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Inhibitive Action of *Piper nigrum* Extract as Corrosion Inhibitor for Mild Steel in 1 N Sulphuric Acid Medium

M. SIVARAJU†, K. KANNAN* and M. SHANKARRAJ
Department of Chemistry, Government College of Engineering, Salem-636 011, India
E-mail: kannan_k2002@yahoo.co.in; sivarajuviji06@yahoo.co.in

The inhibition effect of *Piper nigrum* (black pepper) seeds extracts *i.e.*, acid extract (A) and water extract (W) on the corrosion of mild steel in 1 N sulphuric acid has been studied by mass loss and polarization techniques between 302 and 323 K. The inhibition efficiency increased with increase in concentration of extracts. The corrosion rate increased with increase in temperature and decreased with increase in concentration of inhibitor compared to blank. The inhibition efficiency of the acid extract was greater than aqueous extract (A > W). The adsorption of inhibitor on the mild steel surface has been found to obey Temkin's adsorption isotherm. Potentiostatic polarization results reveal that *Piper nigrum* act as mixed type inhibitor. The values of activation energy (E_a), free energy of adsorption (ΔG_{ads}), heat of adsorption (Q_{ads}), enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) were also calculated.

Key Words: Mild steel, Sulphuric acid, Corrosion inhibition, Temkin's adsorption isotherm, Potentiostatic polarization, *Piper nigrum*.

INTRODUCTION

The study of corrosion of mild steel in sulphuric acid is a subject of practical significance and many engineering applications since the acid is highly corrosive and extensively used in industrial operations[1]. Especially, concentrated mineral acids are used extensively in pickling, cleaning, descaling and oil well. Aciding of metallic materials cause corrosion damage to metals[2,3]. It has been speculated that organic inhibitors are more effective with iron and that polar organic compounds containing sulphur, oxygen and nitrogen atoms are good corrosion inhibitors for the acidic dissolution of metals[4,5]. The effectiveness of these compounds as corrosion inhibitors can be attributed to the number of mobile electron pair present to the π electron character of free electron and to the electron density around the nitrogen atoms. Most of the previous studies were focused on the inhibition of stainless

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†Department of Chemistry, Muthayammal Engineering College, Rasipuram-637 408, India.

steel (or) chromium nickel steel in hydrochloric acid and sulphuric acid solutions using organic compounds containing nitrogen, sulphur and oxygen atoms as corrosion inhibitors[6-10].

Because of toxic nature and high cost of some chemicals currently in use it is necessary to develop environmentally acceptable and less expensive inhibitors. Natural products can be considered as a good source for this purpose. The possible replacement of some expensive chemicals as corrosion inhibitors for metals in acid cleaning process by naturally occurring substances of plant origins has been studied[11].

Piper nigrum is most common plant in the piperaceae family that has alkaloid of piperine compound and its relative toxicity is 1.0 (0-very safe and 3-high toxicity)[12]. The recent trend of using different herbal extracts as corrosion inhibitors was due to their biodegradable, less non-toxic, soluble and highly stable nature in acidic solutions due to their availability in plenty, various parts of plants *viz.*, seeds, fruits, leaves, flowers, *etc.*, have been used as corrosion inhibitors in several studies[13,14].

The present investigation is carried out to examine the inhibitive action of *Piper nigrum* extract towards corrosion of mild steel in 1 N sulphuric acid solution by mass loss method and polarization technique. It is aimed to predict the corrosion rate, inhibition efficiency, surface coverage on mild steel by adsorbed *Piper nigrum* extracts of acid and water at various temperatures and the thermodynamic feasibility such as the values of activation energy (E_a), free energy of adsorption (ΔG_{ads}), heat of adsorption (Q_{ads}), enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) were also calculated. The adsorption characteristic was studied in order to access the adsorption isotherm (S).

Preparation of plant extract: *Piper nigrum* seeds used for this investigation were obtained locally. These were dried in air at room temperature. The dried seeds were grounded into powder and 2.0 g of the powder was digested in 1 L of 1 N sulphuric acid and water separately. These resultant solutions were allowed to stand for 48 h and then filtered. From this stock, solutions of varying concentration of the acid and water extracts were prepared. Already this method was used to prepare *Allium sativum* extract and corrosion inhibitive action on mild steel in acidic medium was examined[15].

EXPERIMENTAL

Mass loss measurements: Mild steel specimens were cut to size of 5 cm × 1 cm from the mild steel sheets having the percentage composition as shown below:

Element	Fe	Ni	Mo	Cr	S	P	Si	Mn	C
Composition (%)	99.686	0.013	0.015	0.043	0.014	0.009	0.007	0.196	0.017

The surface of specimens were polished with emery papers ranging from 110 to 410 grades and degreased with trichloroethylene. The specimens were dried and stored in vacuum desiccators containing silica gel and then initially weighed in an electronic balance. After that the specimens were suspended with the help of PTFE, threads and glass rod in 100 mL beaker containing acid in the presence and absence of inhibitor. The specimens were removed after 3 h of exposure, washed with water to remove any corrosion products and finally washed with acetone. After that they were dried and reweighed. Mass loss measurements were carried out in 1 N sulphuric acid with *Piper nigrum* extract in the concentration range of 2×10^{-6} to 8×10^{-6} g/L as inhibitors and the temperature between 302 and 323 K for an immersion period of 3 h. All the solutions were prepared with AR grade chemicals in double distilled water. Mass loss measurements were performed as per ASTM method described previously[16.17].

Potentiostatic polarization measurements: Polarization measurements were carried out in a conventional three-electrode cell. Mild steel strips coated with lacquer except for an exposed area of 1 cm^2 were used as working electrode. The saturated calomel electrode (SCE) and the platinum foil were used as reference and counter electrodes, respectively. The potentiostatic polarization measurement was carried out using BAS-100A model instrument. The potential of the test electrode was measured with respect to SCE and platinum electrode was used as auxilliary electrode and the experiment was carried out at 302 to 323 K.

RESULTS AND DISCUSSION

Mass loss: Table-1 shows the value of inhibition efficiency [IE %], surface coverage (θ) and corrosion rate obtained at different concentrations of the inhibitors in 1 N sulphuric acid solution for an immersion period of 3 h. From the mass value, the inhibition efficiency and surface coverage were calculated using the following equations[18,19].

$$\text{IE\%} = \frac{\text{Wu} - \text{Wi}}{\text{Wu}} \times 100$$

$$\theta = \frac{\text{Wu} - \text{Wi}}{\text{Wu}}$$

where Wu and Wi are the corrosion rates for mild steel in the absence and presence of inhibitor, respectively at the same temperature.

It could be seen from the Table-1 that the addition of inhibitor to the acid has reduced the corrosion rate. The inhibition efficiency increased with increase in concentration of inhibitors and temperature from 302 to 323 K in 1 N sulphuric acid for both acid and water extract of *Piper nigrum*. The values of the corrosion rate and inhibition efficiency of the inhibitors are known to depend on the molecular structure of the inhibitors.

TABLE-1
CALCULATED CORROSION RATE, INHIBITION EFFICIENCY (IE %) AND SURFACE COVERAGE (θ) FOR ACID AND WATER EXTRACT OF *Piper nigrum* FROM MASS LOSS STUDIES IN 1 N SULPHURIC ACID

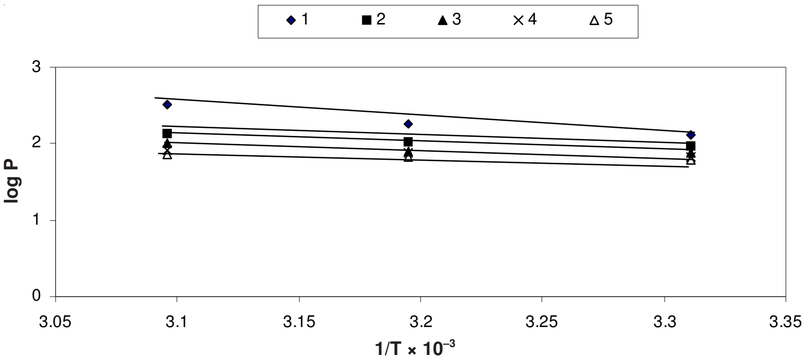
Temp. (K)	Conc. of inhibitor ($\times 10^{-6}$ g/L)	Acid extract			Water extract		
		Corrosion rate	Surface coverage (θ)	IE (%)	Corrosion rate	Surface coverage (θ)	IE (%)
302	Blank	131.6601	–	–	131.6601	–	–
	2	93.9155	0.2867	28.67	122.4468	0.0700	7.00
	4	76.0092	0.4227	42.27	119.8463	0.0897	8.97
	6	67.9847	0.4836	48.36	107.8097	0.1812	18.12
	8	61.1491	0.5356	53.56	99.9338	0.2410	24.10
313	Blank	177.9491	–	–	177.9491	–	–
	2	105.8779	0.4050	40.50	147.5603	0.1708	17.08
	4	80.5415	0.5474	54.74	145.2570	0.1837	18.37
	6	74.4489	0.5816	58.16	137.0840	0.2296	22.96
	8	67.3160	0.6217	62.17	120.7379	0.3215	32.15
323	Blank	320.7542	–	–	320.7542	–	–
	2	134.4092	0.5810	58.10	200.6850	0.3743	37.43
	4	100.6025	0.6864	68.64	165.0209	0.4855	48.55
	6	81.1359	0.7470	74.70	143.1766	0.5536	55.36
	8	73.7059	0.7702	77.02	128.1679	0.6004	60.04

The maximum inhibition efficiency of *Piper nigrum* in acid and water extracts were found to be 77.02 and 60.04 %, respectively in 1 N sulphuric acid with 8 × 10^{-6} g/L of inhibitor concentration at 323 K.

Energy of activation (E_a): Table-2 presents the calculated values of activation energy (E_a) and free energy of absorption (ΔG_{ads}) for mild steel corrosion in 1 N sulphuric acid with and without inhibitors at 302 to 323 K. Energy of activation was calculated from Arrhenius equation[19].

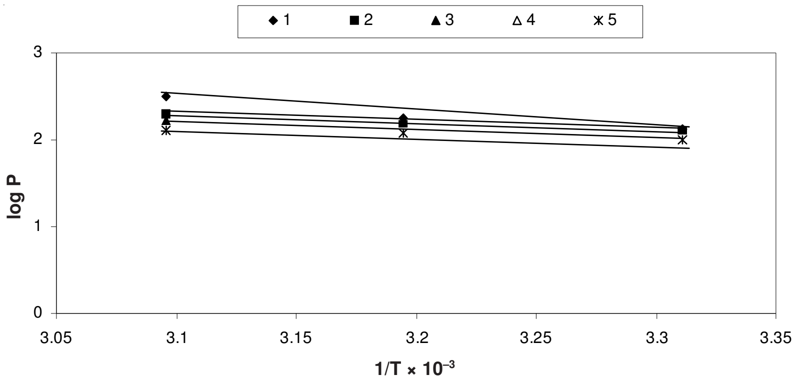
$$\log\frac{P_2}{P_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 \times T_2}\right)$$

where P_1 and P_2 are the corrosion rates at temperatures T_1 and T_2, respectively. The E_a values for 1 N sulphuric acid containing inhibitors are found to be lower than that of without inhibitors. Pultilova *et al.*[20,21] have indicated that this type of inhibitors are effective at higher temperature because the surface area of the metal coverage by the inhibitor molecules increases as the temperature rises and also decrease in activation energy could be attributed to the metal surface *via* chemisorptions[20-22]. E_a values are calculated from the slopes of Arrhenius plot and by using equation are approximately almost similar for both acid and water extracts (Figs. 1 and 2).



1 = Blank, 2 = 2 × 10^{-6} g/L, 3 = 4 × 10^{-6} g/L, 4 = 6 × 10^{-6} g/L, 5 = 8 × 10^{-6} g/L

Fig. 1. Arrhenius plot for corrosion of mild steel in 1 N sulphuric acid with acid extract



1 = Blank, 2 = 2 × 10^{-6} g/L, 3 = 4 × 10^{-6} g/L, 4 = 6 × 10^{-6} g/L, 5 = 8 × 10^{-6} g/L

Fig. 2. Arrhenius plot for corrosion of mild steel in 1 N sulphuric acid with water extract

Heat of adsorption (Q_{ads}): The values of heat of adsorption Q_{ads} were calculated using the following equation[23],

$$Q_{ads} = 2.303R\log\left(\frac{\theta_2}{1-\theta_2}\right) - \left(\frac{\theta_1}{1-\theta_1}\right) \times \left(\frac{T_1 \times T_2}{T_2 - T_1}\right)$$

where θ_1 and θ_2 are the degrees of surface coverage at temperature T_1 and T_2 by the different additives. From Table-2 it is evident that in all the cases, the Q_{ads} values are positive range from 14.46 to 46.43 KJ/mol with *Piper nigrum* acid extract and -14.62 to 18.06 KJ/mol for water extract. The higher value of heat of adsorption (Q_{ads}) also shows that *Piper nigrum* acid extract has greater inhibition efficiency than water extract and confirms the chemisorptions character of the adsorption[24].

TABLE-2
CALCULATED VALUES OF ENERGY OF ACTIVATION (E_a) AND FREE ENERGY CHANGE (ΔG_{ads}) FOR MILD STEEL IN 1 N SULPHURIC ACID WITH WATER (W) AND ACID (A) EXTRACTS OF *Piper nigrum*

Types of extract	Conc. of inhibitor ($\times 10^{-6}$ g/L)	E_a (KJ/mol)		-ΔG			Q_{ads} (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol/k)
		From eqn.	From plot	302 K	313 K	323 K			
Water	Blank	34.39	35.21	–	–	–	–	30.24	–
	2	19.08	18.88	36.54	40.49	44.65	-14.62	14.93	0.1973
	4	12.35	12.94	35.47	38.92	44.01	2.44	8.20	0.1729
	6	10.96	11.62	36.49	38.59	43.65	11.36	6.80	0.1671
	8	9.61	10.16	36.67	39.05	43.40	18.04	5.45	0.1618
Acid	Blank	34.39	35.21	–	–	–	–	30.24	–
	2	13.85	14.30	40.74	43.60	46.90	14.46	9.69	0.1874
	4	10.83	11.10	40.51	43.29	46.27	30.88	6.67	0.1753
	6	6.83	7.52	40.11	42.60	45.98	41.96	2.67	0.1611
	8	7.21	7.12	39.91	42.29	45.55	46.43	3.06	0.1610

Free energy of adsorption (ΔG_{ads}): The free energy of adsorption (ΔG_{ads}) at different temperatures was calculated from the following equation[25].

$$\Delta G(_{ads}) = -RT \ln (55.5 K)$$

where K is equilibrium constant and given by

$$K = \frac{\theta}{C(1-\theta)}$$

where θ is surface coverage on the metal surface, C is concentration of inhibitor in mol/L and 55.5 is concentration of water (mol/L).

The negative values of (ΔG_{ads}) indicate the spontaneous adsorption of the inhibitors. This is usually characteristic of strong interaction with the metal surface. It is found that the ΔG_{ads} values are more negative than -40 KJ/mol indicating that inhibitors are strongly adsorbed on the metal surface[26,27]. The free energy of adsorption (ΔG_{ads}) of *Piper nigrum* extracts in 1 N sulphuric acid can be calculated from the above equation at 302-333 K.

Enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS): The enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) were also calculated from the following equations:

$$\Delta H^o = E_a - RT$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

Table-2 shows that thermodynamic data obtained in this study. It could be seen from the table that the activation energy decreases linearly with increasing efficiency of the inhibitor.

Ideally, a corrosion inhibitor is a substance that greatly increases the activation energy of corrosion. The negative values of (ΔG_{ads}) indicate the spontaneous adsorption of the inhibitor on the surface of mild steel. It's also observed that (ΔS) decreases with increasing efficiency of the inhibitors. The adsorption process is believed to be exothermic process and is always accompanied by a decrease in entropy. Ateya *et al.*[28] have described this situation as due to adsorption of the organic compound, which is accompanied by desorption of water molecules from the surface. While the adsorption process is believed to be exothermic and associated with a decrease in entropy of the solute, the opposite is true for the solvent.

Adsorption isotherms: Adsorption isotherms are very important in determining the mechanism of organo-electrochemical reactions. The most frequently used are those of Langmuir, Frumkin, Parsons, Temkin, Flory-Huggins and Bockris-Swinkels[29-32]. All these isotherms are of the general form,

$$f(\theta,x)\exp(-a\,\theta) = K\,C$$

where $f(\theta,x)$ is the configurational factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm.

The mechanism of inhibition of corrosion is generally believed to be due to the formation and maintenance of a protective film on the metal surface. The plot of surface coverage (θ) obtained by mass loss method *versus* log C at different concentrations of the inhibitors shows a straight line indicating that the adsorption of the inhibitor from acid on mild steel surface follows the Temkin's adsorption isotherm[25]. This also point out that the corrosion inhibition by these compounds is a result of their adsorption on the metal surface. Figs. 3 and 4 show the Temkin's adsorption isotherm plots for acid and water extract, respectively of *Piper nigrum* with 1 N sulphuric acid.

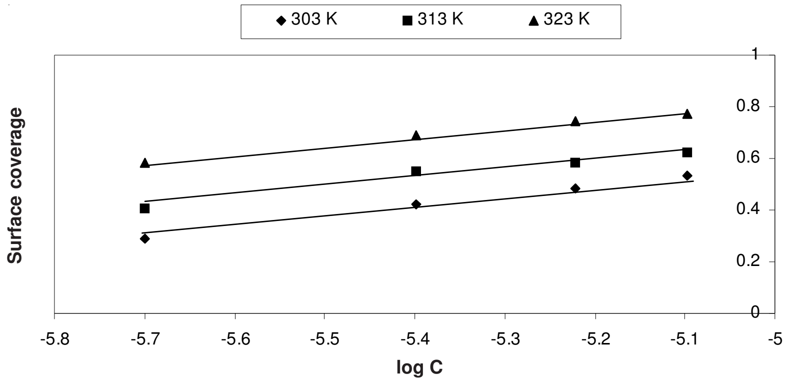


Fig. 3. Tempkin's adsorption isotherm for corrosion behaviour of mild steel in 1 N sulphuric acid with acid extract

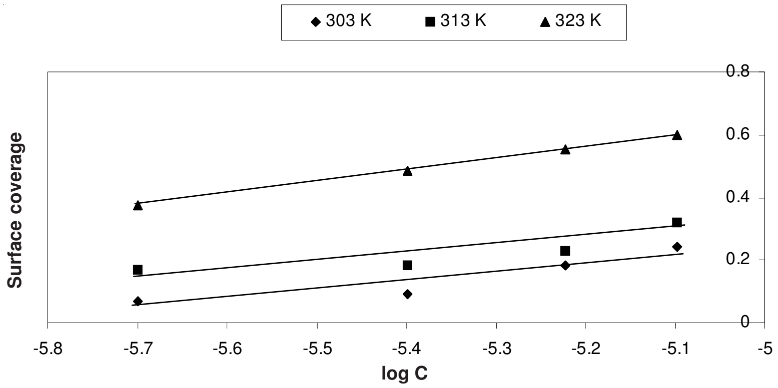
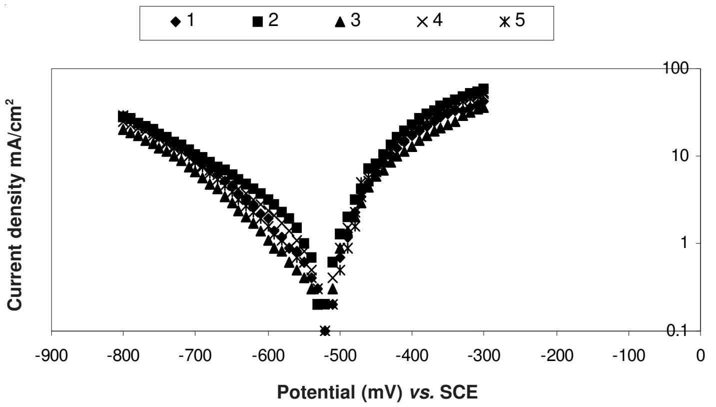


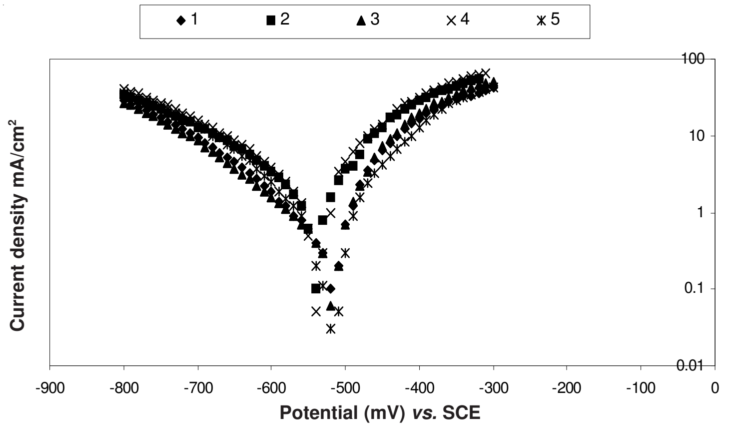
Fig. 4. Tempkin's adsorption isotherm for corrosion behaviour of mild steel in 1 N sulphuric acid with water extract

Potentiostatic polarization studies: The polarization behaviour of mild steel functioning as cathode as well as anode in the test solution is shown in Figs. 5 and 6 for 1 N sulphuric acid with *Piper nigrum* acid and water extracts at room temperature (302 K). The electrochemical data obtained are shown in Table-3. It is evident that *Piper nigrum* extracts bring about considerable polarization of cathode as well as anode. It is therefore inferred that the inhibitive action is of a mixed type and the cathodic and anodic Tafel slopes increase with increasing inhibitor concentration and the increase is predominant in case of the former indicating that the cathodic inhibition dominating through the inhibitive action is of mixed nature. The non-constancy of Tafel slopes for different inhibitor concentrations reveals that the inhibitors act through their interference in the mechanism of the corrosion processes at cathode as well as anode.



1 = Blank, 2 = 2 × 10^{-6} g/L, 3 = 4 × 10^{-6} g/L, 4 = 6 × 10^{-6} g/L, 5 = 8 × 10^{-6} g/L

Fig. 5. Typical potentiostatic curves for mild steel in 1 N sulphuric acid with acid extract



1 = Blank, 2 = 2 × 10^{-6} g/L, 3 = 4 × 10^{-6} g/L, 4 = 6 × 10^{-6} g/L, 5 = 8 × 10^{-6} g/L

Fig. 6. Typical potentiostatic curves for mild steel in 1 N sulphuric acid with water extract

The corrosion parameters deduced from Tafel polarization such as corrosion current I_{corr}, corrosion potential E_{corr}, Tafel constants b_a and $-b_c$ and inhibition efficiency (IE) are given in Table-3. The I_{corr} values decreased with increasing concentration of the inhibitors. The inhibition efficiency values were determined from the values of corrosion current.

TABLE-3
ELECTROCHEMICAL POLARIZATION PARAMETERS FOR THE CORROSION BEHAVIOUR OF MILD STEEL IN 1 N SULPHURIC ACID WITH ACID AND WATER EXTRACTS OF *Piper nigrum*

Temp. (K)	Conc. of inhibitor ($\times 10^{-6}$ g/L)	$-E_{corr}$ *vs.* SCE (mV)	I_{corr} ($\mu A/cm^2$)	Tafel constant (mV/decade)		IE (%)
				b_a	$-b_c$	
1 N Sulphuric acid with water extract						
302	Blank	535	390	60	120	–
	2	530	330	55	110	15.38
	4	520	310	52	100	20.51
	6	525	300	55	90	23.30
	8	520	290	50	95	25.64
313	Blank	520	1100	70	100	–
	2	520	920	55	95	16.36
	4	515	800	55	90	27.27
	6	520	760	50	80	30.90
	8	510	690	45	75	37.27
323	Blank	520	1800	70	120	–
	2	515	1280	65	115	36.55
	4	510	1125	60	120	37.77
	6	520	960	60	110	46.66
	8	505	890	55	105	53.33

Temp. (K)	Conc. of inhibitor ($\times 10^{-6}$ g/L)	$-E_{corr}$ *vs.* SCE (mV)	I_{corr} ($\mu A/cm^2$)	Tafel constant (mV/decade)		IE (%)
				b_a	$-b_c$	
1 N Sulphuric acid with acid extract						
302	Blank	535	390	60	120	–
	2	525	300	50	110	23.07
	4	520	280	50	120	28.20
	6	515	240	55	90	38.46
	8	520	210	50	85	46.15
313	Blank	520	1100	70	100	–
	2	510	720	50	90	34.54
	4	500	700	45	90	36.36
	6	510	660	50	80	40.00
	8	515	490	43	80	55.45
323	Blank	520	1800	70	120	–
	2	510	980	70	100	45.55
	4	505	900	40	90	50.00
	6	515	790	45	80	56.11
	8	495	600	40	90	66.66

Conclusion

The conclusions were made from the study, (1) Corrosion rates of mild steel in 1 N sulphuric acid increased with increasing temperature and decreased with increasing concentration of both acid and water extract of *Piper nigrum* seeds. (2) The inhibition efficiency increased with respect to the concentration of inhibitors as it is assumed that the inhibition efficiency is equal to surface coverage. (3) The inhibition efficiency of both acid and water extract of *Piper nigrum* in 1 N sulphuric acid increased with rise in temperature from 302 to 323 K. (4) The maximum inhibition efficiency of acid and water extract of *Piper nigrum* was found to be 77.02 and 60.04 % in 1 N sulphuric acid at 8 × 10^{-6} g/L inhibitor concentration at 323 K, respectively. (5) The adsorption of extracts on mild steel surface from the acid solution follows Temkin's adsorption isotherm. (6) The negative value of ΔG_{ads} indicated that the extracts resulted in spontaneous adsorption of inhibitor on the surface of mild steel. (7) The inhibition efficiency obtained from mass loss studies and polarization measurement shows fairly good agreement. (8) *Piper nigrum* acid extract shows the better inhibition efficiency than water extract in 1 N sulphuric acid. (9) It is found that the both acid and water extracts of *Piper nigrum* act as mixed type inhibitor. (10) Energy of activation and free energy values indicate chemical adsorption of the inhibitors on metal surface.

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