Technical Report

Effect of Ferrous Gluconate Inhibition on the Electrochemical Behaviour of Mild Steel in 3.5% NaCl

O. Sanni[1], C.A. Loto[1, 2], A.P.I.Popoola[1]

[1]Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, Pretoria, South Africa
[2]Department of Mechanical Engineering, Covenant University, Ota, Nigeria
*E-mail: popoolaapi@tut.ac.za

Inhibitor and corrosion protection of mild steel specimens immersed in 3.5% NaCl solution was investigated using weight loss, polarization measurements and high resolution scanning electron microscopy (HR - SEM). Ferrous gluconate in different concentrations was used as inhibitor. A decrease in the reactions of active corrosion behaviour of the mild steel test specimen in the sodium chloride solution was obtained with the addition of different concentrations of the ferrous gluconate. The inhibiting effect of ferrous gluconate on mild steel surface was attributed to the Langmuir adsorption isotherm. The obtained results showed that ferrous gluconate provides a good protection for mild steel against corrosion in sodium chloride solution for the greater part of the experimental period.

1. INTRODUCTION

Mild steel, an alloy of iron and carbon is used in various industries because of its low cost and easy availability for fabrication of reaction vessels, girders, machine parts, rivets, tanks and pipes. Chloride ions are usually recognized as the main cause of pitting corrosion in mild steel due to their localised nature, leading to passive layer breakdown [1, 2]. The hostility of chloride ion is as a result of its size, diffusivity and strong acidic anionic nature [3]. A lot of research has been made on the corrosion behavior of steel in carbonated-chloride brine [1]. Corrosion caused by chloride can be generally reduced by using inhibitors to minimize the attack of the metal [4-13]. Various thiadiazole compounds have been assessed as good corrosion inhibitors for mild steel in acidic and sulfate solutions [14-20]. Though, a quite number of studies have been done on the corrosion inhibition of

steel in acidic media [14-20], few works have been done in chloride solution. Therefore, it seems interesting to investigate the role of ferrous gluconate (FG) as corrosion inhibitor for mild steel in 3.5% NaCl solution and to consider the influence of FG on the pitting corrosion potential of the mild steel in the sodium chloride medium. In this study, FG as corrosion inhibitor for mild steel in 3.5% NaCl solution has been assessed using weight loss, potentiodynamic polarization methods and SEM observations.

2. EXPERIMENTAL TECHNIQUES

2.1. Materials and methods

The mild steel coupons with dimensions 12 x 12 x 2 mm were cut from a sheet. The chemical composition (wt %) of the mild steel coupons is given in Table 1. Before use, the samples were polished successively by using silicon carbide papers of 80, 120, 220, 320, 800, 1000 and 1200 grades, thoroughly cleansed with distilled water and with ethanol. The specimens were dried and kept in a desiccator until their use. The initial weight of each sample was taken and recorded. Selected specimens for polarization measurement were connected to an insulated flexible wire and cold mounted with methyl methacrylate resin. 3.5% NaCl solution was used for all studies; double distilled water was used to prepare the sodium chloride solutions. FG as inhibitor was used in sodium chloride environment. The molecular structure of the FG is presented in Fig. 1. The experiment was conducted at 28^0C.
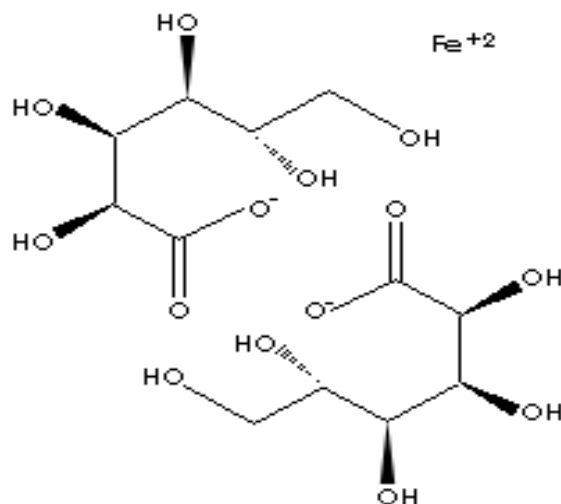

Figure 1. Molecular structure of Ferrous Gluconate

Table 1. Chemical composition of the mild steel used (wt %)

C	Si	Mn	P	S	Ni	Al	Cu	Fe
0.13	0.029	0.397	0.0067	0.018	0.025	0.126	0.036	Balance

2.2. Weight loss method

The corrosion measurement by weight loss method was carried out on the weighed samples with and without FG at 28^0C. The volume of the solution used was 200ml with and without inhibitor. The FG concentration was varied at 0.5, 1.0, 1.5 and 2.0 %g/v in 200ml of 3.5% NaCl solution. For each sample, using weight loss method, the samples were washed, dried and weighed at an interval of 48h of exposure time. The corrosion rate, degree of surface coverage and inhibition efficiency were calculated for the inhibitor concentration at 28^0C. The weight loss was determined by finding the difference between the initial weight of the samples and the final weight using the equation below

$$W = W_O - W_F \qquad\qquad\qquad (1)$$

Where:

W = weight loss in mg, W_O= initial weight, W_F= final weight.

The corrosion rate, surface coverage and inhibition efficiency were determined using equation reported elsewhere [21].

2.3. Potentiodynamic polarization measurement

The potentiodynamic polarization experiments were performed using a typical three electrode cell at 28^0C. The working electrode was mild steel of chemical composition stated above. The exposed area of each sample was 1 cm^2 and the rest being covered by methyl methacrylate resin. A graphite rod was used as counter electrode and saturated Ag/Ag as reference electrode. The polarization studies were conducted in 200 ml 3.5% NaCl solution using AUTOLAB Potentiostat (model Reference-668), this system was connected to a personal computer to control the experiments and the data were analyzed using NOVA software. The linear sections of anodic and cathodic curves were extrapolated with a scan rate of 0.0016V/sec. From the Tafel corrosion technique, the corrosion rate, current density, linear polarization resistance and corrosion potential were obtained in a static solution.

2.4. Surface morphology

The as – received and the corroded mild steel surfaces were studied using high resolution scanning electron microscopy (HR - SEM). The SEM micrographs of the samples were made by JEOL JSM-7600F.

3. RESULT AND DISCUSSIONS

The result of the weight loss measurement for mild steel in 3.5% NaCl – ferrous gluconate is presented in Fig. 2 and 3. The potentiodynamic polarization result is presented in Table 2. The linear polarization curves can be seen in Fig. 4. The HR - SEM micrographs of the as- received and the

corroded inhibited mild steel after 28 days are shown in Fig. 5. Fig. 6 shows the variation of the inhibition efficiency with varied concentrations of the inhibitor for weight loss and potentiodynamic polarization method under different criteria. Fig. 7 illustrates the adsorption isotherm for the inhibitor at different concentration at the studied time.

3.1. Corrosion rate and inhibition efficiency

The effect of addition of ferrous gluconate at different concentrations on the corrosion of mild steel in 3.5% NaCl solutions was investigated using weight loss method at 28^0C after 48 h of immersion period. The corrosion rates of the mild steel coupons in 3.5% NaCl solution with and without different concentrations of inhibitor were determined. The results obtained are presented in Fig. 2. It was deduced from Fig. 2 that the corrosion rate of mild steel increased with exposure time. The corrosion rate of mild steel without inhibitor increased from 0.053 mm/yr at the end of 2 days of exposure time to 0.204 mm/yr at the end of 28 days of exposure time which amount to 74% increment in corrosion rate value after 28 days of exposure time. With FG, the corrosion rate value was drastically reduced from 0.204 mm/yr to 0.055 mm/yr at the end of 28 days of exposure time which also translate to 73% reduction in corrosion rate value at 2.0%g/v concentration of inhibitor. The corrosion rate of mild steel also decreases with an increase in concentration of FG from 0.5 to 2.0%g/v with an interval of 0.5.

Fig. 3 shows the variation of inhibition efficiency (IE) at different concentrations of ferrous gluconate. It was observed that the inhibition efficiencies increase at all the studied concentration of ferrous gluconate. The optimum inhibition efficiency was observed at 0.5%g/v concentration of FG and for all the varied concentration of FG, the IE falls within 70-75% after the 28 days of exposure to the sodium chloride environment.
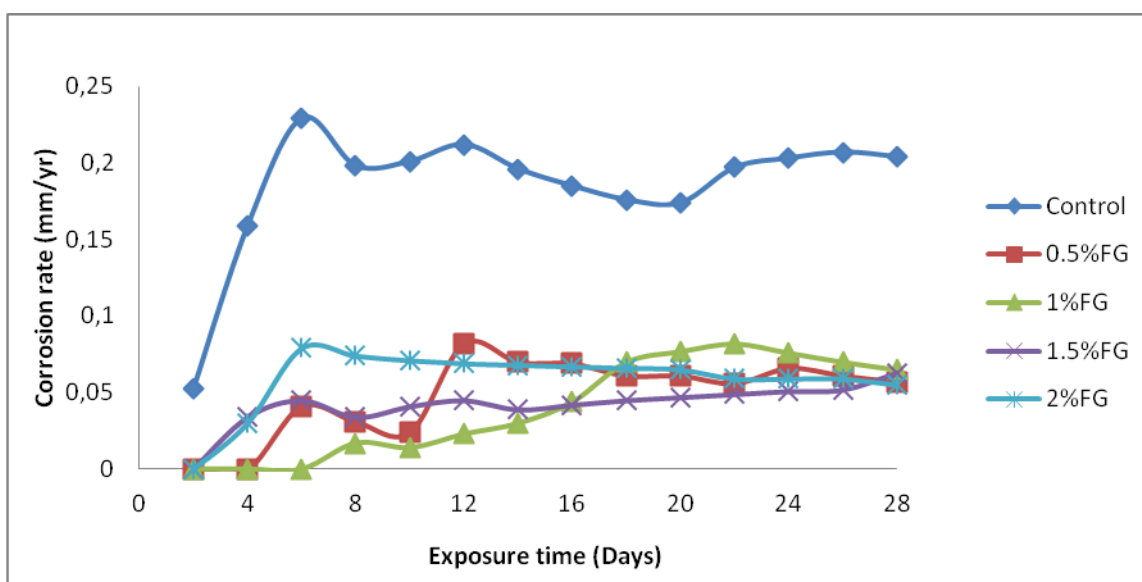

Figure 2. Variation of corrosion rate with exposure time for the mild steel specimen immersed in sodium chloride for different concentration of inhibitor.
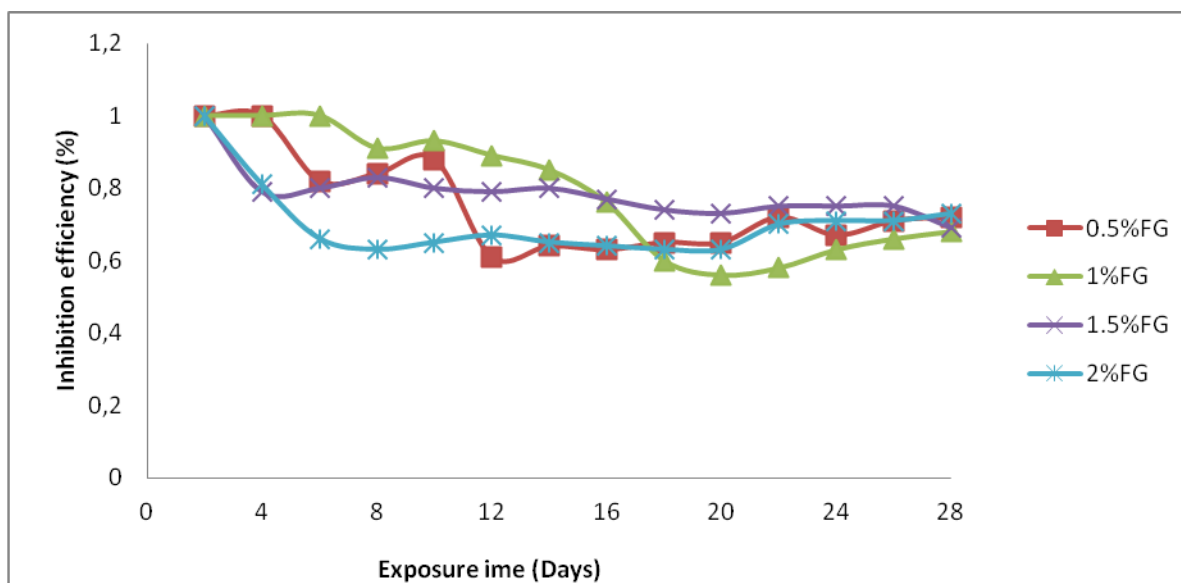
Figure 3. Variation of inhibition efficiency with exposure time for the mild steel specimen immersed in sodium chloride for different concentration of inhibitor.

3.2. Potentiodynamic polarization method

Fig. 4 shows the Tafel polarization curves for mild steel in 3.5% NaCl solution with and without the addition of different concentrations of FG. The important corrosion parameters derived from these curves are presented in Table 2. From Table 2, it is clear that the current density (Icorr) value decreases with the addition of FG. Also, the addition of FG does not alter the value of corrosion potential (Ecorr) significantly. Table 2 also show the variation of polarization resistance of mild steel with the addition of FG in the studied media. The polarization resistance (Rp) values of mild steel in 3.5% NaCl solution increases from 6218 Ω cm^2 of solution without inhibitor to 3.98E+10 Ω cm^2 with 0.5%g/v concentration of inhibitor. Furthermore, the results in Table 2 shows clearly that both current density (Icorr) and corrosion rate (CR) values decrease, while the polarization resistance (*R*p) increases with addition of inhibitor indicating the inhibitory effect of FG on the mild steel in sodium chloride solution.

Table 2. Electrochemical parameters for corrosion of mild steel in 3.5% NaCl with and without varying concentration of ferrous gluconate at 28^{0}C.

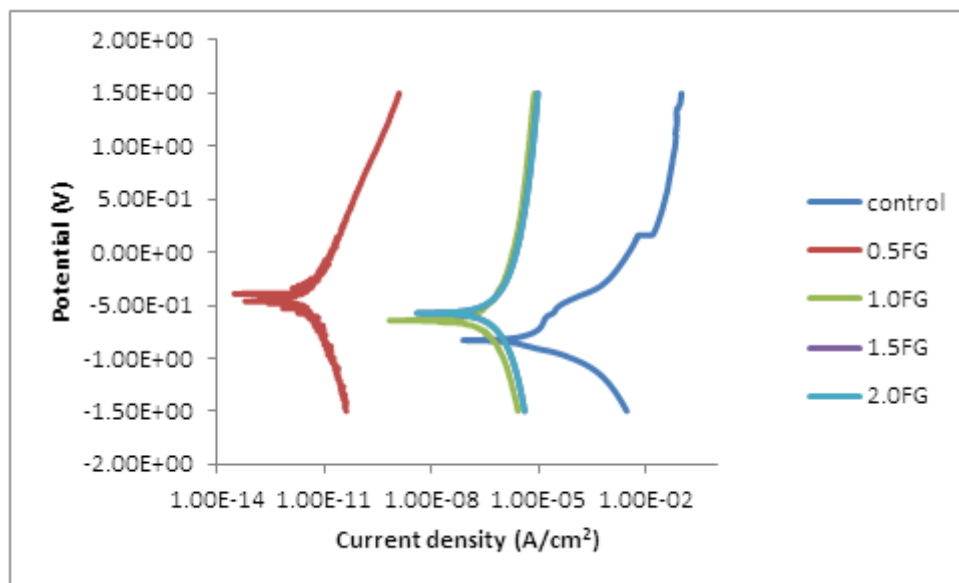| S/N	C(%g/v)	Icorr(A/cm^2)	ba(v/dec)	LPR Rp(Ωcm^2)	-Ecorr(V)	CR(mm/yr)
0	0	4.68E-06	0.45851	6.21E+03	0.82959	0.054382
1	0.5	2.82E-12	0.44503	3.98E+10	0.47559	3.28E-08
2	1.0	1.58E-08	0.28836	2.51E+05	0.64014	0.000184
3	1.5	4.76E-08	0.52491	2.42+E05	0.57366	0.005528
4	2.0	4.76E-07	0.52492	2.42+E05	0.57367	0.005536

Figure 4. Linear polarization of mild steel in 3.5% NaCl solution /ferrous gluconate environment at 28^{0}C.

Generally, for a given inhibitor, Rp value in a solution with inhibitor is greater than its value in corrosive medium without inhibitor, indicating that the corrosion rate of mild steel is more enhanced in sodium chloride media, and that the protective adsorbed layer on the mild steel surface is more stable with the inhibitor [22]. This is in agreement with the present result as Rp value calculated with FG in sodium chloride solution was found to be much higher than the previous value calculated in sodium chloride solution without FG under comparable conditions.

3.3. SEM micrographs

SEM micrographs of the corroded surface of the mild steel samples in 3.5% NaCl solution with and without FG after 28 days immersion were examined using HR - SEM as shown in Fig. 5 (a–c) respectively. Without inhibitor (Fig. 5a), a very rough surface is observed due to rapid corrosion attack of mild steel by the chloride anions. With FG in the solution, the morphology of mild steel surface is quite different from the rough surface without inhibitor, indicating the formation of a protective film with inhibiting power of the FG.
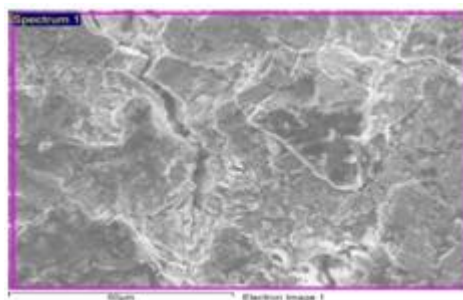

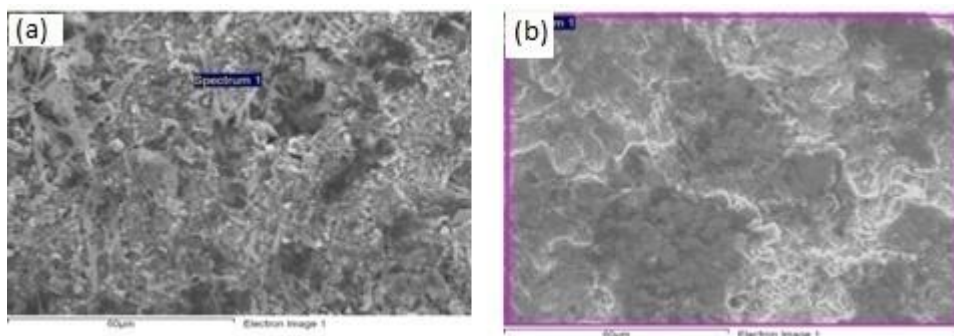**Figure 5a.** SEM micrograph of the as - receive mild steel sample.

Figure 5a and b. SEM micrographs of the surface of mild steel samples after weight loss in 3.5% NaCl solution: (a) without ferrous gluconate (b) With 0.5%g/v ferrous gluconate.

Comparative studies of the SEM images at the same magnification shows that 3.5% NaCl solution with 0.5%g/v ferrous gluconate shows an improvement on the surface morphology of mild steel.

3.4. Inhibitor efficiency and adsorption behavior

Fig. 6 shows the comparative inhibition efficiency parameter for investigating concentration of FG obtained by different methods; weight loss method (WLM), potentiodynamic polarization – corrosion rate (PP–CR), potentiodynamic polarization – current density (PP–Icorr) and linear polarization resistance (LPR) for mild steel in sodium chloride solution.
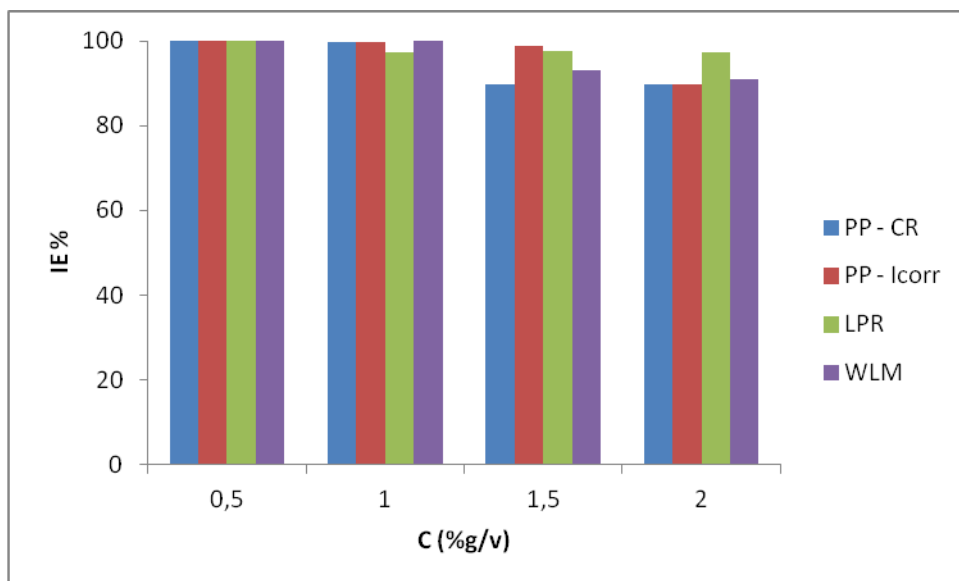

Figure 6. The comparison of inhibition efficiency data (IE %) for mild steel in 3.5% NaCl solution with varying concentration of FG obtained by weight loss and potentiodynamic polarization methods

From the histogram, it is clear that the data obtained by different methods correlates with one another and the inhibition efficiency is high at all the studied concentrations of FG. The optimum concentration was observed at 0.5%g/v FG which gives 100% efficiency.

The corrosion protection mechanism may be explained on the bases of adsorption behavior [23]. The adsorption behavior of FG on mild steel was determined using three frequently used adsorption isotherm namely: Langmuir, Temkin and Freundlich. The effect of inhibitor concentration on the degree of surface coverage (0) was obtained from weight loss method. The data obtained were best fitted with Langmuir isotherm. Plotting $C/0$ against the inhibitor concentration (C) for FG was shown in (Fig. 7) which gives a linear relationship with a slope close to unity.
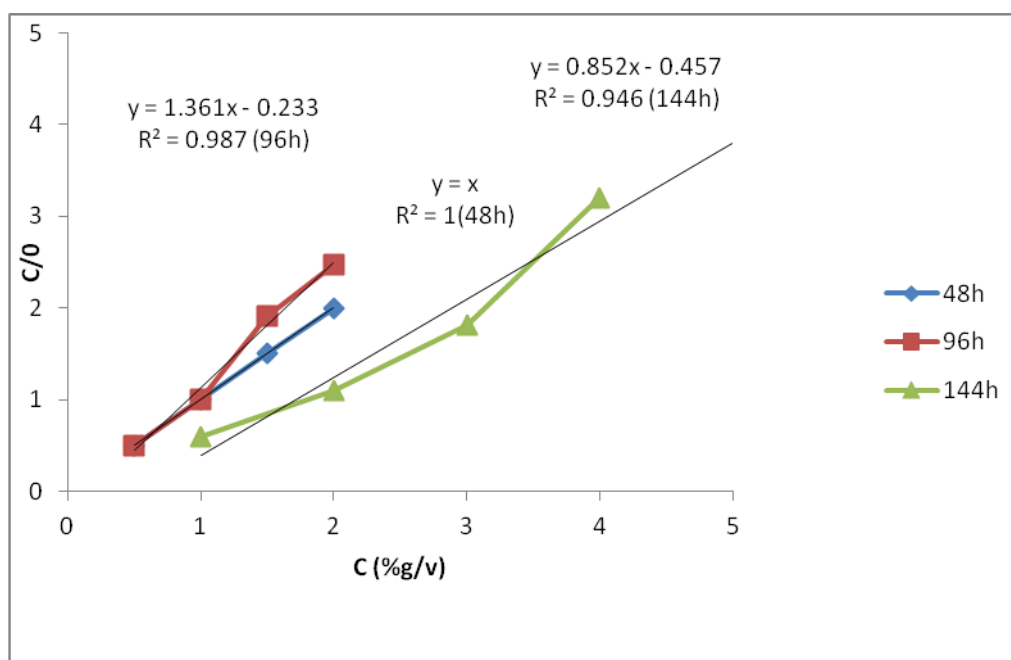

Figure 7. Langmuir isotherm for the adsorption of ferrous gluconate compounds on mild steel surface in 3.5% NaCl solution obtained from weight loss method at 28^0C

4. CONCLUSIONS

From the investigation into the use of FG as an inhibitor in 3.5% NaCl solution, the following deductions were made:

Ferrous gluconate was found to be an effective inhibitor for mild steel in 3.5% NaCl solution.

The results obtained from weight loss tests and potentiodynamic polarization measurements were in good agreement, the adsorption of ferrous gluconate can be attributed to the Langmuir adsorption isotherm.

The inhibitor is recommended to be used at 0.5%g/v concentration in 3.5%NaCl solution for a short period of time.

ACKNOWLEDGEMENTS

References

1. F.M. Al-Kharafi, B.G. Atea and R.M. AbdAlla, *J. Appl. Electrochem.,* 32 (2002) 1363.
2. K. Aramaki and T. Shinura, *Corros. Sci.,* 48 (2006) 209.
3. J.R. Galvele, *Corros. Sci.,* 21 (1981) 551.
4. JO'M .Bockris and B. Yang, *J. Electrochem. Sci.,*138 (1991) 2237.
5. F. Bentiss, M. Traisnel and M. Lagrene`e, *Corros.Sci.,*42 (2000) 127.
6. M. Bouklah, B. Hammouti, M. Benkaddour and Benhadda, *J. Appl. Electrochem.,* 35 (2005) 1095.
7. L. Elkadi, B. Mernari, M. Traisnel, M. Bentiss and M. Lagrene`e, *Corros.Sci.,*42 (2000)703.
8. H.L Wang, R.B Liu and J .Xin, *Corros. Sci.*, 46 (2004) 2455
9. S. S. Mahmoud, *J. Mater. Sci.*, 42 (2007) 989.
10. A.S. Fouda, H.A. Mostafa, S.E. Ghazy and S.A. El-Farah, *Int. J. Electrochem. Sci.* ,2 (2007) 182.
11. W. Villamizar, M. Casales, and J.G. Gonzalez-Rodriguez, *J. Solid State Electrochem.*, 11 (2007) 619.
12. A. Fiala, A. Chibani, A. Darchen, A. Boulkamh and K. Djebbar, *Appl. Surf. Sci.* , 253 (2007) 9347.
13. A.S. Fouda, A .Abd El-Aal and A.B. Kandil, *Desalination.,* 201 (2006) 216.
14. M. Mahdavian and S.A. Ashhari, *Electrochim. Acta.,* 55 (2010) 1720.
15. L. Valek and S. Martinez, *Mater.Lett.,* 61 (2007) 148.
16. M.E. Azhar, B. Mernari, M. Traisnel, F. Bentiss and M. Lagrenée, *Corros. Sci.,* 43 (2001) 2229.
17. M. Lebrini, M. Lagrenée, H. Vezin, M. Traisnel and F. Bentiss, *Corros. Sci.,* 49 (2007) 2254.
18. M. Lebrini, F. Bentiss, H. Vezin and M. Lagrenée, *Corros. Sci. ,* 48 (2006) 1279.
19. M. Lebrini, M. Lagrenée, M. Traisnel, L. Gengembre, H. Vezin and F. Bentiss, *Appl. Surf. Sci. ,* 253 (2007) 9267.
20. F. Bentiss, M. Lebrini, M. Lagrenée, M. Traisnel, A. Elfarouk and H. Vezin, *Electrochim. Acta.*, 52 (2007) 6865.
21. F. El-TaibHeakal, A.S. Fouda and M.S. Radwan*, Int. J. Electrochem. Sci.,* 6 (2011) 3140.
22. S.A. Ali, H.A. Al-Muallem, M.T. Saeed and S.U. Rahman, *Corros. Sci.*, 50 (2008) 664.
23. N.K. Allam, *Appl. Surf. Sci.*, 253 (2007) 4570.