



RESEARCH ARTICLE

Methyl Orange as Corrosion Inhibitor for Carbon Steel in Hydrochloric Acid Solutions

A.S.Fouda¹, S.Rashwan², Y.K.Elghazy¹

1. Department of Chemistry, Faculty of Science, El-Mansoura University, El- Mansoura -35516, Egypt.

2. Department of Chemistry, Ismailia Faculty of Science, Suez Canal University, Ismailia, Egypt.

Manuscript Info**Manuscript History:**

Received: 12 November 2013

Final Accepted: 25 November 2013

Published Online: December 2013

Key words:

Carbon steel, Polarization, EIS, EFM, Acid inhibition

Abstract

The sodium 4-[(4-dimethylamino) phenyldiazenyl]benzene sulfonate (Methyl orange) has been investigated for carbon steel corrosion in 1 M HCl at different concentrations using weight loss measurements, potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) methods. Generally, inhibition efficiency of the investigated compound was found to depend on inhibitor concentration and its structure. The results showed that methyl orange was best inhibitor (gives 98 % inhibition). For this, a detailed study was making for this compound using electrochemical measurements. Potentiodynamic polarization studies clearly reveal that methyl orange acts essentially as mixed inhibitor. The inhibition efficiency increases with concentration. In addition the EIS showed the formation of a protective film. The adsorption of methyl orange on carbon steel surface is found to obey Langmuir adsorption isotherm. Scanning electron microscope (SEM) was used to study the surface morphology of the carbon steel in 1 M HCl solution in the absence and presence of methyl orange.

Copy Right, IJAR, 2013. All rights reserved.

Introduction

Hydrochloric and sulphuric acids are extensively used in processes like acid pickling, acid cleaning, acid descaling and oil well acidizing [1-2]. To ensure only surface scales and deposits are removed and base metal is unaffected, inhibitor is used. Inhibitors are organic molecules which possess π -bonds, hetero atoms like nitrogen, sulphur and oxygen [3-4]. The molecules containing both N and S can claim excellent inhibition compared with those containing only N or S [5-6]. These inhibitors generally act by adsorbing on the metal surface. In acid media, electron rich centers gets protonated to become cation electrostatically binds to cathodic sites of metal thereby hinders cathodic reaction. Electron rich spots of unprotonated molecule finds anodic reactive sites thus reduce anodic reaction. Thus a heterocyclic organic molecule comprehensively acts. Recently considerable amount of effort has been devoted to develop novel and efficient corrosion inhibitors. Bis-thiadiazole derivatives [7], thiosemicarbazide derivatives [8], benzimidazole derivatives [9], purines [10] have been verified to be efficient inhibitors for steel. Many N-heterocyclic compounds, such as imidazoline derivatives [11], 1,2,3-triazole derivatives [12], 1,2,4-triazole derivatives [13-17], tetrazole derivatives [18,19], pyrrole [20], pyridine derivatives [21-23], pyrazole derivatives [24-27], bipyrazole derivatives [28,29], pyrimidine derivatives [30], pyridazine derivatives [31], indole derivatives [32-34], benzimidazole derivatives [35-39], quinoline derivatives [40] and quinoxaline derivatives [41-45] have been used for the corrosion inhibition of iron or steel in acidic media.

The present work was established to study the corrosion inhibition of carbon steel in 1M HCl solution by methyl orange as corrosion inhibitor using different chemical and electrochemical techniques. The thermodynamic parameters were calculated and discussed. Also surface examination was examined.

EXPERIMENTAL METHOD**A. Materials and Chemicals**

All experiments were tested using carbon steel specimens with chemical composition (weight %): 0.200 % C, 0.350 % Mn, 0.024 % P, 0.003 % S, and the remainder Fe. All chemicals and reagents used are with analytical grade and used without further purification (used as received). The aggressive solution used was made of AR grade HCl (37%). Appropriate concentrations of acid were prepared using bidistilled water. 10^{-3} M stock solutions from the investigated compound were prepared by dissolving the appropriate weights of the used chemically pure solid compound in hot bidistilled water.

B. Weight loss measurements

Weight loss measurements were performed on the carbon steel samples with a rectangular form of size 2.5 cm × 2.0 cm × 0.025 cm in 1M HCl solution with and without addition of different concentrations of methyl orange. Carbon steel coupons were abraded with emery paper up to 1200 grade size to give a mirror-like surface, then washed with bidistilled water and acetone, then dried between filter paper. Every sample was weighed by an electronic balance, and then placed in the acid solution (100 mL). The duration of the immersion was 3 h at the temperature range from 25 to 50°C. After immersion, the surface of the specimen was cleaned by bidistilled water followed rinsing with acetone and the sample was weighed again in order to calculate the corrosion rate and the inhibition efficiency (% IE). The experiments were done in triplicate and the average value of the weight loss was noted. For each experiment, a freshly prepared solution was used and the solution temperature was thermostatically controlled at a desired value. The aggressive solutions (1M HCl) were prepared by dilution of an analytical grade HCl (37 %) with bidistilled water. The surface coverage (θ) and inhibition efficiency (%IE) was determined by using following equation:

$$\% \text{ IE} = \theta \times 100 = [1 - (W_i/W_o)] \times 100 \quad (1)$$

where W_i and W_o are the weight loss values in presence and absence of inhibitor, respectively.

C. Electrochemical measurements

Electrochemical measurements, including potentiodynamic polarization curves, electrochemical frequency modulation (EFM) and electrochemical impedance spectroscopy (EIS) were performed in three electrode cell assembly at room temperature ($25 \pm 1^\circ\text{C}$). The carbon steel of 1 cm^2 was the working electrode, platinum electrode was used as an auxiliary electrode, and standard calomel electrode (SCE) was used as reference electrode. The working electrode was abraded with different grades of emery papers, washed with water and degreased with acetone. Prior to the electrochemical measurement, a stabilization period of 30 minute was allowed, which was proved to be sufficient to attain a stable value of E_{corr} . For polarization measurements potential was applied from $\pm 500 \text{ mV}_{\text{SCE}}$ (relative to open circuit with a scan rate of 1 mVs^{-1}). The (% IE) is calculated using the following equation [46, 47]:

$$\% \text{ IE} = \theta \times 100 = [1 - (i_{\text{corr(inh)}} / i_{\text{corr(free)}})] \times 100 \quad (2)$$

where $i_{\text{corr(free)}}$ is corrosion current density in the absence of methyl orange and $i_{\text{corr(inh)}}$ is the corrosion current density in presence of different concentrations of methyl orange.

The EIS spectra were recorded at open circuit potential (OCP) after immersion the electrode for 30 min in the test solution. The AC signal was 5 mV peak to peak and the frequency range studied was between 100 kHz and 0.2 Hz. The inhibition efficiency (% IE) and the surface coverage (θ) of the used inhibitor obtained from the impedance measurements can be calculated by applying the following relations:

$$\% \text{ IE} = \theta \times 100 = [1 - (R_{\text{ct}}^{\circ} / R_{\text{ct}})] \times 100 \quad (3)$$

Where R_{ct}° and R_{ct} are the charge transfer resistances in the absence and presence of inhibitor, respectively.

Electrochemical measurements were performed by using Gamry (PCI 300/4) instrument Potentiostat / Galvanostat/ZRA which includes a Gamry frame work system based on ESA400 Gamry applications include DC 105 for corrosion measurements and EIS 300 for electro chemical impedance spectroscopy and EFM 140 software along with a computer for collecting data, ECHEM analyst 5.58 software was used for plotting, graphing and fitting data.

RESULTS AND DISCUSSION

A. Weight loss measurement

Figure 1 represents the weight loss-time curves carried out at temperature 25°C in 1 M HCl with the absence and the presence of different concentrations of methyl orange for an immersion period of 3 hours. Methyl orange showed maximum inhibition efficiency of 91.5% in HCl and at an optimum concentration of 15×10^{-6} M. Further increase in methyl orange concentration did not cause any significant change in the performance of the inhibitor. The values of percentage inhibition efficiency (%IE) and corrosion rate (C.R.) obtained from weight loss method at different concentrations of methyl orange at 25°C are summarized in Table 1. The results of Table 1 showed that as the methyl orange concentration increases the corrosion rate decreases and inhibition efficiency increases.

B. Potentiodynamic polarization measurements

Polarization curves for carbon steel in presence and absence of different concentrations of methyl orange are shown in Figure 2. The extrapolation of Tafel straight line allows the calculation of the corrosion current density (i_{corr}). The values of i_{corr} , the corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (β_c , β_a) and inhibition efficiency (%IE) are given in Table 2. The small change in β_a and β_c values as shown in Table 2 indicates that adsorption of methyl orange does not modify the mechanism of anodic dissolution as well as cathodic hydrogen evolution [48, 49]. From the Figure 2, it is clear that both the cathodic and anodic reactions are inhibited and the inhibition increases as the inhibitor concentration increases in acid media, but the cathode is more polarized. From the Table 2, it is clear that there was no definite trend in the shift of E_{corr} values, in the presence of various concentrations of methyl orange in 1 M HCl solution. This result indicated that methyl orange can be classified as mixed type of inhibitor in 1 M HCl solution [50, 51].

C. Electrochemical impedance spectroscopy (EIS) measurements

The Nyquist and Bode plots of carbon steel obtained in 1 M HCl solution in the absence and presence of various concentrations of methyl orange and the data obtained are given in Figures 3 & 4, respectively. The related electrochemical parameters were calculated and are shown in Table 3 at open circuit potential in presence and absence of different concentrations of methyl orange (Figure 3). Single distorted semicircles were observed in Nyquist plots suggesting a simple $R-C$ circuit (Figure 5). Increase the methyl orange concentrations decreased the double layer capacitance values (Table 3). Higher charge transfer resistances indicate the decrease in corrosion current densities. The percentage inhibition efficiencies increased with methyl orange concentrations. The values of double layer capacitance (C_{dl}) were decreased and the charge transfer resistance (R_{ct}) increased with inhibitor concentration, which refer to an increasing in thickness of electrical double layer which may corresponding with a decreasing in local dielectric constant, the higher R_{ct} value is indicating the lower corrosion state [52]. The appearance of depressed semicircle is due to high frequency dispersion [53] or due to surface heterogeneity or corrosion products covering the surface at random sites [54]. Both the electrochemical methods offered nearly same % IE values for both inhibitors.

D. Electrochemical frequency modulation (EFM) measurements

EFM is a nondestructive corrosion measurement technique that can directly give values of corrosion current depending on the non-linear nature of the corrosion process, since corrosion is non-linear so the current responses due to a potential perturbation by one or more sine waves will be measure at more frequencies than the applied signal's frequencies [55]. The inhibition efficiency was determined using the following equation:

$$\% \text{IE} = \theta \times 100 = [1 - (i_{\text{corr(inh)}} / i_{\text{corr(free)}})] \times 100 \quad (4)$$

Figure 6 (a-f) shows the frequency spectrum of the current response of carbon steel in absence and presence of different concentrations of methyl orange. EFM results are spectrum of current that response as a function of frequency, the large peaks were used to calculate the corrosion current density (i_{corr}), Tafel slopes (β_c & β_a) and causality factors (CF-2 and CF-3) calculated values are given in Table 4. From this Table, it is clear that i_{corr} values decrease with increasing the inhibitor concentration but the inhibition increases with increasing its concentration. The great strength of the EFM is the causality factors which serve as an internal check on the validity of the EFM measurement [56]. The causality factors obtained under different experimental conditions are approximately equal to the theoretical values (2 and 3) indicating that the measured data are verified and of good quality [57]. The data obtained from polarization and impedance measurements are in good agreement with the results obtained from EFM.

E. Adsorption isotherms

Methyl orange molecules have adsorbed on the carbon steel surface due to Vander Waals forces. The presence of extensively delocalized π -electrons of the phenyl rings and presence of lone pair of electrons on N atoms have favoured greater adsorption [58]. Adsorptions of this organic molecule have displaced the water molecules from the metal surface. The interaction between the organic molecule and the metal surface are obtained from various isotherms. Percentage inhibition efficiency was obtained from weight loss measurements as surface coverage (θ). According to the Langmuir adsorption isotherm, the surface coverage (θ) is related to inhibitor concentration (C) by the following equation:

$$C/\theta = 1/K_{\text{ads}} + C \quad (5)$$

Where K_{ads} is the equilibrium constant. Figure 7 presents the plot of C/θ versus C for both the inhibitors. A straight line fits with a correlation of 0.999 suggests the adsorption obeys Langmuir adsorption isotherm. Using K_{ads} value, ($\Delta G_{\text{ads}}^\circ$) was calculated from the following equation:

$$\Delta G_{\text{ads}}^\circ = -RT \ln 55.5 K_{\text{ads}} \quad (6)$$

Where R is the gas constant and T is the absolute temperature. The value of 55.5 is the concentration of water in solution in M^{-1} . To calculate heat of adsorption (ΔH_{ads}°) a plot of $\log K_{ads}$ vs. $1/T$ was done (Fig.8) the slope would be equal to $\Delta H_{ads}^{\circ}/R$ according to the following equation:

$$\log K_{ads} = (-\Delta H_{ads}^{\circ}/2.303RT) + \text{constant} \quad (7)$$

The entropy of adsorption (ΔS_{ads}°), can be obtained from the following equation:

$$\Delta G_{ads}^{\circ} = \Delta H_{ads}^{\circ} - T \Delta S_{ads}^{\circ} \quad (8)$$

The values of equilibrium constant (K_{ads}), standard free energy of adsorption (ΔG_{ads}°), enthalpy of adsorption (ΔH_{ads}°) and entropy of adsorption (ΔS_{ads}°) are listed in Table 5. The negative values of standard free of adsorption indicated spontaneous adsorption of methyl orange on carbon steel surface and stability of the adsorbed layer on the alloy surface. Generally the values of ΔG_{ads}° less than -20 kJ mol^{-1} are consistent with physisorption, while those greater than -40 kJ mol^{-1} correspond to chemisorption [59]. The calculated standard free energy of adsorption values for the methyl orange are in the range of -42.5 and $-43.8 \text{ kJ mol}^{-1}$ and it can be concluded that the adsorption of methyl orange on carbon steel surface is both physical and chemical, and chemisorption predominates [60, 61]. The negative sign of ΔH_{ads}° reveals that the adsorption of inhibitor molecules is an exothermic process. Generally, an exothermic adsorption process suggests either physisorption or chemisorption while endothermic process is attributed to chemisorption [62]. The unshared electron pairs in investigated molecules may interact with d-orbitals of carbon steel to provide a protective chemisorbed film [63] In the case of methyl orange, the absolute values of enthalpy are relatively high, and not approaching those of chemisorption. The values of ΔS_{ads}° in the presence of investigated compounds are large and negative that is accompanied with exothermic adsorption process [64].

F. Effect of temperature and activation parameters

The dependence of corrosion current density on the temperature can be expressed by Arrhenius equation:

$$k = A \exp(-E_a^*/RT) \quad (9)$$

where A is the pre-exponential factor and E_a^* is the apparent activation energy of the corrosion process. Arrhenius plot obtained for the corrosion of carbon steel in HCl solution is shown in Fig. 9 presents the Arrhenius plot in the presence of different concentrations of methyl orange. Values determined from the slopes of these linear plots are shown in Table 6. The linear regression (R^2) is close to 1 which indicates that the corrosion of carbon steel in 1 M HCl solution can be elucidated using the kinetic model. Table 6 showed that the value of for inhibited solution is higher than that for uninhibited solution, suggesting that dissolution of carbon steel is slow in the presence of inhibitor and can be interpreted as due to physical adsorption [65]. It is known from Eq. 9 that the higher values lead to the lower corrosion rate. This is due to the formation of a film on the carbon steel surface serving as an energy barrier for the carbon steel corrosion [66]. Enthalpy and entropy of activation (ΔH^* , ΔS^*) of the corrosion process were calculated from the transition state theory (Table 6):

$$\text{Rate} = (RT/Nh) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT) \quad (10)$$

Where h is Planck's constant and N is Avogadro's number.

A plot of $\log(k/T)$ vs. $1/T$ for C-steel in 1 M HCl at different concentrations of methyl orange, gives straight lines as shown in Fig. 10. Values of ΔH^* are positive. This indicates that the corrosion process is an endothermic one. The entropy of activation is large and negative. This implies that the activated complex represents association rather than dissociation step, indicating that a decrease in disorder takes place, going from reactants to the activated complex [67].

G. Scanning electron microscopy (SEM)

The effect of corrosion on the surface morphology of the carbon steel sample was analyzed by recording the SEM images of the steel samples in 1M hydrochloric acid for 3 hours of immersion in the absence and presence of $15 \times 10^{-6} \text{ M}$ of methyl orange. Fig. 11 shows SEM images of (a) polished carbon steel with the characteristic features of the polishing lines, Fig. 11(b) damaged carbon steel with rough surface due to attack of hydrochloric acid and Fig.11 (c) carbon steel in presence of 1M hydrochloric acid and $15 \times 10^{-6} \text{ M}$ of methyl orange. It can be seen that the steel surface is less damaged in presence of methyl orange compared to carbon steel surface dipped in 1M hydrochloric acid solution without inhibitor. Thus it can be concluded that methyl orange protects the steel effectively by forming a uniform film on the surface of carbon steel.

Table (1): Inhibition efficiencies (%IE) and corrosion rates (C.R.) of carbon steel in 1 M HCl in presence of different concentrations of methyl orange at 25°C

Compound	[inhibitor] M	Corrosion rate(C.R.) mg cm ⁻² min ⁻¹	Efficiency (% IE)
Methyl orange	5 ×10 ⁻⁶	0.019	64.3
	7 ×10 ⁻⁶	0.013	76.0
	9 ×10 ⁻⁶	0.011	79.3
	11 ×10 ⁻⁶	0.009	84.0
	13 ×10 ⁻⁶	0.006	88.0
	15 ×10 ⁻⁶	0.005	91.5

Table (2): Electrochemical data obtained from Tafel plots for carbon steel in 1 M HCl with different methyl orange concentrations at 25°C

Conc M	i _{corr} ×10 ⁻⁴ μA cm ⁻²	-E _{corr} mV _{SEC}	β _a mVdec ⁻¹	β _c mVdec ⁻¹	C R mmy ⁻¹	θ	%IE
Blank	1680	462	101	155	767.5		
7 ×10 ⁻⁶	390	496	121	150	178.2	0.768	76.8
9×10 ⁻⁶	143	470	93	121	65.37	0.914	91.4
11×10 ⁻⁶	113	469	100	129	51.54	0.933	93.3
13×10 ⁻⁶	47.9	454	81	105	21.9	0.971	97.1
15 ×10 ⁻⁶	35.6	451	69	99	16.29	0.979	97.9

Table (3): EIS data of carbon steel in 1 M HCl with absence and presence of different concentrations of methyl orange at 25°C

Conc M	R _{ct} ×10 ⁻³ μFcm ⁻²	C _{dl} μF cm ²	θ	%IE
Blank	14.8	14.15		
7 ×10 ⁻⁶	139.9	12.05	0.894	89.4
9×10 ⁻⁶	191.5	7.91	0.923	92.3
11×10 ⁻⁶	242.8	6.72	0.939	93.9
13×10 ⁻⁶	246.9	6.54	0.940	94.0
15 ×10 ⁻⁶	335.4	6.17	0.956	95.6

Table (4): EFM data of C-steel in 1 M HCl with absence and presence of different concentrations of methyl orange at 25°C

Conc M	i_{corr}^2 $\mu A\ cm^{-2}$	β_a mV/dec^{-1}	β_c mV/dec^{-1}	CF-2	CF-3	C.R. $mm\ y^{-1}$	θ	%IE
Blank	598.7	97.44	113	1.93	3.21	273.5		
7×10^{-6}	100.9	81.04	135.6	1.94	2.93	46.12	0.831	83.1
9×10^{-6}	82.51	67.34	94.5	2.08	3.19	37.7	0.862	86.2
11×10^{-6}	60.29	46.98	50.3	1.15	2.79	27.55	0.899	89.9
13×10^{-6}	48.73	33.95	35.61	2.26	3.22	22.27	0.918	91.8
15×10^{-6}	24.84	32.19	34.48	2.61	2.98	11.35	0.959	95.9

Table (5): Equilibrium constant and adsorption free energy of the methyl orange adsorbed on carbon steel via Langmuir isotherm

	Temp. $^{\circ}C$	$K_{ads} \times 10^{-5}$ M^{-1}	$-\Delta G_{ads}^{\circ}$ $kJ\ mol^{-1}$	$-\Delta H^{\circ}$ $kJ\ mol^{-1}$	$-\Delta S^{\circ}$ $J\ mol^{-1}K^{-1}$
Methyl orange	25	8.4	43.8	56.4	42.2
	35	2.9	42.5		45.3
	40	2.1	42.4		44.6
	50	1.4	42.7		42.2

Table (6): Activation parameters of the corrosion of carbon steel in 1 M HCl different concentrations of methyl orange

Conc., M	E_a^* $kJ\ mol^{-1}$	ΔH^* $kJ\ mol^{-1}$	$-\Delta S^*$, $J\ mol^{-1}K^{-1}$
Blank	57.8	55.1	85.07
5×10^{-6}	77.0	74.3	29.24
7×10^{-6}	82.2	79.6	14.46
9×10^{-6}	83.9	81.4	9.70
11×10^{-6}	87.0	84.4	1.158

Table (7): surface composition (weight %) of carbon steel after 3 days of immersion in 1 M HCl solution in the absence and presence of 11×10^{-6} M methyl orange

(Mass %)	Fe	Mn	C	O	N	Cl	S	Br
Fresh sample	95.43	0.63	3.94	-	-	-	-	-
Blank	65.45	0.57	3.32	30.15	-	0.51	-	-
Methyl Orange	59.46	0.51	22.51	11.14	5.82	-	0.56	-

H. Energy Dispersion X-ray Spectroscopy (EDX)

Figures 12(a)–12(c) show the EDX spectrum in the absence and presence of methyl orange. In the presence of methyl orange, Figures 12(b) and 12(c), EDX spectra show an additional line characteristic for the existence of N and S. In addition, the intensities of C, and O signals are enhanced. The appearance of the N and S signal and this enhancement in the C and O signals is due to the N, S, C and O atoms constituting the methyl orange which indicate that the inhibitor molecules have adsorbed on the metal surface. Data obtained from the spectra are presented in Table 7. The spectra show also that Fe peaks are considerably suppressed in the presence of inhibitor which is due to the overlying inhibitor film. These results confirm those from electrochemical measurements which suggest that a surface film inhibits the metal dissolution, and hence retarded the hydrogen evolution reaction [68, 69].

Mechanism of corrosion inhibition

The adsorption of organic molecules on the steel surface cannot be considered only as purely physical or chemical adsorption phenomenon. In addition to the chemical adsorption, inhibitor molecules can also be adsorbed on the steel surface via electrostatic interaction between the charged carbon steel surface and charged inhibitor molecule if it is possible [70]. The corrosion inhibition property of methyl orange through adsorption on the surface of the carbon steel can be attributed to the presence of electronegative atoms nitrogen, oxygen, sulphur and also the presence of π electrons on the benzene ring. The carbon steel surface is positively charged in highly acidic medium. The mechanism of adsorption of methyl orange can be predicted on the basis of the mechanism proposed for the corrosion of carbon steel in hydrochloric acid [71]. According to this mechanism, anodic dissolution of carbon steel involves following steps: In highly acidic solutions, the methyl orange molecule undergoes protonation and can exist as a protonated positive species. The protonated species gets adsorbed on the cathodic sites of the steel surface through electrostatic interaction, thereby decreasing the rate of the cathodic reaction. The presence of anions in the solution and their adsorption on the steel surface play an important role in the mechanism of inhibition exhibited by the organic compounds [72]. In a highly acidic medium like the one in the present investigation, the steel surface is positively charged. The protonated species causes the negatively charged chloride ions to get adsorbed on the alloy surface, making the steel surface negatively charged. The positively charged protonated methyl orange molecules interact electrostatically with the negatively charged chloride adsorbed steel surface, resulting in physisorption. The negative charge centers of the methyl orange molecules containing a lone pair of electrons and π -electrons can electrostatically interact with the anodic sites on the carbon steel surface and get adsorbed. The neutral inhibitor molecules occupy the vacant adsorption sites on the alloy surface through the chemisorption mode involving the displacement of water molecules from the carbon steel surface and sharing of electrons by the hetero atoms like nitrogen and oxygen. The presence of methyl orange in the protonated form and the presence of negative charge centers on the molecule are also responsible for the mutual interaction of inhibitor molecules on the steel surface. In acidic solution, the nitrogen and oxygen atoms of the methyl orange molecules can absorb on the cathodic sites of steel in competition with the hydrogen ions.

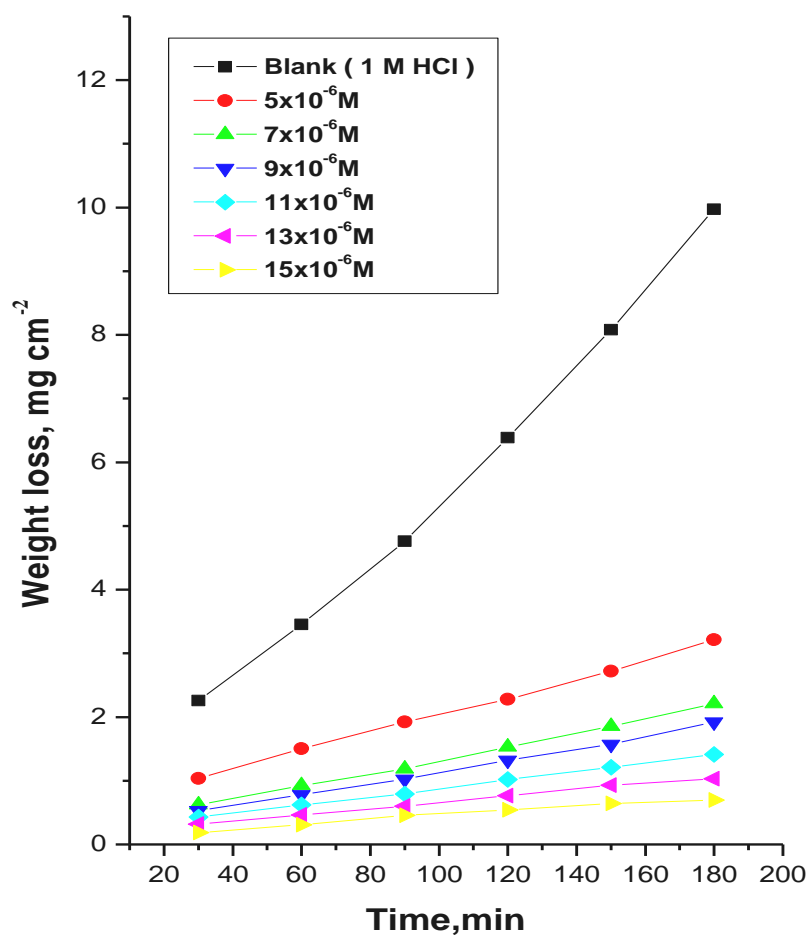


Figure (1): Weight loss-time curves for the corrosion of C-steel in 1 M HCl in the absence and presence of different concentrations of methyl orange at 25°C

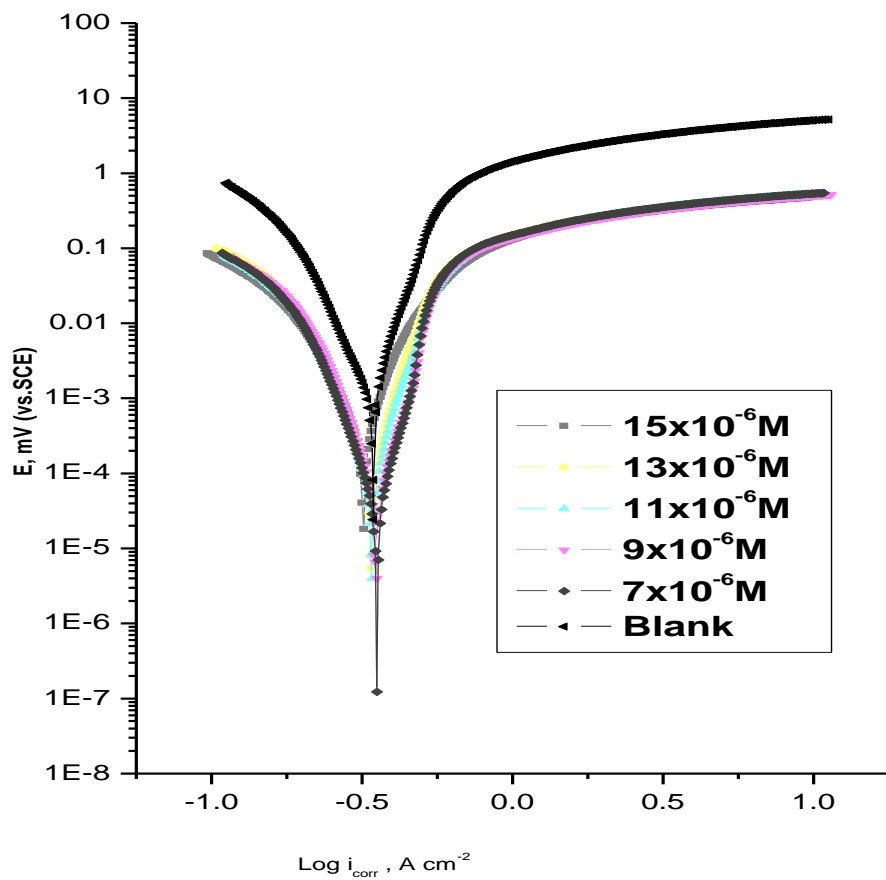


Figure (2): Potentiodynamic polarization curves for the dissolution of C- steel in 1 M HCl in the absence and presence of different concentrations of methyl Orange at 25°C

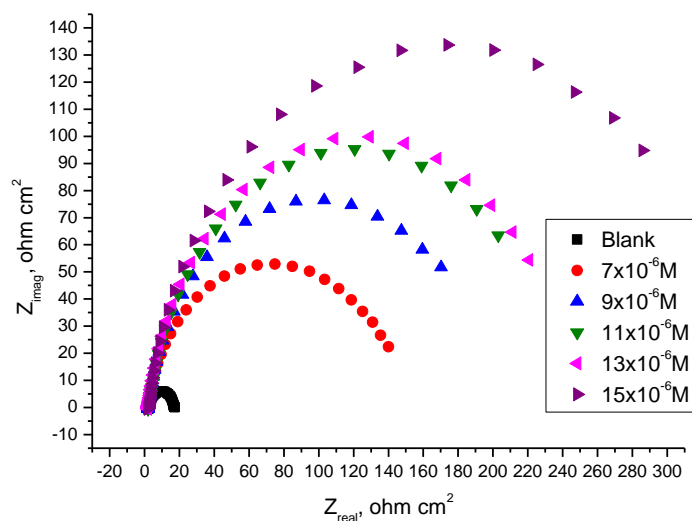


Figure (3): The Nyquist plots of carbon steel in 1 M HCl with or without methyl orange at 25°C

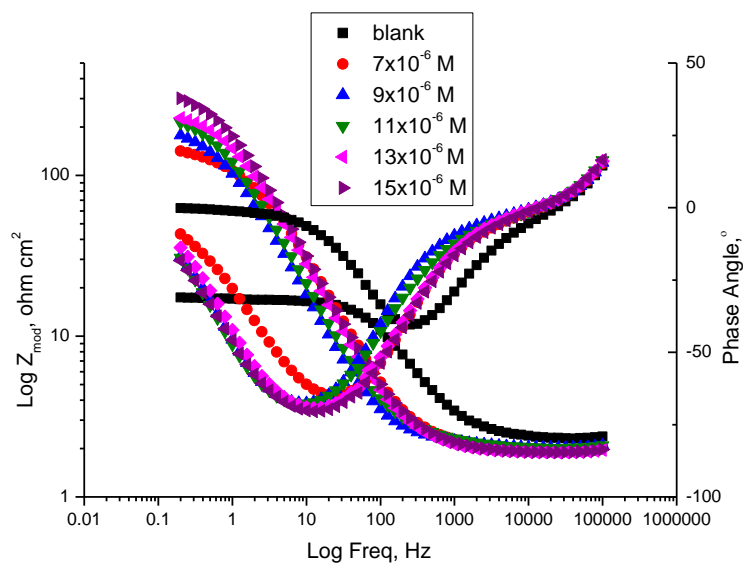


Figure (4): The Bode plots of carbon steel in 1 M HCl with or without methyl orange at 25°C

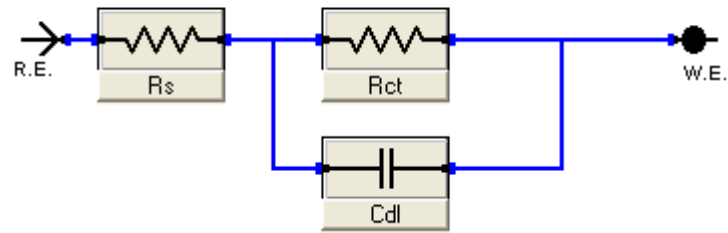


Figure (5): Electrical equivalent circuit model used to fit the results of impedance

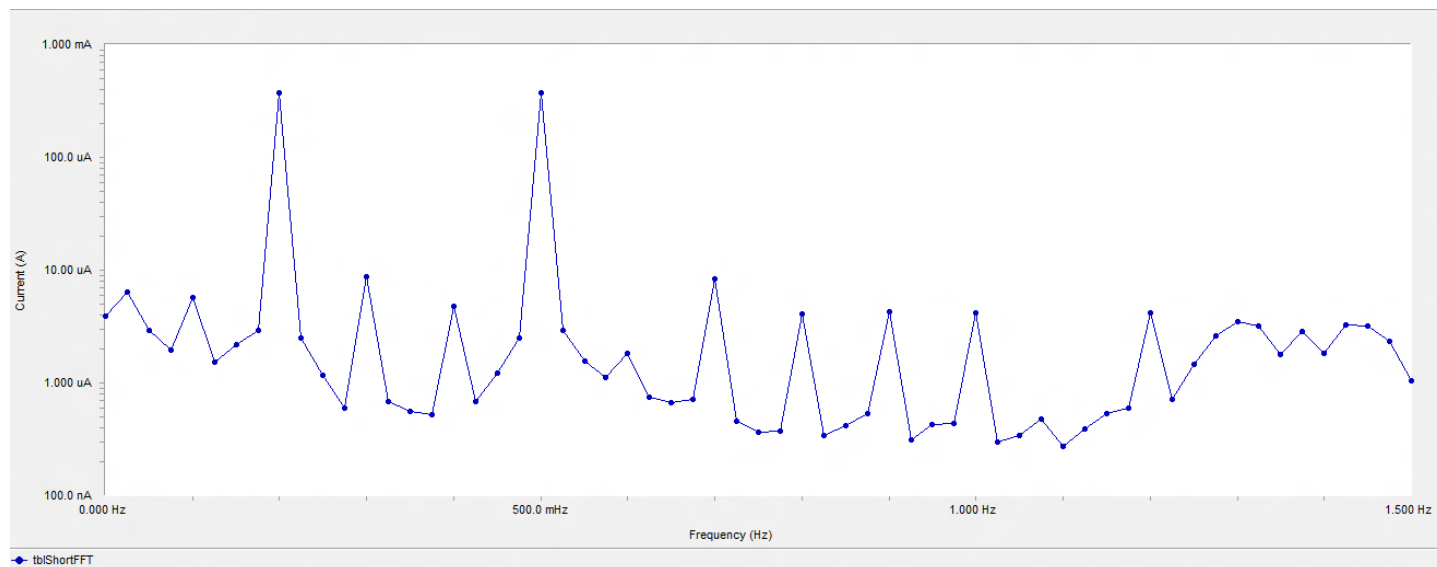


Figure (6a): EFM spectra for C-steel in 1 M HCl (Blank)

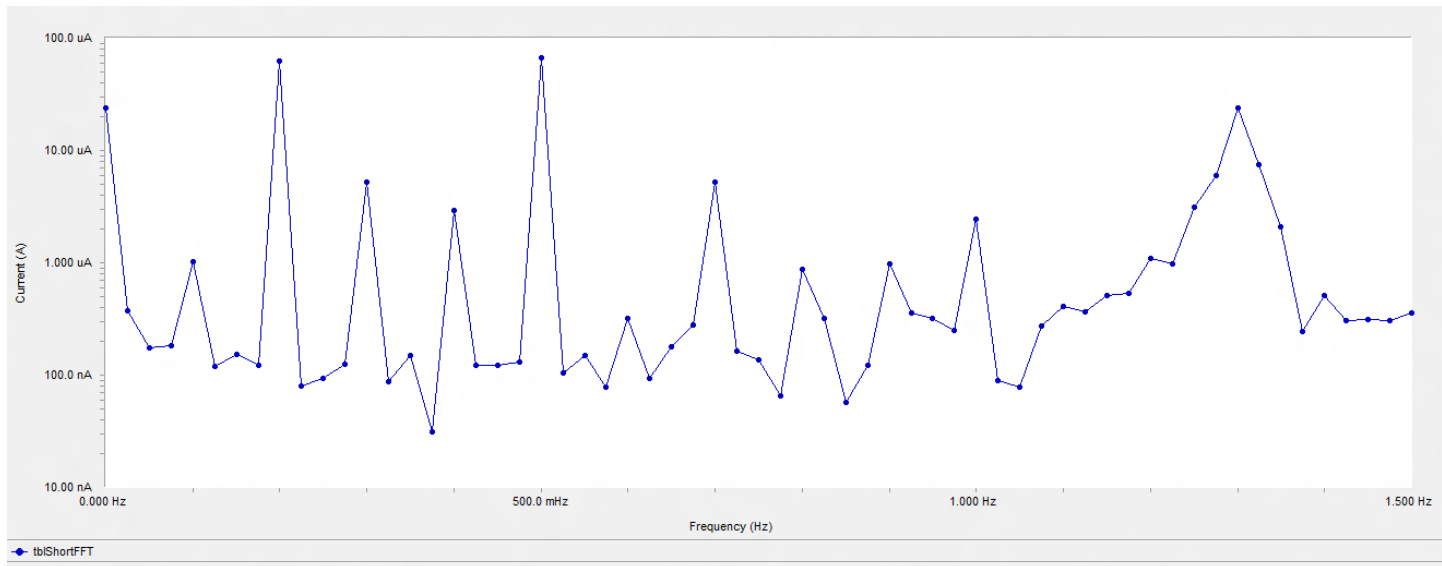


Figure (6b): EFM spectra for C-steel in 1 M HCl in presence of 7×10^{-6} M of methyl orange

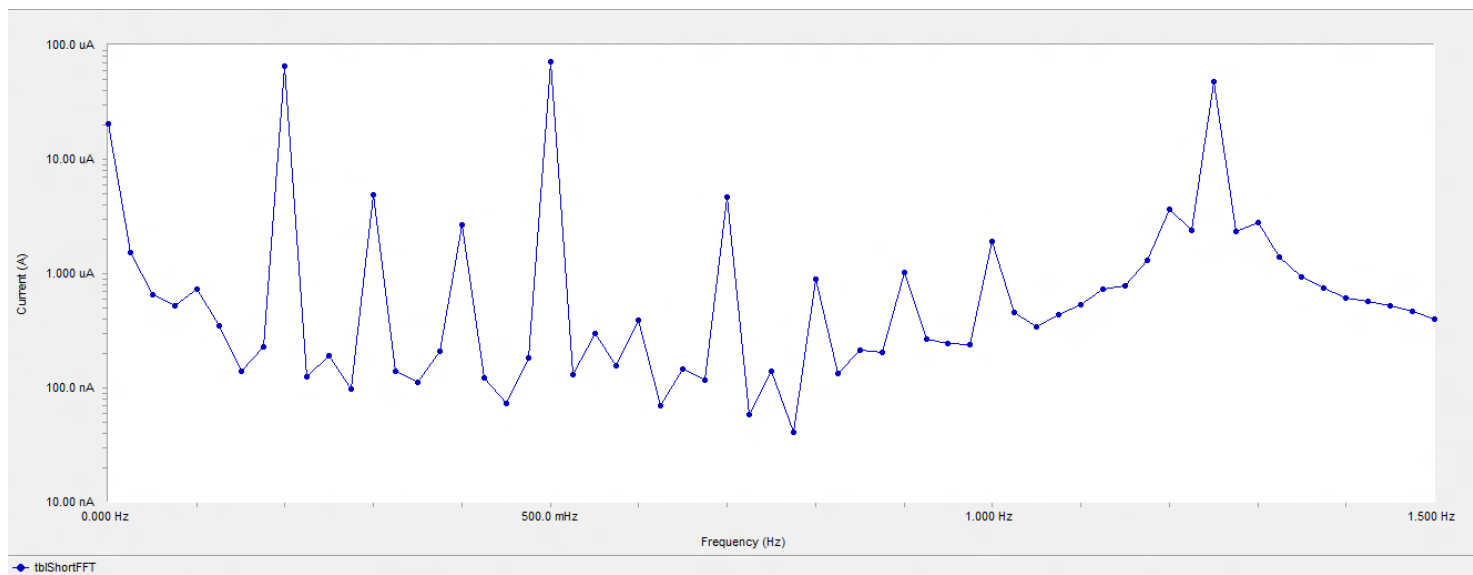


Figure (6c): EFM spectra for C-steel in 1 M HCl in presence of 9×10^{-6} M of methyl orange

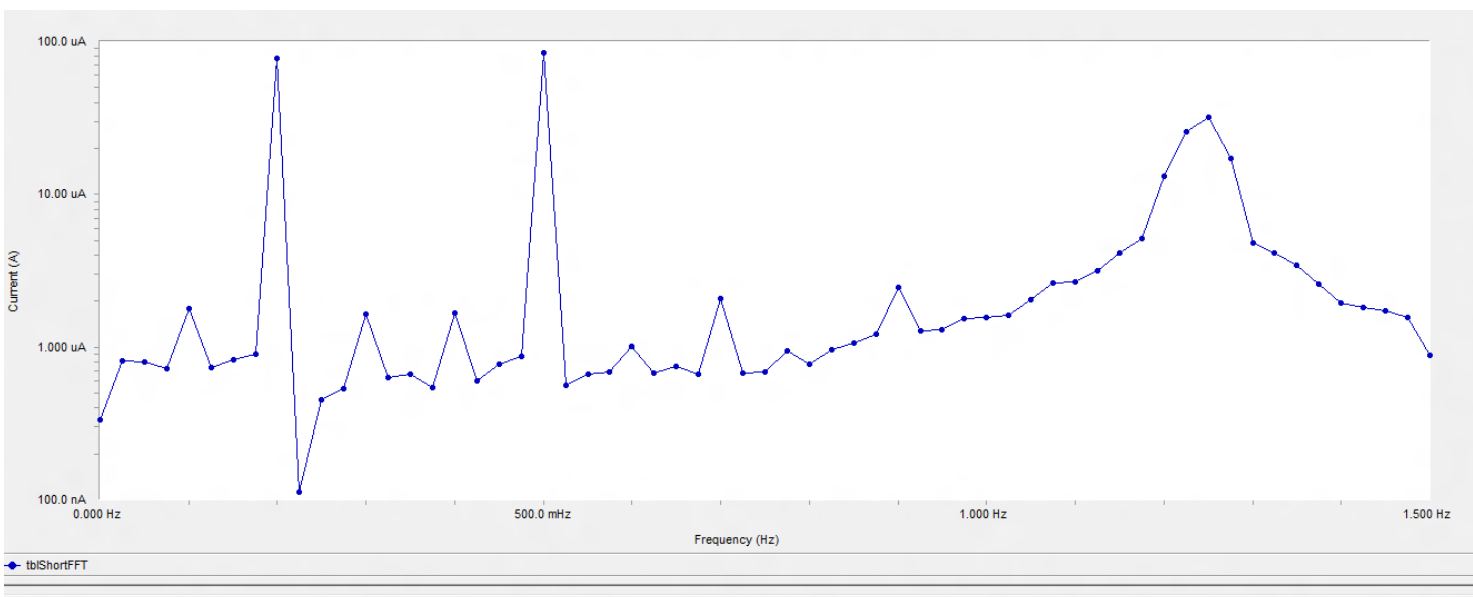


Figure (6d): EFM spectra for C-steel in 1 M HCl in presence of 11×10^{-6} M of methyl orange

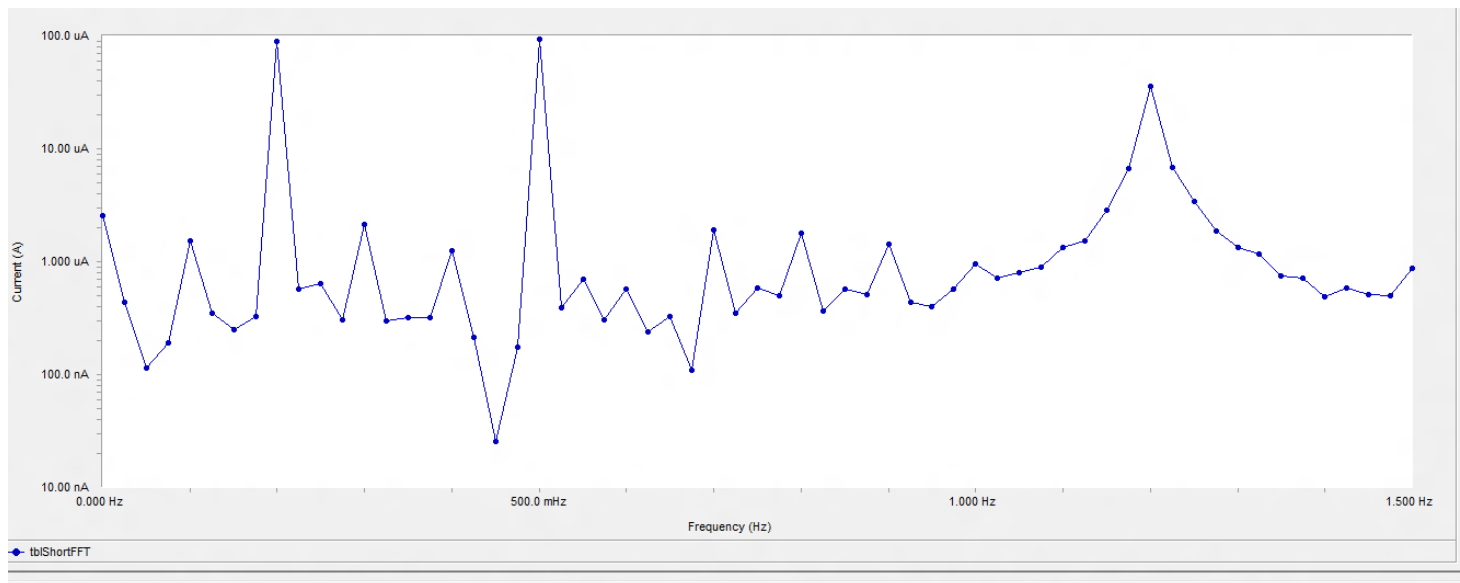
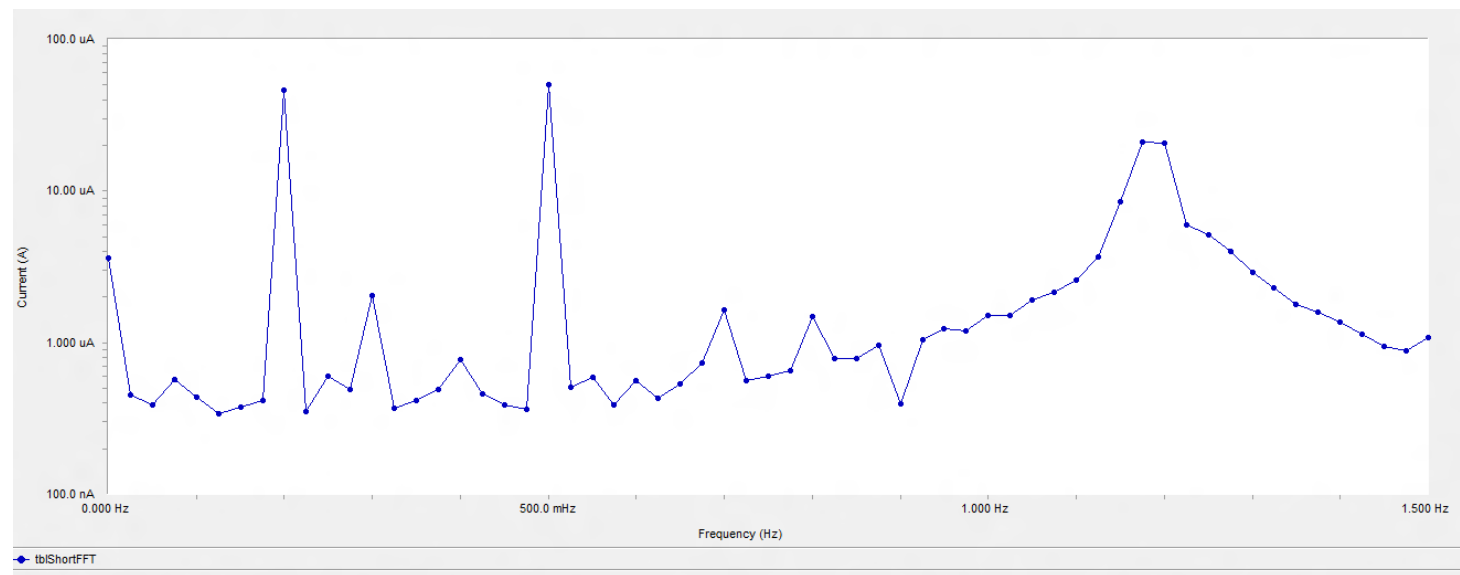


Figure (6e): EFM spectra for C-steel in 1 M HCl in presence of 13×10^{-6} M of methyl orange.

Figure (6f): EFM spectra for C-steel in 1 M HCl in presence of 15×10^{-6} M of methyl orange



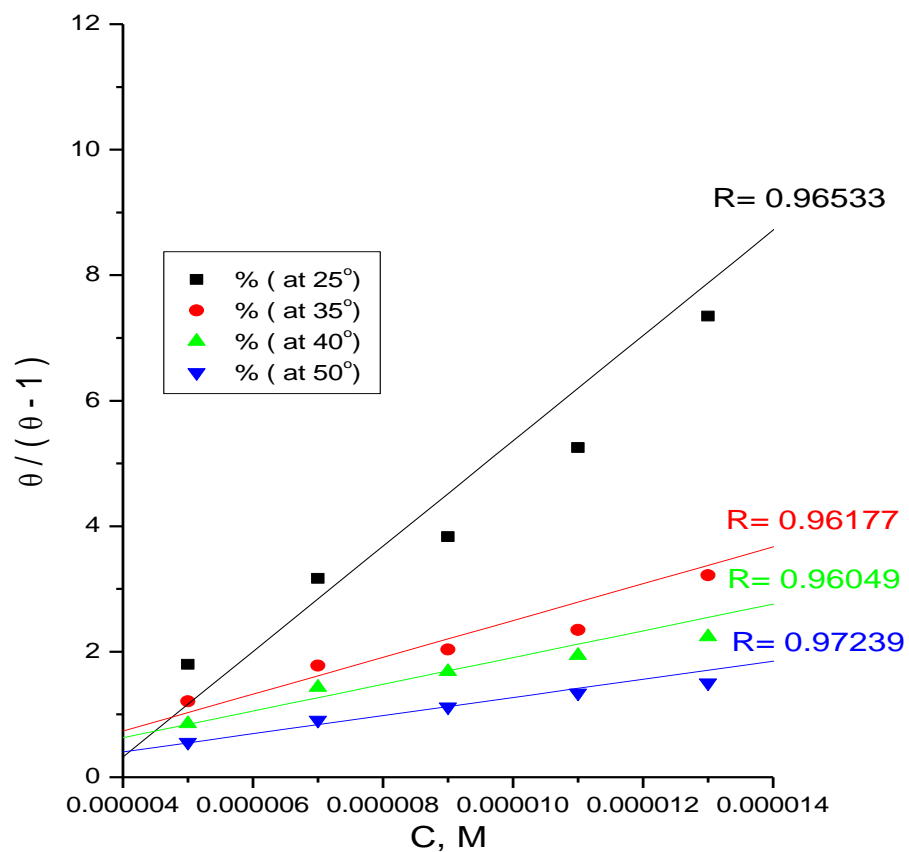


Figure (7): Langmuir adsorption isotherm of methyl orange on C-steel surface in 1 M HCl at different temperatures

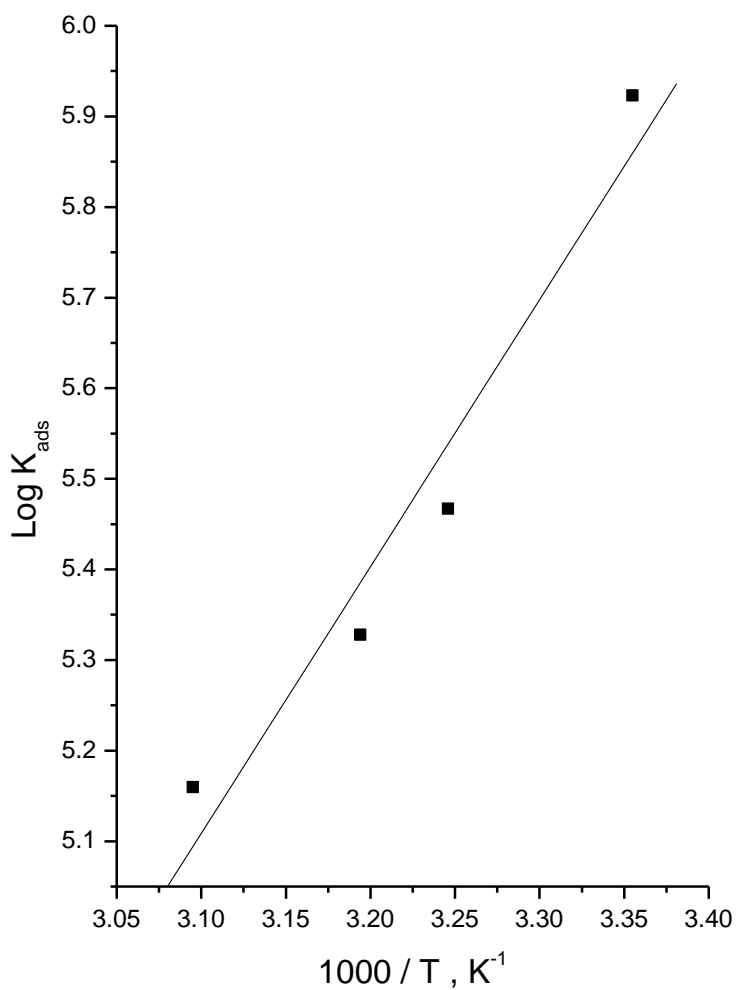


Figure (8): $\log K_{\text{ads}}$ vs. $(1/T)$ for the corrosion of C-steel in 1 M HCl in the presence of methyl orange

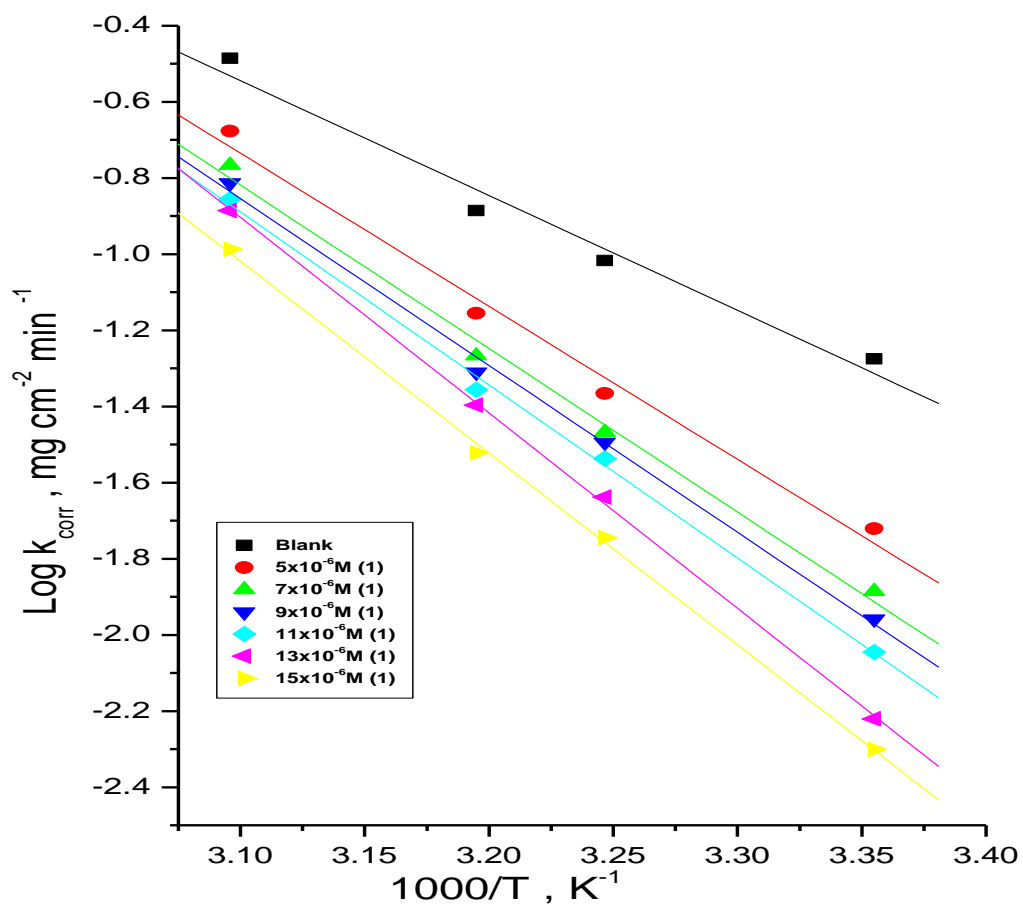


Figure (9): Arrhenius plots for C-steel corrosion rates ($k_{\text{corr.}}$) after 120 min of immersion in 1 M HCl in the absence and presence of various concentrations of methyl orange

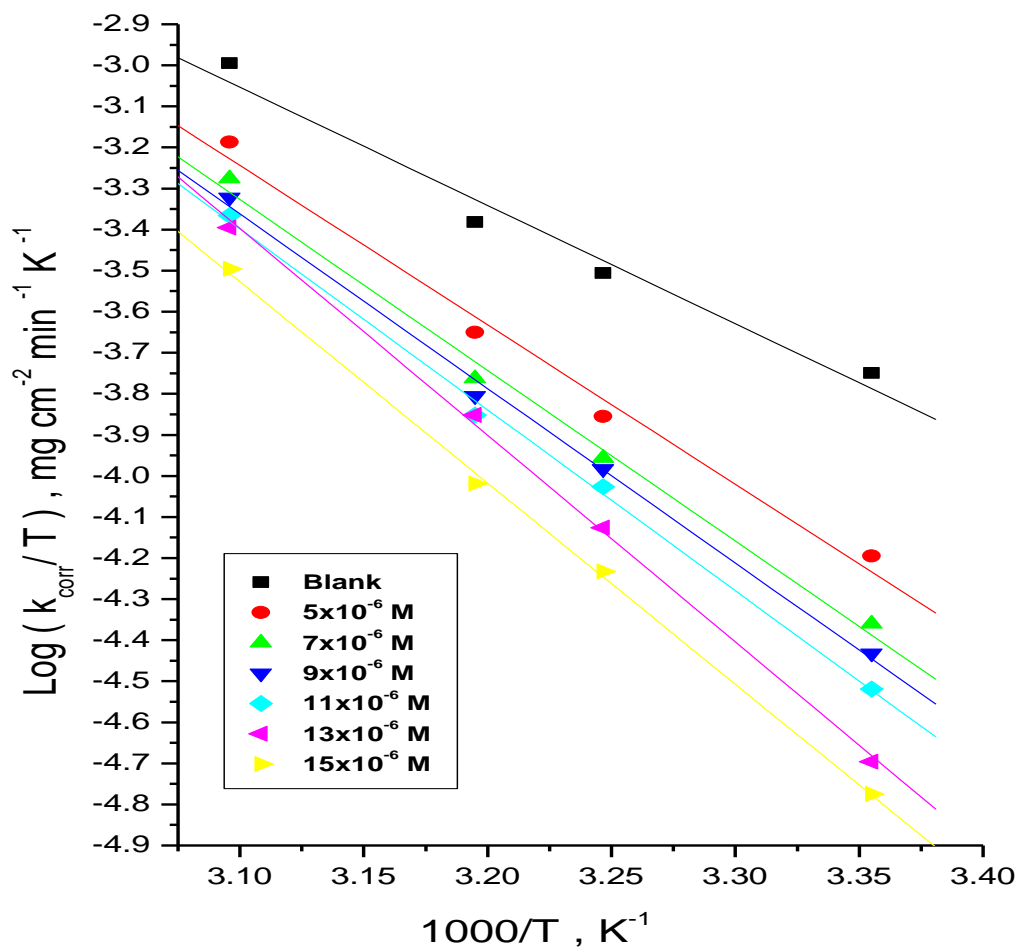


Figure (10): Transition-state for C-steel corrosion rates (k_{corr}) in 1 M HCl in the absence and presence of various concentrations of methyl orange

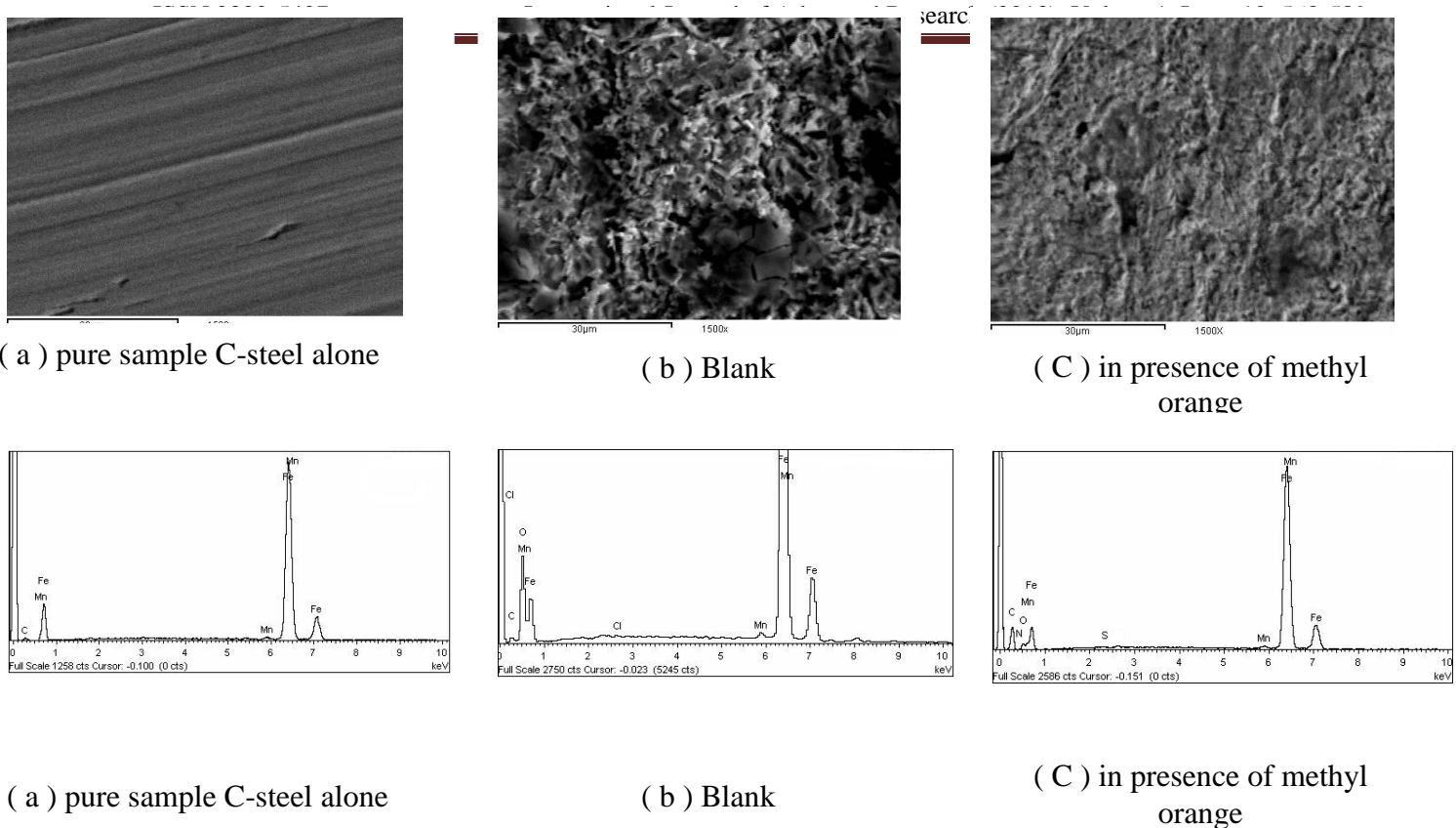


Figure (12): Shows EDS analysis of a C-steel surface alone without any additives (a) and after 3 days immersion in a 1M HCl solution (b) and (c) after 3 days immersion in a 1 M HCl in presence of 15×10^{-6} M of methyl orange

CONCLUSIONS

The investigated methyl orange acts as inhibitor for the corrosion of carbon steel in hydrochloric acid solution. Methyl orange adsorbs on carbon steel surface according to the Langmuir adsorption isotherm. The inhibitor increases the value of activation energy of corrosion and consequently, decreases the rate of dissolution of carbon steel in HCl solution. Polarization data showed that this investigated methyl orange acted as mixed-type inhibitor. The inhibition efficiencies obtained from electrochemical and chemical measurements are in good agreement with each other.

References

- [1] L.R. Chauhan, G. Gunasekaran, Corrosion inhibition of mild steel by plant extract in dilute HCl medium Corros. Sci., 49, 1143-1161, 2007
- [2] K.F. Khaled, Application of electrochemical frequency modulation for monitoring corrosion and corrosion inhibition of iron by some indole derivatives in molar hydrochloric acid, Mater. Chem. Phys., 112, 290-300, 2008
- [3] M.K. Pavithra, T.V. Venkatesha, K. Vathsala, K.O. Nayana, Synergistic effect of halide ions on improving corrosion inhibition behaviour of benzisothiazole-3-piperazine hydrochloride on mild steel in 0.5 M H₂SO₄ medium, Corros. Sci., 52, 3811-3819, 2010.
- [4] Ishtiaque Ahmad, Rajendra Prasad, M.A. Quraishi, Adsorption and inhibitive properties of some new Mannich bases of Isatin derivatives on corrosion of mild steel in acidic media, Corros. Sci., 52, 1472-1481, 2010
- [5] O. Benali, L. Larabi, M. Traisnel, L. Gengembra, Y. Harek, Electrochemical, theoretical and XPS studies of 2-mercapto-1-methylimidazole adsorption on carbon steel in 1 M HClO₄, Appl. Surf. Sci., 253, 6130-6139, 2007
- [6] Y. Abboud, A. Abourriche, T. Saffaj, M. Berrada, M. Charrouf, A. Bennamara, N. Al Himidi, H. Hannache, 2,3-Quinoxalinedione as a novel corrosion inhibitor for mild steel in 1 M HCl, Mater. Chem. Phys., 105, 1-5, 2007
- [7] Ashish Kumar Singh, M.A. Quraishi, The effect of some bis-thiadiazole derivatives on the corrosion of mild steel in hydrochloric acid, Corros. Sci., 52, 1373-1385, 2010

- [8] G.E. Badr, The role of some thiosemicarbazide derivatives as corrosion inhibitors for C-steel in acidic media, Corros. Sci, 51, 2529- 2536 .2009
- [9] J. Aljourani, M.A. Golozar, K. Raeissi, The inhibition of carbon steel corrosion in hydrochloric and sulfuric acid media using some benzimidazole derivatives, Mater. Chem. Phys, 121, 320- 325 , 2010
- [10] Ying Yan, Weihua Li, LankunCai, BaorongHou, Electrochemical and quantum chemical study of purines as corrosion inhibitors for mild steel in 1 M HCl solution, Electrochim. Acta., 53, 5953-5960, 2008
- [11] J. Cruz, R. Martinez, J. Genesca, E. Garcia-Ochoa, Experimental and theoretical study of 1-(2-ethylamino)-2-methylimidazoline as an inhibitor of carbon steel corrosion in acid media, J. Electroanal. Chem. 566, 111–121, 2004.
- [12] A. M. S. Abdennaby, A. I. Abdulhady, S. T. Abu-Oribi, H. Saricimen, The inhibition action of 1(benzyl) 1-H-4,5-dibenzoyl-1, 2,3-triazole on mild steel in hydrochloric acid media, Corros. Sci. 38, 1791–1800, 1996
- [13] F. Bentiss, M. Traisnel, L. Gengembre, M. Lagrenee, A new triazole derivative as inhibitor of the acid corrosion of mild steel: electrochemical studies, weight loss determination, SEM and XPS, Appl. Surf. Sci. 152, 237–249, 1999
- [14] L. Wang, Inhibition of mild steel corrosion in phosphoric acid solution by triazole derivatives, Corros. Sci., 48, 608–616, 2006.
- [15] M. A. Quraishi, H. K. Sharma, 4-Amino-3-butyl-5-mercapto-1,2,4-triazole: a new corrosion inhibitor for mild steel in sulphuric acid, Mater. Chem. Phys. 78 , 18–21, 2002.
- [16] E. Garcia-Ochoa, J. Genesca, Understanding the inhibiting properties of 3-amino-1, 2, 4-triazole from fractal analysis, Surf. Coat. Tech. 184, 322– 330, 2004.
- [17] W. H. Li, Q. He, S. T. Zhang, C. L. Pei, B. R. Hou, “Some new triazole derivatives as inhibitors for mild steel corrosion in acidic medium, J Appl. Electrochem. 38, 289–295, 2008
- [18] S. Kertit, B. Hammouti, Corrosion inhibition of iron in 1M HCl by 1-phenyl-5-mercapto-1,2,3,4-tetrazole, Appl. Surf. Sci., 93, 59–66, 1996.
- [19] P. Morales-Gil, G. Negron-Silva, M. Romero-Romoa, C. Angeles-Chavez, M. Palomar-Pardave, Corrosion inhibition of pipeline steel grade API 5L X52 immersed in a 1 M H₂SO₄ aqueous solution using heterocyclic organic molecules, Electrochim. Acta, 49, 4733–4741, 2004.
- [20] R. M. Hudson, T. J. Bulter, C. J. Warning, The effect of pyrrole-halide mixtures in inhibiting the dissolution of low-carbon steel in sulphuric acid, Corros. Sci., 17, 571–581, 1977
- [21] M. Bouklah, A. Ouassini, B. Hammouti, A. El Idrissi, Corrosion inhibition of steel in 0.5 M H₂SO₄ by [(2-pyridin-4-ylethyl)thio]acetic acid, Appl. Surf. Sci. 250, 50–56, 2005
- [22] M. Lashkari, M.R. Arshadi, DFT studies of pyridine corrosion inhibitors in electrical double layer: solvent, substrate, and electric field effects, Chem. Phys. 299, 131–137, 2004.
- [23] M. A. Veloz, I. G. Martinz, Effect of Some Pyridine Derivatives on the Corrosion Behavior of Carbon Steel in an Environment Like NACE TM0177, Corrosion, 62, 283–292, 2006.
- [24] A. Ouchrif, M. Zegmout, B. Hammouti, S. El-Kadiri, A. Ramdani, 1,3-Bis(3-hydroxymethyl-5-methyl-1-pyrazole) propane as corrosion inhibitor for steel in 0.5 M H₂SO₄ solution, Appl. Surf. Sci., 252, 339–344, 2005.
- [25] G. K. Gomma, Corrosion of low-carbon steel in sulphuric acid solution in presence of pyrazole—halides mixture, Mater. Chem. Phys., 55 241–246, 1998
- [26] M. Abdallah, M. M. El-Naggar, Cu²⁺ cation+3,5-dimethyl pyrazole mixture as a corrosion inhibitor for carbon steel in sulfuric acid solution, Mater. Chem. Phys. 71; 291–298, 2001.
- [27] M. Abdallah, Corrosion behaviour of 304 stainless steel in sulphuric acid solutions and its inhibition by some substituted pyrazolones, Mater. Chem. Phys. 82; 786–792, 2003
- [28] A. Chetouani, B. Hammouti, T. Benhadda, M. Daoudi, Inhibitive action of bipyrazolic type organic compounds towards corrosion of pure iron in acidic media, Appl. Surf. Sci. 249 375–385., 2005
- [29] M. Elayyachy, M. Elkodadi, A. Aouniti, A. Ramdani, B. Hammouti, F. Malek, A. Elidrissi, New bipyrazole derivatives as corrosion inhibitors for steel in hydrochloric acid solutions, Mater. Chem. Phys. 93, 281–285, 2005
- [30] S. A. Abd El-Maksoud, The influence of some Arylazobenzoyl acetonitrile derivatives on the behaviour of carbon steel in acidic media, Appl. Surf. Sci., 206, 129–136, 2003.
- [31] A. Chetouani, A. Aouniti, B. Hammouti, N. Benchat, T. Benhadda, S. Kertit, Corrosion inhibitors for iron in hydrochloride acid solution by newly synthesised pyridazine derivatives, Corros. Sci., 45, 1675–1684, 2003
- [32] G. Moretti, G. Quartarone, A. Tassan, A. Zingales, 5-Amino- and 5-chloro-indole as mild steel corrosion inhibitors in 1 N sulphuric acid, Electrochim. Acta, 41, 1971–1980, 1996.

- [33] M. Dudukcu, B. Yazici, M. Erbil, The effect of indole on the corrosion behaviour of stainless steel, Mater. Chem. Phys. 87, 138–141, 2004.
- [34] A. A. Ismail, S. H. Sanad, A. A. El-Meligi, inhibiting effect of indole and some of its derivatives on corrosion of C-steel in HCl, J. Mater. Sci. Technol. 16 397-400, 2000.
- [35] L. Wang, Evaluation of 2-mercaptobenzimidazole as corrosion inhibitor for mild steel in phosphoric acid, Corros. Sci., 43, 2281–2289, 2001
- [30] A. Popova, M. Christov, T. Deligeorgiev, Influence of the Molecular Structure on the Inhibitor Properties of Benzimidazole Derivatives on Mild Steel Corrosion in 1 M Hydrochloric Acid, Corrosion 59, 756–764, 2003
- [36] A. Popova, M. Christov, S. Raicheva, E. Sokolova, Adsorption and inhibitive properties of benzimidazole derivatives in acid mild steel corrosion, Corros. Sci., 46, 1333–1350, 2004
- [37] K. F. Khaled, The inhibition of benzimidazole derivatives on corrosion of iron in 1 M HCl solutions, Electrochim. Acta, 48, 2493–2503, 2003.
- [38] M. H. Wahdan, The synergistic inhibition effect and thermodynamic properties of 2-mercaptobenzimidazol and some selected cations as a mixed inhibitor for pickling of mild steel in acid solution, Mater. Chem. Phys., 49, 135–140, 1997
- [39] L. B. Tang, X. M. Li, Y. S. Si, G. N. Mu, G. H. Liu, The synergistic inhibition between 8-hydroxyquinoline and chloride ion for the corrosion of cold rolled steel in 0.5 M sulfuric acid, Mater. Chem. Phys. 95, 29–38, 2006
- [40] I. B. Obot, N. O. Obi-Egbedi, N. W. Odozi, Acenaphtho [1,2-b] quinoxaline as a novel corrosion inhibitor for mild steel in 0.5 M H₂SO₄, Corros. Sci., 52, 923-926, 2010
- [41] I. B. Obot, N. O. Obi-Egbedi, Indeno-1-one [2,3-b]quinoxaline as an effective inhibitor for the corrosion of mild steel in 0.5 M H₂SO₄ solution, Mater. Chem. Phys. 122, 325-328, 2010
- [42] Y. Abboud, A. Abourriche, T. Saffaj, M. Berrada, M. Charrouf, A. Bennamara, N. AlHimidi, H. Hannache, 2,3-Quinoxalinedione as a novel corrosion inhibitor for mild steel in 1 M HCl, Mater. Chem. Phys., 105, 1-5, 2007
- [43] M. Benabdellah, K. Tebbji, B. Hammouti, R. Touzani, A. Aouniti, A. Dafali and S. ElKadiri, The effect of temperature on the corrosion of steel in 1M HCl in the presence of quinoxaline compound, Phys. Chem. News, 43, 115-120, 2008.
- [44] M. Benabdellah, R. Touzani, A. Aouniti, A. Dafali, S. Elkadiri, B. Hammouti, M. Benkaddour, Investigation of the inhibitive effect of some quinoxaline compounds on the corrosion of steel in HCl solutions, Phys. Chem. News, 37, 63-69, 2007
- [45] I. El Ouali, B. Hammouti, A. Aouniti, Y. Ramli, M. Azougagh, E. M. Essassi, M. Bouachrine, Thermodynamic characterisation of steel corrosion in HCl in the presence of 2-phenylthieno (3, 2-b) quinoxaline, J. Mater. Envir. Sci. 1, 1-8, 2010
- [46] F. Bentiss, M. Lagrenee, M. Traisnel, 2,5-Bis(n-pyridyl)-1,3,4-oxadiazoles as corrosion inhibitors for mild steel in acidic media, Corrosion 56, 733- 742, 2000
- [47] S. Omanovic, S.G. Roscoe, Effect of linoleat on electrochemical behavior of stainless steel in phosphate buffer, Corrosion, 56, 684- 701, 2000
- [48] T.P. Hoar, R.P. Khera, Proceedings 1st EuropSymp. On Corrosion Inhibitors, Ferrara, Italy, 73-97, 1960.
- [49] S.S. Abdel Rehim, O.A. Hazzazi, M.A. Amin, K.F. Khaled, on the corrosion inhibition of low carbon steel in concentrated sulphuric acid solutions. Part I: chemical and electrochemical (AC and DC) studies, Corros. Sci., 50, 2258–2271, 2008
- [50] J., Aljourani, K., Raeissi, M.A., Golozar, Benzimidazole and its derivatives as corrosion inhibitors for mild steel in 1M HCl solution, Corros. Sci., 51, 1836-1843 ,2009
- [51] H., Amar, A., Tounsi, A., Makayssi, A., Derja, J., Benzakour, A., Outzourhit, Corrosion inhibition of Armco iron by 2-mercaptobenzimidazole in sodium chloride 3% media Corros.Sci., 49, 2936- 2945 , 2007
- [52] T. Pajkossy, “Impedance of rough capacitive electrodes,” Impedance of rough capacitive electrodes, J. Electroanal. Chem., 364 (1-2), 111–125, 1994.
- [53] M. Lebrini, F. Bentiss, H. Vezin, and M. Lagrenée, “The inhibition of mild steel corrosion in acidic solutions by 2,5-bis(4-pyridyl)-1,3,4-thiadiazole: structure-activity correlation,” Corros.Sci., 48(5), 1279–1291, 2006.
- [54] F. B. Growcock and R. J. Jasinski, “Time-resolved impedancespectroscopy of mild steel in concentrated hydrochloric acid,” Journal of the Electrochemical Society, 136(8), 2310–2314, 1989.
- [55] E. Kus, F. Mansfeld; An evaluation of the electrochemical frequency modulation (EFM) technique, Corros. Sci., 48, 965-979 ,2006
- [56] M. Bethencourt, F.J. Botana, J.J. Calvino, M. Marcos; Lanthanide compounds as environmentally-friendly corrosion inhibitors of aluminium alloys: a review Corros. Sci., 40, 1803- 1819 ,1998
- [57] Gamry Echem Analyst Manual, 2003.

- [58] Bayol, K., Kayakirilmaz, M., Erbil, The inhibitive effect of hexamethylenetetramine on the acid corrosion of steel , The inhibitive effect of hexamethylenetetramine on the acid corrosion of steel, Mater.Chem.Phys., 104, 74- 82 , 2007
- [59] O., Benalli, L., Larabi, M., Traisnel, L., Gengembra, Y., Harek, Electrochemical, theoretical and XPS studies of 2-mercapto-1-methylimidazole adsorption on mild steel in 1 M HClO₄, Appl. Surf. Sci., 253 ,6130-6139, 2007
- [60] Z. Szlarska-Smialowska, Crevice corrosion of stainless steels in sodium chloride solution, Corros. Sci. 18; 953-960 . 1978
- [61] A. Yurt, S. Ulutas, H. Dal, Electrochemical and theoretical investigation on the corrosion of aluminium in acidic solution containing some Schiff bases Appl. Surf. Sci.,253 919- 925 ,2006
- [62] Abd El-Rehim S.S., Hassan H.H. and Amin M.A., Corrosion inhibition of aluminum by 1,1(lauryl amido)propyl ammonium chloride in HCl solution, Mater.Chem. Phys. 70, 64-72 .2001
- [63] Tang L., Lie X., Si Y., Mu G. and Liu G., The synergistic inhibition between 8-hydroxyquinoline and chloride ion for the corrosion of cold rolled steel in 0.5 M sulfuric acid, Mater. Chem. Phys., 95, 29- 38 ,2006.
- [64] Mu G., Li X. and Liu G., Synergistic inhibition between tween 60 and NaCl on the corrosion of cold rolled steel in 0.5 M sulfuric acid, Corros.Sci., 47, 1932- 1952 ,2005
- [65] N.M.Guan, L.Xumeing, L.Feimeter. Synergistic inhibition between o-phenanthroline and chloride ion on cold rolled steel corrosion in phosphoric acid, Chem.Phys.,86, 59-68,2004
- [66] E.F., El-Sherbiny , Effect of some ethoxylated fatty acids on the corrosion behavior of mild steel in sulphuric acid solution" Mater. Chem. Phys. 60, 286–290,1999
- [67]-A.S., Fouda, A.A., Al-Sarawy, E.E., El-Katori, Pyrazolone derivatives as corrosion inhibitors for mild steel HCl solution, Desalination, 201 ,1-13, 2006
- [68] L.; Fragoza-Mar, O.Olivares-Xometl.; M. A.; Domnguez-Aguilar, E. A.; P Flores.,; Arellanes-Lozada, F., Jimenez-Cruz, Corrosion inhibitor activity of 1,3-diketone malonates for mild steel in aqueous hydrochloric acid solution, Corros. Sci.61; 171-184, 2012.
- [69] K.; Aramaki, N.Hackermann, Inhibition Mechanism of Medium-Sized Polymethyleneimine, J., Electrochem. Soc., 116,568-574, 1969.
- [70] Ashish Kumar Singh, M. A. Quraishi., Study of Some Bidentate Schiff Bases of Isatin as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution, Int. J. Electrochem. Sci., 7, 3222-3241, 2012
- [71] M.C.Tschapek, , R.M Wasowski., and Torres Sanchez.,_Corrosion of Aluminium in Hydrochloric Acid and Sodium Hydroxide Solutions, J. Electroanal. Chem., 74, 67-76, 1976.
- [72] A.A., Awady, B.A. Abd. El- Nabey, and S.G. Aziz, Thermodynamic and kinetic factors in chloride ion pitting and nitrogen donor ligand inhibition of aluminium metal corrosion in aggressive acid media ,J. Chem. Soc. Faraday Trans., 89, 795-802, 1993