Int. J. Electrochem. Sci., 8 **(2013)** 12088 - 12096

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electro-oxidation Behaviour and Passivation Potential of Natural Oil as Corrosion Inhibitor in Hydrochloric Acid Environment

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Received: 19 July 2013 / *Accepted:* 22 August 2013 / *Published:* 25 September 2013

The electro-oxidation behaviour and passivation potential of natural oil (*Arachis hypogeae)* as corrosion inhibitors for mild steel in 2M HCl solution have been studied using gravimetric and electrochemical techniques. The surface morphology of as-corroded samples was assessed with scanning electron microscopy equipped with energy dispersive spectroscopy (SEM-EDS). The results revealed that corrosion rate of mild steel with *Arachis hypogea* in HCl environment decreased with exposure time. In the gravimetric method, an inhibitor efficiency of 72.69, 75.19 and 47.07% were obtained at 50/20/50%v/v *Arachis hypogeae* addition respectively in 2M HCl solution for 12, 24 and 36h exposure time. Results from the linear polarization indicate a higher potential value and %IE of 94.99 for 100%v/v *Arachis hypogeae* with an increase in the polarization resistance (R_p) and lower current density for the inhibited samples than the uninhibited mild steel. There was an agreement with the methods used for the corrosion evaluation of mild steel-*Arachis hypogeae* in 2M HCl solution.

Keywords: *Arachishypogeae*, Inhibitor efficiency, SEM-EDS, thin film

1. INTRODUCTION

The applications of mild steel in many industries are due to its easy availability, ease of fabrication, low cost and good tensile strength besides various other desirable properties. The degradation of mild steel in acidic environment has become subject of interest among researcher over the years due to the usage of mild steel as an engineering material such as in acid pickling, industrial cleaning, acid descaling, oil-well acid and the petrochemical process [1-4], water cooling system, steam generators and ballast tanks [4]. The wide industrial application of mild steel have been driven by number of issues, in particular its low cost and availability for the manufacturing of reaction vessels; cooling tower reservoirs, pipelines [5]. However, the ability of mild steel to resist corrosion attack in some environment is not sufficient and a continuous search for method(s) for improving this limitation becomes important. Various methods have been developed for the corrosion control and prevention for mild steel in majority of environment. Among the methods, the use of inhibitors for reducing the corrosion rate of mild steel has been reported to be effective [1-14]. Recently, some chemical and synthetic compounds as inhibitors for corrosion prevention have been identified as highly toxic to both human beings and environment [1,6,15]. In this direction, an environmentally (eco-friendly) and nontoxic inhibitors has been area of focus in recent time. Plant and oils have become important as an environmentally acceptable, readily available and renewable source of materials for wide range of corrosion prevention and control [3,16,17] and low-cost substances [1]. The potentials of *Arachis hypogeae* as corrosion inhibitor for aluminium alloy in some acidic [18] and mild steel in tetraoxosulphate iv acid [19] environment have been demonstrated in our previous study. In the present work, an attempt was made to study the electro-oxidation behaviour and passivation potential utilizing the natural oil as an eco-friendly corrosion inhibitor on mild steel in HCl solution using gravimetric and potentiodynamic polarization techniques.

2. MATERIALS AND METHOD

2.1 Materials and sample preparation

Table 1. Chemical composition of the mild steel used

Element	C	Mn	Si	P	S	Cr	Ni	Fe
wt% Composition	0.20	0.65	0.10	0.04	0.13	7.20	3.50	Balance

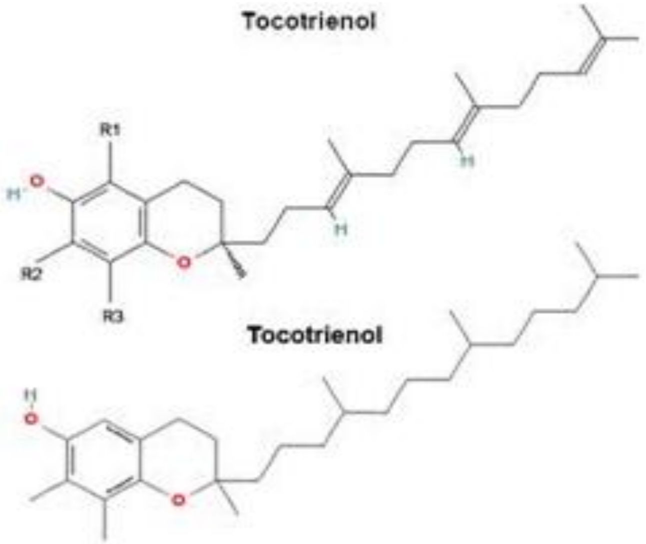

Figure 1. Molecular structure of *Arachis hypogeae*

A mild steel specimen of dimension 20 x 10 x 3 mm with chemical composition shown in Table 1 was used. The samples were degreased in ethanol, dried, weighed and stored in a desiccator. The initial weight of each sample was taken and recorded. A concentration of 2M hydrochloric (HCl) were prepared fresh as required for the experiment. The *Arachis hypogeae* oil was used as inhibitor for mild steel in HCl acidic solution. The natural oil was obtained from chemical shop in Pretoria, South Africa with molecular structure shown in Figure 1. The corrosion measurements were conducted at room temperature (25^{o}C) in a static solution.

2.2 Gravimetric corrosion measurement

The gravimetric corrosion test was carried out on the previous weighed samples with and without inhibitor at 25^{o}C. The volume of the solution was 100 mL with and without the addition of *Arachis hypogeae* inhibitor. The *Arachis hypogeae* inhibitor's concentration was varied from 20, 50 and 100%v/v in 100ml of 2M HCl acidic solution. For each sample with *Arachis hypogeae* inhibitor using gravimetric technique after the corrosion test, the samples was washed, dried and weight taken at interval of 12, 24 and 36 h of immersion time. The corrosion rate (mm/day) and inhibitor efficiency (% IE) were determined along with the degree of surface coverage (θ).

2.3 Potentiodynamic corrosion measurement and surface morphology

The potentiodynamic polarization was used to evaluate the corrosion rate of the mild steel in *Arachis hypogeae*-HCl solution. All the potentiodynamic measurements were obtained using Autolab frequency response analyzer (FRA) coupled to potentiostat that was connected to a computer system. A glass corrosion cell kit with a platinum counter electrode, a saturated Ag/Ag reference electrode and mild steel sample as working electrode were used. The working electrodes samples were positioned at the glass corrosion cell kit, leaving 1 cm^2 surfaces in contact with the solution. Polarization test were carried out in 2M HCl solution at room temperature in a static solution using a potentiostat (model: AuT71791 and PGSTAT 30) with a scan rate of 0.003V/sec. From the Tafel corrosion analysis, the corrosion rate, potential and linear polarization resistance was obtained. The as-corroded uninhibited and inhibited mild steel surfaces were examined with scanning electron microscopy to analyze the extent of surface damage (Model: Joel 6100).

3. RESULTS AND DISCUSSION

3.1 Results

Table 2 shows the corrosion parameters obtained from the gravimetric measurement for mild steel in 2M HCl/*Arachis hypogeae environment*. In Figure 2, the variation of corrosion rate with inhibitor concentrations can be found. While Table 3 represent the electrochemical corrosion data for mild steel in 2M HCl-*Arachis hypogeae* environment. The linear polarization curves can be found in

Figure 3. The SEM micrographs of as-corroded uninhibited/inhibited mild steel were presented in Figure 4 (a and b). Figure 5 shows the variation of inhibitor efficiency against concentration of inhibitors for different corrosion methods used. Figure 6 illustrates the Langmuir adsorption isotherm for the inhibitor using different corrosion evaluation techniques.

3.2 Discussion

3.2.1 Gravimetric measurement

Table 2. Corrosion rate (CR), Inhibition efficiency and surface coverage (θ) for mild steel in 2M HCl without and with varying concentration of *Arachis hypogeae* at 25°C

Time (hr)	Concentration of inhibitor (%v/v)	CR (mm/day) *Arachis hypogeae*	Surface coverage (θ)	Inhibition Efficiency (%)
12	0	1.45×10^{-3}	-	-
	20	1.22×10^{-3}	0.1586	15.86
	50	3.96×10^{-4}	0.7269	72.69
	100	7.70×10^{-4}	0.4690	46.90
	0	1.04×10^{-3}	-	-
24	20	2.58×10^{-4}	0.7519	75.19
	50	6.57×10^{-4}	0.3683	36.83
	100	8.55×10^{-4}	0.1779	17.79
36	0	1.16×10^{-3}	-	-
	20	9.29×10^{-4}	0.1991	19.91
	50	6.14×10^{-4}	0.4707	47.07
	100	7.82×10^{-4}	0.3259	32.59

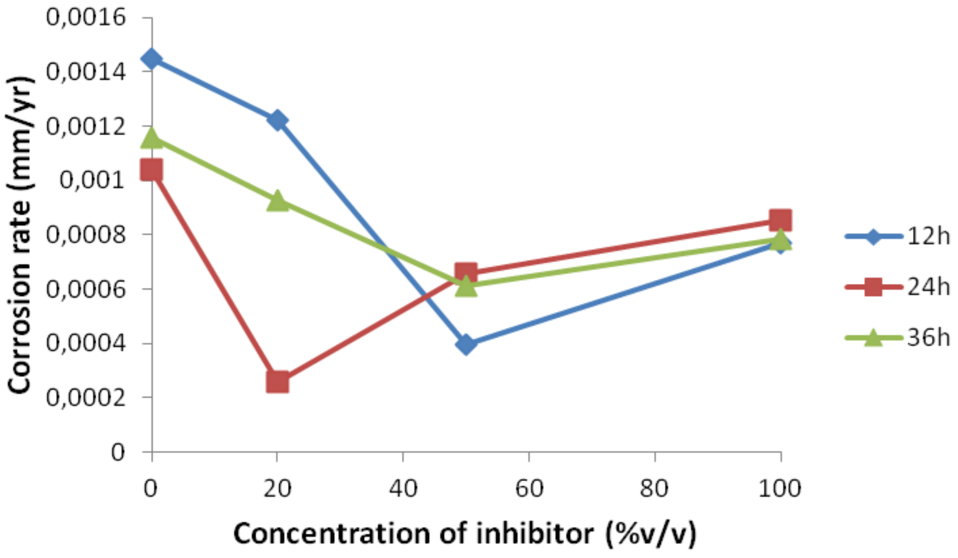

Figure 2. Variation of corrosion rate with concentration of inhibitor for mild steel in 2M HCl without and with varying concentration of *Arachis hypogeae* at 25°C

Natural oil of *Arachis hypogeae* was considered for the study of mild steel-HCl corrosion behavior with different inhibitor concentrations at 25°C. The results indicated that corrosion rate (CR) of the mild steel-HCl decreased with addition of inhibitor and exposure time considered (Table 2; Figure 2). Considering the 2M HCl-*Arachis hypogeae* environment (Figure 2), at 12 h immersion time for 50%v/v *Arachis hypogeae* corrosion rate decreased from 0.00145 to 0.000396 mm/day indicating inhibitor efficiency (IE) of 72.69%. While at 20%v/v *Arachis hypogeae* addition the corrosion rate decreased from 0.00104 to 0.000258 mm/day with IE of 75.19%. The corrosion behavior of mild steel in the HCl containing *Arachis hypogeae* has been attributed to the increase in the element that forms stable oxides as evidenced in the EDS (Figure 4c). The thin layer of the oxides adheres to the metal surface resulting to a decrease in the corrosion rate. This is similar to the results reported elsewhere [11,20,21].

3.2.2 Potentiodynamic polarization

Table 3. Electrochemical corrosion data obtained for mild steel in 2M HCl-varying concentration of *Arachis hypogeae* environment at 25°C

S/N	% inhibitor	I_{corr}(A/cm^2)	b_a(v/dec)	LPR R_p(Ωcm^2)	E_{corr}(V)	CR (mm/yr)
1	0	1.003E-4	0.040	8.489E-1	-0.406	5.482E-1
2	20	2.899E-5	0.043	1.414E+1	-0.415	1.585E-1
3	50	1.482E-5	0.044	2.652E+1	-0.431	8.102E-2
4	100	5.020E-6	0.018	5.227E+0	-0.407	2.744E-2

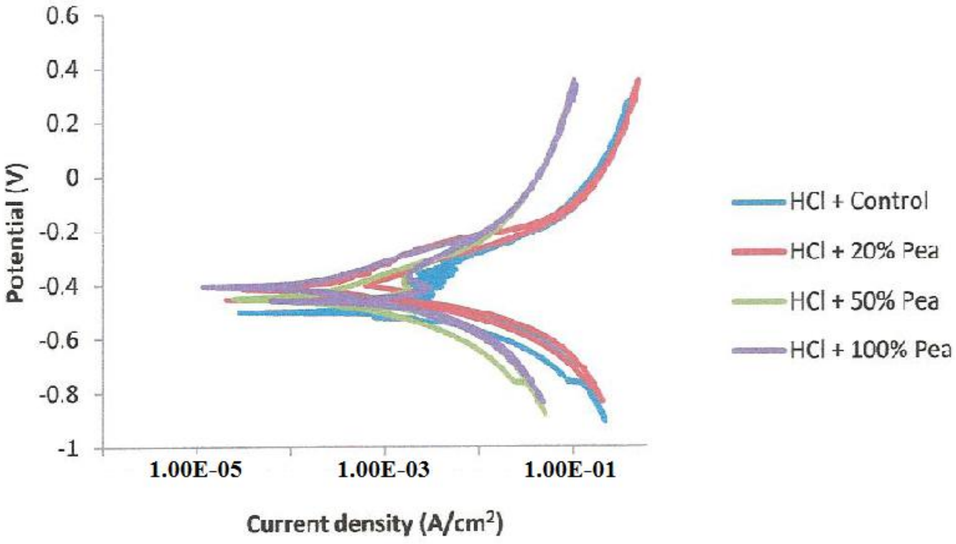

Figure 3. Linear polarization curves for mild steel in 2M HCl solution-*Arachis hypogeae* environment

The potentiodynamic measurement for the mild steel in 2M HCl/*Arachis hypogeae* is presented in Table 3. Potentiodynamic polarization-corrosion rate (PP-CR), potentiodynamic polarization-corrosion density (PP-I_{corr}), and linear polarization resistance (LPR) were used as criteria for evaluation of corrosion resistance of mild steel in the environment. Figure 3 shows the polarization curves for 2M HCl-*Arachis hypogeae* at 25°C. In general, the enhanced environment demonstrated a decreased corrosion rate and current density with addition of the inhibitor at all concentrations. While the corrosion potential (E_{corr}) and polarization resistance (R_p) increases with inhibitor's concentrations. These are in agreement with previous study [22]. The inhibited mild steel in HCl-*Arachis hypogeae* revealed that corrosion rate decreased from 0.5482 mm/yr to 0.1585, 0.08102 and 0.02744 mm/yr at 20, 50, and 100%v/v *Arachis hypogeae* respectively. However, based on the changes in anodic and cathodic branches for the environment, a mixed-type corrosion inhibition has been proposed.

3.2.3. Scanning electron microscope-energy dispersive spectroscopy (SEM-EDS) and Inhibitor efficiency/adsorption behavior of the mild steel in HCl-inhibitor

The SEM micrographs of mild steel surfaces are shown in Figure 4a, b and c. The uninhibited mild steel sample in 2M HCl solution (Figure 4a) indicates a severe pits formation as compared with inhibited mild steel (Figure 4b).

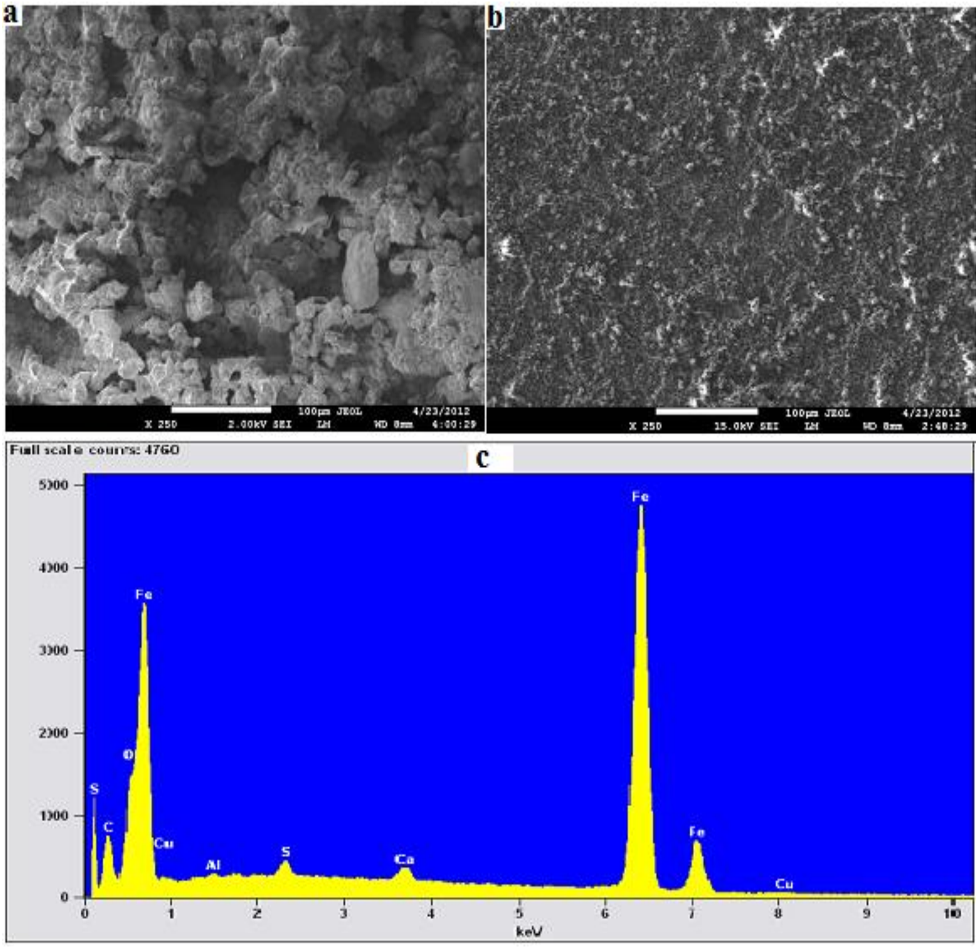

Figure 4. SEM micrographs of a) as-corroded uninhibited b) as-corroded inhibited in 50%v/v *Arachis hypogeae* -2M HCl solution after 36 h of immersion time c) EDS spectral for (b)

In Figure 4b, it is clear that *Arachis hypogeae* natural oil was able to exhibit some degrees of inhibition which retarded the corrosion rate of the mild steel in HCl solution. In addition, the inhibited sample can be said to be protected with thin film layers of the corrosion inhibitor resulting to the decreased in the corrosion rate of the mild steel in the HCl solution. From the EDS in Figure 4c, the occurrence of O is as a result of ferrous hydroxide formation and the combination of C, O and other elements are due to the constituent contained in the structure of the inhibitors (Figure 1). This acts as a good inhibitor which in turn increases the corrosion resistance of the mild steel in the acidic medium.

The percentage inhibitor efficiency (% IE) of the *Arachis hypogeae* inhibitor for mild steel in HCl solution was computed using the equation reported [23]. *Arachis hypogeae* inhibitor was used for the study of mild steel-HCl corrosion behavior with different inhibitor concentrations at 298K. In each concentration, the corrosion rate (mm/yr) was calculated and the inhibitor efficiency IE (%) was determined using equations 1 and 2 below;

$$\mathrm{CR} = \frac{Wo - Wa}{At} \qquad (1)$$

$$\mathrm{IE}\ (\%) = \frac{(CRa - CRp)100}{CRa} \qquad (2)$$

Where Wo and Wa are the specimen weight before and after immersion in the tested solution, A is the area of the mild steel specimen and t is the exposure time (hr). CRa and CRp are the corrosion rate in the absence and presence of inhibitor respectively. The computed data for the IE using gravimetric (GM), potentiodynamic polarization-corrosion rate (PP-CR), potentiodynamic polarization-corrosion density (PP-I_{corr}), and linear polarization resistance (LPR) are presented in Figure 5 for 2M HCl/*Arachis hypogeae* environment. This shows that % IE of the HCl/*Arachis hypogeae* oil increases with an increase in the inhibitor concentrations. The reasons been that, as the inhibitor concentration increases, the surface area covered by these inhibitors increased hence higher %IE were obtained. For example, for mild steel-HCl/*Arachis hypogeae*, IE of 94.99, 97.69 and 96.80% were obtained for PP-CR, PP-I_{corr}, and LPR respectively at 100/100/50%v/v *Arachis hypogeae.*

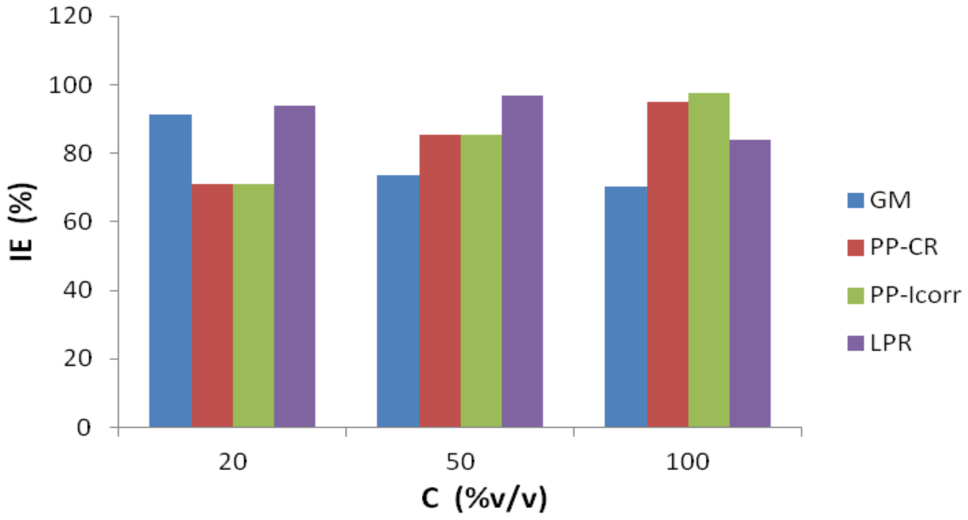

Figure 5. Comparative chart of inhibitor efficiency (IE) for mild steel-2M HCl solution/*Arachis hypogeae* concentration obtained by different techniques

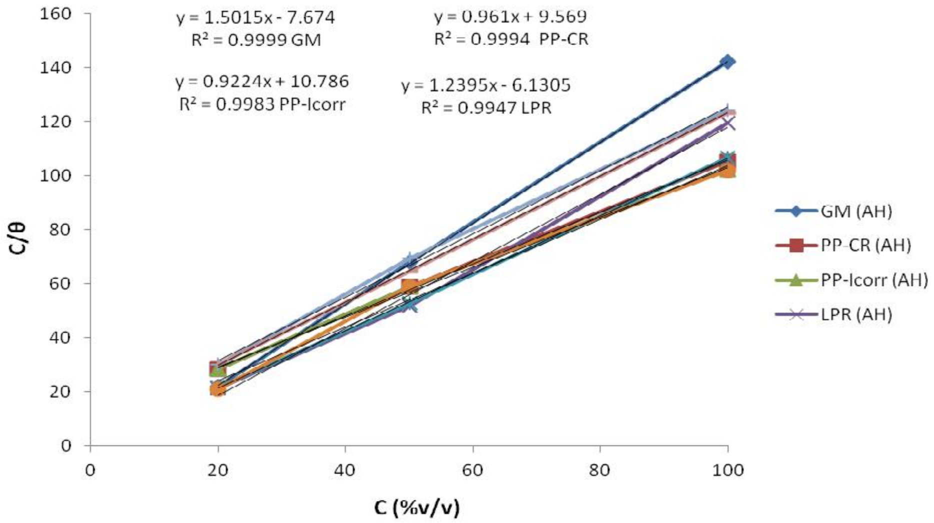

Figure 6. Langmuir isotherm for the adsorption of *Arachis hypogeae* compounds on the mild steel surface in 2M HCl solution at 25^{o}C obtained by gravimetric and potentiodynamic polarization methods

It can be said that the natural oil exhibited a mixed-type corrosion inhibition because of the simultaneous change in the anodic and cathodic region during the electrochemical measurement. These results were found to be in agreement with earlier reported studies [6,19,22,24-26]. The mechanism of adsorption for the oil on to the surface of the mild steel was shown that the relationship between C/θ against C is linear at 25^{o}C (Figure 6). Since the linear regression coefficient (R^2) for mild steel-HCl/inhibitor are almost unity; *Arachis hypogeae,* GM (0.9999)/PP-CR (0.9994)/PP-I_{corr}(0.9983)/LPR (0.9947), the adsorption behavior is believed to have obeyed Langmuir adsorption isotherms under the studied conditions.

4. CONCLUSIONS

1. *Arachis hypogeae* oil been an eco-friendly have been demonstrated to be a good corrosion inhibitor for mild steel-HCl environment at 25^{o}C
2. The corrosion rate of mild steel decreased with addition of *Arachis hypogeae* as inhibitor. This also enhanced inhibitor efficiency as high as 75.19 and 94.99% using gravimetric and electrochemical respectively in HCl-Arachis hypogeae condition.
3. Surface morphology of uninhibited mild steel sample shows severe pits and cracks formation.
4. That the mixed-type corrosion inhibition exist and Langmuir adsorption isotherms were proposed for the mild steel.

ACKNOWLEDGEMENTS

This material is based upon work supported financially by the National Research Foundation. The Technology Innovation Agency, Chemical Station, Ga-Rankuwa, TUT, is appreciated for equipment support.

References

1. A. Ostovari, S. M. Hoseinieh, M. Pei Kari, S. R. Shadizadeh, S. J. Hashemi, *Corrosion Science*, 51(2009) 1935.
2. J. A. Udiandeye, A. O. Okewale, B. R. Etuk, P. K. Igbokwe, *Inter. J. Basic and Appl Sci*, 11(6)(2011) 48.
3. S. Rekkab, H. Zarrok, R. Salghi, A. Zarrouk, Lh. Bazzi, B. Hammouti, Z. Kabouche, R. Touzani, M. Zougagh, *J. Mater. Environ. Sci.* 3 (4) (2012) 627.
4. A. Kosari, M. Momeni, R. Parvizi, M. Zakeri, M. H. Moayed, A. Davoodi, H. Eshghi, *Corrosion Science*, 53 (2011) 3058.
5. G. Quartarone, L. Ronchin, A. Vasasori, C. Tortato, L. Bonaldo, *Corrosion Science*, *64* (2012) 89.
6. N. Lahhit, A. Bouyanzer, J. M. Desjobert, B. Hammouti, R. Salghi, J. Costa, C. Jama, F. Bentiss, L. Majidi, *Portugaliae Eletrochemica Acta*, 29(2) (2011) 127.
7. Corrosion Control and Treatment Manual (CCTM), TM-584C, 1994.
8. O. A. Omotosho, O. O. Ajayi, O. Fayomi, V. O. Ifepe, *Asian J Appl Sci*, 5(2)(2012) 74.
9. A. Bouyanzer, B. Hammouti, L. Majidi, B. Haloui, *Portugaliae Eletrochemica Acta*, 28(3) (2010) 165.
10. F. Bentiss, C. Jama, B. Mernari, H. El-Attari, L. El-Kadi, M. LEbrini, M. Traisnel, M. Lagrenee, *Corrosion Science*, 51 (2009) 1628.
11. A. K. Singh, E. E. Ebenso, M. A. Quraishi, *Int. J. Electrochem. Sci.*, **7***(*2012) 2320.
12. Liu FG, M. Du, J. Zhang, M. Qiu, *Corrosion Science*, 51(2009) 102.
13. I. Muhammad, A. S. Abdulrahman, S. H. Muhammad, *Inter J Eng. Sci. Techn.*, 3(2)(2011) 1742.
14. D. Komatsu, E. C. Souza, E. C. de Souza, L. C. F. Canale, G. E. Totten, *Strojniskivestnik-Journal of Mechanical Engineering*, 56(2**)** (2010) 121.
15. A. A. El-Meligi, *Recent Patents on Corrosion Science*, 2 **(**2010) 22.
16. M. Dakmouche, S. Ladjel, N. Gherraf, M. Saidi, M. Hadjal, M. R. Ouahrani, *Asian Journal of Chemistry*, 21(8) (2009) 6176.
17. L. Bammou, B. Chehi, R. Salghi, L. Bazzi, B. Hammouti, M. Mihit, H. Idrissi, *Green Chemistry Letters and Review*,3(3) (2010) 178.
18. K. Lakshmi Prabha, Shameela Rajam, A. Subramania, *Journal of Chemical and Pharmaceutical Research*, 4(1) (2012) 347.
19. M. Abdulwahab, A. Kasim, O. S. I. Fayomi, F. Asuke, A. P. I. Popoola, *J. Mater. Environ. Sci*., 3 (6) (2012) 1182.
20. M. Znini, G. Cristofari, L. Majidi, A. Ansari, A. Bouyanzer, J. Paolini, J. Costa, B. Hammouti, *Int. J. Electrochem. Sci.*,7 (2012) 3959.
21. N. S. Patel, S. Jauhari, G. N. Mehta, *E-Journal of Chemistry*, 6(S1) (2009) R. Rosliza, A. Nora'aini,
22. W. B. W. Nik, *J Appl Electrochem*, 40 (2010) 833.
23. J. Halambek, K. Berkovic, J. Vorkapic-Furac, *Corrosion Science*, 52 (2010), 3978.
24. N. Haldar, H. S. Shukla, G. Udayabhanu, *Indian Journal of Chemical Technology*, 19 (2012) 173.
25. A. P. I. Popoola, M. Abdulwahab, O. S. I. Fayomi, *Int. J. Electrochem. Sci.*, 7 (2012) 5816.
26. K.S. Raja Muthu Kumar, P.Vijian, J. Samu Solomon and L. John Berchmans, *Elixir Corrosion* 53 (2012) 11717.