Available online at www.derpharmachemica.com

Scholars Research Library

Der PharmaChemica, 2015, 7(5):87-94
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Using pectin extract as eco-friendly inhibitor for steel corrosion in 1M HCl media

N. Saidi[a], H. Elmsellem[a*], M. Ramdani[a], A. Chetouani[a,c], K. Azzaoui[b], F. Yousfi[a], A. Aouniti[a] and B. Hammouti[a]

[a]*LCAE-URAC18, COST, Department of Chemistry, Faculty of Sciences, Mohamed 1st University, Oujda, Morocco*
[b]*Laboratory of Mineral Solid and Analytical Chemistry LMSAC, Department of Chemistry, Faculty of Sciences, Mohamed 1st University, Oujda, Morocco*
[c]*Laboratoire de chimie physique, Centre Régionale des Métiers de l'Education et de Formation "CRMEF", Région de l'Orientale, Oujda, Morocco*

ABSTRACT

Corrosion inhibition of mild steel in 1 M HCl was investigated in the absence and presence of different concentrations of pectin extracted from opuntia cladodes. Weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy techniques were employed. Impedance measurements showed that the double-layer capacitance decreased and charge-transfer resistance increased with increase in the inhibitor concentration and hence increasing in inhibition efficiency. Potentiodynamic polarization study showed that the inhibitor act as cathodic-type inhibitor. The inhibition efficiency was found to increase with inhibitor content to attain 96% in the presence of1g/l at 308K. Data obtained from EIS studies were analyzed to determinate the model inhibition process through appropriate equivalent circuit models. Inhibition efficiency E (%) obtained from the various methods was in good agreement. The associated activation energy has been determined. The adsorption of pectin on the steel surface was found obey to Langmuir's adsorption isotherm.

Keywords: Mild steel, Pectin, cladodes, HCl, Corrosion, Green inhibitor

---

INTRODUCTION

Acid solutions, widely used in industrial acid cleaning, acid descaling, acid pickling, and oil well acidizing, require the use of corrosion inhibitors in order to restrain their corrosion attack on metallic materials. Several factors including cost and amount, easy availability and most important safety to environment and its species need to be considered when choosing an inhibitor. Use of inhibitors is one of the most economical and practical methods for protecting metal against corrosion [1]. Use of organic molecules as corrosion inhibitors is one of the most practical methods for protecting against corrosion [2].

In recent years, research into the use of low-cost and eco-friendly compounds as corrosion inhibitors for mild steel were intensified. Many researchers have studied the use of plant based inhibitor and the results shows that this new type of inhibitors is proven effectively to reduce the corrosion rate on the metal [3-11].The use of natural polymeric structures, derived from extracts of leaves or seeds, as green corrosion inhibitors is receiving strong preference. These chemical substances are safe, cost-effective and renewable sources of materials [12-16]. Pectin is a naturally occurring polysaccharide contained in the primary cell walls of higher plants [17]. In addition, the biodegradability and the eco-friendly role of pectin [18] have adapted it to be used also as an excipient in food industry [19], and as controller for drug delivery systems [20,21] due to its non-toxicity, low production costs and gelling activity

properties. In the literature, Plant extracts containing pectin among many other compounds were tested as corrosion inhibitors [22-24].

Pectin has been reported to be a promising green corrosion inhibitor of aluminum in hydrochloric acid solution. The maximum inhibition efficiency obtained at 10 °C using pectin concentration (8.0 g/L) was 91% [16]. The use of a ternary inhibitor formulation with pectin, propyl phosphonic acid and Zn^{2+} for corrosion control of carbon steel in aqueous solution presented 94 % as inhibition efficiency for 50 ppm of PPA and 20 ppm of Zn^{2+} [25].However, the corrosion inhibition performance of Pectin-Grafted Polyacrylamide and Pectin-Grafted Polyacrylic Acid on mild steel in 3.5% of NaCl was found to be only 85% [26]. Recently, the inhibition corrosion of mild steel in 1 M HCl solution attained a maximum value of 94.2% using 2.0 g /L of pectin solution at 45 °C [27].

The encouraging results obtained in our laboratory by naturally extracts from different plants as corrosion inhibitors of steel in acid solutions permit to test more eco-friendly inhibitor.In the present study, the inhibitive effect of the Pectin extracted from *Opuntia Ficus Indica* cladode on corrosion of mild steel in hydrochloric acid solution was investigated by weight loss, electrochemical polarization measurements and electrochemical impedance spectroscopy.

MATERIALS AND METHODS

2.1. Pectin extraction

300 g of cladodes of *opuntia ficus indica* (Fig.1) were washed with double distilled water. They were cut into small pieces and placed with 100 mL of distilled water in conventional Samsung microwave MS-23F301EFS model set for 15 min at 700 w and 2450 MHz. After cooling, the mixture was centrifuged at 4000 rpm for 10 min to separate the liquid from the solids. The supernatant, containing the NE was filtered with fine cloth. NE was precipitated using absolute ethanol in a 2:3 ratio of supernatant to solvent. The precipitate was washed with ethanol-water mixture (70%) to remove any remaining impurities and left to dry at room temperature overnight. The solid was pulverized and stored at room temperature.

(a) **(b)**

Figure1:(a):*Opuntia* Cladodes, (b):Pectin powder

2.2. Solutions

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 Pectin inhibitor employed was 0.125-1 (g/L).

2.3. Weight loss measurements

Coupons were cut into 1.5× 1.5 × 0.05 cm^3 dimensions having composition (0.09 % P, 0.01 % Al, 0.38 % Si, 0.05 % Mn, 0.21 % C, 0.05 % S and Fe balance) used for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 180, 400, 800, 1000, 1200 grades of emery papers. The specimens are washed thoroughly with bi-distilled water degreased and dried with ethanol. Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser. The solution volume is 100 cm^3. The immersion time for the weight loss is 6 h at (308±1) K. In order to get good reproducibility, experiments were carried out in duplicate. The average weight loss was obtained. The corrosion rate (**v**) is calculated using the following equation:

$$\mathbf{v = W / S.}t \qquad (1)$$

Where W is the average weight loss, S the total area, and t is immersion time. With the corrosion rate calculated, the inhibition efficiency (Ew) is determined as follows:

$$Ew\ \% = \frac{V0-V}{V0}\ X\ 100 \qquad (2)$$

Where$\mathbf{V_0}$ and **V** are the values of corrosion rate without and with inhibitor, respectively.

2.4.Electrochemical tests

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. Inhibition efficiency (Ep %) is defined as Equation3, where $i_{corr(0)}$ and $i_{corr(inh)}$ represent corrosion current density values without and with inhibitor, respectively.

$$Ep\% = \frac{\mathrm{icor(0)-icor(inh)}}{\mathrm{icor(0)}}\mathrm{x}\ 100 \qquad (3)$$

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system, which included a digital potentiostat model Voltalab PGZ100 computer at Ecorr after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 308 K. The impedance diagrams are given in the Nyquist representation. Inhibition efficiency (E_R%) is estimated using the relation 4, where $R_t(0)$ and Rt(inh) are the charge transfer resistance values in the absence and presence of inhibitor, respectively:

$$ER\% = \frac{\mathrm{Rt(inh)-Rt(0)}}{\mathrm{Rt(inh)}}\mathrm{x}\ 100 \qquad (4)$$

RESULTS AND DISCUSSION

3.1. Weight loss measurements

3.1.1. Effect of inhibitor concentration

The weight loss method of monitoring corrosion rate is useful because of its simple application and reliability [28,29]. Therefore, a series of weight loss measurements were carried out after 6h immersion in 1.0 M HCl in the absence and presence of various concentrations of the Pectin.

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

Concentration Pectin (g/l)	V ($mg.cm^{-2}\ h^{-1}$)	E_w (%)
HCl	0.82	---
1	0.05	94
0.5	0.08	90
0.25	0.09	89
0.125	0.13	84

Table 1 shows the calculated values of corrosion rates obtained using Eq. (1) as well as inhibition efficiency values evaluated using the expression given in Eq. (2). The results show that the corrosion efficiencies for Pectin increase with the increasing of inhibitor concentration. The inhibition efficiency attain 94% at a concentration of 1g/L. Also, the corrosion rate decreases with the increase of concentration of the tested inhibitor. From weight loss measurement, we can conclude that Pectinis an excellent corrosion inhibitor for mild steel in 1 M HCl solution.

In comparison with the literature, we obtained comparable results with those obtained recently by Fiori-Bimbi and col. [27] using a higher concentration of pectin 2 g/L instead of 1g/L in our conditions. On the contrary, our results are slightly higher than those obtained by Fares et al. [16] usinga morehigher concentration of pectin 8g / L.

3.1.2. Adsorption isotherm

It is generally assumed that the adsorption of the inhibitors on the metal surface is the essential step in the inhibition mechanism [30].

Attempts were made to fit values of θ to many isotherm including Langmuir, Temkin, Frumkin and Freundlich. The organic compound seems that follows well the Langmuir adsorption isotherm written in the rearranged form [31]:

$$\frac{C}{\theta} = \frac{1}{k} + C \quad (5)$$

The surface coverage values (θ) were tested graphically for fitting a suitable adsorption isotherm. In those cases, the plots of C_{inh}/θ versus C_{inh} yield a straight line, clearly proving that the adsorption of the used inhibitors from 1 MHCl solutions on the mild steel surface obeys the Langmuir adsorption isotherm (Fig. 2).

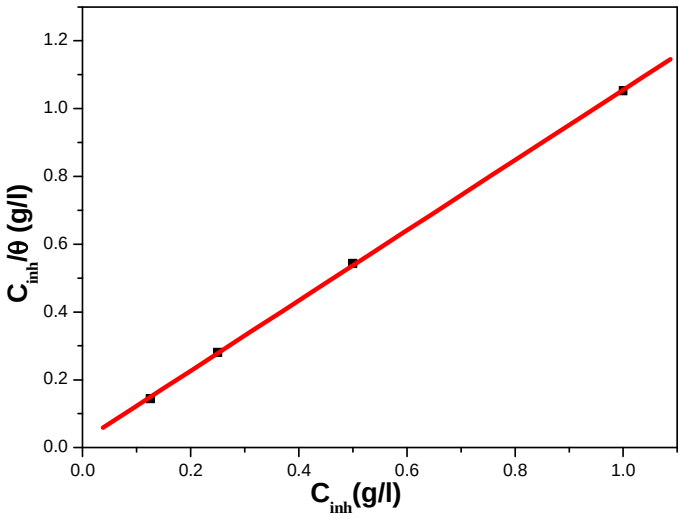

Figure 2: Langmuir isotherm of steel in the 1M HCl in presence of pectincalculated by gravimetric method

The adsorption equilibrium constant (K) is related to the standard adsorption free energy (ΔG°) as shown the following equation (6):

$$K = \frac{1}{55.5}\exp\left(\frac{-\Delta G^{0}}{RT}\right) \quad (6)$$

Where R is the gas constant (8.314 J K^{-1} mol^{-1}), T the absolute temperature (K), and the value 55.5 is the concentration of water in the solution.

Table.2. Thermodynamic parameters for the adsorption of pictine in 1M HCl on the mild steel at 308K(Weight loss method, immersion time is 6 h)

Inhibitor	Linear correlation coefficient (r)	Slope	K (M^{-1})	ΔG°_{ads} ($KJ.mol^{-1}$)
Pectin	0.999	1.021	1.47×10^{-2}	- 22.83

The negative values of (ΔG^{0}_{ads}) suggest that the pectin inhibitor was spontaneously adsorbed on steel–electrolyte interface. It has been reported that values of ΔG^{0}_{ads} up to -20 kJ/mol are consistent with the physisorption; those around -40 kJ/mol or higher are consistent with chemisorptions [32,33]. In the present study, the value of ΔG°_{ads} is - 22.83 kJ mol^{-1}, probably means that the adsorption of Pectin Extract inhibitor on the steel surface exhibits both physical adsorption.

The calculated ΔG_{ads} values, using Eq. (6), were also given in Table 2. The large negative values of ΔG_{ads} ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on the mild steel surface [34,35] as well as a strong interaction betweenpectin and the metal surface [36].

3.2. Potentiodynamic polarization curves:

Potentiodynamic anodic and cathodic polarization plots for mild steel specimens in 1 M HCl solution in the absence and presence of different concentrations of pectinat 308 K are shown in Figure 3. The respective kinetic parameters including corrosion current density (Icorr), corrosion potential (Ecorr), cathodicTafel slope (βc) and inhibition efficiency (IE %) are given in Table 3.

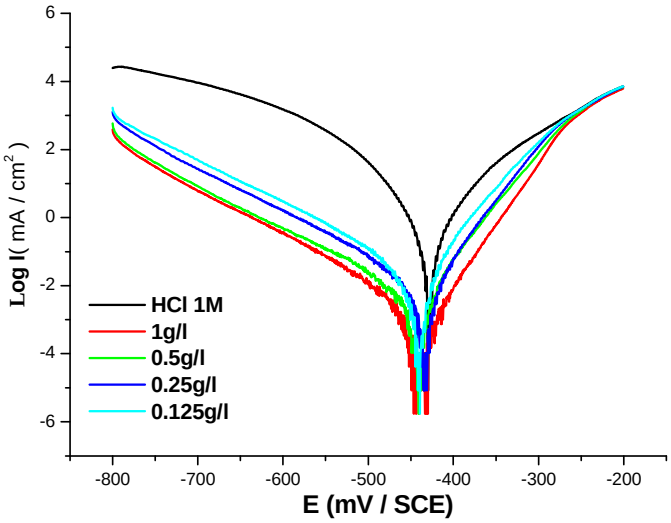

Figure 3: Anodic and cathodic polarization curves of mild steel in solutions of 1 M HCl in the presence and absence of different concentrations of Pectin

Table 3. Electrochemical parameters of mild steel at various concentrations of Pectin in 1M HCl

Concentration Pectin (g/l)	-E_{corr}(mV/SCE)	I_{corr} (µA/cm^2)	-βc	βa	E_p (%)
HCl	429	1788	151	155	
1	434	29	130	64	98.38
0.5	441	98	190	77	94.52
0.25	433	113	170	71	93.68
0.125	441	220	184	82	87.70

Inspection of these results (figure 3, table 3) reveals that in presence of inhibitors, the value of corrosion density (I_{corr}) was decreased. This behaviour reflects its ability to inhibit the corrosion of mild steel in 1M HCl solution. The E(%) increases as the extract concentration is increased. It is also worth noting that the value of βc changes dramatically with the addition of pictin, much more so than the value of βa. This indicates that the pectin behave cathodically more than anodically [37,38].

3.3. Electrochemical impedance spectroscopy

Among the different electrochemical techniques that can be used to study corrosion inhibitors, EIS appears as powerful tool for the information that can provide, as for example, double layer capacitance, C_{dl}, and transfer resistance, R_t, values. Changes in these parameters as a function of time or with respect to other variables, allow obtaining important information about the kinetics of the corrosion process being involved [39,40].

Nyquist plots for mild steel obtained at the interface in the absence and presence of Pectin Extract at different concentrations is given in Figure 4.

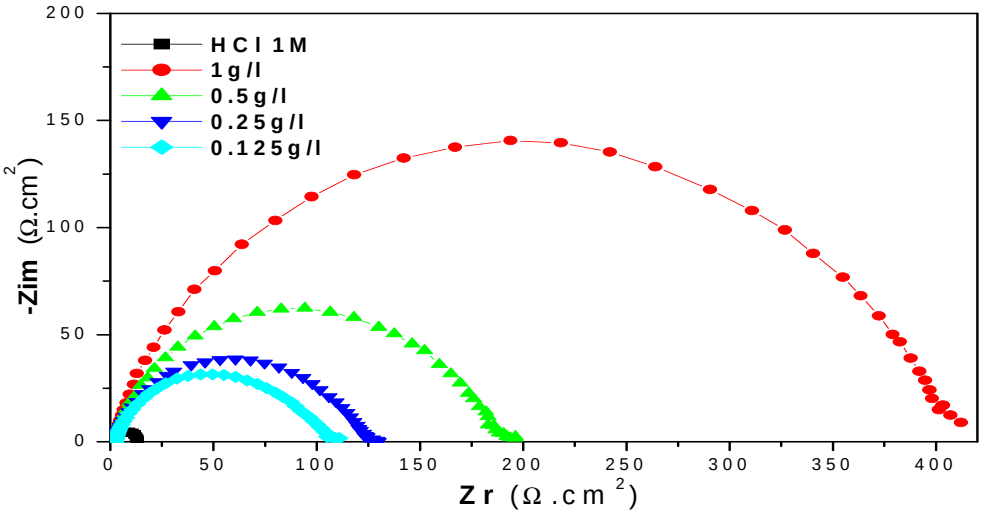

Figure 4:Nyquist plot at different concentrations of Pectin in 1M HCl solution

As shown in Figure 4, in uninhibited and inhibited 1 M HCl solutions, the impedance spectra exhibit one single capacitive loop, which indicates that the corrosion of steel is mainly controlled by the charge transfer process [41]. It is noted that these capacitive loops in 1 M HCl solutions are not perfect semicircles which can be attributed to the frequency dispersion effect as a result of the roughness and inhomogeneous of electrode surface [42]. Furthermore, the diameter of the capacitive loop in the presence of inhibitor is larger than that in blank solution, and enlarges with the inhibitor concentration. This means that the impedance of inhibited substrate increases with the inhibitor concentration, and leads to good inhibitive performance.

The electrochemical parameters of R_t and C_{dl} derived from Nyquist plots and inhibition efficiency E_{Rt} (%) are calculated and listed in Table 4.

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

Concentration Pectin(g/l)	R_{ct} ($\Omega.cm^2$)	C_{dl} ($\mu f/cm^2$)	E (%)
HCl	13.11	353	--
1	397.50	50.65	96.70
0.5	185.90	54.53	92.95
0.25	120.43	66.10	89.11
0.125	103.40	76.89	87.32

From carful inspection of impedance parameters (Table 4), it was revealed that Rt values increased with the Pectin concentration while Cdl values decreased and consequently the inhibition efficiency (E_{Rt}%) increases to 96.70 % at 1 g/l, which indicates a reduction in the steel corrosion rate.

The simplest fit is represented by the Randles equivalent circuit, Fig 5, which is a parallel combination of the charge-transfer resistance (R_t) and the constant phase element (CPE) [43], both in series with the solution resistance (Rs).

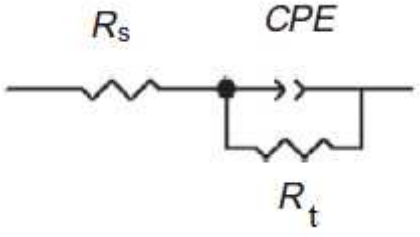

Figure 5. Electrical equivalent circuit model used for the modeling metal/solution

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.

CONCLUSION

The following results can be drawn from this study:
1. Tafel polarization measurements indicates that Pectin act behave cathodically more than anodically.
2. The increase in the charge transfer resistance and decrease in double layer capacitance values, with the increase in the inhibitor concentration, showed that Pectin formed protective layerson the mild steel surface, covering areas where HCl solution degrades and corrodes rapidly.
3. The inhibition efficiency increases with increasing concentration of Pectin.
4. The corrosion process was inhibited by adsorption of the organic matter on the mild steel surface, obtaining the formation of the film on the metal/acid solution interface, decreasing the degradation of the material.
5. Results obtained through weight loss measurements and electrochemical tests demonstrated that Pectin act as efficient corrosion inhibitors of the mild steel in 1 M HCl solution.

REFERENCES

[1] A.S. Fouda, A.S. Ellithy, *Corros. Sci*. **2009,** 51, 868.
[2] A. Zarrouk, B. Hammouti, A. Dafali, F. Bentiss, *Ind. Eng. Chem. Res*. **2013,** 52, 2560.
[3] L. Afia, R. Salghi, L. Bazzi, M. Errami, O. Jbara, SS. Al-Deyab, B. Hammouti. *Int. J. Electrochem. Sci*. **2011,** 6,5918.
[4] L. Bammou. M. Belkhaouda, R. Salghi, O. Benali, A. Zarrouk, SS. Al-Deyab. I. Warad. H. Zarrok, B. Hammouti. *Int. J. Electrochem. Sci.* **2014**, 9, 1506.
[5] H. Bouammali, A. Ousslim, K. Bekkouch, B. Bouammali, A. Aouniti , SS. Al-Deyab, C. Jama, F. Bentiss, B. Hammouti. *Int. J. Electrochem. Sci*. **2013**, 8, 6005.
[6] F. Aouinti, H. Elmsellem, A. Bachiri, ML. Fauconnier, A. Chetouani, B. ChaoukiBelbachir, A. Aouniti, B. Hammouti*Journal of Chemical and Pharmaceutical Research*, **2014**, 6(7), 10
[7] S.M. Ramananda. *J. Mater. Environ. Sci.* **2013 ,**4 (1), 119.
[8] Z. Ghazi, H. ELmssellem, M. Ramdani, A.Chetouani, R. Rmil, A. Aouniti, C. Jama, B. Hammouti, *Journal of Chemical and Pharmaceutical Research*, **2014**, 6(7), 1417.
[9] M.Dahmani, A. Et-Touhami, B.Hammouti, A.Bouyanzer, *Int. J. Electrochem. Sci*. **2010**, 5, 1060.
[10] C.Hellio, D. De La Broise, L.Dufossé, Y. Le Gal, N.Bourgougnon, *Marine EnvironmentalResearch*, **2010**, 52(3),231.
[11] 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.
[12] A.M. Abdel-Gaber, B.A. Abd-El-Nabey, I.M. Sidahmed, A.M. El-Zayady, M. Saadawy, *Corros. Sci*. **2006,** 48**,** 2765–2779.
[13] O.K. Abiola, J.O.E. Otaigbe, O.J. Kio, *Corros. Sci*. **2009,** 51**,** 1879–1881.
[14] N. Lahhit, A. Bouyanzer, J.-M. Desjobert, B. Hammouti, R. Salghi, J. Costa, C. Jama, F. Bentiss, L. Majidi, *Port. Electrochim. Acta*, **2011,** 29, 127-138.
[15] L. Valek, S. Martínez, *Mater. Lett*. **2007,** 61**,** 148–151.
[16] M.M. Fares, A.K. Maayta, M.M. Al-Qudah, *Corros. Sci.* **2012,**60**,** 112–117.
[17] F. Keppler, J.T.G. Hamilton, M. Bra, T. Röckmann, *Nature* **2006,** 439**,** 187–191.
[18] M.M. Fares, Y.R. Tahboub, S.T. Khatatbeh, Y.M. Abul-Haija, *J. Polym. Environ.***2011,** 19**,** 431–439.
[19] L. Liu, M.L. Fishman, J. Kost, K.B. Hicks, *Biomaterials* **2003,** 24**,** 3333–3343.
[20] M.M. Fares, S.M. Assaf, Y.M. Abul-Haija, *J. Appl. Polym. Sci*. **2010,** 117**,** 1945–1954.
[21] S.M. Assaf, Y.M. Abul-Haija, M.M. Fares, *J. Macromol. Sci. Part A: Pure Appl. Chem*. **2011,**48 (6), 493–502.
[22] J. Cardozo da Rocha, J.A. da Cunha Ponciano Gomes, E. D'Elia, *Corros. Sci*. **2010,** 52**,** 2341–2348.
[23] A.Y. El-Etre, *Corros. Sci*. **2003,** 45**,** 2485–2495.
[24] R.M. Saleh, A.A. Ismail, A.A. El Hosary, *Corros. Sci.*, **1983,** 23**,** 1239-1241.
[25] M. Prabakaran, S. Ramesh, V. Periasamy, B. Sreedhar, *Res. Chem. Intermed.*, **2014**, http://dx.doi.org/10.1007/s11164-014-1558-0.
[26] R. Geethanjali, A. Ali Fathima Sabirneeza, and S. Subhashini, *Ind. J. Mat. Sc.*, **2014**, 1-9.
[27] M. V. Fiori-Bimbi, P. E. Alvarez, H. Vaca, C. A. Gervasi. *Corros. Sci.*, **2015,** 92**,** 192-199.
[28] I.B. Obot, N.O. Obi-Egbedi, S.A. Umoren, *Corros. Sci.*, **2009**, 51, 1868.
[29] M. Behpour, S.M. Ghoreishi, N. Mohammadi, N. Soltani, M. Salavati-Niasari, *Corros. Sci.*, **2010,** 52, 4046-4057
[30] A. Asan, M. Kabasakaloglu, M. Is_ıklan, Z. Kılıc, *Corros. Sci.*, **2005,** 47**,** 1534-1544.
[31] N. Labjar, M. Lebrini, F. Bentiss, N. Chihib, S. El Hajjaji, C. Jama, *Mater. Chem. Phys.*, **2010**, 119, 330.

[32] M. B. Mahida and H.G. Chaudhari, *J. Chem. Pharm. Res.*, **2012**, 4, 5195-5201.
[33] F. Bentiss, M. Outirite, M. Traisnel, H. Vezin, M. Lagrenee, B. Hammouti, S.S. Al-Deyab, *Int. J. Electrochem. Sci.*, **2012**, 7, 1699-1723
[34] L. Tang, X. Li, L. Lin, G. Mu, G. Liu, *Mater. Chem. Phys.*, **2006,** 97**,** 301.
[35] K. Tebbji, N. Faska, A. Tounsi, H. Ouddad, M. Benkaddour, B. Hammouti, *Mater. Chem. Phys.*, **2007**, 106, 2144.
[36] G. Mu, X. Li, G. Liu, *Corros. Sci.*, **2005**, 47, 1932.
[37] A.Y. Musa, R.T.T. Jalgham, A.B. Mohamad, *Corros. Sci.*, **2012,** 56**,** 176-183.
[38] A. Popova, M. Christov, A. Vasilev, A. Zwetanova, *Corros. Sci.*, **2011,** 53**,** 679-686.
[39] H. Elmsellem, A. Aouniti, M. Khoutoul, A. Chetouani, B. Hammouti, N. Benchat, R.Touzani, M. Elazzouzi, *J. Chem. Pharm. Res.*, **2014**, 6, 1216-1224.
[40] H. Elmsellem, M. H.Youssouf, A. Aouniti, T. Ben Hadda, A. Chetouani, B. Hammouti. *Russ. J. Appl. Chem.*, **2014**, 87, 744-753.
[41] A. Fouda, A. El-Bendary, M. Diabb, A. Bakra, *Mor. J. Chem.*, **2014**, 2, 302-319.
[42] J. Saranya, P. Sounthari, A. Kiruthuka, K. Parameswari, S. Chitra, *J. Mater. Environ. Sci.*, **2015,** 6**,** 425-444.
[43] 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.