Int. J. Electrochem. Sci., 6 **(2011)** 6542 - 6556

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Corrosion Inhibition of Mild Steel using Potato Peel Extract in 2M HCl Solution

Taleb H. Ibrahim[1,*], *Youssef Chehade*[1] *and Mohamed Abou Zour*[2]

[1]American University of Sharjah, Department of Chemical Engineering, P.O. Box 26666, Sharjah, United Arab Emirates
[2]GE Water & Process Technologies, P.O. Box 261939, Dubai, United Arab Emirates
[*]E-mail: italeb@aus.edu

Received: 9 October 2011 / *Accepted:* 13 November 2011 / *Published:* 1 December 2011

The inhibitive effect of naturally available potato peel extract (PPE) toward the corrosion of mild steel in 2M HCl solution has been investigated by weight loss and electrochemical techniques. The results showed increase in the inhibition efficiency with increasing potato peels extract concentration. A reasonable corrosion inhibition level was obtained at a concentration of 50 ppm (>70% inhibition efficiency). Nyquist plots from Impedance data showed that upon increasing the PPE concentration, the charge transfer resistance increased and the doubled layer capacitance decreased. The adsorption film of extract on the mild steel specimen was also found to follow Langmuir adsorption isotherm.

Keywords: Corrosion inhibition; adsorption; Natural inhibitors; Potato peel; Mild-steel, Corrosion

1. INTRODUCTION

Metals are considered the corner blocks of various industries due to their hard structure which make them suitable for handling and processing various corrosive fluids and gases. Corrosion of metals however is considered to be a serious problem in most industries. Mild steel is commonly used in a wide range of industries due to its cheap cost and availability.

The main setback for this metal is its tendency to corrode easily in an acidic environment. Inorganic acids like HCl and H_2SO_4 are used for drilling, fracturing and acid stimulations at various stages in oil exploration, production and/or descaling operations and in many industrial applications. Wet acidic gases such as CO_2, H_2S and weak acetic and formic acids cause significant amount of corrosion for steel pipelines and storage processing facilities used in the oil and gas production networks. Since these acidic environments cause corrosion of mild steel, several protective measures are to be taken, one of them being the use of corrosion inhibitors.

Corrosion inhibitors can be defined as those compounds that when added in suitable amounts cause lowering in the corrosion rate of the metal without significantly changing the concentration of any other corrosive agent [1]. Corrosion inhibitors help the metal or the alloy maintain its resistance against corrosion via various inhibition mechanisms.

It is generally assumed that inhibition in acid media by chemical compounds added to the electrolyte is to be attributed to the adsorption of the additive, (ion or neutral polar molecule), on the metal-solution interface. It can then retard the cathodic and/or anodic reactions, thus, reducing the corrosion rate.

A number of organic compounds represent this type of inhibition, particularly those containing elements of Group V and VI of the periodic table, such as nitrogen, phosphorous, arsenic, sulphur, oxygen and selenium [2-6]. The interaction of ions or neutral polar molecules at the electrical double-layer changes its properties and structure.

The water molecules pre-adsorbed at the metal surface in contact with aqueous solution are involved in the successive adsorption processes. Organic inhibitors provide the protection for metal surfaces by molecular adsorption into the metal surface and forming a barrier film to decrease the corrosion rate.

One of the main draw backs with most of synthetic type organic inhibitors is their severe environmental hazards. These hazards are including their toxicity, biodegradation and/or bioaccumulation. Therefore, more steps and efforts have been put into researching naturally occurring inhibitors. Recent research aimed at plant extracts as natural sources of corrosion inhibitors and have shown promising results [7-17]. Plant extracts containing ingredients that act as antioxidants could be considered separately or mixed within synthetic formulations to generate cost effective source of corrosion inhibitor actives being renewable, widely available, and they offer the advantage of imposing no hazard to the environment.

Natural corrosion inhibitors are mostly obtained from medicinal plants, aromatic spices, and herbs, but little has been done about researching the capabilities of fruit and vegetable peels' extracts as corrosion inhibitors.

However, such food-processing generated by-products are in fact rich in phenolic groups that can offer a readily available natural source of anitoxidants [18, 19]. Saleh et al. verified that *Opuntia* extract, *Aleo eru* leaves, orange and mango peels give adequate protection to steel in 5% and 10% HCl at 25 and 40 °C. Rehman et al [20] reported that petroleum ether of potato extract to provide a strong antioxidant. Nandita and Rajini [21] demonstrated that potato peel powder has a considerable antioxidant activity.

This study aims to investigate the inhibition effect of potato (Solanum tuberosum L.) peel extract (PPE) on mild steel in 2M HCl solution using weight loss measurements and electrochemical techniques. The inhibitor active components were investigated using FT- IR.

2. EXPERIMENTAL

2.1. Preparation Of Potato Peel Stock Solution Extract

The potato peel was placed in a fluidized bed heater at 80°C for three hours until completely dried. After drying the peel, they were grinded into fine powder. The PPE was prepared by refluxing the ground peel in doubled-distilled water for two hours. The extracted solution was filtered by vacuum filtration. Concentration of the stock solution was determined by drying a sample and measuring the weight of the residue relative to the volume of the sample taken. Using dilution, stocks with different extract concentrations were prepared.

2.2. Preparation Of The Metal Specimens

Mild steel C1018 coupons were used in this investigation. The coupons had the composition of (0.18 wt% C; 0.02 wt% Cr; 0.03 wt% Cu; 0.79 wt% Mn; 0.02 wt% Ni; 0.022 wt% P; 0.024 wt% S; 0.21 wt% Si and balance is iron) The coupons had a surface area of 13.625 cm^2 and were used for the weight loss measurements.

The specimens were first degreased using ethanol followed by immersion for two minutes in 10% HNO_3 to activate the surface. Afterwards, they were washed using doubled-distilled water followed by rinsing with ethanol. Specimens were dried and then weighed. For the electrochemical tests, 1 cm^2 mild steel specimens were assembled into Teflon specimen holder to represent the working electrode to which electrical connectivity was established.

The specimens were first washed using double distilled water, then ethanol, followed by double distilled water, then acetone and finally by double distilled water.

Working and reference electrodes were also used to complete the electrochemical setup and generate electrochemical data.

2.3. Weight Loss Measurement

Mild steel specimens were immersed in 500ml of 2M HCl with various extract concentrations ranging from 0 to 1000ppm for 7 days at a temperature of 25±2°C. The acid solution under investigation represents various real industrial environments including pickling acids, stimulation fluids, and/or cleaning solutions for inorganic carbonate scales. The specimens' surfaces were immersed in a 20% H_2SO_4 for 1 minute, rinsed with ethanol, with doubled-distilled water and finally were dried before taken initial weights.

Inhibition efficiency was calculated using the following relationship

$$\left[\mathrm{IE\%} = \frac{w - w_i}{w}\right] * 100 \qquad (1)$$

where w and w_i are corrosion rates of the mild steel without and with PPE, respectively.

2.4. Electrochemical measurements

The Gill AC Potentiostat, ACM Instruments, was used for the electrochemical measurements. The electrochemical cell consisted of three electrodes: a saturated calomel reference electrode, a platinum auxiliary electrode, and a mild steel working electrode. The cell was filled with 600ml of 2M HCl. Various electrochemical measurements were conducted to generate corrosion inhibition data including, long-term linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and potentiodynamic scans (cyclic sweep, CS)For the LPR test, the polarization was conducted in the linear region around open circuit potential with a magnitude of ±10 mV.. For the AC Impedance, the amplitude used was 20 mV RMS. For the cyclic sweep, the sweep rate used was 1mV/sec.

2.5. Fourier Transform Infrared Spectroscopy (FT-IR)

The identification of the active corrosion inhibitor components within the potato peel a small portion of PPE was left in dry air overnight followed by complete drying in a vacuum oven. A KBr pellet was made from the dry extract and was characterized by a Bomem MB-3000 FT-IR equipped with ZnSe optics and a DTGS detector. Spectrum was obtained at 4 cm^{-1} resolution and 200 scans.

3. RESULTS AND DISCUSSION

Due to increasing environmental awareness, natural corrosion inhibitors are becoming of great important because of their biodegradability, easy availability and non-toxic nature. Plant extracts proved to have effective corrosion inhibition efficiency for various metal and alloys in aggressive environments. In this study, potato peels extract, are evaluated as corrosion inhibition mild steel in 2M HCl corrosive media.. Weight loss data, data from LPR, electrochemical polarization scans and impedance measurements are presented in this section. Furthermore, various electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic and cathodic Tafel slopes (β_a and β_c), charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived and obtained from electrochemical measurements will be used to help determine the mechanism of inhibition.

3.1. Characterization of PPE

FT-IR spectrum of PPE is shown in Figure. 1. The FT-IR shows strong absorption at 3418 cm^{-1} for OH band stretching mode. The absorption at 2938 cm^{-1} is aromatic C-H band stretching mode. The absorption at 1572 cm-1can be assigned to the aromatic C=C stretching mode. The peaks at 1409 and 1154 cm^{-1} indicate the presence of aryl OH. Finally, the absorption at 1081 cm^{-1} shows the stretching mode of C-O [22, 23]. The aqueous extract of PPE contains polyphenolic compound with an antioxidation potential. Among these phonolics are chlorogenic acid, caffeic acid, p-coumaric acid, ferulic acid, salicylic acid and vanillic acid [24].

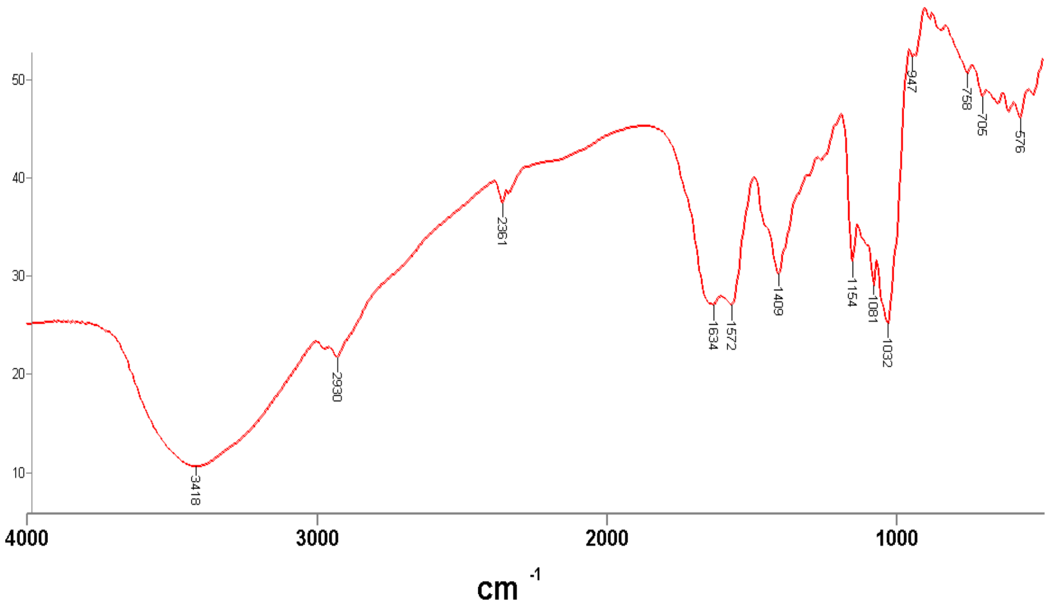


Figure 1. FT-IR spectrum of potato peels extract, PPE

3.2. Weight Loss Measurements

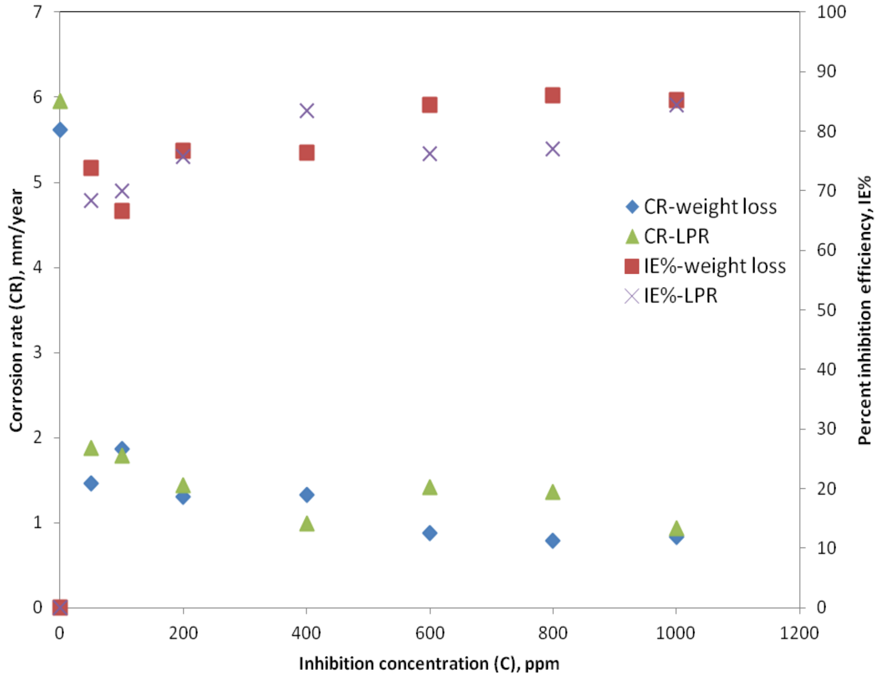


Figure 2. Corrosion rate and inhibition efficiency of mild steel specimens in 2M HCl with and without potato peel extract using the weight loss and LPR methods.

Mild steel coupons were immersed in 2M HCl for one week with different concentrations (0-1000 ppm) of PPE. Figure 2 shows the values of the corrosion rate and inhibition efficiency from the weight loss measurements at 25±2°C. In general, the corrosion rate of the mild steel samples decreases and the inhibition efficiency increases as the concentration of the PPE increases. 50 ppm of PPE was enough to reduce corrosion rate from around 6 mm/yr to below 2 mm/yr. At room temperature, higher PPE concentrations of about 600 ppm was enough to reduce corrosion rate to less than 1 mm/yr which translates to inhibition efficiency of 85%.

3.3. Adsorption Behavior

The reduction in corrosion rate illustrates the inhibition effectiveness of the PPE. The behavior could be explained in terms of the increase in the molecular adsorption of the PPE molecules to the mild steel surface as the concentration increases. It is well known that the inhibition efficiency (*IE%*) is directly proportional to the fraction of the surface covered by the adsorbed inhibitor molecules (θ). The degree of surface coverage θ is calculated using the relation $\theta = IE\%/100$.

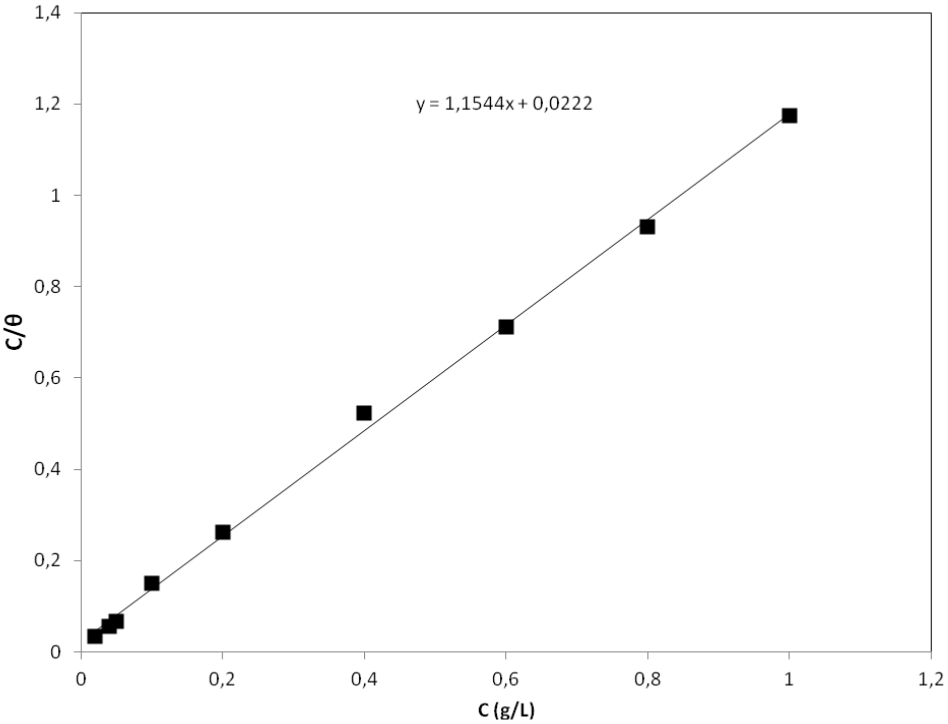


Figure 3. Langmuir isotherm for adsorption of potato peels extract onto mild steel surface in 2M HCl

Figure 3 demonstrates that the value of surface coverage increases with increasing in the inhibitor concentration. If we assume that the adsorption of PPE is monolayer adsorption and neglecting the interaction between the inhibitor molecules, then Langmuir adsorption isotherm can be applied. The Langmuir adsorption could be represented by the following equation:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (2)$$

where K is the adsorption constant and

$$K = \frac{1}{55.5} exp\left(\frac{-\Delta G^0_{ads}}{RT}\right) \tag{3}$$

Where R is the ideal gas constant, T is the absolute temperature and ΔG^0_{ads} is the standard free energy of adsorption. The calculated value of ΔG^0_{ads} was found to be -19.38 kJ/mole. The negative sign indicates that the adsorption of PPE molecules onto the steel surface is a spontaneous process. The value of ΔG^0_{ads} indicates a physical adsorption [25]. The phenolic compounds adsorb on the steel surface through the lone pairs of electrons on oxygen and nitrogen atoms forming an isolating layer film. The oxygen and nitrogen atoms are present at opposite extreme end on the phenolic structure [26]. This arrangement of the oxygen and nitrogen atoms may lead to the conclusion that the phenolic molecules are forced to be adsorbed horizontally to the mild steel surface. The high inhibition efficiency obtained with relatively low PPE concentration and the observed constant value of inhibitor efficiency (85%) for PPE concentration $\geq$ 600 ppm could imply that a large coverage area for the metal surface achieved with the initial small number of adsorbed PPE molecules.

3.4 Electrochemical Studies

3.4.1. Linear Polarization Resistance (LPR)

LPR is one of the most common techniques employed to determine corrosion rate. In LPR measurement, the corrosion rate is made by measuring two resistances (the solution resistance, R_s, and the polarization resistance, R_P). R_s is the resistance between the corroding interface and the reference electrode and R_P is related to the corrosion rate (equal to the slope of the voltage (E) versus the current density (I) near the free corrosion potential). For high conductivity solutions, the R_s of aqueous environments is negligible relative with R_P and can be ignored in calculating the corrosion rate. The relationship between the polarization resistance (R_p) and corrosion rate (CR) can be approximated by the following equation:

$$CR = \frac{\beta_a \beta_c M}{2.3(\beta_a + \beta_c) R_p F Z \rho} \tag{4}$$

where β_a, β_c are the anodic and cathodic Tafel slopes, respectively, M is the molecular weight of the metal, F is Faraday's constant, Z is the metal's valence, and ρ is the metal's density. The inhibition efficiency was evaluated using the relationship:

$$IE\% = \frac{I^0 - I}{I^0} x100 \tag{5}$$

Where I^0 and I are the current density of steel without and with inhibitor, respectively

Figure 2 shows that at room temperature, the overall trend is that the corrosion rate is reduced as the concentration of the PPE is increased. No additional real benefit was obtained by increasing the

PPE concentration >400-600 ppm. This could be attributed to the competitive effect between inhibitor molecules to reaching the metal surface which prevent some of them from reaching the metal surface and/or due to the flat nature of the inhibitor molecules (as FTIR indicated) which allow only some of them to provide surface coverage and no active inhibition from rest of molecules in bulk solution.

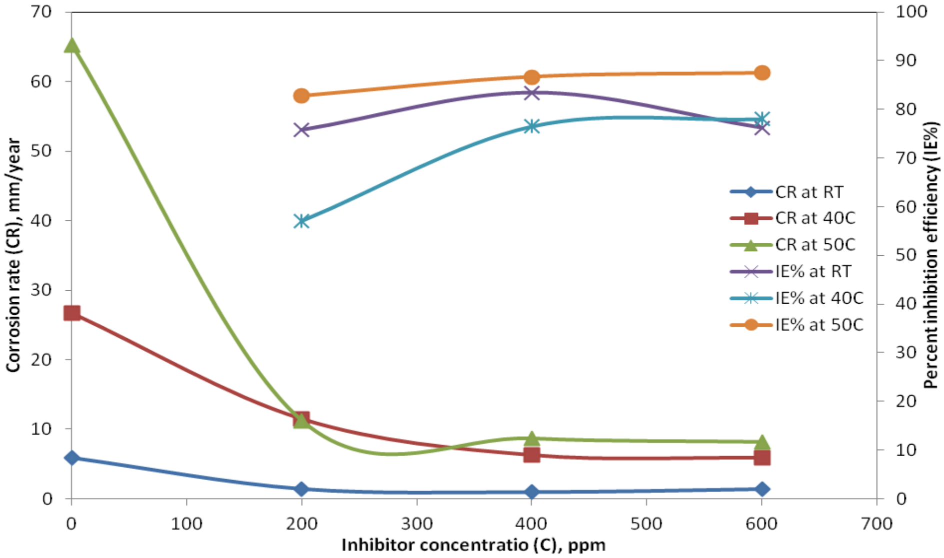


Figure 4. Corrosion rate and inhibition efficiency of mild steel in 2M HCl with and without potato peels extract at different temperatures using LPR.

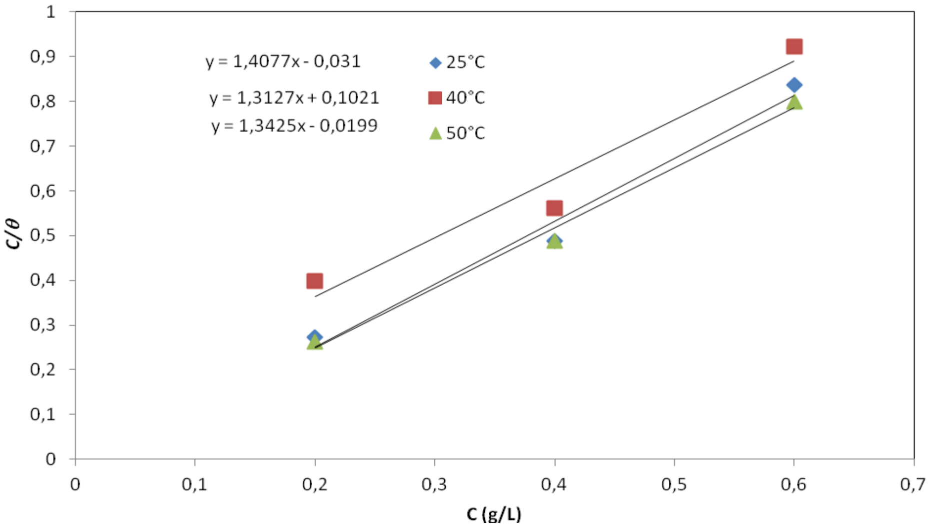


Figure 5. Langmuir isotherm for adsorption of potato peels extract onto mild steel surface in 2M HCl at different temperatures

Figure 4 shows the LPR results at selective concentrations at different temperatures (25, 40 and 50°C). The PPE inhibition efficiency increased as the PPE concentration increased at all the different temperatures tested. The CR increased as the temperature increased. The various concentrations of the PPE were also effective in decreasing the corrosion rates at the elevated temperatures. Inhibition efficacies as high as 90 % were calculated for PPE at 50°C, at 600ppm... The increase in corrosion rate with increasing temperature is due to faster reaction kinetics at both the anodic and the cathodic sites. Increasing corrosion rates and corresponding inhibition efficiencies with the PPE indicate that the adsorption mechanism is physical and not chemical. Physiosorption concludes weak adsorption at increasing temperatures unlike chemiosorption that would show higher inhibition at higher temperatures [27].

The C/θ versus C were plotted for the various temperatures based on the LPR results. Figure 5 shows that plot of C/θ versus C give a straight line with almost unit slope at all temperatures. This again supports the previous observed behavior from the weight loss method. The adsorbed PPE on the mild steel follows Langmuir adsorption isotherm over the range of concentrations and temperature studied. The calculated values of ΔG^0_{ads} for the different temperatures are: -18.56 kJ/mole at 25°C; -16.39 kJ/mole at 40°C and -26.87 kJ/mole at 50°C. The negative signs $\Delta G^0_{ads}\ values$ indicate that the adsorption of PPE onto the mild steel surface is a spontaneous process.

The activation energy of the corrosion reaction with and without PPE was calculated using Arrhenius equation:

$$CR = K_0 exp\left(-\frac{E_a}{RT}\right) \tag{6}$$

Where E_a is the apparent activation corrosion energy, T is the absolute temperature, K_0 is the Arrhenius pre-exponential constant and R is the ideal gas constant.

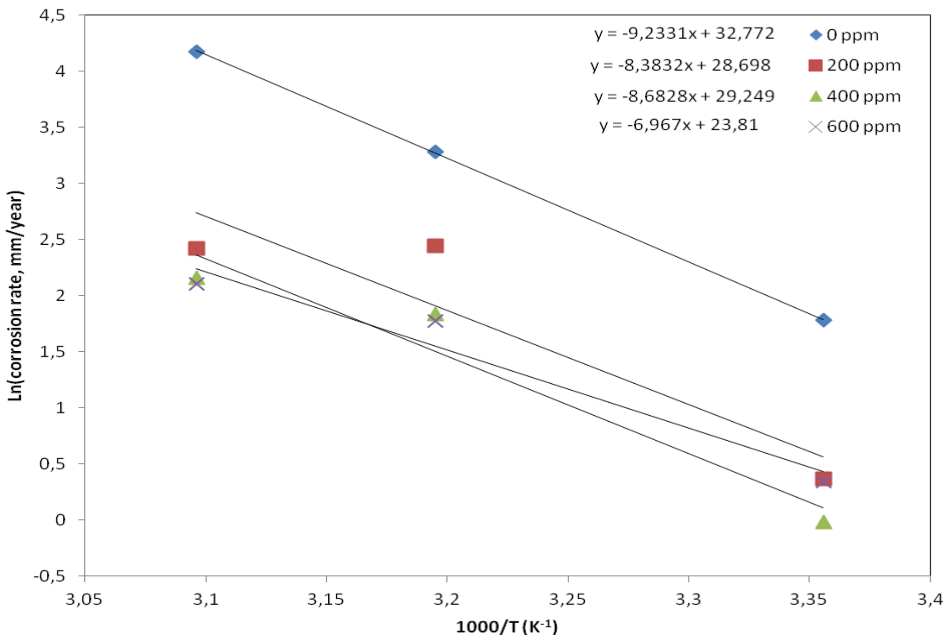


Figure 6. Arrhenius plots for the corrosion rate of mild steel in 2M HCl with and without potato peels extract at different temperatures.

Values of E_a were determined from the slope of the plots of *ln(CR)* versus *1/T* at different inhibitor concentration, figure 6. In general, E_a values tend to increase as the concentration of PPE extract (200 and 400ppm) increased (69.70 and 72.19 kJ/mole, respectively). However, the E_a value at 600ppm decreased (E_a = 57.92 kJ/mole) due to slight desorption of the inhibitor. Similar behavior was observed with the inhibition efficiency.

3.4.2. Potentiodynamic Scans, Cyclic Sweeps (CS)

The cyclic sweeps were run with a sweep rate of 60 mV/min and was started at a potential of -150 mV.

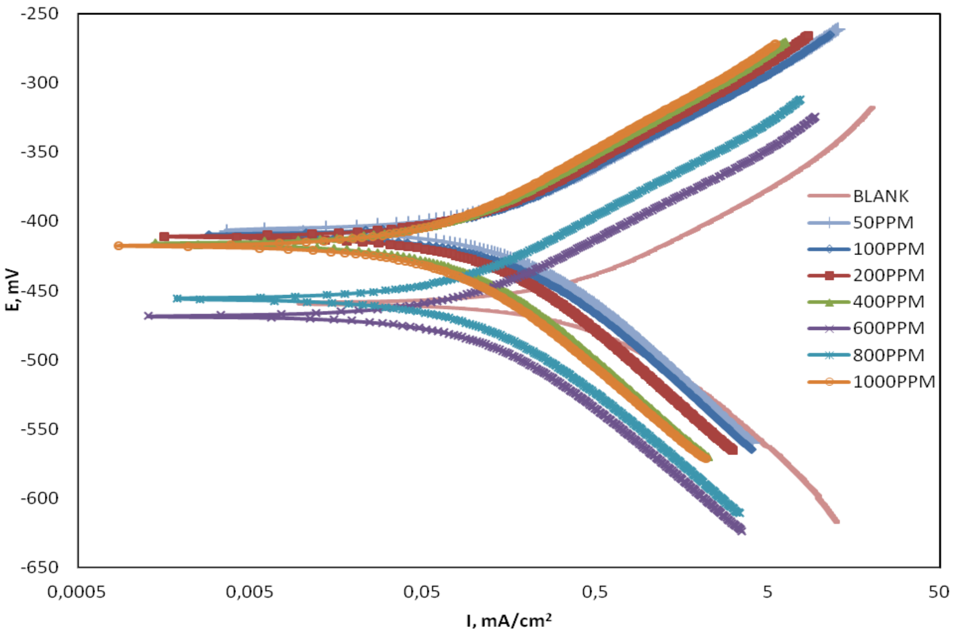


Figure 7. Cyclic sweep of mild steel immersed in 2M HCl with or without potato peel extract at room temperature.

Figure 7 shows the polarization scans for mild steel in 2M HCl and treated with various concentration of PPE. It can be seen that addition of PPE affected the open circuit potential values and both anodic and cathodic parts of the curves. The scans shows more apparent reduction in the current density of the cathodic part for the higher PPE concentrations when compared to the uninhibited scan, blank (0 ppm), Lower PPE concentrations showed some reduction in cathodic current but to a lesser extent.

Various values and parameters were derived from the sweeps in Figure 7. The data in Table 1 validates the inhibitive effect PPE exhibits as the corrosion rate of mild steel decreases with the increasing concentration of PPE in the 2M HCl solutions. This is in agreement with the behavior observed from the LPR results. In general, the increase in the inhibition efficiency could be attributed to the increased coverage of the surface area of the mild steel by PPE molecules as it blocks the available sites for reaction on the surface.

Table 1. Kinetic parameters of cyclic sweep for mild steel in 2 M HCl with or without PPE at different temperatures.

Temparature	PPM	Rest Potential (mV)	β_a (mV)	β_c (mV)	Icorr (mA/cm²)	IE%
25 °C	0	-459.16	85	110	1.27	-
	50	-406.88	79	116	0.49	62
	100	-409.99	78	113	0.44	65
	200	-411.00	79	112	0.34	73
	400	-415.97	76	108	0.23	82
	600	-468.58	74	105	0.36	72
	800	-455.58	78	106	0.30	76
	1000	-417.02	76	105	0.20	84
40 °C	0	-462.51	122	146	3.72	-
	200	-443.17	101	129	1.85	50
	400	-461.12	99	121	1.07	71
50 °C	0	-446.70	160	185	9.03	-
	200	-427.30	110	123	2.16	76
	400	-448.48	111	152	1.63	82

An inhibitor can be classified as cathodic or anodic type if the displacement in corrosion potential is more than 85 mV with respect to corrosion potential of the blank [28]. Compared to the blank solution, the cathodic corrosion potential has shifted by 5-6 mV. This indicates that the potato peels' extract acts as a mixed inhibitor. Both of the Tafel slopes, β_a, associated with the anodic metal dissolution of the mild steel, and β_c, associated with the cathodic hydrogen evolution reveal the inhibitive effect of the PPE as they decrease in value in respect to the increase in concentration, which can be translated as decreased corrosion rate. The corrosion current density data also supports PPE inhibitive characteristics.

3.4.3. Electrochemical Impedance Spectroscopy (EIS)

Impedance data for mild steel specimens in 2M HCl with various concentration of PPE (0-1000 ppm) are presented as Nyquist plots in Figures 8 and 9. They show a main e semicircle at all PPE concentrations. A second small semi-circle could also be observed towards the lower frequency. This indicates that the inhibition is mainly affected by charge transfer and once the surface is covered by inhibitor molecules some competitive diffusion resistance is taking place between molecules to reach metal surface.

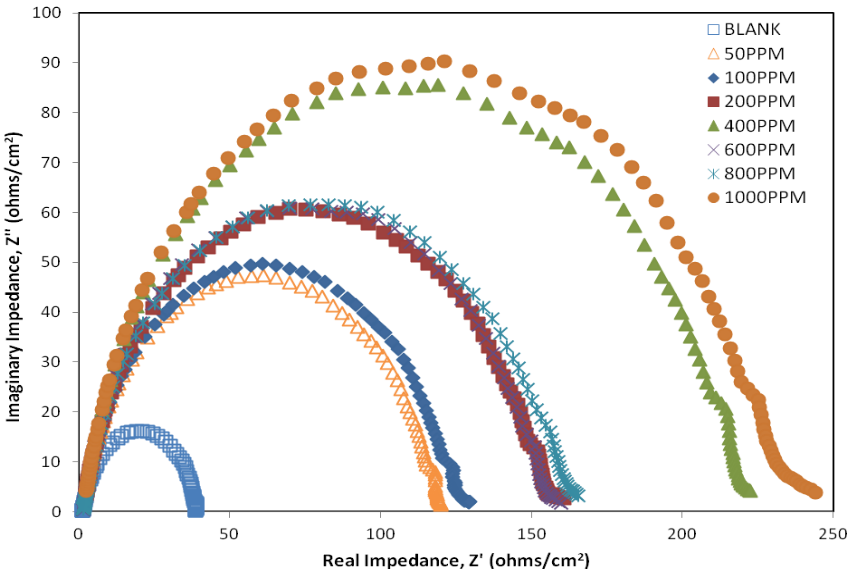
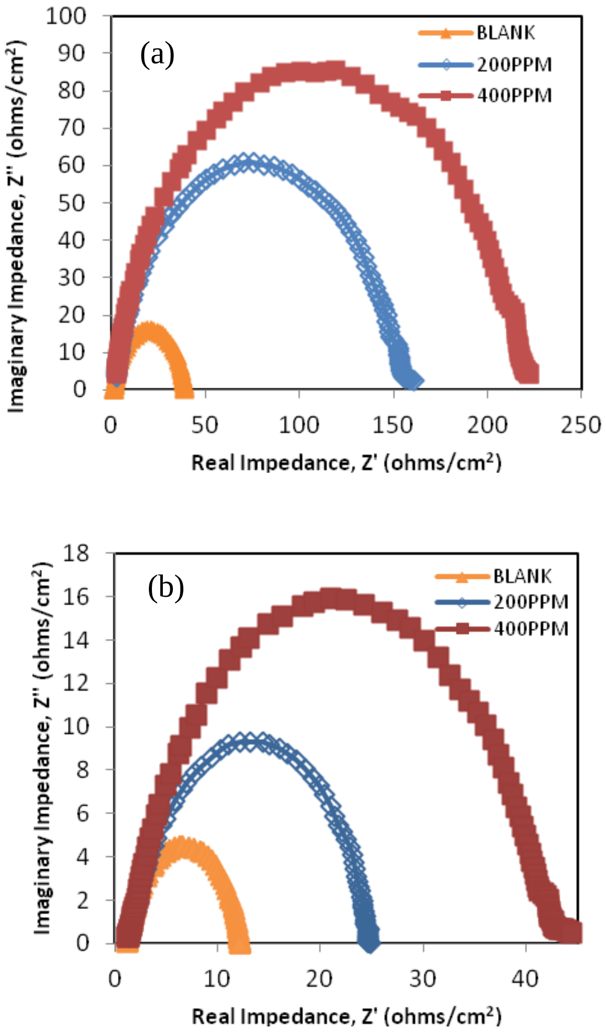


Figure 8. Impedance plots of mild steel in 2M HCl with or without potato peels extract.



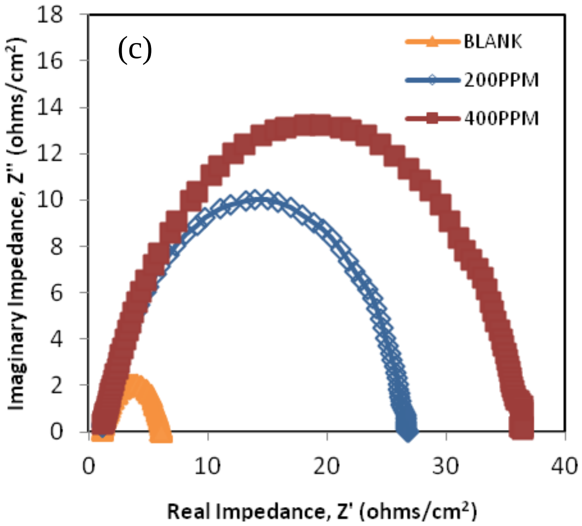


Figure 9. Impedance plots of mild steel in 2M HCl with or without potato peels extract at (a) 25°C, (b) 40°C and (c) 50°C.

Table 2. Kinetic parameters obtained from EIS of mild steel in 2 M HCl with or without PPE at different temperatures

Temparature	PPM	R_{ct} (ohms.cm²)	C_{dl} (µF)	I_{corr} (mA/cm²)	Corr. Rate (mm/yr)	IE%
25 °C	0	37.48	252	0.555	6.43	-
	50	116.60	137	0.175	2.03	68
	100	122.70	141	0.164	1.90	70
	200	151.90	126	0.132	1.53	76
	400	216.00	104	0.090	1.04	84
	600	151.50	147	0.125	1.45	77
	800	158.10	170	0.124	1.43	78
	1000	227.30	104	0.084	0.97	85
40 °C	0	10.93	894	2.649	30.70	-
	200	23.41	320	1.054	12.22	60
	400	40.95	308	0.567	6.57	79
50 °C	0	5.01	720	7.436	86.19	-
	200	25.51	318	0.991	11.48	87
	400	35.21	240	0.792	9.18	89

This is in full agreement with data presented earlier from both weight loss and LPR and showed that inhibition is achieved via relatively lower optimum PPE concentrations and higher concentrations do not add much to the inhibition. The increasing diameter of the Nyquist plots in relation to the PPE concentration increase indicates a decrease in the corrosion rate accordingly. In general, the higher the inhibition efficiency, the lower the calculated double layer capacitance. Some results are outside this fashion but are considered within the experimental error range.

EIS measurements were also performed for mild steel in 2M HCl with and without PPE extract at 40-50°C (Figure 9). As can be seen from the Nyquist plots, the diameter is increased as the concentration of inhibitor increased. Table 2 shows that the R_{ct} values increased and C_{dl} values decreased indicating a more controlled anodic and cathodic processes and the decrease in the capacitance values are attributed to the formation of a protective layer at the mild steel surface [29]. Similarly as before, the inhibition efficiency is increased as the inhibitor concentration increased at all temperatures.

There are few studies on the use of fruit and vegetable peels' extracts as corrosion inhibitors (30-33). The potato peels' extract showed higher inhibition efficiency for mild steel in 2M HCl when compared to those reported in literature.

4. CONCLUSIONS

1. Potato peels' extract was found to provide excellent inhibitive characteristics for mild steel in 2M HCl. Under test conditions it provided inhibition efficiencies as high as 85-90% with various PPE concentrations.
2. It was demonstrated that the potato peels' extract follows the Langmuir adsorption isotherm, however, when concentration reaches optimum levels, no significant further adsorption takes place and inhibitor molecules remain in bulk solution..
3. According to the conducted electrochemical tests, it was found that the PPE behaves as a mixed type inhibitor. The results confirmed the inhibitive effect of extract.
4. The electrochemical studies conducted at higher test temperatures demonstrated that the PPE are still effective and achieved higher inhibition efficiencies.
5. PPE provide naturally available, environmentally friendly chemistry that should be considered for commercial formulations to minimize environmental impact that synthetic chemistries pause.
6. Lab evaluations are generally for screening purposes and optimal inhibitor concentrations are to be evaluated based on actual real industry demand and optimized using realistic corrosion monitoring information.

References

1. Xia Z., Chou C. and Smialowska ZS. *Corrosion* 45, 8 (1989): p. 636.
2. R. Hasanov, M. Sadikoglu, S. Bilgic, *Appl. Surf. Sci*. 253 (2007): p. 3913.
3. M. Bouklah, B. Hammouti, M. Lagrenee, F. Bentiss, *Corros. Sci*. 48 (2006): p. 1279.
4. A. Yildirim, M. Cetin, *Corros. Sci*. 50 (2008): p. 155.
5. I.B. Obot, N.O. Obi-Egbedi, *Colloid Surf. A Physicochem Eng. Aspects* 330 (2008): p. 207.
6. K.F. Khalid, M.M. Al-Qahtani, *Mater. Chem. Phys*. 113 (2009): p. 150.
7. A.Y. El-Etre, *Coll. and Interf. Sci*. 314 (2007): p. 578.

8. M. Benabdellah, M. Benkaddour, B. Hammouti, M. Bendahhou, A. Aouniti, *Appl. Surf. Sci*. 252 (2006): p. 6212.
9. A.K. Satapathy, G. Gunasekaran *, S.C. Sahoo, Kumar Amit, P.V. Rodrigues, *Corros. Sci*. 51 (2009): p. 2848.
10. A. Bouyanzer, B. Hammouti, L. Majidi, *Mater. Lett*. 60 (2006): p. 2840.
11. A.Y. El-Etre, M. Abdallah, Z.E. El-Tantawy, *Corros. Sci*. 47 (2005): p. 385.
12. K.O. Orubite, N.C. Oforka, *Mater. Lett*. 58 (2004): p. 1768.
13. A.Y. El-Etre, *Corros. Sci*. 45 (2003): p. 2485.
14. G.O. Avwiri, F.O. Igho, *Mater. Lett*. 57 (2001): p. 3705.
15. H. Al-Sehaibani, *Mater. Wissen. Werkst. Tech*. 31 (2000): p. 1060.
16. S. Martinez, I. Stern, *Appl. Surf. Sci*. 199 (2002): p. 83.
17. R.M. Saleh, A.A. Ismail, A.A. El Hosary, *Corros. Sci*. 17 (1982): p. 131.
18. A. A. Mohdaly, M. A. Sarhan, I. Smetanska1, and A. Mahmoud. *J. Sc. Food and Agri*. 90, 2 (2010): p. 218.
19. R.M. Saleh, A.A. Ismail, A.A. El Hosary, *Br. Corros. J*. 17, 3 (1982): p. 131.
20. Z. Rehman, F. Habib, W.H. Shah, *Food Chem*. 85 (2004): p. 215.
21. S. Nandita, P.S. Rajini, *Food Chem*. 85 (2004): p 611.
22. J.J. Benitez, A.J. Matas, A. Heredia, *J. Structural Biology* 147 (2) (2004) 179.
23. N. Cordeiro, M.N. Belgacem, A.J.D. Silvestre, C. Pascoal Neto, A. Gandini, *Int. J. Biological Macromolecules* 22(2) (1998) 71.
24. P.P. Singh, M.D.A. Saladna, *Food Research Int*. (2011), in press.
25. M. Donahue, K. Nobe, *J. Electrochem. Soc*. 112 (1965): p. 886.
26. A. Schieber, M.D. Aranda-Saldana, *Food* 3, 2 (2009): p. 23.
27. E.E. Oguzie, *Corros. Sci*. 50 (2008): p. 2993.
28. Y. Yan, W. Li, L. Cai, B. Hou, *Electrochim. Acta* 53 (2008): p. 5953.
29. F. Bentiss, M. Traisnel, M. Lagrene'e, *J. Appl. Electrochem*. 31 (2001): p. 41.
30. R.M. Saleh, A.M. Shams El Din, *Corros. Sci.* 12 (9) (1972) 689.
31. N.O. Eddy, E.E. Ebenso, *Afr. J. Pure Appl. Chem.* 2(6) (2008) 46.
32. T. Ibrahim, M. Habbab, Int. J. Electrochem. Sci. 6 (2011) 5357.
33. J.C. da Rocha, J.A. Gomes, E. D'Elia, *Corr. Sci*. 52 (201) 2341.