Journal of materials and Environmental Sciences
ISSN : 2028-2508

JMES, 2017 Volume 8, Issue 1, Page 298-309

http://www.jmaterenvironsci.com/

5-Chloro-1*H*-indole-2,3-dione derivative as corrosion inhibitor for mild steel in 1M H_3PO_4: weight loss, electrochemical and SEM studies

Z. Tribak[1], A. Haoudi[1], M.K. Skalli[1], Y. Kandri Rodi[2], M. El Azzouzi[3], A. Aouniti[3], B. Hammouti[3], O. Senhaji[4*]

[1] *Laboratory of Applied Chemistry, Sidi Mohamed Ben Abdellah University, Faculty of Science and Technology of Fes, Morocco.*
[2] *Laboratory of Applied Organic Chemistry, Sidi Mohamed Ben Abdellah University, Faculty of Science and Technology of Fes, Morocco.*
[3] *LCAE-URAC18, Faculty of Science, Mohammed first University, Po Box 717, 60000 Oujda, Morocco.*
[4] *Laboratory of Applied Physical Chemistry, Moulay Ismaïl University, Faculty of Sciences and Technology of Errachidia, Morocco.*

Received 12 July 2016,
Revised 21 Oct 2016,
Accepted 25 Oct 2016

Keywords
- ✓ 5-Chloroisatin derivative,
- ✓ corrosion,
- ✓ mild steel,
- ✓ 1M H_3PO_4,
- ✓ inhibition,
- ✓ weight loss

ossenhaji@yahoo.fr
Tel: +212661963819

Abstract

The detailed study of 5-Chloroisatin derivative against the corrosion of mild steel in a 1M H_3PO_4 solution at 303 K was carried out using the method of weight loss measurements, Tafel polarization techniques, electrochemical impedance spectroscopy (EIS) and also scanning electron microscopy (SEM). The results showed that the 5-chloro-1- (2-(dimethylamino) ethyl) indoline-2,3-dione (Indo1) is a good inhibitor and its inhibition efficiency reached 91% at 10^{-3}M. Polarization measurements revealed that the 5-chloro-1-(2- (dimethylamino) ethyl) indoline-2,3-dione behaves as mixed-type. The adsorption of 5-chloro-1 (2(dimethylamino) ethyl) indoline-2,3-dione on a mild steel surface obeys the Langmuir isotherm, has been studied at different temperatures. The kinetic parameters, and thermodynamic activations for the corrosion of mild steel, respectively, were calculated and discussed.

1. Introduction

Corrosion may be defined as an electrochemical reaction between a metal and its environment, which causes a slow deterioration, regular and irreversible in the metal, both its physical and chemical properties. These phenomena have major implications in various fields, particularly in industry.

A variety of acidic solutions are generally used in the industry, this causes corrosion of metals is a major problem that must be confronted for the safety, environmental and economic reasons [1]. Especially for metals and alloys, mild steel chosen because of the low cost and easy availability has found wide applications in a wide range of industries and machinery, despite his tendency to corrosion, the inhibition of corrosion of steel is thus an important issue theoretical as well as practical [2-9].

Generally, the inhibitors are commonly used to reduce the corrosive attack on metallic materials [10] among the many inhibitors; there N-heterocyclic systems are considered the most effective corrosion inhibitors [11-13]. For steel in acidic media, the pyrazine derivatives [14, 15], derivatives of triazoles [16-18] pyridine derivatives [19], diamine derivatives [20-22] offer excellent performance of corrosion inhibition.

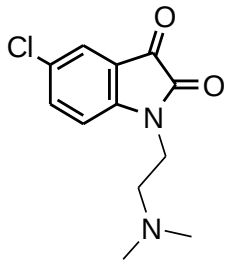
In this article, we studied the corrosion inhibition of 5-Chloroisatin derivative on mild steel in 1M phosphate solution using the method of weight loss measurement at different concentration, Tafel polarization techniques, the electrochemical impedance spectroscopy (EIS) and also the morphology of the metal surface by the analysis of scanning electron microscope, all of the kinetic and thermodynamic parameters are calculated and discussed in detail [23].

1. Materials and methods

1.1. Inhibitor tested.

In this part, we are interesting to study the inhibition of corrosion of mild steel in phosphoric acid with the derivatives of 5-Chloroisatin already synthesized and analyzed (Tribak et al., 2016)[24] the chemical structure of this compound is given in Figure 1. The inhibitory activity of corrosion of this organic compound was successively examined by weight loss,

potentiodynamic polarization curves, electrochemical impedance spectroscopy (EIS). The kinetics and adsorption parameters of the corrosion inhibition processes are also evaluated.



5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione
Figure 1: Chemical formula of Indo1

1.2. Preparation of Material

In this study, mild steel that was used includes the 0.370% C element, 0.230% Mn 0.680% Si, 0.016% S, 0.077% Cr, 0.011% Ti, 0.059% Ni, 0.009% Co, 0.160% of Cu and the balance being iron (Fe), the steel was mechanically cut to size of 1.5 x 1.5 cm coupons subsequently mild steel samples were pre-treated prior to the experiments by grinding with emery paper of SiC (grades 400, 600 and 1200), then washed thoroughly with double distilled water, degreased with acetone, and finally dried at room temperature before use.

1.3. Solutions

The preparation of the acid solutions (1M H_3PO_4) was performed by diluting a quality of analytical reagent H_3PO_4 85% with bidistilled water. The concentration range of 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione used was 10^{-6} M to 10^{-3} M, to compare their corrosion inhibiting properties with those similar heterocyclic compounds.

1.4. Corrosion tests

Weight loss tests were carried out in rectangular specimens of size (1.5 cm x 1.5 cm x 0.3 cm) in a 1M H_3PO_4 solution, added to the system in different concentrations in a range of 10^{-6} to 10^{-3}M the immersion time for weight loss was 6h at 303 K.

After the corrosion test, steel samples were thoroughly washed with distilled water twice, dried and then weighed. The experiments were repeated in triplicate in each case and the mean value of the weight loss is shown using an analytical balance (accuracy ± 0.1 mg). Weight loss has allowed us to calculate the corrosion rate and of course the efficiency of inhibition.

The effect of temperature on the reaction inhibited acid-metal is very complex because many changes occur on the metal surface, why experimental tests were carried out by different temperatures (303- 333 K) for 1 hour in the absence and presence of 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione in order to study the change of the corrosion rate and the inhibition efficiency with temperature in the acid 1M H_3PO_4.

Electrochemical tests were monitored using the potentiostat PGZ 100 controlled by a software VoltaMaster, electrochemical measurements were performed in a system of three cylindrical electrodes electrolysis Pyrex glass cell, the working electrode (WE) is in the form a disk cut from the steel sheet, the area that is exposed to the corrosive solution was 1 cm^2. A saturated calomel electrode (SCE) and a platinum electrode were used respectively as reference and auxiliary electrode.

Measures the electrochemical impedance spectroscopy (EIS) are made with the electrochemical system includes a digital model of potentiostat computer VoltaLab PGZ100 to E_{corr} after immersion in solution without bubbles.

The identification of the current in the stable state to a corrosion potential, sine wave voltage (10 mV) peak-to-peak at frequencies between 100 kHz and 10 MHz is superimposed on the resting potential.

After immersion, computer programs automatically controlled measurements at the potentials at 303K, and then the impedance diagrams are given in the Nyquist representation.

Steel surface morphologies studied soft inhibited or uninhibited, before and after immersion was examined by scanning electron microscope (FEI Quanta 200) equipped with EDAX probe for microanalysis of surfaces.

2. Results and discussion

2.1. Weight Loss study

By applying the method of weight loss measurements at 303 K we studied the effect of the addition of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione tested at different concentrations on corrosion of mild steel in 1M H_3PO_4 after 6 hours of immersion.

The corrosion rate (C_R), the inhibition efficiency $\eta_{WL}(\%)$ and surface coverage (θ) were summarized in Table 1 and were calculated according to equations 1 and 2 [25], respectively:

$$C_R = \frac{W_b - W_a}{At} \quad (1)$$

$$\eta_{WL}(\%) = \left(1 - \frac{w_i}{w_0}\right) \times 100 \quad (2)$$

$$\theta = \left(1 - \frac{w_i}{w_0}\right) \quad (3)$$

With W_b and W_a is the weight of the sample before and after immersion in the test solution, w_0 and w_i are the values of weight loss corrosion of mild steel in uninhibited and inhibited solutions, respectively, A the surface of the mild steel specimen (cm^2) and t is the exposure time (h).

Table 1: Parameters obtained from weight loss measurements for mild steel in 1M H_3PO_4 at different concentrations of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione, at 303 K for 6h

Concentration (M)	C_R $(mg.cm^{-2}.h^{-1})$	η_{WL} **(%)**	θ
Blank	0.470	--	--
10^{-3}	0.038	91.91	0.919
5.10^{-4}	0.065	86.21	0.862
10^{-4}	0.076	83.91	0.839
5.10^{-5}	0.164	65.16	0.652
10^{-5}	0.227	51.73	0.517
10^{-6}	0.237	49.60	0.496

η_{WL} *(%)* change with the concentration is shown in Fig. 2.

From the results, it is clear that the values of corrosion rate (C_R) decreases continuously with increasing the concentration of 5-chloro-1 additive (2 (dimethylamino) ethyl) indoline-2,3 -dione to 303 K.

While the efficiency values η_{WL} *(%)* increase with increased concentration up to a maximum efficiency η_{WL} *(%)* is 91.9% to 10^{-3}M (Table 1, Fig. 2). The plausible mechanism for the inhibition of corrosion of mild steel in 1M H_3PO_4 additive to 303 K, can be explained by the adsorption of molecules of 5-chloro-1 (2 (dimethylamino) ethyl) indoline 2,3-dione on the metal surface.

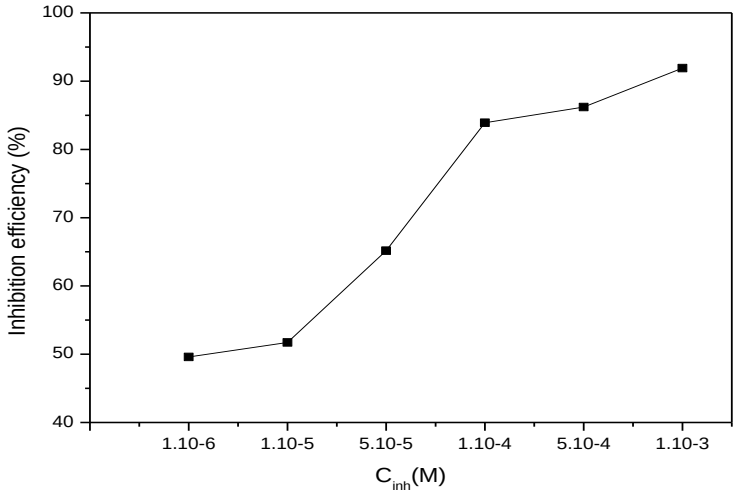


Figure 2: Variation of inhibition efficiency of mild steel in 1M H_3PO_4 containing various concentrations of 5-chloro-1- (2-(dimethylamino) ethyl) indoline-2,3-dione.

2.2. Potentiodynamic measurements:

2.2.1. Tafel polarisation study

The polarization of electrochemical measurements was performed in order to understand the process of the kinetics of the anodic and cathodic reactions.

Fig. 3 shows the potentiodynamic polarization curves typical of mild steel in the phosphoric acid in the absence and presence of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione at varying concentrations.
Experiments were carried out by the method of extrapolation of Tafel [26] allow determine. The electrochemical corrosion of parameters such that the corrosion current density (I_{corr}), the corrosion potential (E_{corr}), cathodic Tafel slope (βc) and an efficiency of inhibition use the following equation [27]:

$$E_I\% = \frac{I_{corr} - I_{corr\ (inh)}}{I_{corr}} \times 100 \qquad (4)$$

Where I_{corr} and $I_{corr(inh)}$ are the corrosion current densities for steel electrode in the uninhibited and inhibited solutions, respectively.

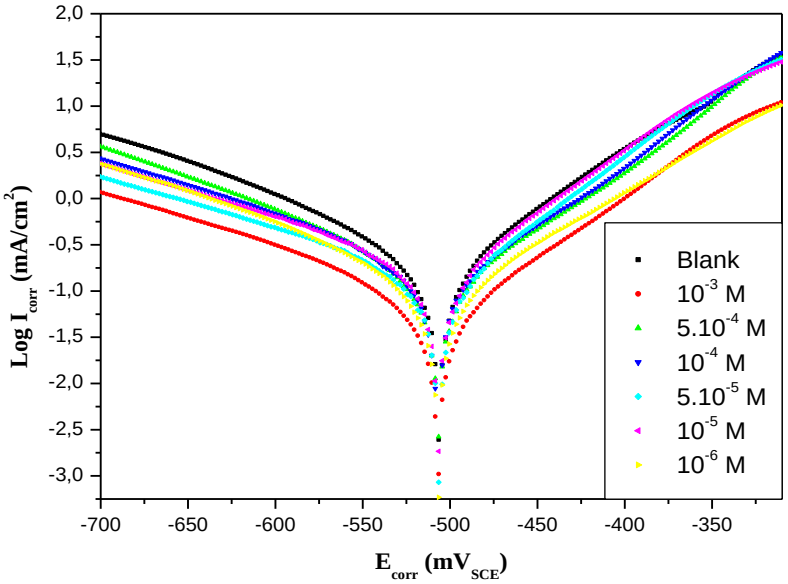


Figure 3: Curves of mild steel potentiodynamic polarization at various concentration of 5-chloro-1-(2-(dimethylamino) ethyl)indoline-2,3-dione in a solution of phosphoric acid 1M.

Table 2: Potentiodynamic polarization parameters at different concentrations of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione in 1M H_3PO_4

	Conc (M)	$-E_{corr}$ (mV/SCE)	$-\beta_c$ (mV/dec)	I_{corr} (µA/cm²)	E_I (%)
Blank	--	520.2	151.7	2516	--
Product	10^{-6}	510.6	157.2	1481	41.13
	10^{-5}	504.7	160.8	1327	47.25
	5.10^{-5}	506.4	166.1	1069	57.51
	10^{-4}	507.8	171.5	806	67.96
	5.10^{-4}	512.6	178.3	657	73.88
	10^{-3}	501.9	184.7	489	80.56

It was remarkable that from figure 3 addition of 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione affects both anodic and cathodic polarization curves suggesting that 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione could be classified as a type of mixed inhibitor because it is observed that a decrease in both the anode and cathode tafel slope with a decline most pronounced in the cathodic branch (reducing the dissolution of mild steel, as well as the release of hydrogen). This could be the result of the adsorption of organic molecules of inhibitor on the metal surface (working electrode).
It was clearly seen from the table 2 that the values of the corrosion current density (I_{corr}) decreases as the concentration of 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione increased. This shows that the addition of inhibitor reduces the metal dissolution process.

2.2.2. Ac impedance study

In order to complete and compare the results obtained previously, the behavior of the corrosion of mild steel in a phosphoric acid solution with and without inhibitor 5-chloro-1- (2- (dimethylamino) ethyl) indoline 2,3-dione, was studied by electrochemical impedance spectroscopy (EIS)[28,29] at 303K (Fig. 4).

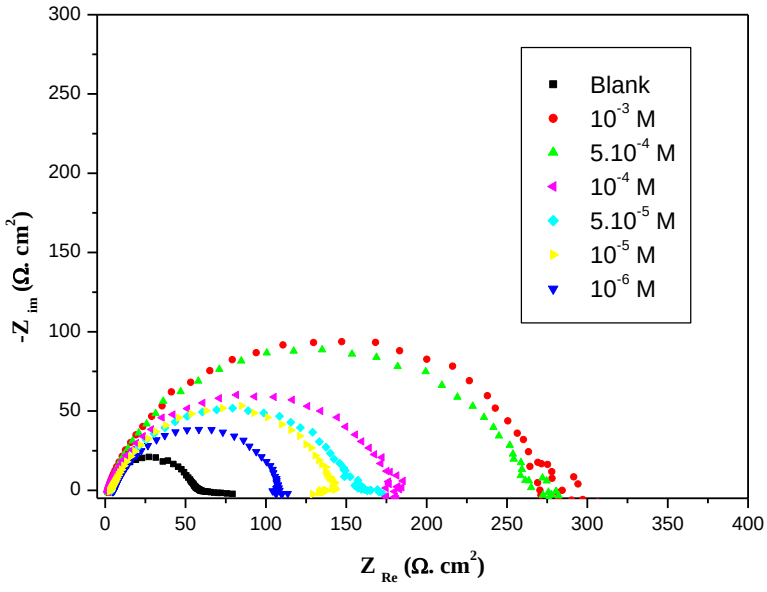


Figure 4: Impedance plot of mild steel obtained in the absence and presence of various concentrations of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione in 1M H_3PO_4

The efficiency values of inhibition and the capacity double layer (C_{dl}) were calculated from the equations (5) and (6).

$$\eta\% = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100 \quad (5)$$

Where R_{ct} and $R_{ct(inh)}$ are the charge transfer-resistance values with and without the inhibitor, respectively.

$$C_{dl} = \frac{\varepsilon_0 \varepsilon}{\delta} S \quad (6)$$

Where δ is the thickness of the deposit, S is the surface of the electrode, ε_0 is the permittivity of the air, and ε is the medium dielectric constant.

Table 3: Characteristic parameters evaluated from the impedance diagram for steel in 1M H_3PO_4 at various concentrations of Indo 1.

	Conc (M)	R_t (Ω. cm^2)	R_{ct} (Ω. cm^2)	C_{dl} (μF/cm^2)	η (%)
Blank	--	2.45	61.8	58.36	--
Product	10^{-6}	3.56	112.6	57.06	45.11
	10^{-5}	1.45	121.4	54.27	49.09
	5.10^{-5}	2.64	154.6	49.57	60.02
	10^{-4}	2.19	185.7	47.51	66.72
	5.10^{-4}	1.57	277.1	43.87	77.69
	10^{-3}	3.04	300.9	41.95	79.46

In all cases, the charge transfer resistance is increased with increasing concentration of 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione. Inspection of Table 3 data clearly shows that the charge transfer resistance R_{ct} and capacitance values of double-layer C_{dl} tend opposed any concentration range (R_{ct} increases and C_{dl} decreases with the concentration of inhibitor) involves R_t is associated with a slower corrosion system.

The decrease in C_{dl} values with the addition of the inhibitor is due to adsorption inhibitory molecules instead of water at the metal-solution interface which leads to the decrease in local dielectric constant and / or an increase in thickness of the electric double layer [30].

2.3. Effect of temperature

2.3.1. Corrosion kinetic study

The variation in the inhibition efficiency with concentration of 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione at different temperatures (303-333 K) into the acid 1M H_3PO_4 after immersion is shown in Table 4.

Table 4: corrosion parameters obtained from the weight loss for mild steel in 1M H_3PO_4 at different concentrations of 5-chloro-1-(2-(dimethylamino) ethyl)indoline-2,3-dione at different temperatures at 1h

Température	C_{inh} (mol/L)	C_R (mg.cm^{-2}.h^{-1})	η (%)	θ
303	Blank	0.113	---	---
	10^{-3}	0.00	94.1	0.941
	10^{-4}	0.025	77.7	0.777
	10^{-5}	0.037	67.1	0.671
	10^{-6}	0.054	52.1	0.521
313	Blank	0.138	---	---
	10^{-3}	0.011	92.0	0.920
	10^{-4}	0.034	75.6	0.756
	10^{-5}	0.055	60.4	0.604
	10^{-6}	0.074	46.3	0.463
323	Blank	0.386	---	---
	10^{-3}	0.039	89.9	0.899
	10^{-4}	0.150	61.0	0.610
	10^{-5}	0.251	34.8	0.348
	10^{-6}	0.313	18.8	0.188
333	Blank	0.644	---	---
	10^{-3}	0.127	80.3	0.803
	10^{-4}	0.286	55.6	0.556
	10^{-5}	0.426	33.8	0.338
	10^{-6}	0.550	14.5	0.145

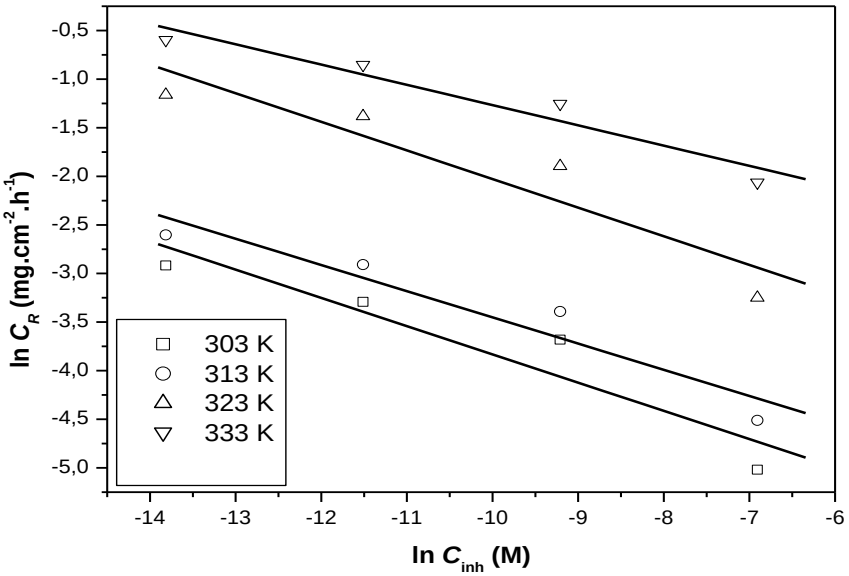


Figure 5: Change Ln*C*R with Ln*C*inh for mild steel in 1M H_3PO_4 containing 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione at different temperatures

It is observed that the efficiency of inhibition increases with increasing concentration of 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione, but decreases with increasing temperature. This translates as adsorption and desorption of inhibitory molecules are consistently produced at the metal surface and that the balance exist between the two processes, at a given temperature. With increasing temperature, the equilibrium between the adsorption and desorption process is shifted results in a higher desorption rate than adsorption until equilibrium is again established at a different values of equilibrium constant [31].

Assuming that the corrosion rate of mild steel against the concentration of inhibitor studied obeys the following kinetic relation [32]:

$\mathrm{Ln}C_R = \mathrm{BLn}C_{\mathrm{inh}} + \mathrm{Ln}k$ (7)

Where k is the rate constant and equal to C_R to the concentration of inhibitor unit, B is the constant for the reaction which in this case is a measure of the effectiveness of the inhibitor and C_{inh} is the concentration of inhibitor.
Negative values of B reflect the corrosion process rate is inversely proportional to the concentration of the inhibitor, which means that the inhibitor becomes more effective with increasing the concentration
The variation of C_R with the inhibitor concentration accelerates at high negative value for constant B which reflects good inhibiting properties studied inhibitor [33].

Table 5: Kinetic parameters for the corrosion of mild steel in 1M H_3PO_4 containing 5-chloro-1-(2- (dimethylamino) ethyl) indoline-2,3-dione at different temperatures

Temperature (K)	*B*
303	-0,290
313	-0,269
323	-0,294
333	-0,208

It is clear from table 4 that in the presence of the 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione, the corrosion rate of steel decreases at any given temperature as the inhibitor concentration increases due to the increase the degree of surface coverage.
Equations Arrhenius.1 and 2 were used to calculate the thermodynamic activation of the corrosion process parameters, [34]

$$C_R = Aexp\left(-\frac{E_a}{RT}\right) \quad (8)$$

$$C_R = \frac{RT}{Nh}\, exp\left(\frac{\Delta S_a}{R}\right)\, exp\left(-\frac{\Delta H_a}{RT}\right) \quad (9)$$

With E_a is the energy of corrosion apparent activation, R is the universal gas constant, A is the Arrhenius pre-exponential factor, T is the absolute temperature, h is Plank's constant, N is the number of Avogadro, and ΔS_a, ΔH_a successively are entropy and enthalpy of the activation.
The linear regression between ln(C_R) and 1000/T to calculate the values of the apparent activation energy of corrosion (E_a) of mild steel in 1M H_3PO_4 in the presence of 5-chloro -1- (2- (dimethylamino) ethyl) indoline-2,3-dione at various concentrations, the results are given in table 5. Arrhenius plots of the rate of mild steel (ln (C_R) versus 1000/ T) to corrosion are given in figure 6.

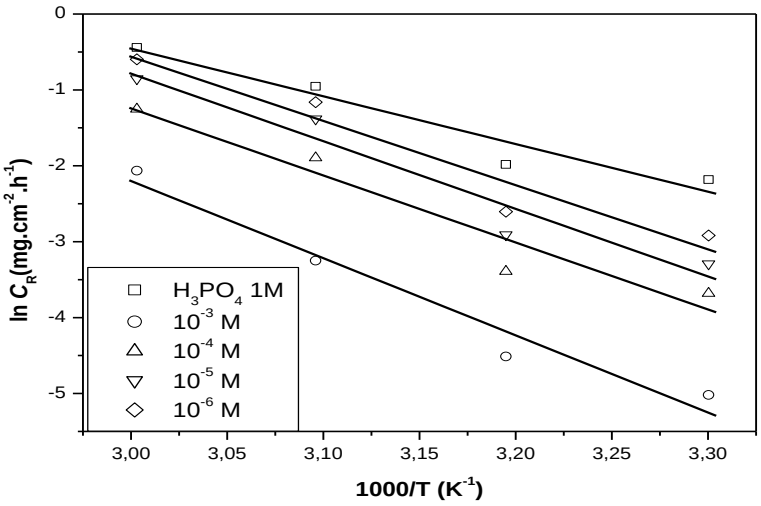


Figure 6: Arrhenius plots for mild steel corrosion rates (C_R) in 1M H_3PO_4 in the absence and presence of various concentrations of 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2, 3-dione

The obtained linear regression coefficients are close to 1 that reflects the corrosion of steel in phosphoric acid can be elucidated by applying the kinetic model [35-37].
The obtained values of the activation energy E_a of the corrosion process [38-40] in 1M H_3PO_4 is in the temperature range commonly cited[41-43], are grouped between 61.01 kJ mol-1 and 91.48 kJ mol-1.
From Table 6, it is clear that the values of the activation energy E_a increase with the concentration of 5-chloro -1- (2- (dimethylamino) ethyl) indoline-2,3-dione, but all the E_a values in the range of concentration tested, were superior to that of the uninhibited solution (blank).

Table 6: Corrosion kinetic parameters in absence and presence of different concentrations of 5-chloro -1- (2- (dimethylamino) ethyl) indoline-2,3-dione for steel in 1M H_3PO_4

C_{inh} (mol/L)	E_a (kJ.mol^{-1})	ΔH_a (kJ.mol^{-1})	ΔS_a (J.mol^{-1}.K^{-1})	E_a-ΔH_a
Blank	61.01	59.45	-70.80	1.56
10^{-6}	70.33	67.70	-46.99	2.64
10^{-5}	73.35	71.62	-37.55	2.73
10^{-4}	80.65	77.76	-21.49	2.89
10^{-3}	91.48	89.66	2.67	2.81

Figure 7 shows a graph of ln (C_R / T) against 1000/ T. A straight lines are obtained with a slope (-ΔH_a / R) and an interception (Ln R / Nh + ΔS_a / R) from which the values of ΔH_a and ΔS_a are calculated are summarized in Table 6. Inspection of these data suggests that ΔH_a values for the dissolution reaction of mild steel in 1M H_3PO_4 in the presence of 5-chloro -1- (2- (dimethylamino) ethyl) indoline-2,3-dione are higher (67.70 to 89.66 kJ mol-1) than in the absence of inhibitors (59.45 kJ mol-1).
Positive signs values ΔH_a reflects the endothermic nature of mild steel dissolution process suggesting that the dissolution of mild steel is slow [44]
*E*a values are larger than the analogous values ΔH_a implying that the corrosion process must result in a reaction gas, which allows us to verify the equation between thermodynamics and E_a, ΔH_a.
$\Delta H_a = E_a - RT$ (10)
It is observed that the average value of the difference E_a - ΔH_a is about 2.64 kJ mol^{-1}, approximately around the average value of the ambient temperature, indicating that the corrosion process is a reaction monomolecular.
For the entropy of activation (ΔS_a), shown in Table 6 that a large ΔS_a negative value is obtained presence of 5-chloro -1- (2- (dimethylamino) ethyl) indoline-2,3-dione, a negative value is also observed in the uninhibited solution. This observation is consistent with the results of other workers [45].

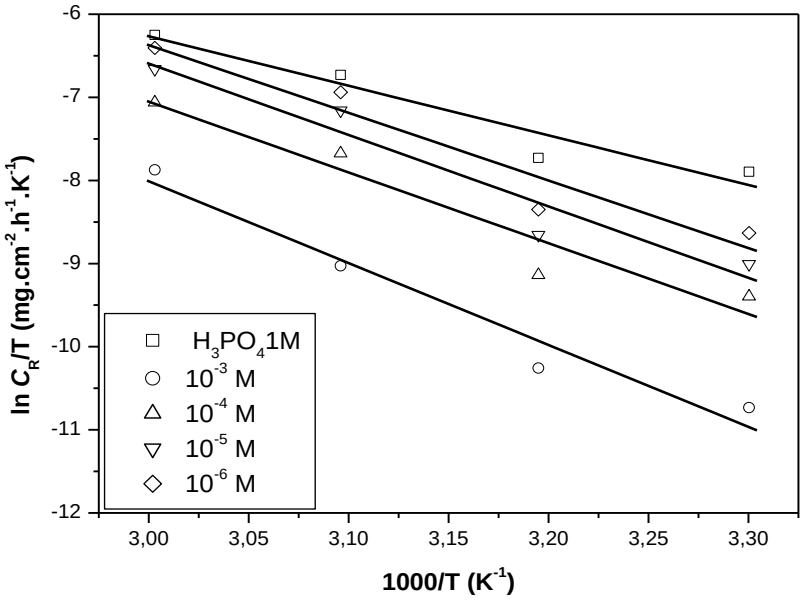


Figure 7: Transition-state plots in absence and in presence of different concentrations of 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione for mild steel corrosion rates (C_R) in 1M H_3PO_4

1.1.1. Adsorption isotherm and thermodynamic parameters

the efficiency of inhibition is directly linked to the metal cover level by inhibitory adsorbed for each concentration of 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione it has a value of the cover surface in the temperature range from 303 to 333 K were used to explain the best Isotherm to determine the adsorption process. From weight loss measurements compared can determine easily the surface coverage fraction (θ). It is possible to obtain different expressions adsorption isotherms plots and therefore the degree of surface coverage (θ) can be plotted against the concentration of inhibitor tested [46, 47]. The best model that describes the adsorption behavior of 5-chloro-1- (2-(dimethylamino) ethyl) indoline-2,3-dione is the adsorption isotherm Langmuir. In this case, the cover surface (θ) of the inhibitor on the steel surface is related to the concentration of the inhibitor in the solution according to the following equation:

$$Ln\frac{\theta}{1-\theta} = LnK + yLnC_{inh} \qquad (11)$$

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (12)$$

With θ is the degree of surface coverage, C_{inh} is the inhibitor concentration in the electrolyte and k is the equilibrium constant of the adsorption process.

The values of K can be considered as measures of the strength of the adsorption forces between inhibitory molecules and the metal surface

The adsorption parameters were calculated, straight lines were drawn by the least squares method. Experiences (points) and calculated isotherms (lines) are plotted in Figure 8.

The values of k_{ads} were determined from the intersections of straight lines C_{inh} / θ - axis and gathered on table. We can observe that the k_{ads} values decrease with temperature of 303-333 K; this is related to the temperature increase which causes the adsorption of some inhibitory molecules adsorbed on the metal surface.

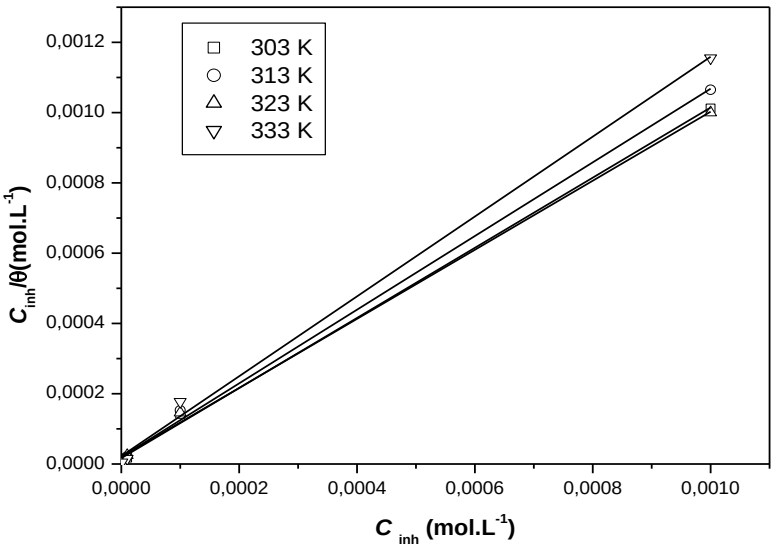


Figure 8: Langmuir's isotherm adsorption model of 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione on the mild steel surface in 1M H_3PO_4 at different temperatures.

Thermodynamic adsorption parameters are: the free energy of adsorption ($\Delta G°_{ads}$), standard adsorption enthalpy ($\Delta H°_{ads}$) and the adsorption entropy $\Delta S°_{ads}$, can be calculated based estimated values of adsorption isotherms at different temperatures. The adsorption constant, k_{ads}, is related to the standard free energy of adsorption, $\Delta G°_{ads}$, with the following equation [48]:

$$K_{ads} = \frac{1}{C_{H_2O}} exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \qquad (13)$$

Where R is the universal gas constant, T is the thermodynamic temperature and C_{H2O} is the concentration of water in the solution in mol / l. The data is recovered in the following Table 8.

In this process, the covalent bond is formed by load sharing or transfer from the inhibitory molecules of the metal surface [49,50]. Theoretically if the absolute value of the $\Delta G°_{ads}$ is in the range of -20 kJ mol-1 or lower adsorption is considered physisorption, when the absolute value of $\Delta G°_{ads}$ is of the order of - 40 kJ mol-1 or higher, adsorption may be regarded as chemisorption. In the temperature range studied the values of $\Delta G°_{ads}$ are in the range that, go from -40.5 to -37,70 kJ mol-1, which automatically reflects that the adsorption mechanism of 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione of mild steel in the 1M H_3PO_4 solution corresponds to a chemisorption (table 8).

Besides the regular temperature dependence is very clear from the obtained values of $\Delta G°_{ads}$ reflects a good correlation between thermodynamic parameters.

Table 8: Thermodynamic parameters at different temperatures on the mild steel in 1M solution of H_3PO_4 for the adsorption of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione

T (K)	K_{ads} (mol/L)	$\Delta G°_{ads}$ (kJ.mol^{-1})
303	167546,2	-40,5
313	93586,64	-40,2
323	36508,58	-39,13
333	13279,43	-37,70

$\Delta G°_{ads}$ is relatively related to the standard enthalpy and entropy of the adsorption process, $\boldsymbol{\Delta H°_{ads}}$ and $\boldsymbol{\Delta S°_{ads}}$ represented by means of the equation. (14):

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\,\Delta S^{\circ}_{ads} \qquad (14)$$

A plot of $\Delta G°_{ads}$ vs. T gives straight lines (Figure 9) with the slope equal to - $\Delta S°_{ads}$, and the value of $\Delta H°_{ads}$ can be calculated from intercept (Table 9).

Table 9: Thermodynamic parameters on mild steel in 1M H_3PO_4 solution at different temperatures for the adsorption of Indo 1.

T (K)	$\boldsymbol{\Delta H°_{ads}}$ (KJ.mol^{-1})	$\boldsymbol{\Delta S°_{ads}}$ (J.mol^{-1}.K^{-1})	$\boldsymbol{\Delta H°_{ads}}$ (KJ.mol^{-1})	$\boldsymbol{\Delta S°_{ads}}$ (J.mol^{-1}.K^{-1})	$\boldsymbol{\Delta H°_{ads}}$ (KJ.mol^{-1})	$\boldsymbol{\Delta S°_{ads}}$ (J.mol^{-1}.K^{-1})
	Method 1		Method 2		Method 3	
303	-69.49	-94	-71.39	-89.04	-69	-94.05
313						-92.01
323						-92.47
333						-93.99

And the standard enthalpy of adsorption ($\boldsymbol{\Delta H°_{ads}}$) can be calculated according to the Van't Hoff equation (Method2) [51]:

$$Ln\,K_{ads} = -\frac{\Delta H^{\circ}_{ads}}{RT} + constant \qquad (15)$$

To optimize the thermodynamic parameters ($\boldsymbol{\Delta H°_{ads}}$ and $\boldsymbol{\Delta G^{\circ}_{ads}}$) using the Gibbs-Helmholtz equation (Method 3), which is as follows [52, 53]:

$$\left[\frac{\partial(\Delta G^{\circ}_{ads}/T)}{\partial T}\right]_p = -\frac{\Delta H^{\circ}_{ads}}{T^2} \qquad (16)$$

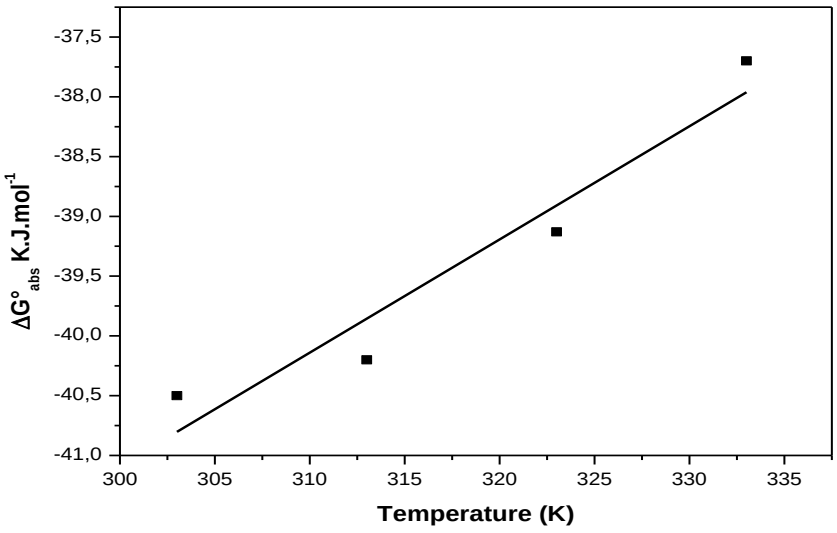


Figure 9: Variation of ΔG_{ads} versus T on mild steel in 1M H_3PO_4 containing 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione

1.2. Surface analysis by scanning electron microscopy (SEM)

The observation of each sample by the scanning electron microscope was carried out to observe the morphology [54] of mild steel plates before and after the immersion in phosphoric acid in the absence and presence of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione are shown in figures: fig10(a) Metallic surface after being polished, fig.10(b) metallic surface after 6 h immersion in 1M H_3PO_4 and fig.10(c) metallic surface after 6 h immersion in 1M H_3PO_4 with 10^{-3} M of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione.

More information on the inhibition of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione on mild steel was provided by electron microscopy by Surface Analysis (SEM) on the surface of the mild steel.

In absence of the inhibitor the case of figure 10(b) we can be observed on the surface of the mild steel, it has been strongly attacked by phosphoric acid with evidence of the formation of the well, while the presence of 5-chloro-1-(2-(dimethylamino) ethyl) indoline-2,3-dione figure10 (c) reduced the level of the attack on the metal surface which involves the remarkable protective efficacy of the inhibitor in phosphoric acid.

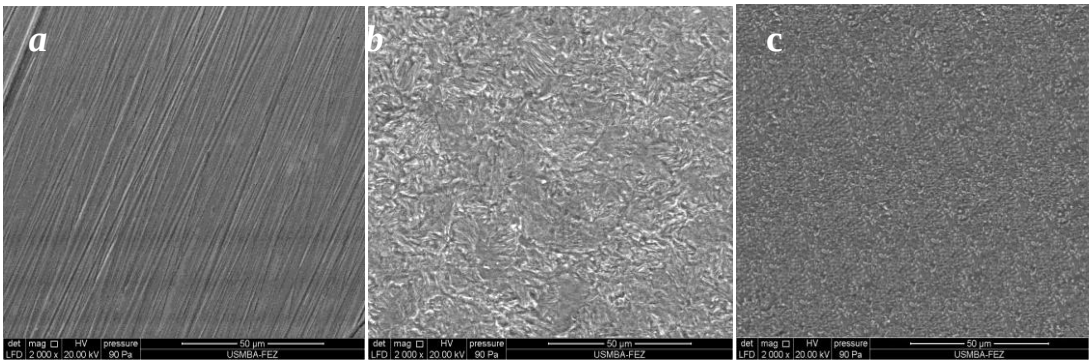


Figure 10: SEM micrographs of the mild steel surface in the absence and presence of 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione 10^{-3} M after 6 hours of 'immersion in 1M H_3PO_4

Conclusion

The new 5-Chloroisatin derivative shows excellent inhibition properties for the corrosion of mild steel in 1 M H_3PO_4 at 303 K, and the inhibition efficiency, $\eta_{WL}(\%)$, increases with increase of the Indo 1 concentration but, It decreases with temperature (303-333 K). The Tafel polarization results indicated that 5-chloro-1- (2- (dimethylamino) ethyl) indoline-2,3-dione can be classified as mixed inhibitor..

The Indo 1 inhibits the corrosion process by getting adsorbed on steel surface following a Langmuir isotherm model.

In addition, the calculated values of ΔG°_{ads} and ΔH°_{ads} show that the adsorption mechanism of 5-chloro-1- (2-(dimethylamino) ethyl) indoline-2,3-dione on a steel surface in 1M H_3PO_4 solution is mainly chemisorption.

The inhibition efficiencies determined by weight loss, potentiodynamic polarization, EIS techniques and Micrographs SEM are in reasonably good agreement.

References

1. Abed Y., Hammouti B., Touhami F., Aouniti A., Kertit S., Mansri A., Elkacemi K., *Bull. Electrochem.*, 17 (2001) 105.
2. Patel A.S., Panchal V.A., Trivedi P.T., and Shah N.K., *Portugaliae. Electrochim. Acta., 30(3)*(2012) 163-175
3. Belfilali I., Chetouani A., Hammouti B., Aouniti A., Louhibi S., Al-Deyab SS., *Int. J. Electrochim. Sc., 7 (*2012) 3997.
4. Zarrok H., Zarrouk A., Salghi R., Oudda H., Hammouti B., Ebn Touhami M., Bouachrine M., and Boukhris S., *Portugaliae*. *Electrochimi. Acta.*, 30 (2012) 405.
5. Bentiss F., Lebrini M., Chihib N.E., Abdalah M., Jama C., Lagrenee M., Al-Deyab S.S., *Int. J. Electrochim. Sc.*, 7(2012), 3947.
6. Benabdellah M., Hammouti B., Warthan A., Al-Deyab S.S., Jama C., Lagrenee M., Bentiss F., *Int. J. Electrochim. Sc.*, 7(2012) 3489.
7. Suraj B., Ade, Deshpande M.N., Kolhatkar D.G., *J. Chem. Pharm. Res.*, 4 (2012),1033.
8. Shanmugam R., Thangavelu C., Annamalai G., *J. Chemi. Pharm. Res.*, 4 (2012), 4836.
9. Aljohani T.A., Hayden B.E., Anastasopoulos A., *Portugaliae*. *Electrochim. Acta.*, 76 (2012), 389.
10. Zhang, Q.B., Hua, Y.X., *Electrochim. Acta.*, 54 (2009) 1881.
11. Popova A., Sokolova E., Raicheva S., Christov M., *Corros. Sci*., 45 (2003) 33.
12. Noor E.A., Corros. Sci., 47 (2005) 33.
13. Mansri A., Bouras B., Hammouti B., Warad I., Chetouani A., *Res. Chem. Intermed*., 10 (2012) 1007.
14. Marei M., Elajaily, Fatma I. Abdullah, Ramadan A. Akasha, Mohamed S. Suliman, *J. Chem. Pharm. Res*, 5 (2013), 1144.
15. Bouklah M., Attayibat A., Kertit S., Ramdani A., Hammouti B., *Appl. Surf. Sc.*, 242 (2005), 399.
16. Eddy N.O., Ameh P.O., Gwarzo M.Y., Okop I.J., Dodo S.N., *Portugaliae*. *Electrochim. Acta.*, 31 (2013), 79.
17. Joseph B., Prajila M., Joseph A., *J. Dispersion. Sc. Technol., 33*(2012) 739.

18. Kabanda M.M., Murulana L.C., Ozcan M., Karadag F., Dehri I., Obot I.B., Ebenso E.E., *Int. J. Electrochem. Sci.*, 7 (2012), 5035.
19. Bouhrira K., Ouahiba F., Zerouali D., Hammouti B., Zertoubi M., Benchat N., *E-J. Chem.*, 7(2010) S35-S42.
20. Samide A. *J. Env. Sci. Healt., 48 (*2013) 159.
21. Avramovic Z.A, Antonijevic M.M, Petrovic NI. *Metalurgia. Int.*, 17(2012) 59.
22. Herrag L., Bouklah M., Patel N.S., Mistry B.M., Hammouti B., Elkadiri S., Bouachrine M., *Res. Chem. Intermediates.*, 38 (2012) 1669.
23. Tourabi M., Nohair K., Nyassi A., Hammouti B., Jama C., Bentiss F., *J. Mater. Environ. Sci.*, 5 (2014) *1133.*
24. Tribak, Z., Kharbach, Y., Haoudi A., Skalli M.K., Kandri Rodi Y., El Azzouzi M., Aouniti A., Hammouti B., Senhaji, O. *J. Mater. Environ. Sci.* 7 (2016) *2006.*
25. Zarrok H., Zarrouk A., Hammouti B., Salghi R., Jama C., Bentiss F., *Corros. Sci.* 64 (2012) 243.
26. Lebrini M., Bentiss F., Chihib N., Jama C., Hornez J. P., Lagrenée M., *Corros. Sci.* 50 (2008) 2914.
27. Bouklah M., Benchat N., Aouniti A., Hammouti B., Benkaddour M., Lagrenée M., Vezin H., Bentiss F., *Prog. Org. Coat.* 51 (2004) 118.
28. Bentiss F., Traisnel M., Lagrenee M., *Corros. Sci*., 42 (2000) 127.
29. Umoren S.A., Ebenso E.E., *Mater. Chem. Phys*., 106 (2007) 387.
30. Murlidharan S., Phani K.L.N., Pitchumani S., RavichandranS., *J. Electrochem. Soc.*, 142 (1995) 1478.
31. Bentiss F., Lagrenée M., Traisnel M., Mernari B., Elattari H., *J. Heterocyclic Chem.*, 36 (1999) 149.
32. Boumhara K., Bentiss F., Tabyaoui M., Costa J., Desjobert J.M., Bellaouchou A., Guenbour A., Hammouti B., Al-Deyab S. S., *Inter. J. Electrochem. Sci.*, 9 (2014) 1187.
33. Singh A. K., Quraishi M. A., *Corros. Sci.*, 52 (2010) 1529.
34. Bockris J. O.M., Reddy, A. K. N., Modern Electrochem, Plenum Press, New York., 2 (1977) 1267.
35. Umoren S.A., Eduok U.M., Oguzie E.E., *Portugaliae. Electrochim. Acta*., 26 (2008) 533.
36. Bouanis F.Z., Jama C., Traisnel M., Bentiss F., *Corros. Sci*., 52 (2010) 3180.
37. Belkaid S., Tebbji K., Mansri A., Chetouani A., *Res. Chem. Intermed.*, 38 (2012) 2309.
38. Gesmundo F., Viani F., *Mater. Chem. Phys*., 20 (1988) 513.
39. Doner A., Solmaz R., Ozcan M., Kardas G., *Corros. Sci*., 53 (2011) 2902.
40. Bentiss F., Lagrenee M., Traisnel M., Mernari B., Elattari H., *J. Appl. Electrochem*., 29 (1999) 1073.
41. Bouanis F.Z., Jama C., Traisnel M., Bentiss F., *Corros. Sci*., 52 (2010) 3180.
42. Bouklah M., Attayibat A., Kertit S., Ramdani A., Hammouti B., *Appl. Surf. Sci*., 242 (2005) 399.
43. Doner A., Kardas G., *Corros. Sci*., 53 (2011) 4223.
44. Fouda A.S., Al-Sarawy A.A., El-Katori E.E., *Desalination*, 201 (2006) 1.
45. Bouklah M., Benchat, N., Hammouti, B., Aouniti, A., Kertit, S., *Mater. Lett.* 60 (2006) 1901.
46. Dada A.O., Olalekan A.P., Olatunya A.M., Dada O., *IOSR J. App. Chem.*, 3 (2012) 38.
47. Voudrias E., Fytianos F., Bozani E., *Global Nest, The Int. J*., 4 (2002) 75
49. El Azhar M., Traisnel M., Mernari B., Gengembre L., Bentiss F., Lagrenée M., *App. Surf. Sci.*, 185 (2010) 197.
49. Donahue F. M., Nobe, K., *J. Electrochem. Soc.*, 112 (1965) 886.
50. Kamis E., Bellucci F., Latanision R. M., El-Ashry E. S. H. *Corrosion* 47 (1991) 677.
51. Bouklah M., Hammouti B., Lagrenée M., Bentiss F., *Corros. Sci.* 48 (2006) 2831.
52. Kharbach Y., Haoudi A., Skalli M.K., Kandri Rodi Y., Aouniti A., Hammouti B., Senhaji, O., Zarrouk A., *J. Mater. Environ. Sci.*, 6 (2015) 2906.
53. El Azhar M., Traisnel M., Mernari B., Gengembre L., Bentiss F., Lagrenée M., *App. Surf. Sci.* 185 (2010) 197.
54. Olusegun S.J., Oluwasina O.O., Alaneme1 K.K., Olubambi P.A., *J. Mater. Environ. Sci.*, 7 (2016) 1086.

(2017) ; http://www.jmaterenvironsci.com