'x' represents the number of water molecules replaced by the adsorption of a molecule of the Schiff's base. For organic compounds, which impede the metal dissolution reaction in acid media, the surface coverage can be evaluated as a function of the inhibitor efficiency (IE%). The link between the surface coverage and the inhibitor efficiency at constant temperature gives an insight into the adsorption process.

In the present study, various adsorption isotherms were tested and it was found that the adsorption of Schiff's base on the mild steel surface in acid media follows the Langmuir adsorption isotherm

According to Langmuir's isotherm, surface coverage is related to inhibitor concentration (C) by the following equation [22]

$$C/\theta = 1/K_{\text{ads}} + C \quad (4)$$

where K_{ads} is the equilibrium constant for adsorption process. The plot of C/θ versus C yields a straight line (Fig. 5) with regression coefficient (R²) close to 1 suggests that the adsorption of inhibitor molecules follow Langmuir adsorption isotherm. The K_{ads} values can be calculated from line intercept on C/θ axis and is related to standard free energy change of adsorption (ΔG°_{ads}) as follows [23]

$$\Delta G^{\circ}_{\text{ads}} = -2.303RT \log (55.5 K_{\text{ads}}) \quad (5)$$

where R is molar gas constant (8.314 J mol⁻¹ K⁻¹), T is absolute temperature (K) and value 55.5 is the concentration of water (in mol dm⁻³) in the solution.

A second order polynomial of the adsorption free energy versus temperature is shown in following equation (6):

$$\Delta G = 0.1733T^2 - 206.45T + 19133 \quad (6)$$

The most common independent variables are T and P, and from Gibbs equations we can obtain temperature dependences of free energy, G, which is expressed as(7)

$$dG = -SdT + VdP \quad (7)$$

At constant P we write $dP = 0$ and we can obtain Eq. (8)

$$\Delta S = - (dG/dT)_P \quad (8)$$

If the second order polynomial expression (6) is derived according to T at constant P, Eq. (9) is obtained.

$$\Delta S = -0.3466T + 206.45 \quad (9)$$

Thus ΔS_{ads} values can be calculated at all studied temperature from Eq. (9).

ΔH_{ads} values are also calculated at all studied temperatures applying the ΔG_{ads} and ΔS_{ads} values in Eq.10[24]

$$\Delta H_{ads} = \Delta G_{ads} + T\Delta S_{ads} \quad (10)$$

The calculated thermodynamic parameters are listed in Table 2. The positive values of ΔH_{ads} reflect that inhibitor adsorbs onto the mild steel surface through endothermic reaction. This could be explained in the following way: the adsorption of inhibitors from the aqueous solution can be regarded as quasi-substitution process between the organic compound in the aqueous phase and water molecules at the mild steel surface. Here, the adsorption of BHDPA molecules is accompanied by desorption of water molecules from the surface which results in positive enthalpy[25]. ΔS_{ads} values were positive, this can be explained as the inhibitor molecules were earlier free to move in bulk solution but after inhibitor molecules were orderly adsorbed onto steel surface, as a result, a decrease in entropy observed. The large negative ΔG_{ads}° and high K_{ads} values insure spontaneity of adsorption, stability of the adsorbed layer on the mild steel surface and hence better inhibition efficiency. Its well known that values of ΔG_{ads}° of the order of 20 kJ mol⁻¹ or lower indicate a physisorption; those of order of 40 kJ mol⁻¹ or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [26, 27]. In accordance with this, it could be said that the interaction seems to be physical; however a chemical contribution may act on adsorption mechanism.

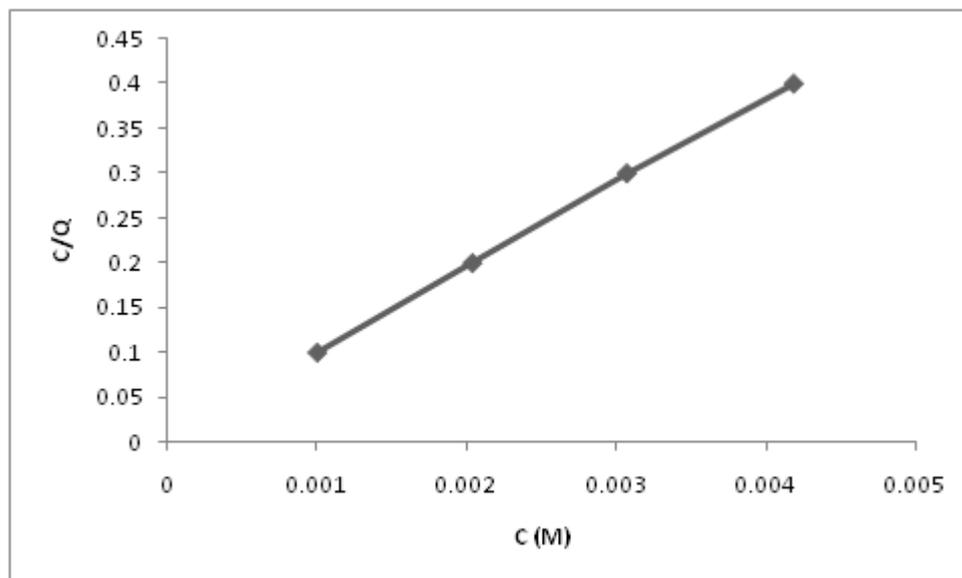


Fig. 5. Langmuir adsorption isotherm of the inhibitor in 1.0 M H₂SO₄ at 25 °C:

Table 2. Thermodynamic adsorption parameters for BHDPA on mild steel in 1.0 M H₂SO₄ solution at 298.

Compound	K _{ads}	R ²	ΔG° _{ads} (kJ/mol)	ΔS _{ads} (j/mol)	ΔH _{ads} (j/mol)
BHDPA	1.53 × 10 ²	0.9996	22.43	103.16	8311.68

CONCLUSIONS:

The Schiff base Benzhydrylidene-(2, 5-dimethyl-phenyl)-amine was synthesized and tested as possible corrosion inhibitor for mild steel in 0.5M H₂SO₄ solution.

According to results obtained, the following points can be emphasized:

1. The BHDPA Schiff base has better corrosion inhibition efficiency than the corresponding amine group. The inhibition efficiency of Schiff base studied depends on its concentration. The excellent inhibition efficiency was attributed to the adsorption of inhibitor molecules and protective film formation on the metal surface.
2. The potentiodynamic polarization curves indicated that the BHDPA Schiff base inhibits both anodic metal dissolution and also cathodic hydrogen evolution reactions.
3. The adsorption of BHDPA molecules on the metal surface from 0.5M H₂SO₄ solution obeys Langmuir adsorption isotherm. The high value of adsorption equilibrium constant and the negative value of standard free energy of adsorption suggested that, the BHDPA molecules were strongly adsorbed on mild steel surface and this adsorption took place spontaneously.

4. The standard free energy of adsorption has been found close to -22 kJ mol^{-1} which indicated that the adsorption is seen more a physical form than chemical adsorption.

References

- [1] Maruthamuthu, S.; Kumar, B. D.; Ramachandran, S.; Anandkumar, B.; Palanichamy, S.; Chandrasekaran, M.; Subramanian, P.; Palaniswamy, N. Microbial corrosion in petroleum product transporting pipelines. *Ind. Eng. Chem. Res.* 2011, 50, 8006.
- [2] Ji, G.; Shukla, S. K.; Dwivedi, P.; Sundaram, S.; Prakash, R. Inhibitive effect of *Argemone mexicana* plant extract on acid corrosion of mild steel. *Ind. Eng. Chem. Res.* 2011, 50, 11954.
- [3] Wang, H. L.; Fan, H. B.; Zheng, J. S. Corrosion inhibition of mild steel in hydrochloric acid solution by a mercapto-triazole compound. *Mater. Chem. Phys.* 2002, 77, 655–661.
- [4] Yadav, M.; Behera, D.; Sharma, U. Development of Corrosion Inhibitors Used in Acidization of Petroleum Oil Well. *Chem. Sin.* 2012, 3, 262–268.
- [5] Ahamad, I.; Quraishi, M. A. Bis (benzimidazol-2-yl) disulphide: An efficient water soluble inhibitor for corrosion of mild steel in acid media. *Corros. Sci.* 2009, 51, 2006–2013.
- [6] Zhang, Q. B.; Hua, Y. X. Corrosion inhibition of mild steel by alkylimidazolium ionic liquids in hydrochloric acid. *Electrochim. Acta* 2009, 54, 1881–1887.
- [7] Quraishi, M. A.; Sardar, N.; Ali, H. Study of Some New Acidizing Inhibitors on Corrosion of N80 Alloy in 15% Boiling Hydrochloric Acid. *Corrosion* 2002, 58, 317–321.
- [8] E. Sadeghi Meresht, T. Shahrabi Farahani, J. Neshati, Failure analysis of stress corrosion cracking occurred in a gas transmission steel pipeline, *Eng Fail Anal* 18 (2011) 963–970.
- [9] E. Sadeghi Meresht, T. Shahrabi Farahani, J. Neshati, 2-Butyne-1, 4-diol as a novel corrosion inhibitor for API X65 steel pipeline in carbonate/bicarbonate solution, *Corros. Sci.* 54 (2012) 36–44.
- [10] A. Madhankumar, N. Rajendran, A promising copolymer of p-phenylenediamine and o-aminophenol: chemical and electrochemical synthesis, characterization and its corrosion protection as pecton mild steel, *Synth. Met.* 162 (2012) 176–185.
- [11] Tamilselvi, S.; Raman, V.; Rajendran, N. Corrosion inhibition of mild steel by benzotriazol derivatives in acidic medium. *J. Appl. Electrochem.* 2003, 33, 1175–1182.
- [12] Antonijevic, M. M.; Bogdanovic, G. D.; Radovanovic, M. B.; Petrovic, M. B.; Stamenkovic, A. T. Influence of pH and Chloride Ions on Electrochemical Behavior of Brass in Alkaline Solution. *Int. J. Electrochem. Sci.* 2009, 4, 654–661.

- [13] Bentiss, F.; Lebrini, M.; Vezin, H.; Lagrenee, M. Experimental and theoretical study of 3-pyridyl-substituted 1, 2, 4-thiadiazole and 1, 3, 4-thiadiazole as corrosion inhibitors of mild steel in acidic media. *Mater. Chem. Phys.* 2004, 87, 18–23.
- [14] Bentis F, Transnel M, Chaibi N, Mernari B, Vezin H, Lagrenee M. 2, 5- Bis(*n*-methoxyphenyl)-1, 3, 4-oxadiazoles used as corrosion inhibitors efficiency and chemical structure. *Corros Sci* 2002; 44: 2271-2289.
- [15] M. Gopiraman, N. Selvakumaran, D. Kesavan, R. Karvembu, Adsorption and corrosion inhibition behaviour of N-(phenylcarbamoithioly)benzamide on mild steel in acidic medium, *Prog. Org. Coat.* 73 (2012) 104–111.
- [16] S.T. Zhang, Z.H. Tao, W.H. Li, B.R. Hou, The effect of some triazole derivatives as inhibitors for the corrosion of mild steel in 1 M hydrochloric acid, *Appl. Surf. Sci.* 255 (2009) 6757–6763.
- [17] Mohsen Lashgari, Mohammad-Reza Arshadi, Somaieh Miandari, The enhancing power of iodide on corrosion prevention of mild steel in the presence of a synthetic-soluble Schiff-base: electrochemical and surface analyses, *Electrochim. Acta* 55 (2010) 6058–6063.
- [18] Ayse Ongun Yuce, Gulfeza Kardas, Adsorption and inhibition effect of 2-thiohydantoin on mild steel corrosion in 0.1 M HCl, *Corros. Sci.* 58 (2012) 86–94.
- [19] K.C. Emregul, O. Atakol, Corrosion inhibition of mild steel with Schiff base compounds in 1M HCl, *Mater. Chem. Phys.* 82 (2003) 188–193.
- [20] M. Behpour, S.M. Ghoreishi, M. Salavati-Niasari, B. Ebrahimi, Evaluating two new synthesized S–N Schiff bases on the corrosion of copper in 15% hydrochloric acid, *Mater. Chem. Phys.* 107 (2008) 153–157.
- [21] M.S. Morad, A.A.O Sarhan, *Corros. Sci.* 50 (2008) 744.
- [22] E. Machnikova, K.H. Whitmire, N. Hackerman, *Electrochim. Acta* 53 (2008) 6024.
- [23] J.M. Cases, F. Villieras, *Langmuir* 8 (1992) 1251–1264.
- [24] S.S. Abd El Rehim, M.A.M. Ibrahim, K.F. Khalid, The inhibition of 4-(2-amino-5-methylphenylazo) antipyrine on corrosion of mild steel in HCl solution, *Mater. Chem. Phys.* 70 (2001) 268.
- [25] A.K. Singh, M.A. Quraishi, Investigation of adsorption of isoniazid derivatives at mild steel/hydrochloric acid interface: electrochemical and weight loss methods, *Mater. Chem. Phys.* 123 (2010) 666.
- [26] F.M. Donahue, K. Nobe, *J. Electrochem. Soc.* 112 (1965) 886–891.
- [27] E. Kamis, F. Belluci, R.M. Latanision, E.S.H. El-Ashry, *Corrosion* 47 (1991) 677–686.