Available online at www.derpharmachemica.com

Scholars Research Library

Der Pharma Chemica, 2015, 7(6):64-70
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Anti-corrosive properties of *Nigella sativa* L extract on mild steel in molar HCl solution

El Mounsi[1*], H. Elmsellem[2*], A. Aouniti[2], H. Bendaha[1], M. Mimouni[1], T. Ben Hadda[1], H. Steli[3], M. Elazzouzi[2], Y. EL Ouadi[1] and B. Hammouti[1]

[1]Laboratoire de la chimie des matériaux (LCM), Faculté des Sciences, Université Mohammed Premier, Oujda, Morocco
[2]Laboratoire de Chimie Appliquée et Environnement (LCAE-URAC18), Faculté des Sciences, Université Mohammed Premier, Oujda, Morocco
[3]Laboratoire mécanique & énergétique, Faculté des Sciences, Université Mohammed Premier, Oujda, Morocco

---

ABSTRACT

*Corrosion inhibition effect of Nigella Sativa L extract (**SE NS**) on corrosion of mild steel in 1 M HCl solution was investigated using weight loss measurements, electrochemical polarization and EIS methods. Results obtained reveal that Nigella Sativa L extract acts as a mixed inhibitor without modifying the hydrogen reduction mechanism. The inhibition efficiency increases with increased Nigella Sativa L extract concentration to attain a maximum value of 99% at 2 g/L. The adsorption of natural product on the steel surface was found obey to Langmuir's adsorption isotherm.*

Keywords: Mild steel, Nigella Sativa L, Extract, HCl, Corrosion, Green inhibitor

---

INTRODUCTION

In recent days, studies on steel corrosion phenomena have become an academic and industrial topic, especially in acid environments [1-3]. Currently, research in corrosion is focused on green corrosion inhibitors that show good inhibition efficiency with low risk of environmental pollution [4]. The term green inhibitor'or ecofriendly inhibitor'refers to substances that are biocompatible such as plant extracts since they are of biological origin [5]. Thus natural products (derived from plant materials) are being studied for their corrosion inhibition potential as they are showing good corrosion protection and are more environment friendly [6–10]. We have successfully reported many green corrosion inhibitors for metalsin acid media from various plant sources like mangrove tannins [11], Kopsia singapurensis [12], Xylopia ferruginea [13] and catechins [14].

Currently, research in corrosion is focused on ‘‘green corrosion inhibitors’’, that show good inhibition efficiency with low risk of environmental pollution [15].

Thus natural products (derived from plant materials) are being studied for their corrosion inhibition potential as they are showing good corrosion protection and are more environment friendly [16, 17].

Nigella Sativa L, also known under the names: Cumin Black Habbat El Baraka, Al Haba Souda Sounidj English Black Seed is an annual, herbaceous aillant 30-60 cm high. The pinnate leaves, divided into narrow lobes are lanceolate to linear and have nectar tabs, the lower leaves are small and petaloid and higher are long [18, 19]. The plant is hermaphrodite autonomous reproduction whose fruit is a capsule formed from March to June carpels welded together to the base of persistent styles. [19] Each capsule contains multiple whitish, triangular seeds mature, they open and exposure of seeds to air makes black seeds are ovoid 2 to 3.5 mm are 3-4 angles with a top face and finely granular crosslinked [19]. It is used as a popular culinary herb and spice. In medicine, it is used as a natural remedy for a number of diseases as like anti-cancer, anti-fungal, anti-bacterial, anti-asthm, anti-cough, anti-hypertension, anti-bronchitis, anti-diabetes, against headaches, eczema, fever, inflammation, and other diseases [20].

The encouraging results obtained of of Nigella Sativa L extract as inhibitor of corrosion of copper and steel in aqueous media [21-23] incited us to examine its effect for mild steel in 1M HCl solution using gravimetric method and electrochemical techniques such as linear polarization and impedance spectroscopy (EIS).

MATERIALS AND METHODS

1. Preparing sample of Nigella Sativa L extract:

Nigella sativa L. seeds samples were purchased from a local market at Oujda (Morocco). Harvesting of Nigella sativa seeds was performed in Saudi Arabia in the month of October 2010 which is characterized by its warm, dry climate in this season. After collection, the seeds are stored in the dark at room temperature until use.

The seeds of Nigella sativa previously cleaned and crushed (m_{seeds} = 50 g). The Soxhlet extraction is started at first with hexane (fisrt extract **SH NS**) and then by a mixture of water / methanol (20:80 v / v), the methanol was evaporated in rota evaporator (second extract **SE NS**).

The aggressive solutions of 1.0 M HCl were prepared by dilution of an analytical grade 37% HCl with double distilled water. The concentration range of green inhibitor employed was 0.5– 5 (g/l).

The chemical composition of the working electrode, a mild steel electrode, is given in Table 1. The steel electrode was mounted in polyester. It was mechanically polished with 400, 600, 800, 1200 emery paper, washed in acetone and bi-distilled water and put into the cell.

Table 1 Chemical composition of steel specimens

Elements	**Fe**	**C**	**Si**	**P**	**Mn**	**S**	**Al**
Mass %	99.21	0.21	0.38	0.08	0.05	0.05	0.01

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltamaster soft-ware. This potentiostat is connected to a cell with three electrode thermostats with double wall. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. Anodic and cathodic potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from −800 mV to −200 mV at 308 K. The solution test is there after de-aerated by bubbling nitrogen

The weight loss of steel specimens of size 1.5× 1.5 × 0.05 cm^3in 1 M HCl with and without the addition of different concentrations of inhibitors was determined after immersion in acid solution over 6 h at 308K.

RESULTS AND DISCUSSION

1. Weight loss measurements:

Values of the inhibition efficiency and corrosion rate obtained from the weight loss measurements of mild steel for different concentrations of **SE NS**in 1 M HCl at 35 °C after 6 h of immersion are given in table 2.

Table 2: Corrosion parameters for mild steel in 1 M HCl in absence and presence of different concentrations of SE NS obtained from weight loss measurements at 35° C for 6h

Inhibitors	Concentration (g/l)	V ($mg.cm^{-2} h^{-1}$)	Ew (%)
1M HCl	-	0.82	---
Nigella Sativa L extract (**SE NS**)	0,5	0.0821	90
	1	0.0213	97
	2	0.0091	99
	3	0.0001	**100**
	5	0	**100**

It is clear that the corrosion rate decreases with the increase of concentration of the tested inhibitor and in turn the inhibition efficiency (Ew%) increases to attain 99% (at 2g/l). From weight loss measurement, we can conclude that **SE NS** is the excellent inhibitor.

1.1. Adsorption isotherm

It is well established that the first step in corrosion inhibition of metals and alloys is the adsorption of organic inhibitor molecules at the metal/solution interface and that the adsorption depends on the molecule's chemical composition, the temperature and the electrochemical potential at the metal/solution interface. In fact, the solvent water molecules could also adsorb at metal/solution interface. So the adsorption of organic inhibitor molecules from the aqueous solution can be regarded as a quasi-substitution process between the organic compounds in the aqueous phase [Org(sol)] and water molecules at the electrode surface [$H_2O_{(ads)}$].

$$\text{Org(sol)} + n\text{(H2O)(ads)} \rightleftharpoons \text{Org(ads)} + n\text{H2O(sol)} \quad \mathbf{(5)}$$

Where: Org(sol) and Org(ads) are the organic specie dissolved in the aqueous solution and adsorbed onto the metallic surface, respectively, H_2O(ads) is the water molecule adsorbed on the metallic surface and n is the size ratio representing the number of water molecules replaced by one organic adsorbate. Basic information on the adsorption of inhibitors on the metal surface can be provided by adsorption isotherm. In order to obtain the isotherm, the fractional surface coverage values (θ) as a function of inhibitor concentration must be obtained.

Surface can be provided by adsorption isotherm. Several isotherms including Frumkin, Langmuir, Temkin isotherms are employed to fit the experimental data. It is found that the adsorption of studied inhibitors on steel surface obeys the Langmuir adsorption isotherm equation [24, 25]:

$$\frac{C}{\Theta} = \frac{1}{k} + c \qquad (6)$$

where: C is the concentration of inhibitor, K the adsorption equilibrium constant, and ϴ is the surface coverage and expressed by the ration E%/100.

The surface coverage values θ were tested graphically for fitting a suitable adsorption isotherm. The plot of C/θ versus C yielded a straight line with a slope 1.04. This was observed clearly proving that the adsorption of the citrus aurantium oil from acid solutions on the mild steel surface obey the Langmuir adsorption isotherm (Fig 1).

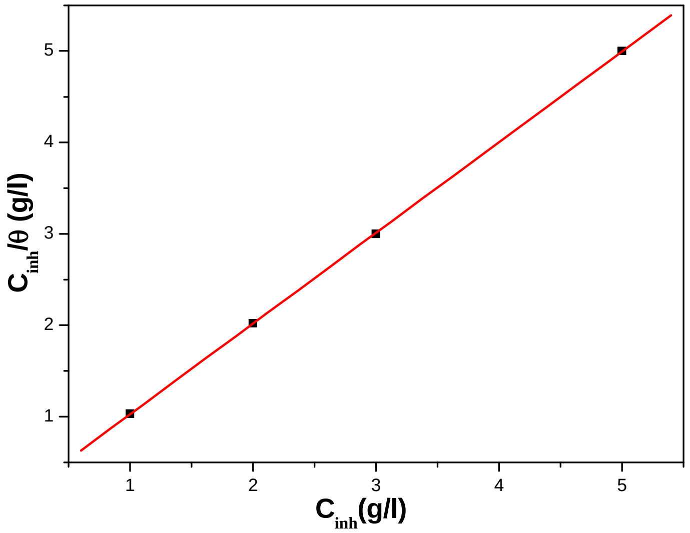

Fig1: Langmuir isotherm of steel in the 1M HCl in presence of SE NS at calculated by gravimetric method

Plotting of C vs. C/θ results in a linear correlation, shown in Fig. 1. The standard free energy of adsorption ($\Delta G°_{ads}$) was estimated by the following equation:

$$\text{K} = \frac{1}{55.5}\exp\left(\frac{\Delta G^0 ads}{RT}\right) \qquad (7)$$

Where 55.5 is the molar concentration of water in the solution expressed in molarity units (M) [26].

As shown in Table 3, the negative $\Delta G°_{ads}$ value (-36.65) obtained indicates that the adsorption process of SE NS to the surface is spontaneous and the interaction of the adsorbed layer with the steel surface is stable [27]. Meanwhile, it could be deduced that inhibitor **SE NS** adopts both electrostatic-adsorption and chemisorptions on the mild steel surface in 1 M HCl with the latter being privileged [28, 29].

Table 3 The calculated value of K_{ads} and $\Delta G°_{ads}$ for mild steel in 1 M HCl containing SE NS at 35 °C

Inhibitor	R^2	Slope	K (M^{-1})	ΔG^0_{ads}(Kj.mol^{-1})
SE NS	0.999	1.04	18.26 10^3	-36.65

1.2. Potentiodynamic polarization curves:

Potentiodynamic polarisation curves of steel in 1M HCl in the presence and absence of the tested inhibitor (**SE NS**) is shown in Fig. 2. The corrosion parameters including corrosion current densities (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (βc), anodic Tafel slop (βa) and inhibition efficiency (EI %) are listed in Table 4.

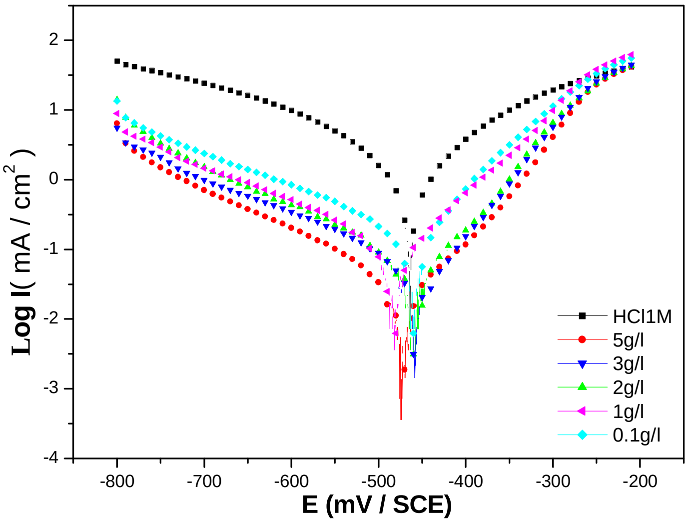

Fig 2: Tafel plot of mild steel with different concentrations of SE NS in 1M HCl solution

The examination of Fig. 2 shows that the addition of SE NS affects both anodic dissolution of steel and cathodic reduction reactions indicating that the compound could be classified as mixed-type inhibitor. The values of corrosion potential (E_{corr}) remain almost constant upon the addition of inhibitor concentration. We also remark that the cathodic current–potential curves give rise to parallel Tafel lines, which indicate that hydrogen evolution reaction is activation controlled and that the addition of the SE NS does not affected the mechanism of this process (Fig.2) [30].

Table 4: Tafel polarization parameters obtained at different concentrations of SE NS

Inhibitors	Concentration (g/l)	-E_{corr} (mV/SCE)	I_{corr} (μA/cm^2)	-βc	βa	E_p (%)
1M HCl	-	464	1386	164	135	--
Nigella Sativa L extract (SE NS)	**0.5**	460	162	196	85	88
	1	480	83	177	90	94
	2	459	18	141	64	99
	3	460	17	130	61	99
	5	473	16	149	81	99

Inspections of the electrochemical parameter values given in Table. 4, reveal that, inhibition efficiency increases with an increase of the concentration of inhibitor. The maximum inhibition efficiency observed at higher inhibitor concentration indicates that more inhibitor molecules are adsorbed on the metal surface. These compounds are then acting as adsorption inhibitors. We note that the corrosion current density were more significantly reduced in the presence of SE NS. The best efficiencies obtained in the presence of SE NS is 99% at 2g/L.

1.3. Electrochemical impedance spectroscopy

EIS experiments were undertaken mainly, as an independent and complementary tool to determine corrosion rates in a rapid and accurate way. Additionally, EIS allowed to gain insight into kinetics of electrochemical processes and the inhibition mode which occur at the mild steel/1 M HCl interface modified by the presence of SE NS. Fig. 3

shows impedance spectra as Nyquist plots that were obtained for mild steel in the absence and presence of different concentrations of SE NS. Nyquist plots typically show a single depressed capacitive semicircle for the blank solution and for the inhibitor-containing solutions, over the studied frequency range.

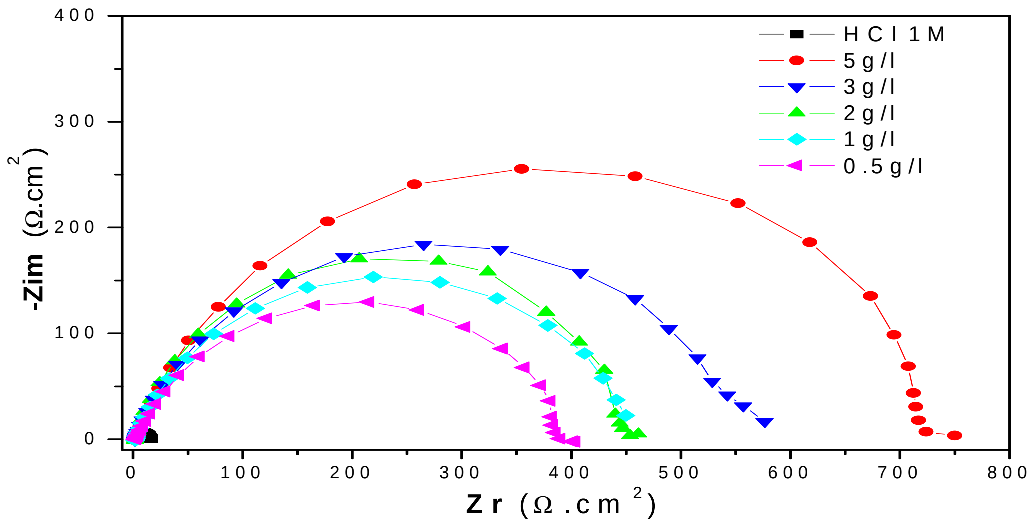

Fig 3:Nyquist plot at different concentrations of SE NS in 1M HCl solution

Table 4: Impedance parameters for mild steel in 1M HCl in the absence and presence of different concentrations of SE NS

Inhibitor	Concentration (g/l)	R_t ($\Omega.cm^2$)	f_{max} (Htz)	C_{dl} ($\mu f/cm^2$)	E (%)
1M HCl	-	14.57	54.64	200	--
Nigella Sativa L extract (SE NS)	**0.5**	382	25.96	35.23	96.19
	1	445	10.16	34.58	96.73
	2	460	10.01	28.42	96.83
	3	560	10.01	21.55	97.40
	5	738	10.01	16.06	98.03

From careful inspection of impedance parameters (Table 4), it was revealed that R_t values increased with the extracts SE NS concentration while C_{dl} values decreased. An increase in charge transfer resistance values could be ascribed to the molecular adsorption of organic moieties of the extracts at metal–acid interface, which effectively blocked the movement of charges across the interface and hence corrosion inhibition acknowledged. This fact was well documented by decrease in C_{dl} values, which could be further explained with the help of equation given below [31]:

$$C_{dl}=(\varepsilon_0\varepsilon/t).A \qquad \textbf{(8)}$$

From Eq. (8) it is obvious that double layer capacitance varies directly with dielectric constant of locally formed film ε, dielectric constant of free space ε_0 and effective exposure area A, while changes inversely with thickness of film formed at the interface t. C_{dl} values decreased with increase in inhibitor concentration, suggesting that either thickness of protective layer increased, or local dielectric constant of film decreased, or both occurred simultaneously.

The results obtained from the polarization technique in acidic solution were in good agreement with those obtained from the electrochemical impedance spectroscopy (EIS) with a small variation.

The EIS data were analyzed by fitting to the equivalent circuit model shown in Fig. 4 which fits well with the experimental results. The circuits comprise a solution resistance Rs, in series with the circuit. CPE is the constant phase element. The Nyquist plots were not perfect semicircles as expected from the theory of EIS.
The Nyquist plots obtained in the real system represent a general behavior where the double layer on the interface of metal/solution does not behave as a real capacitor.

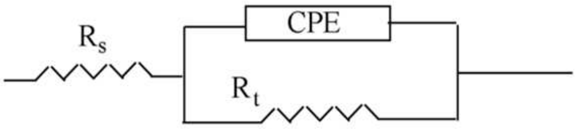

Fig.4.Electrochemical equivalent circuit used in fitting impedance data for metal-electrolyte interface of 1M HCl+inhibitor

CONCLUSION

From the results obtained, the following points were concluded:

✓ Nigella Sativa L extract successfully retarded mild steel corrosion in HCl solutions, and the efficiency of inhibition increases with increased inhibitor concentration.

✓ Tafel polarization curves advocated that SE NS restricted mild steel corrosion via reducing mild steel dissolution, which the impedance study suggested was occurred through molecular adsorption of organic moieties of the extracts on steel surface.

✓ Thus, it is clear from the study that Nigella Sativa L extract can be used as an effective solution of steel corrosion in acid media.

REFERENCES

[1] H. Elmsellem, H. Nacer, F. Halaimia, A. Aouniti, I. Lakehal, A .Chetouani, S. S. Al-Deyab, I. Warad, R. Touzani, B. Hammouti. *Int. J. Electrochem. Sci.*, **2014,** 9 ; 5328 – 5351
[2] L. Afia, R. Salghi, El. Bazzi, L. Bazzi, M. Errami, O. Jbara, S. S. Al-Deyab, B. Hammouti. *Int. J. Electrochem. Sci.*, **2011**, 6, 5918 – 5939
[3] H. Elmsellem, M. H.Youssouf, A. Aouniti, T. Ben Hadda, A. Chetouani, B. Hammouti. *Russian Journal of Applied Chemistry*, **2014**, 87(6), 744−753
[4] M.A. Amin, Hammouti B., Aouniti A., Ramli Y., Azougagh M., Essassi E.M., Bouachrine M. *J. Mater. Environ. Sci.*, **2010,** 1, 1-8
[5] D. Ben Hmamou, R. Salghi, A. Zarrouk, M. Messali, H. Zarrok, M. Errami, B. Hammouti, L. Bazzi, A. Chakir, *Der Pharma Chemica*, **2012,** 4(4), 1496–1505.
[6] A.Y. El-Etre, M. Abdallah, Z.E. El-Tantawy, *Corros. Sci.* **2005**, 47, 385–395.
[7] O.K. Abiola, A.O. James, *Corros. Sci.* **2010**, 47, 661–664.
[8] S. Deng, X. Li, *Corros. Sci.* **2012**, 55, 407–415.
[9] S. Banerjee, V. Shrivatsava, M.M. Singh, *Corros. Sci.* **2012**, 59, 35–41.
[10] S. Garai, S. Garai, P. Jaisankar, J.K. Singh, A. Elango, *Corros. Sci.* **2012**, 60, 193–204.
[11] A.A. Rahim, E. Rocca, J. Steinmetz, M.J. Kassim, *Corros. Sci.* **2008**, 50, 1546–1550.
[12] P.B. Raja, A.A. Rahim, H. Osman, K. Awang, *Acta Phys. Chim. Sin.* **2010**, 26, 2171–2176.
[13] P.B. Raja, A.A. Rahim, H. Osman, K. Awang, *Int. J. Miner. Metall. Mater.* **2011**, 18, 413–418.
[14] S. Nofrizal, A.A. Rahim, B. Saad, P.B. Raja, A.M. Shah, S. Yahya, *Metall. Mater. Trans. A*, **2011**, 43A 1382–1393.
[15] M.A. Amin, S.S. Abd El-Rehim, E.E.F. El-Sherbini, R.S. Bayoumi, *Electrochim. Acta* **2007**, 52, 3588–3600.
[16] M. Ramdani, H. Elmsellem, N. Elkhiati, B. Haloui, A. Aouniti, M. Ramdani, Z. Ghazi, A. Chetouani and B. Hammouti. *Der Pharma Chemica*, **2015**, 7(2), 67-76
[17] F. Aouinti, H. Elmsellem, A. Bachiri, M-L. Fauconnier, A. Chetouani, C. belbachir, A. Aouniti, B. Hammouti, *Journal of Chemical and Pharmaceutical Research*, **2014**, 6(7), 10-23
[18] Bonnier, G. « La grande flore en couleur ». Ed Belin, Paris. Tome 1, **1990**, pp : 17.
[19] Ghedira, K. La nigelle cultivée : Nigella Sativa L. (Ranunculaceae). *Phytothérapie*,, **2006**,4, 1-7.
[20] B.H. Ali, G. Blunden, Pharmacological and toxicological properties of Nigella sativa, *Phytother. Res.* **2003**, *17*, 299–305.
[21] A.M. Abdel-Gaber , B.A. Abd-El-Nabey, I.M. Sidahmed, A.M. El-Zayady, M. Saadawy. *Corros. Sci.* **2006**, 48, 2765.
[22] M. Emad, M. Al-Rasheedi, *J. Mat. Envir. Sci.*, **2015,** 6 (1), 201-206
[23] Y.F. Barakat, A.M. Hassan, A.M. Baraka, *Materialwissenschaft und Werkstofftechnik*, **1998**, 29 365-370
[24] M. Bouklah, M. Kaddouri, Y. Toubi, B. Hammouti, S. Radi, E. E. Ebenso *Int. J. Electrochem. Sci.*, **2013**, 8, 7437 – 7454
[25] H. Elmsellem, A. Aouniti, M. Khoutoul, A. Chetouani, B. Hammouti, N. Benchat, R.Touzani, M. Elazzouzi. *Journal of Chemical and Pharmaceutical Research*, **2014**, 6(4), 1216-1224
[26] M.A. Amin, S.S. Abd El Rehima, H.T.M. Abdel-Fatah, *Corros. Sci.* **2009**, 51, 882–894.
[27] M. Lebrini, M. Lagrenée, H. Vezin, M. Traisnel, F. Bentiss, *Corros. Sci.* **2007**, 49, 2254–2269.

[28] M. Scendo, *Corros. Sci.* **2007**, 49, 373–390.
[29] S.A. Abd El Maksoud, *Corros. Sci.* **2002**, 44, 803–813.
[30] L. Bammou, M. Mihit, R. Salgh, A. Bouyanzer, S.S. Al-Deyab, L. Bazzi, B. Hammouti. *Int. J. Electrochem.* Sci., **2011**, 6, 1454.
[31] B. Ateya, B.E. El-Anadouli, F.M. El-Nizamy, *Corros. Sci.* **1984**, 24, 509–515.