STUDY ON THE PERFORMANCE OF GREEN CORROSION INHIBITOR IN PROTECTION OF API5LX60 IN SEAWATER ENVIRONMENT

Nour El Houda SOBHI,[a,c,*] Amel BOUKHOUIETE,[b] Malika FOUDIA[c] and Sofiane BENIDIR[d]

[a] Department of chemistry, Water and Environment Science and Technology Laboratory, Mohamed Cherif Messaadia University, Souk-Ahras, Algeria, n.sobhi@univ-soukahras.dz
[b] Department of chemistry, University Badji-Mokhtar, Annaba, Algeria, amelboukhouiete@yahoo.fr
[c] Laboratory of energy and electrochemistry of solid (LEES), University Ferhat Abbas 1, Setif, Algeria, foudiam@yahoo.fr
[d] Laboratory of Electrochemistry and Materials (LEM), Processes Engineering Dept., Faculty of Technology, University Ferhat Abbas-Setif 1, Setif, Algeria, sofianebenidir@yahoo.fr

The corrosion inhibition of metals in seawater can be achieved by the addition of inhibitors to the system that prevent corrosion from taking place on the metal surface. The effect of ascorbic acid on carbone steel corrosion in seawater were investigated by means of different techniques: gravimetric method, electrochemical polarization and electrochemical impedance spectroscopy and the scanning electron microscopy (SEM). The results obtained show that the acid ascorbic effectively inhibits the corrosion of steel X60. The optimal inhibitory efficiency is obtained at a concentration of 0.05 g/L of the inhibitor, with a maximum value of 77%. This inhibitor presents a mixed inhibition character. SEM studies confirm the absence of the deterioration products on the surface of the specimens.

INTRODUCTION

Corrosion is one of the major contributing factors of engineering structural damage in aquatic ecosystems, caused by chemical or electrochemical interactions between metals and the marine environment. The presence of microorganisms and bacteria in chemical solvents increases corrosion[1–3] for the majority of metallic items utilized in the marine sector. The action of these may damage their mechanical, physical, and chemical properties.

Organisms that adhere themselves on the surfaces of metallic structures. Microorganism growth on metal particles may alter the electrochemical response at the biofilm/metal contact. This mechanism has the potential to either suppress or accelerate corrosion.[4,5] There are numerous strategies available for avoiding metal corrosion to avoid the dangers connected with corrosion. For example, utilizing antirust solutions and corrosion inhibitors to provide barrier protection, galvanization, and cathodic protection, coating the surfaces or by adding some materials

* Corresponding author: n.sobhi@univ-soukahras.dz

such as inorganic or organic compounds to play as corrosion inhibitors, and cathodic protection.[6-16]

Ascorbic acid is a typical monacid found in animals and plants that are non-toxic, inexpensive, and ecologically acceptable.[17,18] Ascorbic acid is made up of a five-membered lactone ring and four hydroxyl groups, one of which is prone to dissociation due to the conjugation effect.[19] As a result, the ascorbic acid molecule becomes heavy and acidic, with a pK_a of 4.25.[20]

However, because ascorbic acid is reductive, it may diminish the substrate's self-corrosion potential, hence minimizing corrosion to the substrate.[17,21] In this regard, the current study assessed the effectiveness of ascorbic acid in inhibiting the corrosion of steel X60 in seawater.

EXPERIMENTAL

Material

API 5L X60 pipeline steel with the following weight percentage chemical composition was employed as a working electrode: C 0.102 max, Mn 1.06 max, Si 0.34 min, P 0.018 max, S 0.17 max, Ni 0.18max, Nb 0.019 max, Ti 0.023 max. As cylindrical, the specimens were cut from petroleum pipes.

Electrochemical studies were carried out on cylindrical specimens having a diameter of 1 cm. These specimen's surfaces were physically polished with silicon carbide paper ranging from 320 to 2000, cleaned with distilled water, and degreased with acetone.

Medium.

Natural seawater is the corrosive solution

Inhibitor.

The inhibitory solution is obtained by directly powdering ascorbic acid (AA) in seawater

Corrosion testing experiments

Following the initial mass of the total X60 coupons, mass loss studies were performed. The samples were immersed thoroughly. In this context, the uncontrolled seawater solution is referred to as 'blank,' whereas the corrosive solution with the inhibitor is referred to as 'inhibited.' Coupons were taken out of the test solutions.

The electrochemical impedance spectroscopy (EIS) experiments, the open circuit potential (OCP) of the corroding system was monitored for 1h to ensure a steady-state condition. The EIS experimental parameters used were initial frequency = 100 KHz, final frequency = 10 mHz, amplitude signal = 10 mV acquiring 10 points/decade at OCP.

The PDP studies were done out at a scan rate of 0.5 mV/s from -250 mV to +250 mV vs. OCP. This low speed allows us to perform tests under quasi-stationary conditions. All tests were conducted out in a typical three-electrode cell with a platinum counter electrode (CE) and a saturated calomel electrode (SCE) as the reference electrode, utilizing a potentiostat/Galvanostat with Nova 2.0 software. The Luggin capillary was placed near the working electrode to reduce ohmic contribution (WE).

The examination was undertaken by using scanning electron microscopy SEM to examine the electrode surface.

RESULTS AND DISCUSSION

Gravimetric method

Gravimetric analysis is one of the older ways of measuring corrosion rate and inhibitory efficiency when applying an inhibitor. Following that, the mass of the coupons was measured, and the mass loss was computed using the equation below $(mg / j \cdot cm^2)$:

$$V_{corr} = \frac{\Delta m}{St} \tag{1}$$

The value of the inhibitory efficiency is given by the following equation:

$$E(\%) = \left(\frac{V_{corr} - V_{inhi}}{V_{corr}}\right) \times 100 \tag{2}$$

with, V_{corr} and V_{inh} reflect the corrosion rates in the absence and presence of an inhibitor, respectively. At room temperature (25 ± 1 °C), the tests are carried out in saltwater with varying doses of inhibitor.

We prepare five samples of the steel item. Each sample is 5×4 cm^2 in size and ready to be immersed in a solution, as illustrated in Fig. 1.

Fig.1 – The test pieces after immersion

Variation of the inhibitory efficiency with concentration

Experiments were performed out at varying concentrations of the inhibitor at a set time (48 h). The acquired findings are presented in the Table 1.

The results of Table 1 are shown in the following figure.

The corrosion rate of steel in saltwater is decreased with the addition of the inhibitor AA, according to the data shown in Table 1. It is also the most effective inhibitor, with inhibitory effectiveness reached at a dosage of 0.05 g / L inhibitor.

Table 1

Variation of the inhibitory efficiency of carbon steel the concentration of Ascorbic Acid

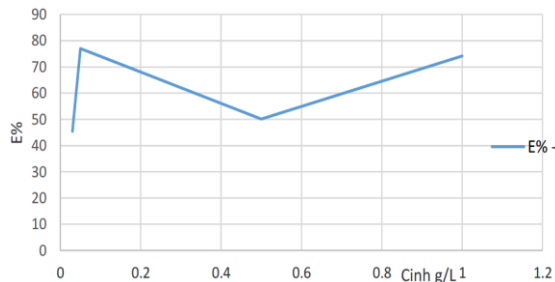| [AA] (g·L⁻¹)	V_{corr} (g·cm⁻²·h)	E (%)
0.00	$8.368 \cdot 10^{-6}$	–
0.03	$3.311 \cdot 10^{-5}$	45.48
0.05	$2.516 \cdot 10^{-5}$	77.01
0.5	$3.650 \cdot 10^{-5}$	50.09
1	$2.190 \cdot 10^{-5}$	74.16

Fig. 2 – Evolution of inhibitory efficiency with a concentration of AA in seawater.

Evolution of inhibitory efficiency with immersion time

The following table summarizes the findings of this study of the variation in ascorbic acid inhibitory efficiency as a function of immersion duration at a constant concentration of 0.05g/L. These findings reveal that the inhibitory effect of AA improves over time, peaking at 77 % after 48 hours and subsequently decreasing somewhat to 60 %.

Table 2

Inhibition efficiencies for corrosion of X60 steel in seawater by the AA as a function of immersion time

Time (h)	Δm (g)	V_{corr} (g·cm⁻²·h)	E (%)
24	0.0047	$8.368 \cdot 10^{-6}$	59.61
48	0.0372	$3.311 \cdot 10^{-5}$	77.01
72	0.0424	$2.516 \cdot 10^{-5}$	74
96	0.082	$3.650 \cdot 10^{-5}$	60.15
168	0.0424	$2.190 \cdot 10^{-5}$	64.43

After 168 hours of immersion, inhibition efficiency climbs to 65 %. This is explained by the presence of a very persistent inhibitory coating on the steel's surface.
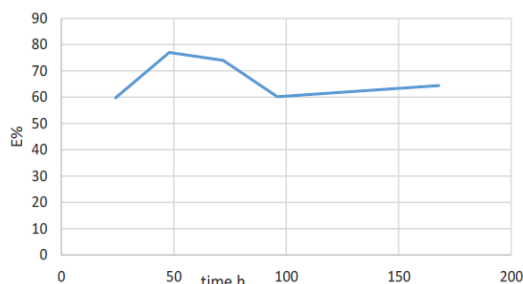

Fig. 3 – Evolution of the inhibitory efficiency of AA in the function of immersion time in seawater.

Electrochemical techniques

Open circuit potential (OCP) curves

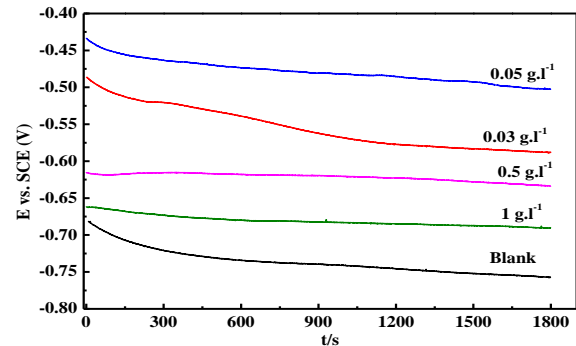The variation of the open circuit potential (OCP) versus time was observed in Fig. 4.

Fig. 4 – Variation of OCP versus immersion time for the systems with and without inhibitor.

It can be shown that the medium containing AA displayed a consistent increase in potential, which corresponded to a consistent decrease in the rate of corrosion of metals within the same time period. This increase is due to the formation of a protective film on the surface of the steel.

The plot of this curve indicates that the corrosive system progresses to larger positive values relative to the potential of the inhibited system.

The potential stabilisation in the aggressive medium may be due to the formation of hydroxide or oxide corrosion products, which results in the increase of potential being abundant.

Polarization analysis

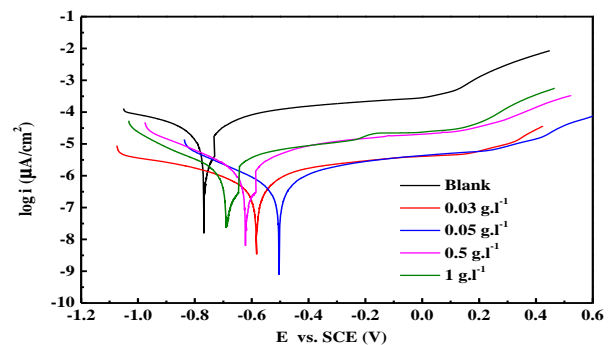The examination of the polarization curves in Fig. 5.

Fig. 5 – polarization curve of steel in seawater without and with the addition of different concentrations of (AA).

The addition of the AA inhibitor allows the corrosion potential to change to higher positive values, reducing the anode partial currents on the anode branches. Other than that, we are seeing a

modest rise in current on the cathode branches. This present rise is caused by the reduction reaction.

Table 3 represents the electrochemical characteristics retrieved from polarization curves

(Fig. 5). Show that the introduction of AA into the corrosive media causes a shift in corrosion potential toward more noble values as compared to the unfettered medium, with the E_{corr} changing from –0.71 to –0.66 V *vs*. SCE.

Table 3

Polarization parameters for X60 steel in seawater with various concentrations of AA inhibitor

[AA] (g·L^{-1})	E_{corr} (V *vs* SCE)	i_{corr}·10^{-3} (mA·cm^{-2})	β_a (V·dec^{-1})	$-\beta_c$ (V·dec^{-1})	IE (%)
0	–0.76	8.97	0.13	0.14	–
0.03	–0.58	4.34	0.10	0.07	51
0.05	–0.50	3.94	0.09	0.06	56
0.5	–0.62	5.70	0.11	0.11	36
1	–0.68	5.79	0.20	0.14	35

The slight change in Tafel slopes (βa and βc), in the absence and presence of the inhibitor, shows that the proton reduction reaction is modified by the addition of the corrosion inhibitor and proceeds by a pure activation mechanism.[22] The change in Tafel slope indicates that AA is acting as a mixed corrosion inhibitor. The i_{corr} of the AA inhibited corrosive media is much lower as compared to the blank. The i_{corr} value decreased from 8.97 A·cm^{-2} in the unprotected medium to 3.94 A·cm^{-2} in the system inhibited with 0.05 g. L^{-1} AA. This equated to corrosion inhibition of 56 %. Finally, the

findings produced by the gravimetric approach are in good conformity.

Electrochemical Impedance Spectroscopy (EIS)

In the investigation of corrosion and adsorption events, electrochemical impedance is a valuable instrument.[23,24] To complete the knowledge of the corrosion and inhibition mechanisms of steel X60 in saltwater in the absence and presence of inhibitor (AA), electrochemical impedance measurements at the abandonment potential in the corrosive media were performed.
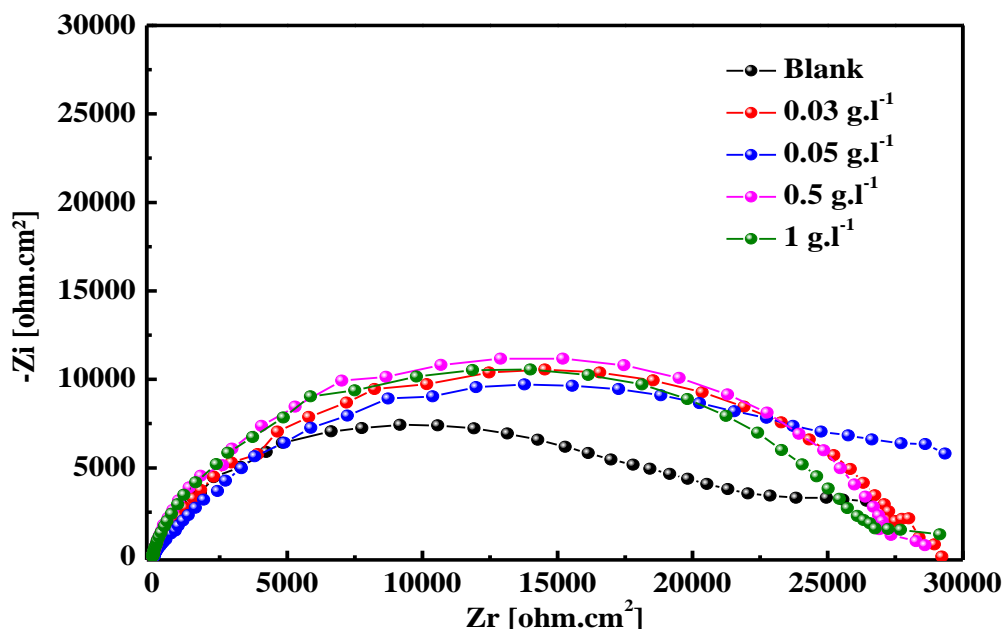

Fig. 6 – Electrochemical impedance diagram of X60 steel in seawater, in the absence and in the presence of AA at different concentrations.

In the high-frequency regions, the resulting diagrams (Fig. 6) reveal a single capacitive loop.

This suggests that a charge transfer process is in charge of the corrosion reaction. The capacitive

loop is not a perfect semicircle, which is owing to the dispersion of the frequency of the interfacial impedance.[25] which is caused by the heterogeneity of the electrode surface. Roughness, contaminants, dislocations, inhibitor adsorption, and the creation of porous layers[26,27] might cause this heterogeneity. This style of figure is often understood to represent a charge transfer process on a heterogeneous and uneven surface.[28,29] The size of the loop increases clearly with the addition of inhibitor, particularly at the 0.05 $g \cdot L^{-1}$ concentration. This reflects, over again, a better inhibitory efficiency of this concentration.

The electrochemical impedance spectra were further investigated using an equivalent circuit. As shown in Fig. 7, R_s signifies the solution resistance, R_{ct} the charge transfer resistance, and CPE the constant phase element. The expression[30] describes the impedance function of CPE :

$$Z_{CPE} = Y_0^{-1} (j \, \omega)^{-n}$$

where Y_0 is a proportional factor, ω is the angular frequency, j means the virtual root, and n can be used as an index of the surface irregularity. When $n = 0$, -1, and 1, CPE represent resistor, inductor, and pure capacitor, respectively. The double layer capacity (C_{dl}) was obtained by the following formulas :[31]

$$C_{dl} = Y_0 \, (\omega_{max})^{n-1} \; = Y_0 \, 2\pi f \, (Z_{im-max})^{n-1}$$

where ω_{max} stands for the frequency at which the imaginary impedance possesses the highest value. $R_{ct,0}$ and R_{ct} stand for charge transfer resistance in the absence and presence of ascorbic acid, respectively. The values of the electrochemical parameters and the inhibition efficiency E (%) for different concentrations of AA obtained by electrochemical impedance spectroscopy are given in Table 4.

Table 4

ESI parameters of steel X60 in seawater without and with differents concentrations of AA

[AA] ($g \cdot L^{-1}$)	$R_t(\Omega)$	$C_{dc}(\mu F.cm^{-2})$	E(%)
0	21	12.0	–
0.03	80	7.85	34
0.05	87	6.72	75
0.5	50	7.92	57
1	34	8.75	27

We can find that the R_{ct} values increases sharply after adding AA. The corrosion inhibition efficiency reaches the maximum value (75%) when inhibitor concentration is 0.05g/L. Indeed, as the film formation is increased, the capacity of the double layer decreases according to the expression of the Helmholtz model:[32]

$$C_{dl} = (\varepsilon^0 \, \varepsilon/d) \cdot S$$

where: ε^0 – and ε is the permittivity of the medium and vacuum respectively; S – the active surface area of the sample; d – the thickness of the film formed on the surface.

This is the result of the formation of a protective film on the surface of the metal[33] and can be related to the adsorption of the inhibitor molecules to the surface thus forming a protective film at the interface.
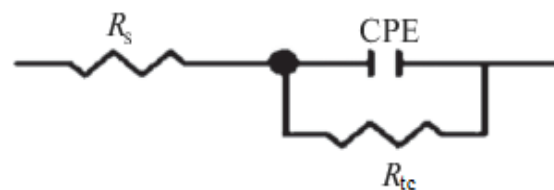

Fig. 7 – Model of the equivalent electrical circuit used in the modeling of the interface metal/solution.

Characterization of the surface by electron microscopy (SEM)

The SEM micrographs for the API5L X60 pipeline steel samples immersed in natural seawater in the absence and presence of AA with concentration equal to 0.05 $g \cdot L^{-1}$ for 48 hours are shown in Fig. 8.

The SEM images reveal that the surface is strongly damaged in the absence of an inhibitor (active corrosion). But in the presence of inhibitor (AA), the micrograph reveals that there is a decrease in the corrosion sites and pits over the surface of the API5L X60 steel (Fig. 8d). This is due to the formation of the adsorption layer of inhibitor on the metal surface (Fig. 8e). From these observations, we can say that the inhibitor gives a good inhibition effect for the mild steel and thus confirms the results obtained from other techniques.
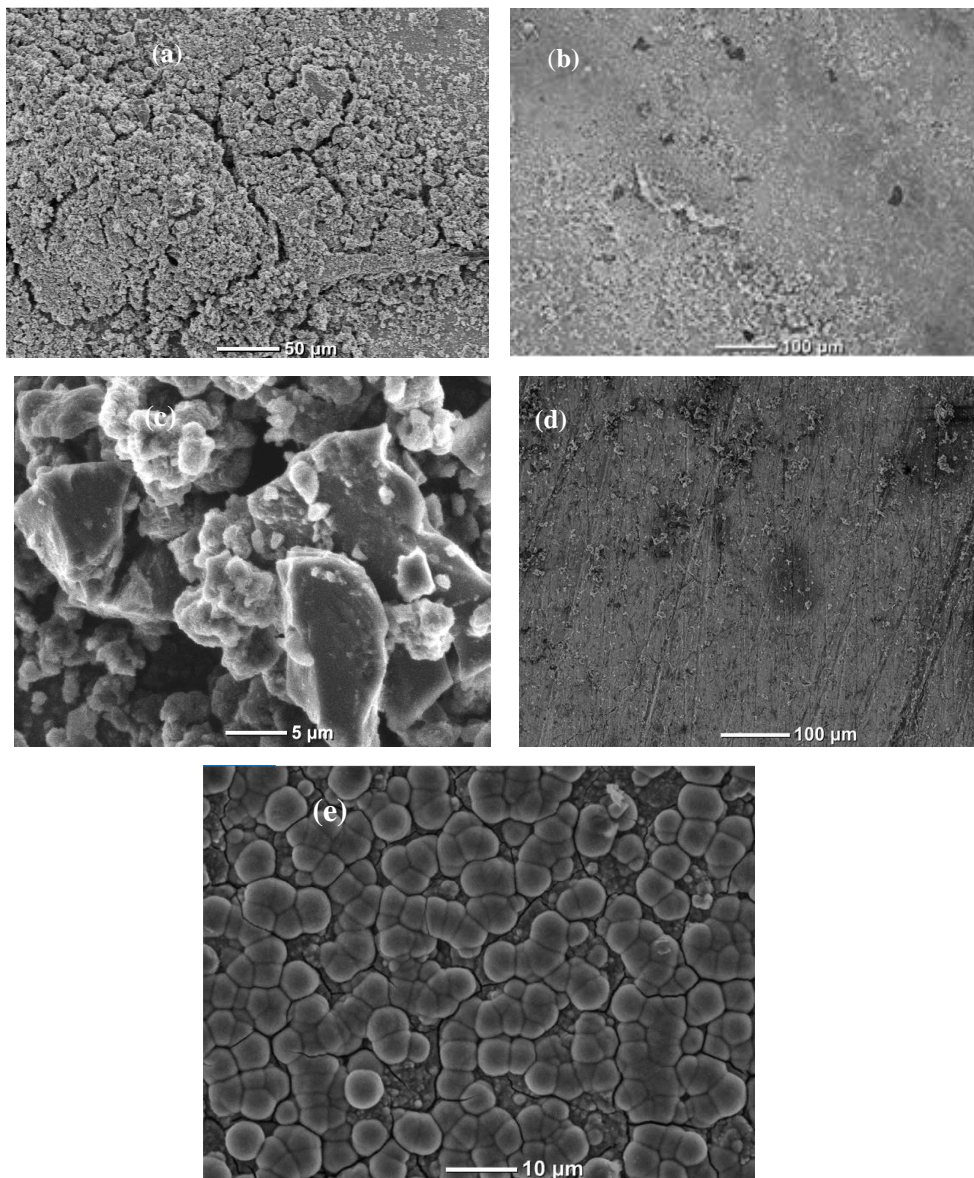
Fig. 8 – SEM micrographs of X60 steel electrodes after 48 hours, (a, b, c) without AA and, (d, e) with AA at 0.05g/L.

CONCLUSION

In conclusion, it is clear that:

Ascorbic acid (AA) has a strong inhibitory power from low concentrations.

The product tested, has been identified as a mixed inhibitor and shows better efficacy for the concentration of 0.05 g·L^{-1}.

The inhibitory efficiency of AA in seawater reaches a value of 77%.

The agreement between the impedance results and those obtained by gravimetry is perfect.

Scanning Electron Microscope reveals the formation of a dense protective layer in the presence of inhibitor.

REFERENCES

1. L. Abdoli and J. Huang, H. LI., *Mater. Chem. and Phys.*, **2016**, *173*, 62–69.
2. P. Wang., Z. Lu and D. Zhang, *Corrosion. Sci.*, **2015**, *93*, 159–166.
3. B. J. Little and J. S. Lee, "Causative organisms and possible mechanisms. Microbiologically influenced corrosion", John Wiley & Sons Inc., New Jersey, 2007, p. 22–55.
4. N. O. San., H. Nazir and G. Donmez, *Corr. Sci.,* **2012**, *65*, 113–118.
5. P. J. Antony, S. H. Chongdar, P. Kumar and R. Ramana., *Electro. Acta,* **2007**, *52*, 3985–3994.
6. R. G. Md. A. Macedo., Nd. N. Marques., J. Tonholo and Rd. C. Balaban, *Carbohydr. Polymer.,* **2019**, *205*, 371–376.
7. W. Wei, S. Geng., D. Xie and F. Wang, *Corr. Sci*., **2019**, *157*, 382–391.

8. A. O. AIjaola, P. K. Farayibi and E. Asmatulu, *J. Nat. Gas Sci. Eng.*, **2020**, *83*, 103544.
9. B. D. B. Tiu and R. C Advincula, *React. Funct. Polymer.*, **2015**, *95*, 25–45.
10. Singh, V. K. Singh and. M.A. Quraishi, *J. Mat. Envi. Sci.*, **2010**, *1*, 162–74.
11. J. D. Talati and D. K. Gandhi, *Mater. and Corr.*, **2004**, *33*, 155–63.
12. M. W. Ranney, Noyes Data Corporation, Park Ridge, NJ, 1976.
13. M. Elachouri, MS. Hajji, M. Saleem, S. Kertit, J. Aride, R. Coudert and E. Essassi, *Corr. Sci.*, **1996**, *37*, 381–389.
14. M. Elayyachy, A. E. Idrissi and B. Hammouti., *Corr. Sci.*, **2006**, *48*, 2470–2479.
15. A. Veawab and A. Tontiwachwuthikul, *Indus. & Eng. Chem. Res.*, **2001**, *40*, 4771–4777.
16. M. M. Arshadi, M. G. Hosseini, and M. Ghorbani, *Brit. Corr. J.*, **2002**, *37*, 76–80.
17. T. Ishizaki, N. Kamiyam, E. Yamamoto, S. Kumagai, T. Sudare and N. Saito, *J. Electrochem. Soc.*, **2015**, *162*, 741–743.
18. N. F. El Boraei and S. S. Abd El Rehim, *Mater. Chem. Phys.*, **2018**, *215*, 332–338.
19. H. Akrout, S. Maximovitch. S. L. Bousselmi, E. Triki and F. Dalard, *Mater. Corr.*, **2007**, *58*, 202–206.
20. E. E. Oguzie, Y. Li and H. F. Wang, *J. App. Electroch.*., **2007**, *37*, 1183–1190.
21. M. S. Hong, S. H. Kim, S. H. Im and J. G. Kim, *Metal. Material. Interna.*, **2016**, *22*, 621–629
22. F. Christian, *Engineering Techniques, Treated Metallic Materials,* M160.
23. H. Lizhi, K. Toyoda and I. Ihara., *J. of Food Eng.*, **2010**, *9*, 167–171.
24. A. Aït Aghzzaf, B. Rhouta, E. Rocca and A. Khalil, J. Steinmetz, *Corr. Sci.*, **2013**, *80*, 46–52.
25. M. Sikine, Y. K. Rodi, H. Elmsellem, O. Krim, H. Steli, Y. Ouzidan, F. O. Chahdi, N. K. Sebbar and E. M. Essassi, *J. Mat. Envi. Sci.*, **2016**, *7*, 1386–1395.
26. K. F. Khaled, *Appl. Surf. Sci.*, **2010**, *256*, 6753–6763.
27. A. Zouitini, Y. K. Rodi, H. Elmsellem, H. Steli, F. O. Chahdi, M. A. Shariati, A. E. Janati, Y. Ouzidan, N. K. Sebbar and E. M. Essassi, *J. of Mater. Envi. Sci.*, **2017**, *8*, 4105–4116.
28. M. Moradi, J. Duan and X. Du, *Corr. Sci.*, **2013**, *69*, 338–345.
29. H. Plonski, in "Modern aspects of Electrochemistry", Springer, Boston, MA, 1996, p. 203–318.
30. G. J. Brug, A. L. G. Vandeneeden and M. Sluytersrehbach, J. H. Sluyters, *J. Electroanal. Chem.*, **1984**, *176*, 275–295.
31. A. M. Beccaria and C. Bertolotto, *Electrochim. Acta*, 42, **1997**, *42*, 1361–1371.
32. Haque, V. Srivastava, D. S. Chauhan, H. Lgaz and M. A. Quraishi., *ACS Omega*, **2018**, *3*, 5654–5668.
33. X. Li, S. Deng and H. Fu, *Corr. Sci.*, **2010**, *52*, 3413–3420.