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# ***Emblica Officinalis* (Indian Gooseberry) Leaves Extract as Corrosion Inhibitor for Mild Steel in 1N HCl Medium**

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**Abstract:** Corrosion inhibition efficiency of acid extract of dry *Emblica officinalis* leaves for mild steel in 1N HCl medium is investigated in the present study. Experimental methods include weight loss, potentiodynamic polarization and impedance studies. The results indicate *Emblica officinalis* leaves to be a good corrosion inhibitor of a mixed type and having efficiency of 87.9% at 2% v/v inhibitor concentration. Corrosion inhibition may be due to the spontaneous physical adsorption of the plant constituents on the mild steel surface. Experimental data fitted the Langmuir, Temkin, Freundlich and Flory-Huggins adsorption isotherms.

**Keywords:** *Emblica officinalis*, Indian gooseberry leaves, Corrosion inhibitor, Mild steel, HCl medium.

## **Introduction**

Use of chemical corrosion inhibitors is common in production and processing operations. Development of new corrosion inhibitors which effectively inhibit corrosion under a variety of conditions while being environmentally safe and acceptable is a challenging task. Acid solutions are widely used in industry such as acid pickling, acid cleaning or acid de-scaling of metallic materials. The frequently used acid is HCl. Several studies have investigated the inhibition of metal corrosion by various types of organic and inorganic compounds<sup>1-8</sup>. Extracts of naturally occurring products like henna<sup>9</sup>, *Datura metel*<sup>10</sup>, aloe vera<sup>11</sup>, tobacco<sup>12</sup>, hibiscus<sup>13</sup>, *zenthoxylum alatum*<sup>14</sup>, phyllanthus amarus<sup>15</sup>, *Michelia champaca*<sup>16</sup>, khillah seeds<sup>17</sup>, black pepper<sup>18</sup>, plant exudate gums<sup>19-22</sup>, *Ficus carica*<sup>23</sup>, *Piper guinensis*<sup>24</sup> etc have been reported as corrosion inhibitors for mild steel in acid media. In the present work inhibitive properties of acid extract of *Emblica officinalis* (Indian gooseberry) leaves is studied using weight loss, polarization and impedance studies.

## Experimental

Green leaves of the plant *Emblica officinalis* (EOL) were collected washed, and shade dried. 50 g of dried powder of leaves were boiled in 1000 mL 1N HCl with reflux condenser for three hours and kept over night. Next day it was filtered and the filtrate volume was made up to 1000 mL using 1N HCl. The extract so prepared was taken as stock solution and from this other concentrations were diluted.

Rectangular samples of area  $1 \times 5 \text{ cm}^2$  have been cut from a big sheet of mild steel locally bought. The specimens (mild steel coupons) were mechanically polished; a hole drilled at one end for free suspension and numbered by punching. The specimens were degreased with acetone, washed with distilled water and well polished with emery paper, cleaned, rinsed and dried and then stored in desiccators, for further study.

Weight loss of rectangular coupons in triplicate immersed in 100 mL of 1N HCl with and without the different concentrations of plant extract was determined after different immersion periods (1 h, 3 h, 5 h, 7 h, 12 h and 24 h) at 303 K. Weight loss determinations were carried out at different temperatures *viz.* 303, 313, 323, 333 and 343 K. After initial weighing, the specimens in triplicate were immersed in 100 mL of 1N HCl in the absence and presence of different concentrations (0.01%, 0.05%, 0.1%, 0.5% and 1% v/v) of the plant extracts at the different temperatures for 1 h duration. The thermostat was set to the appropriate temperature and after 1 h immersion the specimens were removed, washed, dried and reweighed.

Polarization experiments were carried out in the three electrode polarization cell containing platinum auxiliary electrode, saturated calomel reference electrode and polished mild steel specimen as working electrode. All the measurements were carried out using SOLARTRON 1280 B - Electrochemical system. The mild steel specimen was lacquered so as to expose 1 sq. cm area. 100 mL of acid was taken in the electrochemical cell. The polished electrode was then introduced and held for 5 minutes to attain a constant potential. Potentiodynamic anodic and cathodic polarization curves were obtained with a scan rate of 2 mV/s in the potential range from -0.2V to -1V relative to the corrosion potential. In Tafel extrapolation method, plots of applied potential *vs* current are made and extrapolation of linear portion to the corrosion potential gives the corrosion current. In the Linear polarization method current versus voltage curve is recorded very near to the open circuit potential (10 mv). A numerical fit of the curve yields polarization resistance  $R_p$ . Inhibition efficiency (IE%) was calculated as follows

### Tafel method

$$\text{IE \%} = \left[ \frac{I_{\text{corr}}(\text{blank}) - I_{\text{corr}}(\text{additive})}{I_{\text{corr}}(\text{blank})} \right] \times 100$$

Where,  $I_{\text{corr}}(\text{additive})$  and  $I_{\text{corr}}(\text{blank})$  are the corrosion currents with and without the inhibitors respectively

### LPR method

$$\text{IE \%} = \left[ \frac{R_p(\text{additive}) - R_p(\text{blank})}{R_p(\text{additive})} \right] \times 100$$

Where  $R_p(\text{additive})$  and  $R_p(\text{blank})$  are the resistance polarizations with and without the inhibitor respectively.

Impedance spectra were recorded at  $E_{\text{corr}}$  in the frequency range 0.1 to 20000Hz. Impedance parameters  $R_{\text{ct}}$  and  $C_{\text{dl}}$  were computed using EIS software Z VIEW. Inhibition efficiency (IE%) was calculated as follows

$$IE \% = [(C_{dl} - C_{dl.inh}) / C_{dl}] \times 100$$

$$IE \% = [(R_{ct.inh} - R_{ct}) / R_{ct.inh}] \times 100$$

Where,  $C_{dl.inh}$ ,  $C_{dl}$  are double layer capacitances and  $R_{ct.inh}$ ,  $R_{ct}$  are charge transfer resistances with and without the inhibitor respectively.

## Results and Discussion

### *Effect of plant extract concentration and immersion time on IE of plant extract in 1N HCl medium*

Inhibition efficiency (IE) calculated from weight loss measurements of mild steel samples immersed for different time intervals in 1N HCl in absence and presence of different concentrations of EOL extract are given in the Table 1. At lower concentrations the inhibition efficiency increases invariably with increase of inhibitor concentration. This is associated with increase of surface coverage by the constituents present in the extract, which retards the corrosion of mild steel and hence IE increases. The rate of increase of IE with concentration of the extract is appreciable at lower concentration range and at higher concentrations around 1%, the change in IE is not much. The maximum inhibition efficiency for 1 h immersion period for EOL extract is 87.69% at 2%. Thus EOL extract is found to be a good inhibitor for mild steel corrosion in HCl medium. There is a general increase in IE with immersion time. The changes in IE with immersion time can be explained as due to changes in adsorption-desorption equilibria. The inhibitor shows maximum inhibition efficiency at 24 h immersion time. Prolonged immersion of the sample in the medium with plant extract leads to greater adsorption of plant constituents.

**Table 1.** IE (%) of EOL in 1N HCl at different concentrations and different immersion periods.

| Conc. of plant extract { %v/v } | IE, % |       |       |       |       |       |
|---------------------------------|-------|-------|-------|-------|-------|-------|
|                                 | 1 h   | 3 h   | 5 h   | 7 h   | 12 h  | 24 h  |
| 0.01                            | 30.00 | 27.40 | 30.48 | 35.00 | 43.65 | 38.00 |
| 0.05                            | 59.14 | 59.00 | 60.35 | 62.33 | 74.06 | 62.74 |
| 0.1                             | 64.37 | 68.23 | 65.00 | 70.56 | 82.00 | 78.63 |
| 0.5                             | 80.00 | 79.00 | 82.14 | 85.00 | 91.00 | 97.00 |
| 1                               | 85.00 | 87.00 | 89.85 | 92.00 | 94.38 | 98.00 |
| 1.5                             | 85.12 | 87.35 | 91.2  | 92.08 | 93.76 | 97.68 |
| 2                               | 87.69 | 86.93 | 92.42 | 91.03 | 90.15 | 98.45 |

The results of weight loss experiments of corrosion of mild steel in 1N HCl in the presence of plant extract in the temperature range 303K to 343K are shown in Table 2 IE decreases with increase in temperature for all concentrations in the case of plant extract. Decrease in IE with increase in temperature may be explained by the fact that the time lag between the process of adsorption and desorption of inhibitor molecule over the metal surface becomes shorter with increase in temperature. Hence metal surface remains exposed to the acid environment for a longer period thereby increasing the CR which results in reduces IE at elevated temperature.

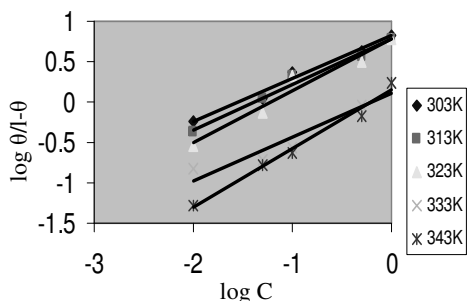
**Table 2.** IE, % of EOL in 1N HCl at different concentrations and different temperatures.

| Conc. of plant extract {%v/v} | IE, % |       |       |       |       |
|-------------------------------|-------|-------|-------|-------|-------|
|                               | 303K  | 313K  | 323K  | 333k  | 343k  |
| 0.01                          | 37.00 | 30.00 | 22.00 | 13.00 | 5.00  |
| 0.05                          | 53.00 | 52.00 | 43.00 | 16.00 | 14.00 |
| 0.1                           | 70.00 | 68.00 | 68.00 | 21.00 | 19.00 |
| 0.5                           | 81.00 | 79.00 | 76.00 | 47.00 | 40.00 |
| 1                             | 87.00 | 86.00 | 86.00 | 63.00 | 64.00 |

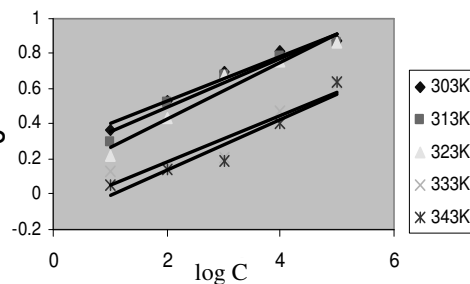
The experimental data obtained with the different inhibitor concentrations of the plant extract in the HCl medium at different temperatures from 303 K to 343 K were applied to different adsorption isotherm equations. Degree of surface coverage  $\Theta$  was calculated based on inhibition efficiency from weight loss measurements as

$$\Theta = (IE \% / 100)$$

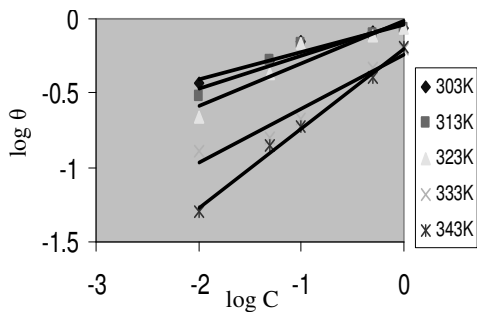
It is found that the data fitted the Langmuir adsorption, Temkin, Freundlich and Flory-Huggins adsorption isotherms with correlation coefficients of > 0.9.



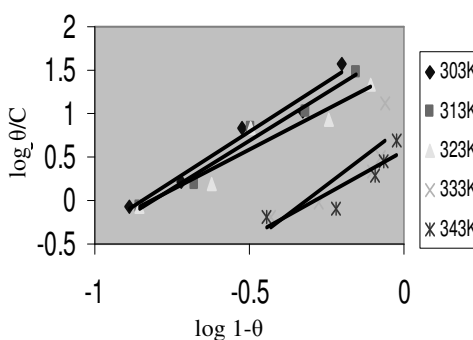
**Figure 1.** langmuir Adsorption EOL in HCl



**Figure 2.** Temkin adsorption EOL in HCl.



**Figure 3.** Freundlich adsorption ELO in HCl



**Figure 4.** Flory-Huggins adsorption EOL in HCl

The values of  $\Delta G_{ads}$  calculated are in the range -14 to -23 kJ/mol indicating that the plant constituents are adsorbed on the metal surface by a strong physical adsorption process. Negative sign indicates that the adsorption of the plant constituents on to the metal surface is a spontaneous process.  $\Delta G_{ads}$  values are found to decrease as the temperature

increases. This may be due to the predominant desorption of the constituents in the adsorption- desorption equilibrium as the temperature increases

**Table 3.** Thermodynamic parameters of adsorption for mild steel in 1N HCl in presence of EOL extract.

| Extract<br>Conc.,% v/v | -ΔG, kJ/mol |       |       |       |       | ΔS,<br>kJ/mol | -ΔH,<br>kJ/mol |
|------------------------|-------------|-------|-------|-------|-------|---------------|----------------|
|                        | 303 K       | 313 K | 323 K | 333 K | 343 K |               |                |
| .01                    | 20.36       | 20.21 | 19.73 | 18.58 | 16.16 | 0.10          | 51.35          |
| .05                    | 18.54       | 18.43 | 18.05 | 14.80 | 14.79 | 0.10          | 48.90          |
| .1                     | 19.22       | 18.38 | 18.97 | 13.80 | 13.86 | 0.13          | 58.36          |
| 0.5                    | 17.03       | 15.68 | 15.72 | 12.68 | 12.25 | 0.09          | 45.03          |
| 1                      | 16.85       | 15.15 | 15.64 | 12.57 | 13.07 | 0.06          | 34.34          |

Negative value for enthalpy of adsorption indicates that the adsorption process is exothermic suggesting physical adsorption. ΔS<sub>ads</sub> values do not show any gradual increase or decrease with respect to inhibitor concentration. A similar trend is observed for ΔG<sub>ads</sub> and ΔH<sub>ads</sub> as well. This may be attributed to the fact that adsorption of the phytoconstituents is not only dependent on concentration but is also influenced by other factors like presence of other constituents, electronic and steric interaction of the inhibitor constituents among themselves as well as with the other constituents present in the corrosive media, orientation of the constituents *etc.*

From Table 4, it can be noticed that E<sub>corr</sub> values are centered on 0.5 V and do not show much variation. This shows that the plant extract acts through mixed mode of inhibiting both the anodic and cathodic reactions equally. I<sub>corr</sub> values show steady decrease from the blank acid to inhibited acid with increasing concentration of inhibitor. This clearly shows that the corrosion rate decreases with inhibitor concentration. The same trend has also been observed in the weight loss method confirming that the inhibitor mechanism involves adsorption of the extract constituents on the surface of metal.

**Table 4.** Potentiodynamic polarization parameters for mild steel in 1N HCl in the presence of EOL extract

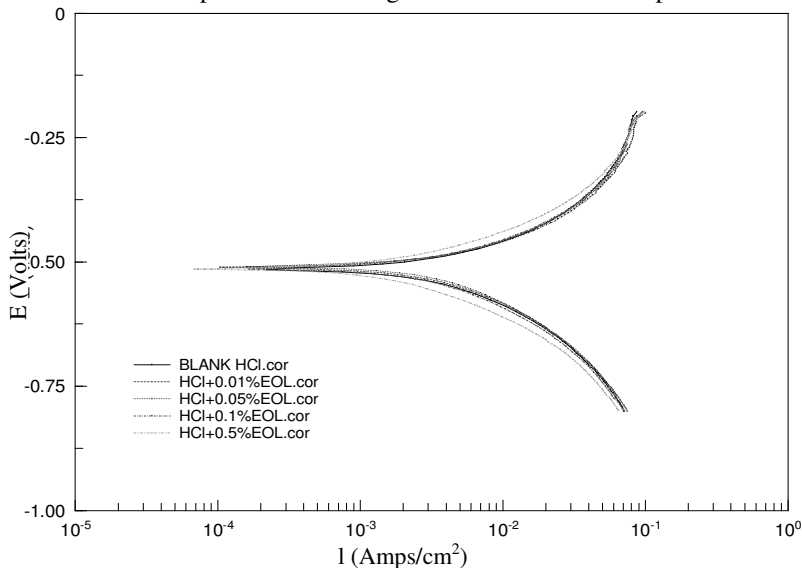
| Concentration of<br>Inhibitor, % w/v | -E <sub>corr</sub><br>mV | I <sub>corr</sub><br>mAmp/Cm <sup>2</sup> | b <sub>a</sub><br>mV/dec | b <sub>c</sub><br>mV/dec | R <sub>p</sub><br>Ohm<br>cm <sup>2</sup> | % Inhibitor<br>Efficiency |        |
|--------------------------------------|--------------------------|---|--------------------------|--------------------------|--|---------------------------|--------|
|                                      |                          |   |                          |                          |  | Tafel                     | Linear |
| Blank                                | 0.5122                   | 4.0524                                    | 178.12                   | 136.8                    | 7.2117                                   | -                         | -      |
| 0.05                                 | 0.5059                   | 3.6071                                    | 171.1                    | 122.46                   | 7.2381                                   | 11.1                      | 0.3    |
| 0.1                                  | 0.5106                   | 3.2178                                    | 164.34                   | 123.79                   | 7.8555                                   | 20.5                      | 8.2    |
| 0.5                                  | 0.5138                   | 2.3363                                    | 153.38                   | 121.33                   | 12.947                                   | 42.2                      | 44.3   |

Inhibition efficiency has been calculated by both Tafel method as well as linear polarization method by using computer software CORRWARE @ for Tafel fit and R<sub>p</sub> fit. IE% values calculated by these methods are found to increase with increase in the concentration of the extract. It is further noticed that values of both anodic and cathodic Tafel constants are markedly changed in the presence of plant extract. This may be attributed to the formation of oxides on the metal surface in the presence of the inhibitor. Different components in the extract might act by specific mechanism and the overall effect may be a mixed mode of inhibition.

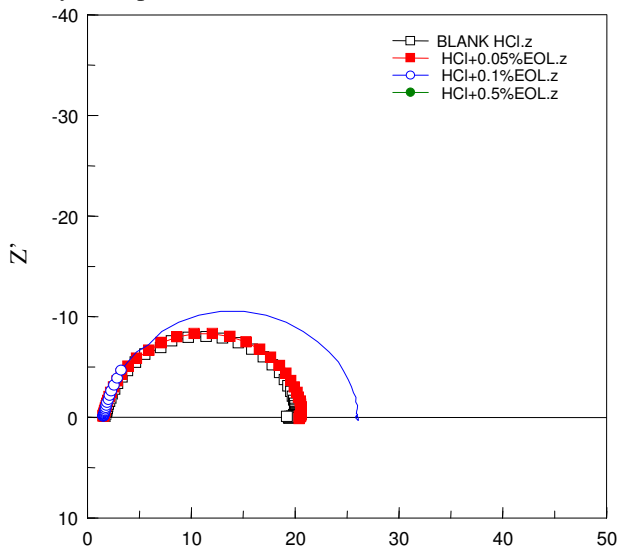
Potentiodynamic polarization curves for mild steel in 1N HCl in the absence and presence of different concentrations of the plant extract are shown in Figure 5. Polarisation plots reveal that the presence of the extract shifts the anodic curves towards the more positive potential direction and the cathodic curves towards the negative direction. This behaviour confirms the

inhibitive effect of the additive. The shapes of Tafel plots also indicate that the electrodic reactions are kinetically controlled.

Figure 6 shows the Nyquist plot for mild steel in 1N HCl without and with the different concentrations of the EOL extract. Nyquist plots show that the mild steel- inhibitor system is under charge transfer resistance control without any loops that could indicate inductive behaviour in the low frequency region. Thus it may be inferred that the inhibitor is selectively adsorbed in specific places on the mild steel surface. According to this mechanism the inhibitor could be adsorbed at active points thus causing the corrosion rate to drop.



**Figure 5.** Potentiodynamic polarization of mild steel in 1N HCl in the absence and presence of EOL.



**Figure 6.** Nyquist plot – mild steel in 1N HCl in the absence and presence of EOL.

Table 5 indicates that  $C_{dl}$  values are less for inhibited systems as compared to those for uninhibited system and  $R_{ct}$  values are higher for inhibited systems. These observations suggest that the plant extract inhibits corrosion by getting adsorbed on the metal surface which increases the impedance (resistance) of the metal surface which in turn decreases  $C_{dl}$  values. Charge transfer resistance is a characteristic quantity indicative of the speed of the electrode reaction. Higher value of  $R_{ct}$  implies a slow reaction

**Table 5.** Impedance parameters for mild steel in the absence and presence of EOL in 1N HCl.

| Concentration of Inhibitor, % v/v | $C_{dl}$<br>$\mu\text{F cm}^{-2}$ | $R_{ct}$<br>$\text{Ohm cm}^2$ | % Inhibitor Efficiency |          |
|-----------------------------------|-----------------------------------|-------------------------------|------------------------|----------|
|                                   |                                   |                               | $C_{dl}$               | $R_{ct}$ |
| Blank HCl                         | 230.5                             | 11.3                          | -                      | -        |
| 0.05                              | 183.95                            | 18.164                        | 20.19                  | 37.78    |
| 0.1                               | 158.9                             | 19.065                        | 31.96                  | 40.74    |
| 0.5                               | 132.92                            | 24.507                        | 42.34                  | 53.89    |

The inhibition mechanism may be predominantly by the adsorption of the plant constituents on the metal by the interaction of  $\pi$  electrons or lone pair electrons of hetero atoms with the metal. The phytoconstituents (Emblicanin A and B, Phyllanthin, punigluconin and pedunculagin) are found to be big molecules capable of covering a large surface area on adsorption. This results in a high IE at relatively low concentration of the extract. This also explains the observation that increase of extract concentration above 1% does not further increase the IE.

## Conclusion

Acid extract of *Emblica officinalis* leaves acts as good corrosion inhibitor for mild steel in 1N HCl medium. Inhibition efficiency increases with inhibitor concentration and maximum inhibition efficiency was 87.69% at the inhibitor concentration 2%v/v. Corrosion inhibition may be due to the spontaneous physical adsorption of the plant constituents on the mild steel surface. Polarisation studies indicate the inhibitor to be of a mixed type inhibiting both cathodic as well as anodic reactions.

## References

1. Abdallah M, El-Etre A Y, Soliman M G and Mabrouk E M, *Anti-Corros Methods Mater.*, 2006, **53**, 2, 118-123.
2. Abiola O K, *J Chil Chem Soc.*, 2005, **50**, 4, 685-690.
3. Adriana O S Leite, Walney S Araújo, Isabel C P Margarit, Adriana N Correiaa and Pedro de Lima-Neto, *J Braz Chem Soc.*, 2005, **16**(4), 756-762.
4. Ayse Tosun and Mübeccel Ergun, *GU J Sci.*, 2006, **19**(3), 149-154.
5. Behpour M, Ghoreishi S M, Soltani N, Salavati-Niasari M, Hamadani M and Gandomi A, *Corros Sci.*, 2008, **50**, 8.
6. El Achouri M, Kertit S, Gouttaya H M, Nciri B, Bensouda Y, Perez L, Infante M R and Elkacemi K, *Prog Org Coatings*, 2001, **43**, 4, 267-273.
7. Hayashi T, Nishihara H and Aramaki K, *Corros Sci.*, 1996, **38**(6), 867-879.
8. Leila Herrag, Balkheir Hammouti, Abdelouahad Aouniti, Sghir El Kadiri and Rachid Touzani, *Acta Chim Slov.*, 2007, **54**, 419-423.
9. El-Etre A Y, Abdallah M and El-Tantawy Z E, *Corros Sci.*, 2005, **47**, 385-395.
10. Sethuraman M G and Raja P B, *Pigment Resin Technol.*, 2005, **34**(6), 327.
11. Saleh R M, Ismail A A and El Hosary A A, *Br Corros J.*, 1982, **17**, 131.

12. Guy D Davis and Von Fraunhofer J A, *Materials Performance*, 2003, **42**(12), 56-59.
13. Oguzie Emeka E, *Port Electrochimica Acta.*, 2008, **26**, 303-314.
14. Chauhan L R and Gunasekaran G, *Corros Sci.*, 2007, **49**, 1143- 1161.
15. Okafor P C, Ikpi M E, Uwah I E, Ebenso E E, Ekpe U J and Umoren S A, *Corros Sci.*, 2008, **50**, 2310-2317.
16. Saratha R, Savitha R and Sivakamasundari S, *J Electrochem Soc India*, 2003, **52**(2), 59-63.
17. El-Etre A Y, *Appl Surf Sci.*, 2006, **252**, 8521.
18. Pandian Bothi Raja and Sethuraman M G, *Mater Lett.*, 2008, **62**(17-18), 2977-2979.
19. Umoren S A and Ebenso E E, *Pigment Resin Technol.*, 2008, **37**, 173 -182.
20. Umoren S A, Obot I B, Ebenso E E and Obi-Egbedi N, *Port Electrochim Acta*, 2008, **26**(2), 199-209.
21. Umoren S A, Obot I B, Ebenso E E and Okafor P C, *Port. Electrochim Acta.*, 2008, **26**(3), 267-282.
22. Umoren S A, Ogbobe O, Igwe I E and Ebenso E E, *Corros Sci.*, 2008, **50**, 1998-2006.
23. Abdel-Gaber A M, Abd-El-Nabey B A, Khamis E and Abd-El-Khalek D E, *Desalination*, 2008, **230**(1-3), 314-328
24. Ebenso E E, Eddy N O and Odiongenyi A O, *Afr J Pure Appl Chem.*, 2008, **2**(11), 107-115.