Adsorption and Thermodynamic Characteristics of *Plumeria rubra* Plant Extracts on Mild Steel Corrosion in Industrial Water Medium

C. B. Pradeep Kumar[1] and K. N. Mohana[1*]

[1]*Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore-570 006, India.*

Authors' contributions

This work was carried out in collaboration between all authors. Author KNM designed the study, managed the analyses of the study and supervised the work. Author CBP performed the analyses and wrote the first draft of the manuscript. All authors read and approved the final manuscript.

ABSTRACT

The inhibition effect of *Plumeria rubra* (PR) extracts on the corrosion of mild steel in industrial water medium was studied by mass loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. The results show that the protection efficiency increased with increase in inhibitor concentration and decreased with temperature. Electrochemical impedance spectroscopic measurements indicated that charge transfer resistance increases with increasing inhibitor concentration. The adsorption of PR extracts on mild steel surface obeys Langmuir isotherm model. Potentiodynamic polarization studies revealed that PR extracts act as a mixed-type inhibitor. Scanning electron microscopy (SEM) was used to analyze the surface adsorbed film.

_____

*Corresponding author: Email: drknmohana@gmail.com;

1. INTRODUCTION

Corrosion is a serious environmental problem in the oil, fertilizer, metallurgical and other industries [1–4]. Corrosion of mild steel is a significant problem in the oil and gas production and transportation systems which cause significant economic loss. In order to prevent degradation of these systems varieties of corrosion control techniques have been employed. The use of inhibitors is one of the most practical and efficient methods to prevent metals against corrosion. Most of the reported inhibitors are synthetic organic compounds containing heterocyclic atoms (nitrogen, sulphur, oxygen and phosphorous) with aromatic rings [5-7]. Even though, these synthesized molecules have shown high corrosion inhibitive effect, they pollute the environment during the process of their synthesis and applications [8]. Therefore, their use as corrosion inhibitors is limited. Thus, efforts have been made to develop cheap and non-toxic corrosion inhibitors. The plant extracts are considered as an incredibly rich source of environmentally acceptable corrosion inhibitors. This area of research is of much importance because in addition to being environmentally friendly and ecologically acceptable, that can be extracted by simple procedures with low cost. A number of natural compounds have been used as corrosion inhibitors for metals and their alloys in various aggressive environments [9-16].

Plumeria rubra is one of the antioxidant medicinal plants belonging to family Apocynaceae. The essential oils from the flowers used for perfumery and aromatherapy purposes [17]. The leaves are used in ulcers, leprosy, inflammations and rubefacient [18]. Besides these phytoconstituents the leaves and bark of the plant contains plumieride, resinic acid, fulvoplumierin, mixture of terpenoids, sterols, large quantities of plumieride, cytotoxic iridoids, fulvoplumierin, allamcin, allamandin, 2,5-dimethoxy- pbenzoquinone, plumericin, and lignan liriodendron [19]. In the light of these reported Phytochemistry of *Plumeria rubra*, the present investigation reports the corrosion inhibition performance of *Plumeria rubra* plant extracts on mild steel (MS) at various temperatures and concentrations in industrial water medium. Effects of inhibitor concentration, temperature and immersion time on the corrosion rate were investigated and discussed. Various activation and adsorption thermodynamic parameters are computed and discussed. Mass lass and electrochemical techniques were employed to study the mechanism of corrosion inhibition. The morphology of the inhibited MS surface was analyzed using scanning electron microscopic studies.

2. MATERIALS AND METHODS

2.1 Preparation of Plant Extracts

Healthy, disease free, mature leaves of *Plumeria rubra* (PR) collected from Western Ghats, Karnataka, India, were used for the preparation of methanolic extracts. Thoroughly washed leaves were shade dried and then powdered with the help of a blender. The powder was extracted with methanol using a Soxhelt extractor. The extracts were concentrated using rotary flash evaporator and preserved at ± 5ºC in airtight bottle until further use.

2.2 Materials

The specimens used for corrosion tests were mild steel (MS) coupons which have the following composition (wt %): 0.051 C: 0.023 Si: 0.005 P: 0.103 Al: 0.179 Mn: 0.023 S and the remainder iron. The test solution was industrial water collected from heat exchangers and reboilers of the chemical industries in and around Mysore city, India. The chemical

composition of the industrial water (ppm) obtained from ionic chromatograph was: 7500 Cl⁻; 64 Ca^{2+}; 3440 SO_4^{2-}; 23 Mg^{2+}; 140 Na^+; 0.28 PO_4^{3-}. Prior to gravimetric and electrochemical measurements, the surface of the specimens was polished under running tap water using emery paper (SiC, grade 220-600), rinsed with distilled water, dried on a clean tissue paper, immersed in benzene for 5 s, dried and immersed in acetone for 5 s, and dried with clean tissue paper. Finally, the specimens were kept in desiccators until use. At the end of the gravimetric experiment, the specimens were carefully washed with acetone and benzene, dried, and then weighed. For polarization and electrochemical impedance studies, the MS specimen was embedded in epoxy resin to expose a geometrical surface area of 1cm² to the electrolyte.

2.3 Methods

2.3.1 Mass loss measurements

Gravimetric experiments were carried out in a glass cell and the solution volume was 100 cm³. The temperature of the environment was maintained by thermostatically controlled water bath (Weiber, India) with an accuracy of ± 0.2 °C under aerated condition. The mild steel specimens used were rectangular with a dimension of 1 cm × 1 cm × 0.1 cm. The initial weight of the specimen was recorded using an analytical balance (precision ± 0.1 mg). After the corrosion test in industrial water with and without inhibitor, the specimens were carefully washed in double distilled water, dried and then weighed. The weight loss of the specimen was determined after an immersion period of 15 to 55 h at the temperature range of 303 to 333 K. Triplicate experiments were performed in each case and the average mass loss was reported. The corrosion rate (C_R) and inhibition efficiency (% IE) are calculated using the equations (1) and (2).

$$C_R = \frac{\Delta W}{St} \tag{1}$$

$$\% \ IE = \frac{(C_R)_a - (C_R)_p}{(C_R)_a} \times 100 \tag{2}$$

Where, ΔW is the weight loss, S is the surface area of the specimen (cm²) t is the immersion time (h) and $(C_R)_a$ and $(C_R)_p$ are corrosion rates in the absence and presence of the inhibitor, respectively.

2.3.2 Electrochemical Impedance Spectroscopy (EIS)

The EIS tests were performed in a three electrode assembly. The cell arrangement used was a conventional three-electrode cell with platinum counter electrode, saturated calomel electrode as reference electrode and test material (mild steel) as working electrode. All potentials are reported vs. saturated calomel electrode. The measurements were done after 30 min of immersion in the testing solution. EIS measurements were performed using CH-analyzer model CH1660D with a frequency range of 10.000 Hz to 0.1 Hz and amplitude of 0.005 V. The IE (%) was calculated using the charge transfer resistance as follows:

$$\% \ IE = \frac{{}^1/_{(R_{ct})_a} - {}^1/_{(R_{ct})_p}}{{}^1/_{(R_{ct})_a}} \times 100 \tag{3}$$

where $(R_{ct})_a$ and $(R_{ct})_p$ are charge transfer resistances in the absence and presence of inhibitor, respectively.

2.3.3 Potentiodynamic polarization

The electrochemical character of MS sample in inhibited and uninhibited solution was investigated by recording anodic and cathodic potentiodynamic polarization curves. Potentiodynamic polarization curves were recorded after immersion of the working electrode (MS) for 30 min in the electrolyte. Measurements were carried out in industrial water medium containing different concentrations of the extracts in the potential range from -100 to -900 mV with a scan rate of 0.4 mV s^{-1}. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain corrosion current densities (I_{corr}). The % IE was calculated using the following equation:

$$\% \, IE = \frac{(I_{corr})_a - (I_{corr})_p}{(I_{corr})_a} \times 100 \tag{4}$$

where, $(I_{corr})_a$ and $(I_{corr})_p$ are the corrosion current density ($\mu A \, cm^{-2}$) in the absence and presence of the inhibitors, respectively.

2.3.4 Morphological investigation

The surface morphology of the MS samples in the absence and presence of PR extracts (1750 ppm in industrial water) was investigated by Scanning Electron Microscopy (SEM) technique (Model JSM-5800).

3. RESULTS AND DISCUSSION

3.1 Mass loss studies

Weight loss of MS was determined in industrial water medium in the absence and presence of different concentrations of PR extracts. The Inhibition efficiency of MS without and with different concentrations of PR extracts was determined after 45 h at room temperature, and the results are depicted in Table 1. It has been observed that, the corrosion rate of MS decreased on increasing the inhibitor concentration upto 1750 ppm. This behavior could be attributed to the increase in adsorption of the inhibitor at the metal/solution interface [20], and reduces the surface area that is available for direct attack on the metal surface. The % IE at different concentrations of PR extracts decreases with increasing temperature from 303 K to 333 K (Fig. 1). This is due to increased rate of dissolution process of MS and partial desorption of the inhibitor from the metal surface with temperature [21].
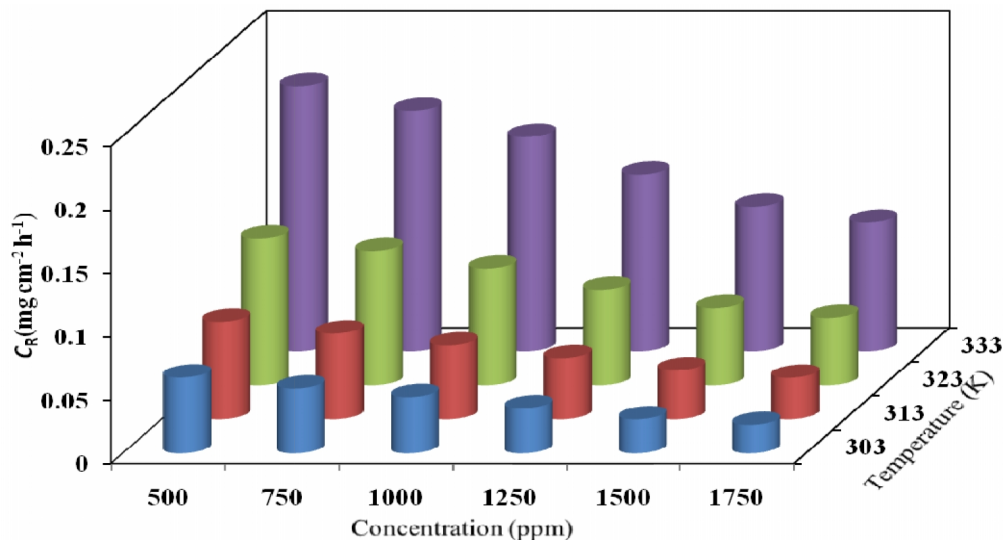
Fig. 1. Variation of C_R with temperature and inhibitor concentration in the absence and presence of different concentrations of PR extracts

Inspection of the Fig. 1 revealed that inhibition efficiency decreases with increase in temperature. This is attributed to increase in the solubility of the protective films and of any reaction products precipitated on the surface of the metal that may inhibit the reaction [22], and also due to the dissolution of MS or the partial desorption of the inhibitor from the metal surface at higher temperature [23].

The inhibitive effect of PR extracts is due to the presence of diverse phytochemical constitution in the extracts. PR extracts is rich in organic compounds of high molecular weight with heteroatoms and π centers in their molecular structures. These include several plumieride, resinic acid, fulvoplumierin, mixture of terpenoids, sterols, plumieride, iridoids, allamcin, allamandin, 2,5-dimethoxy- pbenzoquinone, plumericin, and lignan liriodendron.

Table 1. C_R and % IE obtained from weight loss measurements of MS in industrial water medium containing various concentrations of PR extracts at different temperatures

C (ppm)	Temperature							
	303 K		313 K		323 K		333 K	
	C_R (mg cm^{-2} h^{-1})	IE %	C_R (mg cm^{-2} h^{-1})	IE %	C_R (mg cm^{-2} h^{-1})	IE %	C_R (mg cm^{-2} h^{-1})	IE %
0	0.1204	-	01428	-	0.2048	-	0.3326	-
500	0.0598	50.23	0.0769	46.17	0.1158	42.24	0.2091	37.14
750	0.0511	57.55	0.0676	52.68	0.1061	48.19	0.1895	43.03
1000	0.0443	63.20	0.0582	59.26	0.0919	55.12	0.1691	49.16
1250	0.0355	70.51	0.0482	66.26	0.0755	63.13	0.1396	58.03
1500	0.0268	77.74	0.0386	72.98	0.0608	70.31	0.1141	65.69
1750	0.0223	81.47	0.0328	77.04	0.0532	74.02	0.1015	69.48

3.2 Effect of Temperature

In order to determine the effect of temperature on inhibition efficiency and corrosion rate, the mass loss measurements were carried out as a function of temperature (303 – 333 K) and concentration of PR (500 - 1750 ppm) extracts at 45 h of immersion time. The inhibition efficiency (% IE) and corrosion rate (C_R) are summarized in Table 1. The activation parameters play an important role in understanding the inhibitive mechanism of the inhibitors. The apparent activation energy and pre-exponential factor for different concentrations of PR extracts were calculated from the plots of logarithm of C_R versus $1/T$ (Fig. 2) using Arrhenius-type equation (3).

$$C_R = A \exp\left(-\frac{E_a}{RT}\right)$$
(5)

Where E_a is the apparent activation energy, T is the absolute temperature, A is the Arrhenius pre-exponential constant and R is the universal gas constant. The values of E_a and k at various concentrations of PR extracts are calculated from slopes and intercepts, respectively, and the results are shown in Table 2. The linear regression coefficients are close to unity.
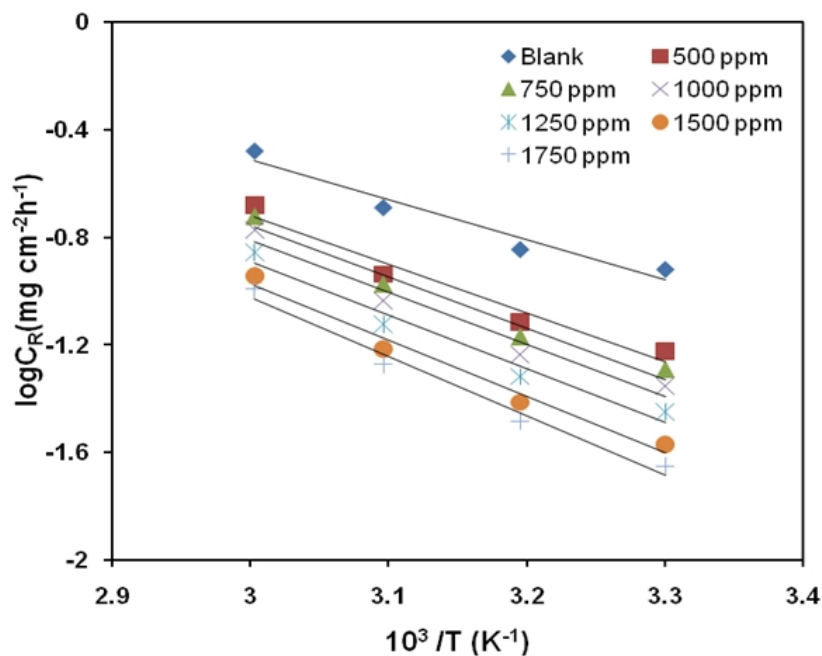

Fig. 2. Arrhenius plots for MS in industrial water medium in the absence and presence of different concentrations of PR extracts
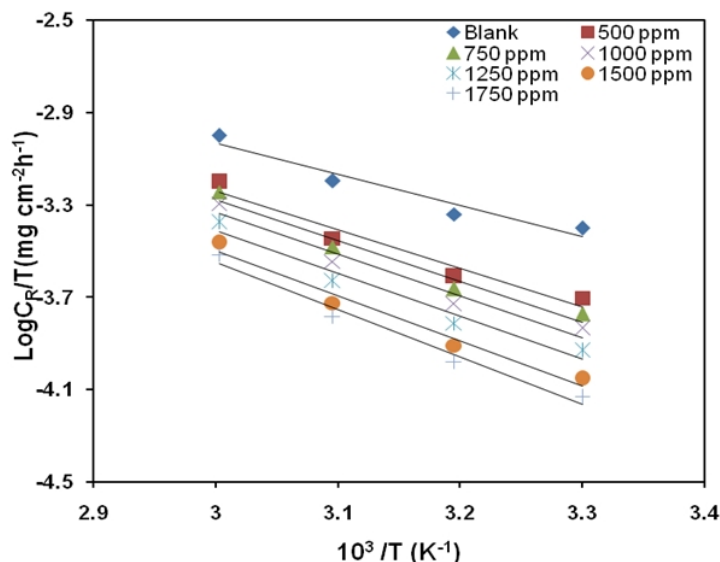
Table 2. Activation parameters for MS in industrial water medium in the absence and presence of different concentrations of PR extracts

C (ppm)	E_a^* (kJ mol^{-1})	K (mg cm^{-2} h^{-1})	ΔH^* (kJ mol^{-1})	$\Delta H^* = E_a^* - RT$ (kJ mol^{-1})	ΔS^* (J mol^{-1}K^{-1})
0	28.41	5701	25.77	25.89	-178
500	34.73	18793	32.09	32.21	-163
750	36.59	94841	33.94	34.07	-158
1000	37.33	110153	34.69	34.81	-157
1250	38.04	117489	35.40	35.52	-156
1500	40.11	204173	37.47	37.59	-152
1750	42.02	364753	39.38	39.50	-147

It can be observed from Table 2 that the activation energy in the presence of PR extracts is high compared to that in the blank. Enthalpy and entropy of activation were calculated by using the following alternative form of Arrhenius equation,

$$C_R = \frac{RT}{Nh} \exp \frac{\Delta S}{R} \exp \left(-\frac{\Delta H}{RT}\right) \tag{6}$$

where h is Planck's constant and N is Avogadro's number, R is the universal gas constant, ΔH is the enthalpy of activation and ΔS is the entropy of activation. Using Eq. (4), plots of log (C_R/T) versus $1/T$ gave straight lines with a slope of ($-\Delta H/2.303R$) and an intercept of [log (R/Nh) + $\Delta S/2.303R$] (Fig. 3) from which the values of ΔH and ΔS are calculated and tabulated in Table 2. It was found that, the positive sign of the activation enthalpy (ΔH) in presence of the extracts reflects the endothermic nature of the MS dissolution process and dissolution is difficult [24]. The increase of ΔS in the presence of plant extracts reveals that an increase in disordering takes place on going from reactant to the activated complex [25].

Fig. 3. Alternative Arrhenius plots for MS in industrial water medium in the absence and presence of different concentrations of PR extracts

The values of ΔH could also be obtained from the following equation:

$$\Delta H = E_a - RT \tag{7}$$

The values of ΔH obtained using Eq. (5) are in very good agreement with those obtained from Eq (4), confirming the endothermic process of MS dissolution in industrial water medium.

3.3 Effect of Immersion Time

In order to evaluate the effect of immersion time on inhibitive behavior of PR extracts, mass loss measurements were carried out in industrial water medium in the absence and presence of 1750 ppm of PR extracts for 15 to 55 h immersion time at 303 K. It can be seen from Fig. 4 that the inhibition efficiency (% IE) in the presence of extracts was increased with increasing immersion time from 15 to 55 h. This increase in % IE reflects the strong adsorption of PR extracts on the MS surface, resulting in a strong protective layer. But after 45 h, the % IE slightly decreases. This decrease in % IE for long period of immersion can be attributed to the depletion of available inhibitor molecules in the solution due to chelate formation between metal and the inhibitor [26,27].
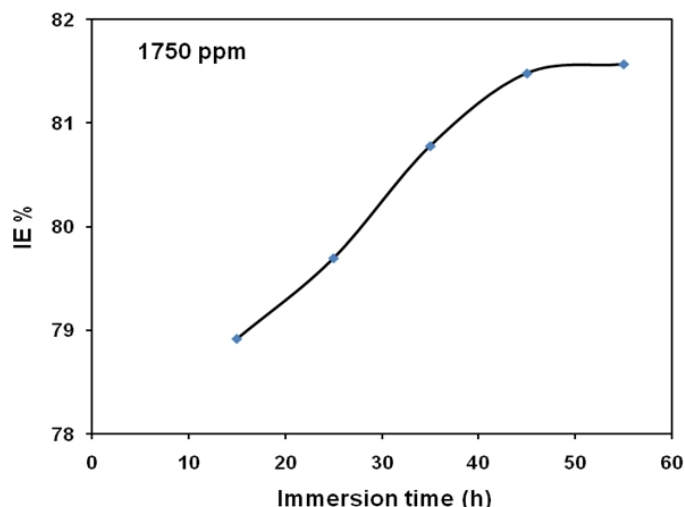

Fig. 4. Effect of immersion time on % IE of PR extracts

3.4 Adsorption Studies

In order to understand the mechanism of corrosion inhibition, the adsorption behavior of the inhibitor on the metal surface has to be known. The data were tested graphically by fitting to various isotherms including Langmuir, Frumkin and Temkin. However, the best fit is obtained from Langmuir and Temkin adsorption isotherm (Figs. 5 and 6) for PR extracts.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + c \qquad \text{(Langmuir isotherm)} \tag{8}$$

$$\text{Exp } (-2a\theta) = KC \qquad \text{(Temkin isotherm)} \tag{9}$$

where K_{ads} is the equilibrium constant for adsorption, C is the concentration of the inhibitor, θ is the surface coverage and a is the molecules interaction parameter. The values of correlation coefficient (R^2) were used to judge the best fit isotherm. In the present study, the strong correlation ($R^2 > 0.99$) suggests that the adsorption of PR extracts on the MS surface obeyed Langmuir isotherm. The free energy of adsorption is related to the equilibrium constant of adsorption using following equation (8),

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right)$$
(10)

where, R is the universal gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution (mol L^{-1}).
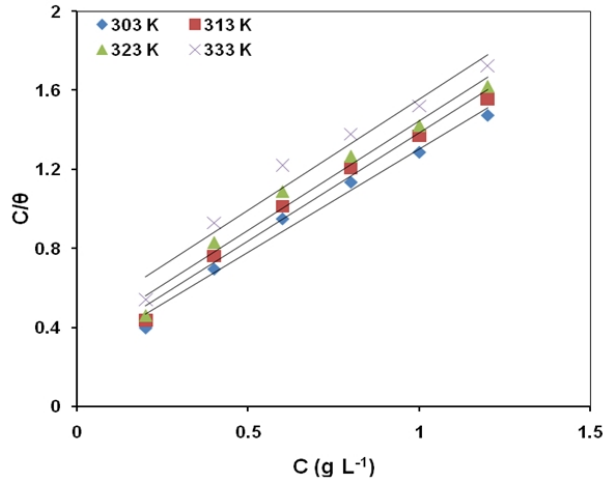

Fig. 5. Langmuir adsorption isotherm of PR extracts on MS in industrial water medium at different temperatures
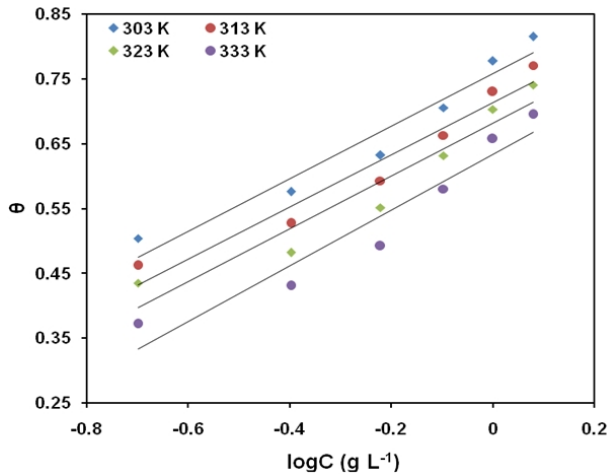

Fig. 6. Temkin adsorption isotherm of PR extracts on MS in industrial water medium at different temperatures

Table 3. Thermodynamic adsorption parameters for adsorption of PR extracts on MS in industrial water medium at different temperatures from Langmuir adsorption isotherm

Temperature (K)	K_{ads} (L mol^{-1})	ΔG_{ads} (kJ mol^{-1})	ΔH_{ads} (kJ mol^{-1})	ΔS_{ads} (J mol^{-1}K^{-1})	ΔG_{ads}= ΔH_{ads} -T ΔS_{ads} (kJ mol^{-1})
303	3921.5	-30.96			-31.20
313	3436.4	-31.64	-14.39**(a)**	54.90**(a)**	-31.57
323	2958.5	-32.25	-14.54**(b)**	54.00**(b)**	-32.12
333	2320.1	-32.58			-32.67

(a) values obtained by Eq. (9)
(b) values obtained by Eq.(10)

The values of Langmuir adsorption parameters obtained are recorded in Table 3. The negative values of ΔG_{ads} in PR extracts suggest that the adsorption of inhibitors onto MS surface is a spontaneous phenomenon. Generally, the values of ΔG_{ads} up to - 20 kJ/mol are consistent with the electrostatic interaction between the charged molecules and the charged metal (physisorption), while those negative values higher than - 40 kJ/mol involve sharing or transfer of electrons from the inhibitors to the metal surface to form a co-ordinate type of bond (chemisorption) [28]. In the present study the values for ΔG_{ads} for PR extracts on the MS surface are in the ranges of 31.20 to – 32.67 kJ/mol, suggesting the combination of both physical and chemical adsorption. The negative values of ΔG_{ads} indicated spontaneous adsorption of the inhibitors on the metal surface. The enthalpy and entropy of adsorption (ΔH_{ads} and ΔS_{ads}) can be calculated using the following equation:

$$\ln K_{ads} = \ln\frac{1}{55.5} - \frac{\Delta H_{ads}}{RT} + \frac{\Delta S_{ads}}{R} \qquad (11)$$

Using Eq. (9), the values of ΔH_{ads} and ΔS_{ads} were evaluated from the slope and intercept of the plot of $\ln K_{ads}$ versus $1/T$ (Fig. 7). The values ΔH_{ads} are negative, suggesting that the adsorption of the inhibitor is an exothermic process. The value of ΔS_{ads} is positive in the adsorption process indicating that, the presence of inhibitor increases the solvent entropy [29]. The values of ΔH_{ads} and ΔS_{ads} can also be calculated by using following equation:

$$\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads} \qquad (12)$$

Using Eq. (10), the plot of ΔG_{ads} versus T gives a straight line (Fig. 8) with a slope of - ΔS_{ads} and intercept of ΔH_{ads}. The values obtained are well correlated with those obtained from Eq. (9), confirming the exothermic behavior of the adsorption of the studied plant extract on the MS in industrial water medium.
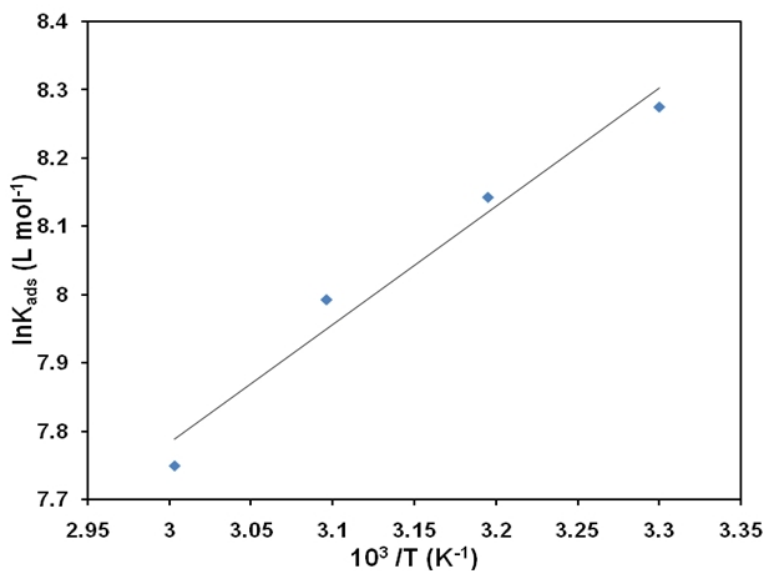
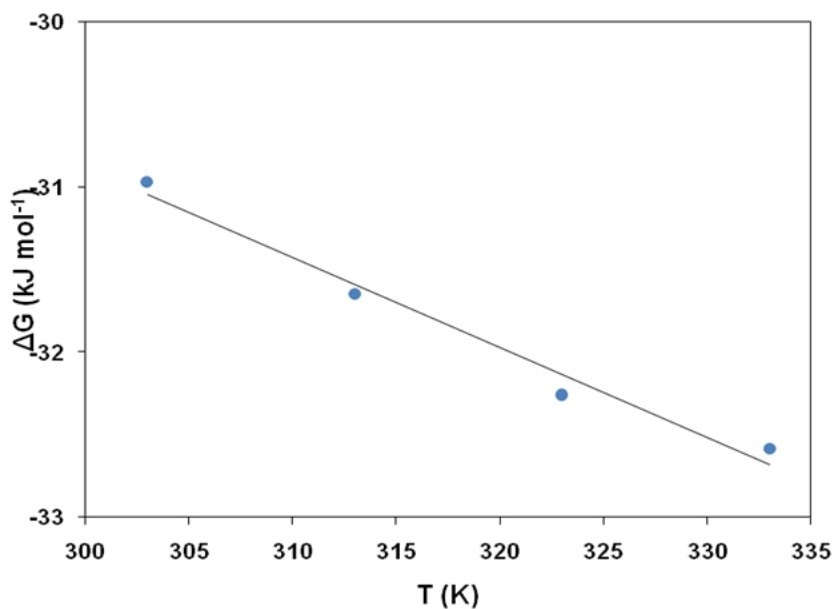**Fig. 7. Plot of ln K_{ads} versus 1/T**

Fig. 8. Plot of Gibbs free energy versus absolute temperature

3.5 Electrochemical Impedance Spectroscopy (EIS)

The impedance response of MS in industrial water medium containing different concentrations of PR extracts is shown in Fig. 9. Nyquist impedance plots were analyzed by fitting the experimental data to a simple circuit model (Fig.10). The fitted values of R_{ct}, C_{dl} and % IE are listed in Table 4. It is clear that by increasing the inhibitor concentration, the C_{dl}

values decrease, R_{ct} and the inhibition efficiency values increases. The addition of inhibitors provide lower C_{dl} values, this situation was the result of an increase in the thickness of the electrical double layer and decrease in local dielectric constant [30]. The increase in size of the semicircle and R_{ct} values with increasing inhibitors concentration, indicating the charge transfer process is the main controlling factor of the corrosion of MS. Considering the impedance diagrams (Fig 9), the size of the capacitive loop increased by increasing the concentration of PR extracts, indicated that PR extracts increased the charge transfer resistance and hence have inhibiting effect on mild steel corrosion in industrial water medium. All impedance plots contains a depressed semicircle which can be attributed to the frequency dispersion effect as a result of the roughness and inhomogeneous of electrode surface [31].
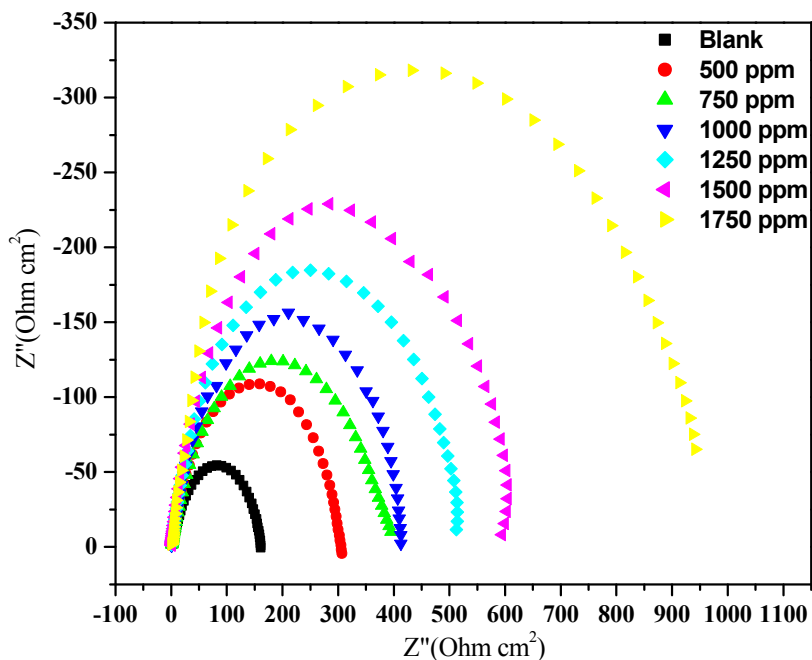

Fig. 9. Nyquist plots for MS in industrial water medium containing different concentrations of PR extracts.
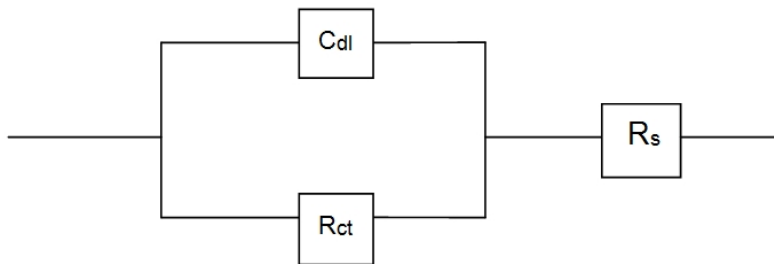

Fig. 10. Equivalent circuit diagram

3.6 Potentiodynamic Polarization

The anodic and cathodic polarization curves of MS electrode in industrial water medium in the absence and presence of various concentrations of PR extracts are shown in Fig. 11. The electrochemical parameters such as corrosion potential (E_{corr}) and corrosion current density (I_{corr}) were calculated from the intersection of anodic and cathodic Tafel slopes of the polarization curves are shown in Table 4. It is clear from Fig. 11 that both the cathodic and anodic curves showed lower current density in the presence of the PR extracts than those recorded in the solution without PR extracts. This indicates that PR extracts inhibits the corrosion process. Generally, an inhibitor can be classified as cathodic or anodic type if the shift of corrosion potential in the presence of the inhibitor is more than 85 mV with respect to that in the absence of the inhibitor [32]. From the results, the changes of E_{corr} are less than 85 mV for studied plant extract, which indicate that PR extracts act as a mixed type inhibitor for the corrosion of MS in industrial water medium.
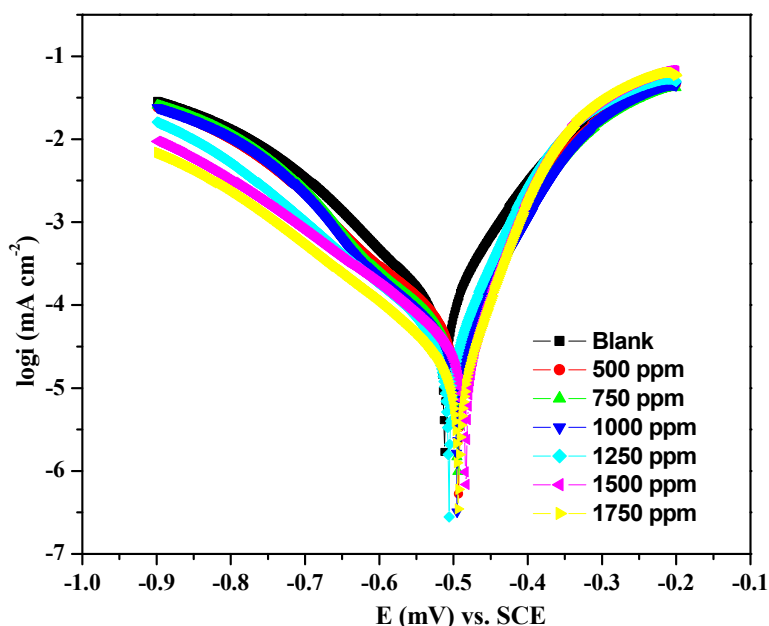

Fig. 11. Potentiodynamic polarization curves for MS in industrial water medium containing different concentrations of compound PR extracts

3.7 Scanning Electron Microscopy (SEM)

The formation of protective film of PR extracts on the MS surface was studied by SEM observations. Figs. 12(a), 12(b) and 12(c) represent the SEM images of MS surface after immersion in industrial water medium in the absence and presence of 1750 ppm concentrations of PR extracts. Fig. 12(a) represents the polished image of MS before placing in industrial water medium. Fig.12(b) shows the surface after immersed in the industrial water solution for 45 h. The morphology of MS surface in Fig. 12 (b) is highly damaged with cracks and pits due to rapid corrosion attack in industrial water medium. However, in the presence of PR extract [Fig. 12(c)], it was observed that the corrosion of MS decreases

considerably. The smooth and less corroded surface morphology of MS in inhibited solution might be due to the adsorption of PR extracts on MS surface.

Table 4. E_{corr}, I_{corr}, R_{ct}, C_{dl} and IE % obtained from polarization and impedance measurements for mild steel in industrial water medium containing various concentrations of PR extracts

C (ppm)	EIS			Polarization		
	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	IE %	E_{corr} (mV)	I_{corr} (μA cm^{-2})	IE %
0	126.5	60.19		-0.512	109.3	
500	246	46.23	48.54	-0.493	55.03	49.65
750	284	42.78	55.45	-0.494	46.00	57.91
1000	333	40.93	62.04	-0.495	37.75	65.46
1250	416	35.44	69.59	-0.506	33.33	69.50
1500	506	32.36	75.00	-0.483	25.00	77.12
1750	742	25.70	82.95	-0.494	14.3	86.91
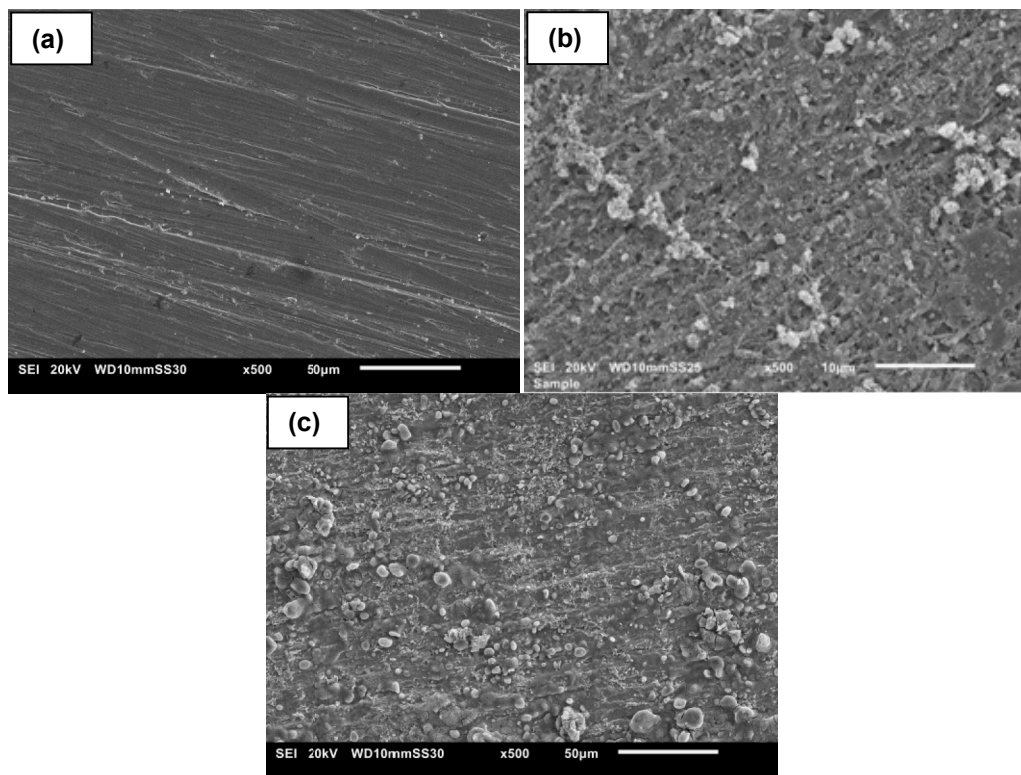
Fig. 12. SEM images of MS in industrial water medium after 40 h of immersion (a) before immersion (polished), (b) Without inhibitor (blank), (c) With 1750 ppm of PR extracts

4. CONCLUSION

PR extracts are eco - friendly and low-cost corrosion inhibitor for MS in industrial water medium. The % IE of PR extracts increased with increasing concentration and decreased with temperature. The results obtained by mass loss, electrochemical impedance spectroscopy and polarization measurements are in good agreement with each other. The adsorption of PR extracts on mild steel was found to obey the Langmuir adsorption isotherm. The values of Gibbs free energy calculated indicated that the adsorption of PR extracts on MS in industrial water medium is the combination of both physisorption and chemisorption. The adsorbed film containing the investigated PR extracts was identified by SEM analysis.

ACKNOWLEDGEMENTS

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Eddy NO. Part 3. Theoretical study on some amino acids and their potential activity as corrosion inhibitors for mild steel in HCl. Mol Simul. 2010;36(5):354-63.
2. Eddy NO, Mamza PAP. Inhibitive and adsorption properties of ethanol extract of seeds and leaves of Azadirachta indica on the corrosion of mild steel in H_2SO_4. Port Electrochim Acta. 2009;27(4):443-56.
3. Aytac A, Ozmen U, Kabasakaloglu M. Investigation of some Schiff bases as acidic corrosion of alloy AA3102. Mater Chem Phys. 2005;89(1):176-81.
4. Eddy NO. Ethanol extracts of phyllanthus amarus as a green inhibitor for the corrosion of mild steel in H_2SO_4. Port Electrochim Acta. 2009;27(5):579-89.
5. Benabdellah M, Hammouti B, Warthan A, Al-Deya SS, Jama C, Lagrenee M, Bentiss F. 2,5-Disubstituted 1,3,4-oxadiazole derivatives as effective inhibitors for the corrosion of mild steel In 2M H_3PO_4 solution. Int J Electrochem Sci. 2012;7(4):3489-3500.
6. Joseph Raj X, Rajendran N. Effect of some oxadiazole derivatives on the corrosion inhibition of brass in natural seawater, JMEPEG, 2012;21(7):1363-1373.
7. Seifzadeh D, Basharnavaz H, Bezaatpour A. A Schiff base compound as effective corrosion inhibitor for magnesium in acidic media. Mater Chem Phys. 2013;138(2):794-802.
8. Quraishi MA, Jamal D. Corrosion inhibition by fatty acid oxadiazoles for oil well steel (N-80) and mild steel. Mater Chem Phys. 2001;71(2):202-205.
9. Soltani N, Tavakkoli N, Khayatkashani M, Jalali MR, Mosavizade A. Green approach to corrosion inhibition of 304 stainless steel in hydrochloric acid solution by the extract of *Salvia officinalis* leaves. Corros Sci. 2012;62(1):122-135
10. Raja PB, Qureshi AK, Rahim AA, Osman H, Awang K. Neolamarckia cadamba alkaloids as eco-friendly corrosion inhibitors for mild steel in 1 M HCl media. Corros Sci. 2013; 69(4):292-301.

11. Abiola OK, Otaigbe JOE. The effects of phyllanthus amarus extract on corrosion and kinetics of corrosion process of aluminum in alkaline solution. Corros Sci. 2009;51(11):790–2793.

12. Abiola OK, Otaigbe JOE, Kio OJ. *Gossipium hirsutum* L. extracts as green corrosion inhibitor for aluminum in NaOH solution. Corros Sci. 2009;51(8):1879-1881.

13. Abiola OK, James AO. The effects of Aloe vera extract on corrosion and kinetics of corrosion process of zinc in HCl solution. Corros Sci. 2010;52(2):661-664.

14. Behpour M, Ghoreishia SM., Khayatkashania M, Soltani N. Green approach to corrosion inhibition of mild steel in two acidic solutions by the extract of punica granatum peel and main constituents. Mater Chem Phys. 2012;131(3):621– 633.

15. Deng S, Li X. Inhibition by ginkgo leaves extract of the corrosion of steel in HCl and H_2SO_4 solutions. Corros Sci, 55(2);2012:407–415.

16. Deng S, Li X. Inhibition by jasminum nudiflorum lindl. Leaves extract of the corrosion of aluminium in HCl solution, Corros Sci. 2012;64(11):253–262.

17. Shaida FS, Salmy SY, Tan ML, Tengku STM. Chemical components of the essential oils from three species of malaysian plumeria and their effects on the growth of selected microorganisms. Jour Bio. 2008;19(2):1–7.

18. Bobbarala V, Katikala PK, Naidu KC, Penumajji S. Antifungal activity of selected plant extracts against phytopathogenic fungi aspergillus niger F2723, Indian J Sci Technol. 2000;2(4):87-90.

19. Zaheer Z, Konale AG, Patel KA, Khan S, Ahmed RZ. Comparative phytochemical screening of flowers of plumeria alba and plumeria rubra. Asian J Pharm Clin Res. 2010;3(4):88-89.

20. Hussin MH, Kassim MJ. The corrosion inhibition and adsorption behavior of uncaria gambir extract on mild steel in 1M HCl. Mater Chem Phys. 2011;125(3):461-468.

21. Schorr M. Yahalom J. The significance of the energy of activation for the dissolution reaction of metal in acids. Corros Sci. 1972;12(11):867-868.

22. Singh AK, Quraishi MA. The effect of some bis-thiadiazole derivatives on the corrosion of mild steel in hydrochloric acid. Corros Sci. 2010;52(4):1373-1385.

23. Ali SA, Shareef AME, Al Ghamdi RF, Saeed MT. The isoxazolidines: the effects of steric factor and hydrophobic chain length on the corrosion inhibition of mild steel in acidic medium. Corros Sci. 2005;47(11):2659-2678.

24. Avci G. Corrosion inhibition of indole-3-acetic acid on mild steel in 0.5 M HCl. Colloids Surf A. 2008;317(1-3):730-736.

25. Li X, Deng S, Fu H, Mu G. Inhibition effect of 6-benzylaminopurine on the corrosion of cold rolled steel in H_2SO_4 solution. Corros Sci. 2009;51(3):620-634.

26. Bensajjay E, Alehyen S, El Achouri M, Kertit S. Corrosion inhibition of steel by 1-phenyl 5-mercapto 1,2,3,4- tetrazole in acidic environments. Anti-Corros Meth Mater 2003;50(6):402-409.

27. Hameed RSA, Aminolysis of polyethylene terephthalate waste as corrosion inhibitor for carbon steel in HCl corrosive medium, Adv Appl Sci Res, 2011;2(3): 483-499.

28. Khaled KF. The inhibition of benzimidazole derivatives on corrosion of iron in 1 M HCl solutions. Electrochim Acta. 2003; 48(17):2493-2503.

29. Li W, He Q, Zhang S, Pei C, Hou B. Some new triazole derivatives as inhibitors for mild steel corrosion in acidic medium. J Appl Electrochem. 2008;38(3):289-295.

30. Oguzie EE, Li Y, Wang FH. Effect of 2-amino-3-mercaptopropanoic acid (cysteine) on the corrosion behaviour of low carbon steel in sulphuric acid. Electrochim Acta. 2007;53(2):909-914.

31.   Lebrini M, Lagrenée M, Vezin H, Traisnel M, Bentiss F. Experimental and theoretical study for corrosion inhibition of mild steel in normal hydrochloric acid solution by some new macrocyclic polyether compounds. Corros Sci. 2007;49(5):2254-2269.
32.   Li W, He Q, Zhang S, Pei C, Hou B. Some new triazole derivatives as inhibitors for mild steel corrosion in acidic medium, J Appl Electrochem. 2008;38(3):289-295.