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Murraya koenigii as green corrosion inhibitor for mild steel in nitric acid medium

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The inhibition behaviour of *Murraya koenigii* (curry) leaves extract on the corrosion resistance of mild steel (MS) in nitric acid medium has been studied by gravimetric (or weight loss) measurements and scanning electron microscopy. The inhibition efficiency increases with inhibitor concentration and decreases with increase in immersion time period. The temperature effect on the corrosion behaviour of mild steel without and with inhibitor has been studied. Temperature studies reveal that the activation energy increases to 18 kJ/mol with the addition of 500 ppm inhibitor. Mild steel corrosion inhibition efficiency of 62% is obtained with 600 ppm of extract in 0.1N HNO_3. The adsorption isotherm studies and the thermodynamic analysis of the results indicate physical adsorption of the inhibitor molecules on the mild steel surface. Scanning electron microscopic studies show the presence of pitting corrosion in uninhibited sample. The energy-dispersive X-ray spectroscopy studies reveal higher carbon content in the inhibited sample which attributs to the presence of adsorbed inhibitor molecules.

Keywords: Green inhibitors, Corrosion inhibitors, Mild steel, *Murraya koenigii* leaves, Nitric acid

Corrosion is the deterioration or destruction of metals as a result of chemical reaction between the metal and the surrounding environment, which is unavoidable but controllable process. Mild steel (MS) is the most common form of steel because of its properties that are acceptable for many applications particularly in food, petroleum, chemical and electrochemical industries. Mild steel faces problem of severe corrosion in acidic medium, as it is exposed to acid during cleaning process. Every year industries spend huge amount of money in corrosion prevention and maintenance of process equipment[1]. There are many ways to prevent corrosion, for example, appropriate material selection and application of coating. One of the methods used to reduce the rate of metallic corrosion is addition of inhibitors. Most of the well-known acid inhibitors are organic compounds especially those with N, O and S showed an effective corrosion inhibition[2,3]. These compounds are not only expensive but also toxic for living beings. Hence, there is a need of new "eco-friendly" inhibitors, which can be of selective plant extract.

Now-a-days, research work on naturally occurring substances exhibiting a strong affinity for metal surfaces for the development of environmentally benign corrosion inhibitors has increased tremendously. Plant extracts are an incredibly rich source of natural chemical compounds that can be extracted by simple procedures with low cost and are biodegradable in nature. Corrosion inhibition property of the extracts of leaves and bark of mango, tobacco, cashew and neem plants[4], *Spirulina platensis*[5], *Hibiscus sabdariffa*[6], *Apricot juice*[7], *Rosemary*[8], *Neolamarckia cadama*[9], *Gossipium hirsutum*[10], *Salvia aucheri mesatlantica*[11], *Osmanthus fragran*[12], *Aspilia africana*[13], *Azadirachta indica*[14], *Dodonaea viscosa*[15], *Spondias mombin*[16], *Gnetum africana*[17], *Carica papaya* and *Camellia Sinensis*[18], *Mentha rotundifolia*[19], *Eucalyptus globulus*[20], *Mangrove tannin*[21], *Piper longum*[22], *Punica granatum*[23], *Andrographis paniculata*[24] have been studied for mild steel.

Murraya koenigii has been reported to offer good corrosion protection for mild steel in hydrochloric and sulfuric acid solutions[25]. The inhibition efficiency of *M. koenigii* was claimed to be due to its main components like monoterpene hydrocarbons (Pinene, Camphene, Limonene etc.) and monoterpene alcohols (Linalool, Nerol, Geraniol etc.). The essential constituents of *M. koenigii* leaves are murrafoline-I, pyrayafoline-D and mahabinine-A[24]. However, the effect of *Murraya koenigii* leaves extract on corrosion inhibition for mild steel in nitric acid medium has not been studied yet. The objective of the present work is to study the inhibitive action of *Murraya koenigii* extract commonly known as curry leaves as a cheap, green and naturally occurring substance on corrosion behaviour of mild steel in nitric acid using gravimetric (weight loss) studies. The surface of the samples treated with acidic medium with and without inhibitor was characterized using scanning electron microscopy.

Experimental Section

Extract preparation

M. koenigii leaves (curry leaves) were washed with double distilled water and then dried for a week and was then powdered. The extract was prepared by refluxing 5 g of powdered dry leaves in methanol for 2 h at 55-60°C. Then the solution was filtered using Whatman No. 1 filter paper and concentrated with the help of hot air oven at 60°C for 2 h.

Weight loss measurements

MS specimen of 2.5 cm diameter and 1 cm thick was used for the corrosion study. Weight loss measurements or gravimetric experiments are widely used for corrosion studies as it gives reliable degree of accuracy, when performed in a procedural manner. The MS specimen was weighed before and after immersion in 200 mL of test solution using an analytical balance. The effect of nitric acid concentration on corrosion rate of MS specimen was studied by immersion of the specimen for a minute duration with different concentration of nitric acid solution. Experiments were also conducted to study the effect of inhibitor concentrations for mild steel coupons in 0.1 N HNO_3 with different inhibitor concentrations. The effect of immersion time and temperature were also studied by immersion of the coupon in 0.1 N nitric acid solutions with and without 500 ppm of inhibitor. Each experiment was performed at least for three times and the average weight loss was used for further calculations of corrosion rate. The corrosion rate (*CR*) in mm/y was calculated using equation 1[25]:

$$CR = \frac{87.6 \times w}{\rho \times a \times t} \qquad \ldots (1)$$

where, w is the weight loss (mg), ρ is the density of MS (7.83 g/cm^3) and a is the area of MS coupon (cm^2), t is the exposure time (h). The inhibition efficiency (*IE*) in % was calculated using equation 2[22]:

$$IE(\%) = \left(\frac{w_o - w_i}{w_o} \right) \times 100 \qquad \ldots (2)$$

where, w_o and w_i is the weight loss of MS specimen in absence and in presence of inhibitor respectively.

Scanning electron microscopy (SEM) analysis

Surface characterization of the MS specimens immersed in 0.1 N HNO_3 solutions in the presence and absence of 500 ppm of inhibitor for an immersion period 6 h was made using scanning electron microscopy (ZEISS EVO 18).

Results and Discussion

Gravimetric analysis

Effect of nitric acid concentration

The corrosion rate (CR) of the MS samples in various concentration of nitric acid has been studied. Mild steel corrosion rate increases with HNO_3 concentration for a constant immersion period of 1 min. As the concentration of the nitric acid increases, dissolution of metal surface also increases. The CR increases from 84.9 mmpy at 0.1 N to 352.6 mmpy at 0.5 N. The CR increases with HNO_3 concentration due to increased H^+ concentration and hence increased rate of chemical reaction as in equation 3[26,27].

$$Fe + 4HNO_3 \rightarrow Fe(NO_3)_2 + 2H_2O + 2NO_2 \qquad \ldots (3)$$

Effect of inhibitor concentration

Figure 1(A) shows the corrosion rate and inhibition efficiency of MS coupons immersed in 0.1N and 1N HNO_3 with various concentrations of inhibitor. The corrosion inhibition efficiency increases with extract concentration and also with the increase in nitric acid concentration. An inhibition efficiency of 89% was obtained for the mild steel coupons treated with 1N HNO_3 with 600 ppm of inhibitor. The inhibition efficiency increases from 36.8% at 100 ppm inhibitor concentration to 61.7% at 600 ppm. Further increase in concentration does not increase the inhibition efficiency. The increase in inhibition efficiency with inhibitor concentration up to 400 ppm is due to increased adsorption of the inhibitor molecules on the metal surface which protects it from corrosion[28].

Effect of immersion time

The corrosion rate and inhibition efficiency of mild steel immersed in nitric acid containing with and without inhibitor as a function of immersion time period are shown in Fig. 1(B). As the immersion period of MS specimen in the medium increases, the corrosion rate decreases for both the cases. The inhibition efficiency increases with immersion period. The observed increase in the IE with immersion period is due to the formation of a time dependent protective film on the mild steel surface which is due to the adsorption of the inhibitor molecules[29].

SEM and EDS analysis

The scanning electron microscopy (SEM) was used to analyze the surface morphology of the MS coupons immersed in 0.1 N HNO_3 with and without inhibitor. Figure 2(A) and (B) show the surface morphology of the MS specimen exposed to the medium in absence and presence of *M. koenigii* extract respectively. The composition of the MS specimen exposed to the medium without and with inhibitor is presented in Table 1. The surface of the uninhibited sample shows the occurrence of pitting corrosion. The inhibited MS coupon's surface showed relatively lower signs of corrosion compared to the blank material (as shown in Fig.4(B)). This could be due to the formation of a protective film on the MS surface. The EDAX analysis shows that the specimen exposed to the nitric acid containing *M. koenigii* showed an increased percentage of carbon and oxygen. This may be due to the adsorption of constituent molecules via oxygen active centers of the flavonoids monomer of *M. koenigii* leaf extract on the metal surface[25].

Effect of temperature

Figure 3 shows the effect of temperature on corrosion rate of mild steel in 0.1 N HNO_3 with and without 500 ppm inhibitor. It revealed that CR increases with temperature of nitric acid solution in either case. Also, the inhibition efficiency was found to be gradually decreasing. This can be attributed to the increased rate of chemical reaction between the metal surface and the medium with temperature. As a result, metal corrodes at a faster rate. However, with the addition of 500 ppm inhibitor to the nitric acid, the corrosion rate significantly decreases due to inhibition effect of *M. koenigii*. This shows the corrosion inhibition effect of *M. koenigii* at higher temperature up to some extent. In order to study the effect of temperature and evaluate the thermodynamic activation parameters of the corrosion of mild steel in nitric acid medium, weight loss measurements were carried out in the temperature range from 298 to 338K in the absence and presence of 500 ppm inhibitor. The activation parameters play an important role in understanding the mechanism of inhibition[30].

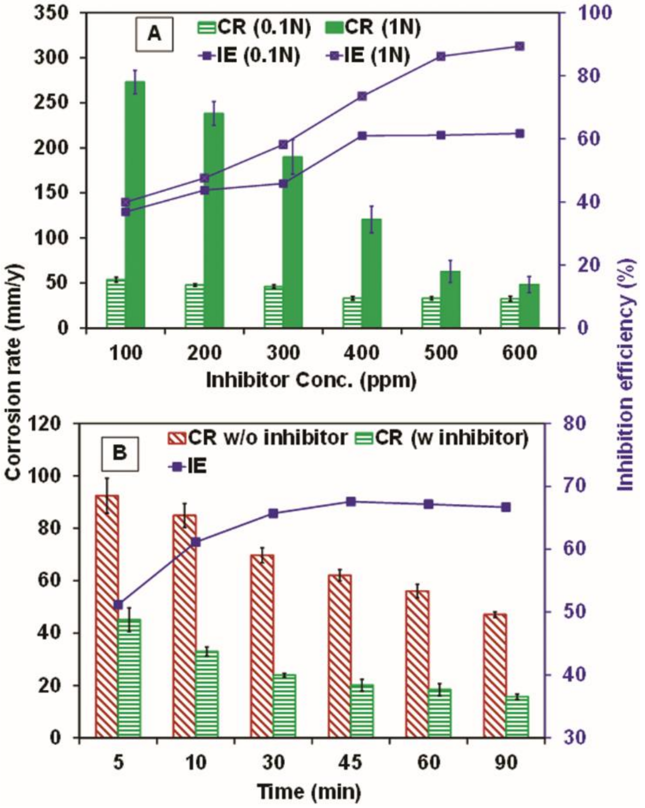

Fig. 1 (A) — Effect of inhibitor concentration on corrosion rate and inhibition efficiency of MS specimen in 0.1N and 1N HNO_3 for 10 min and (B) Effect of immersion time on corrosion rate and inhibition efficiency of MS specimen in 0.1N HNO_3 with and without inhibitor of 500 ppm concentration.

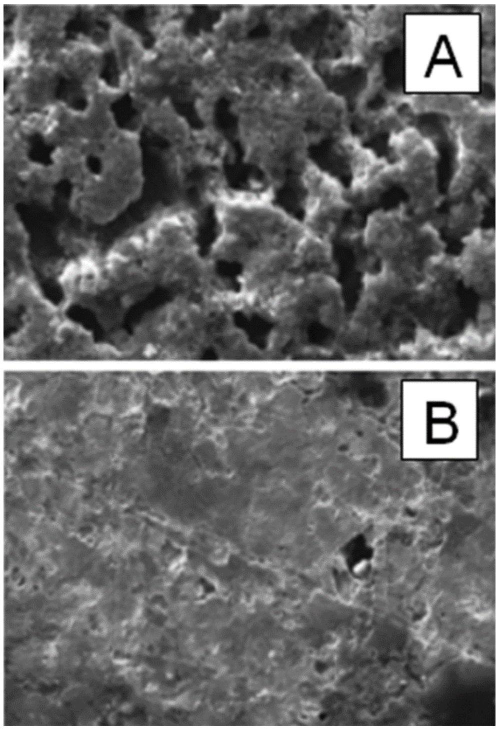

Fig. 2 — SEM image of mild steel specimen immersed in 0.1N HNO_3 medium for 6 h (A) absence of inhibitor and (B) presence of inhibitor.

Table 1 — EDAX composition of MS specimen exposed to medium in absence and presence of 500 ppm *M. koenigii* extract. All the values are in wt%.

Element	Absence of inhibitor	Presence of inhibitor
Fe	53.8	47.8
O	36.4	10.5
C	9.8	41.7

Arrhenius equation given by equation 4 is used to calculate the activation parameters[31]

$$\log(CR) = \log A - \frac{E_a}{2.303RT} \qquad \dots (4)$$

The activation energy and pre-exponential factor were calculated from the plot of logarithm of *CR* versus 1/*T*, which is shown in Fig. 4(A) where, E_a is the activation energy, *T* is the absolute temperature, *A* is the Arrhenius pre-exponential factor and *R* is the universal gas constant. The inhibitor addition increases the activation energy from 8.677 kJ/mol to 18.094 kJ/mol. An increase in activation energy with inhibitor addition could be described by the increased energy barrier of the corrosion reaction[28]. Physical adsorption is believed to occur in the cases where an increase in activation energy is observed with the inhibitor addition[28]. The increased dissolution of the metal resulting from desorption of weakly physisorbed inhibitor molecules results in decreased inhibition efficiency at high temperatures[28]. Literatures state an E_a value less than 40 kJ/mol represents physical adsorption and those above 80kJ/mol indicate chemisorption[28]. In the present study, the E_a value is less than 40 kJ/mol which represents physical adsorption.

However, E_a is not a reliable tool to arrive at a conclusion regarding the nature of the adsorption phenomenon going on in the system. This is due to the competitive adsorption with water molecules which needs some activation energy for the removal of the adsorbed water molecules[28].

Enthalpy and entropy of activation were calculated using transition state equation shown in equation 5[28].

$$\log\left(\frac{CR}{T}\right) = \log\left(\frac{R}{Nh}\right) + \frac{\Delta S_{\text{act}}}{2.303R} - \frac{\Delta H_{\text{act}}}{2.303RT} \qquad \dots (5)$$

where, *h* is Planck's constant(6.626176×10^{-34} J-s), *N* is Avogadro's number (6.02252×10^{23} mol^{-1}), *R* is the universal gas constant, ΔH_{act} is the enthalpy of activation and ΔS_{act} is the entropy of activation. The plot of log (*CR*/*T*) versus 1/*T* is plotted in shown in Fig. 4(B), which gives a straight line with a slope of ($-\Delta H_{act}$ /2.303*R*) and an intercept of [log (*R*/*Nh*) + (ΔS_{act} /2.303*R*)], from which the values of ΔH_{act} and ΔS_{act} are calculated and presented in Table 2[25]. The positive sign of enthalpy (ΔH_{act}) reflects the endothermic nature of the mild steel dissolution process. The increase in ΔH_{act} with inhibitor addition

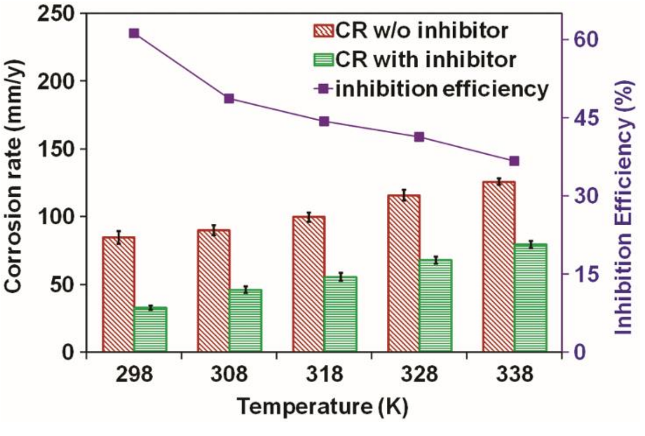

Fig. 3 — Effect of temperature on the corrosion rate and inhibition efficiency in the absence and presence of 500 ppm inhibitor concentration in 0.1N HNO_3solution.

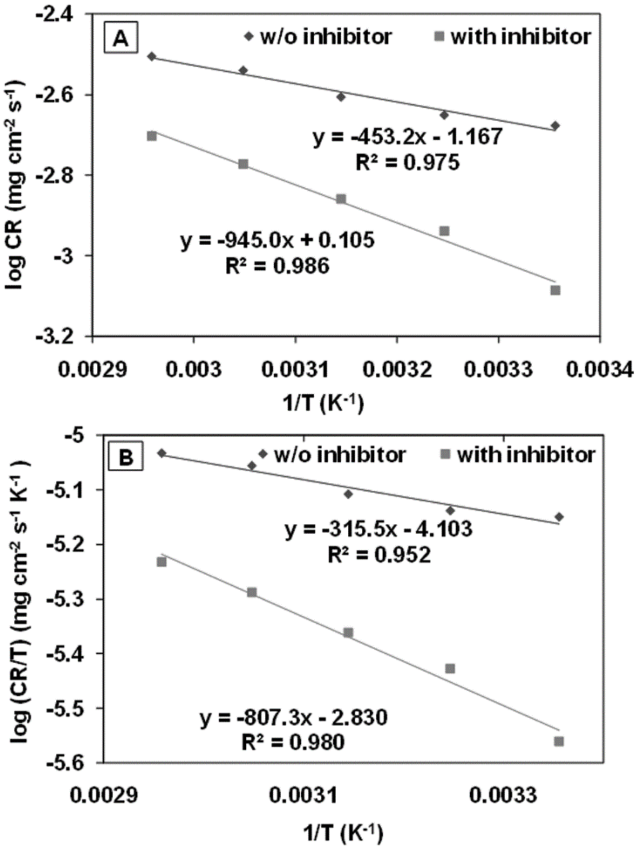

Fig. 4 — Arrhenius plots for MS specimen in 0.1N HNO_3 solution with and without 500 ppm inhibitor (A) log (CR) vs. 1/T and (B) log (CR/T) vs. 1/T.

Table 2 — Activation parameters of mild steel in 0.1N nitric acid with and without 500 ppm inhibitor.

Solution	E_a (kJ/mol)	ΔH_{act} (kJ/mol)	ΔS_{act} (J/mol.K)
Uninhibited	8.677	6.041	-276
Inhibited	18.094	15.457	-251

shows that the energy for dissolution increases which causes a drop in *CR*[28]. The increase of entropy (ΔS_{act}) in the presence of inhibitor reveals that an increase in disordering takes place on going from reactant to the activated complex which is the driving force for the adsorption of inhibitor onto the mild steel surface[24]. The adsorbed molecules hinder the liberation of hydrogen resulting in increased disorderliness[28]. A negative value of ΔS_{act} indicates that the dissolution process is controlled by activation complex[28].

Under constant pressure conditions, the heat of adsorption of the process (Q_{ads}) is considered to be same as the enthalpy of adsorption ΔH_{ads}[28]. The Q_{ads} can be calculated from equation 6[28].

$$\log\left(\frac{\theta}{1-\theta}\right) = \log A + \log C - \frac{Q_{\text{ads}}}{2.303RT} \qquad \ldots (6)$$

where, θ is the surface coverage, *A* is a constant, *C* is the concentration of the inhibitor and Q_{ads} is heat of adsorption. The surface coverage (θ) is calculated by dividing the inhibition efficiency by 100[28]. The value of Q_{ads} at constant inhibitor concentration was calculated using above equation[31]. A plot of log(θ/(1- θ)) vs. 1/*T* is constructed, which is shown in Fig. 5 using the surface coverage values for the weight loss experiments with 500 ppm extract in the temperature range from 25°C to 65°C. The slope of the straight line is $-\Delta H_{ads}/2.303R$ and ΔH_{ads} was calculated to be -19.42 kJ/mol. The negative value of ΔH_{ads} represent that the adsorption of inhibitor on MS specimen is an exothermic process. An absolute ΔH_{ads}value of lower than 41.86 kJ/ mol is considered to be physisorption and higher than 100 kJ/mol is chemisorption[31]. Therefore ΔH_{ads} calculated as -19.42 kJ/mol can be considered as physical adsorption.

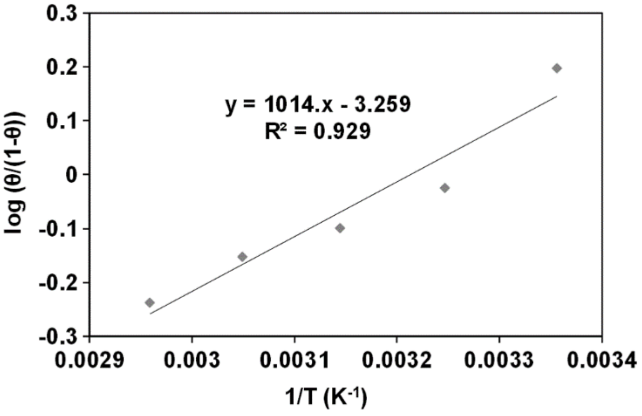

Fig. 5 — Plot of log (θ/(1-θ)) vs. 1/*T* for mild steel in 0.1N HNO_3 in the presence of 500 ppm inhibitor.

Adsorption isotherm

The weight loss studies show that the inhibitor molecules adsorb on the surface of the mild steel resulting in minimized corrosion. The surface coverage of the molecules during adsorption process can be calculated from the inhibition efficiency. The surface coverage can be used to investigate the type of adsorption that the inhibitor molecules follow. Langmuir adsorption isotherm can be expressed by the following equation7[28]

$$\frac{C}{\theta} = \frac{1}{k_{\text{ads}}} + C \qquad \ldots (7)$$

where, C is concentration of the inhibitor, θ is the surface coverage and k_{ads} is the equilibrium constant for adsorption desorption process[31]. The value of equilibrium constant (k_{ads}) was calculated from the reciprocal of the intercept of isotherm line. The plot of C/θ versus *C* (Fig. 6 (A)) yields a straight line with correlation coefficient of 0.9645 and slope of 1.3105.

The Temkin isotherm can be expressed using the equation 8[28]

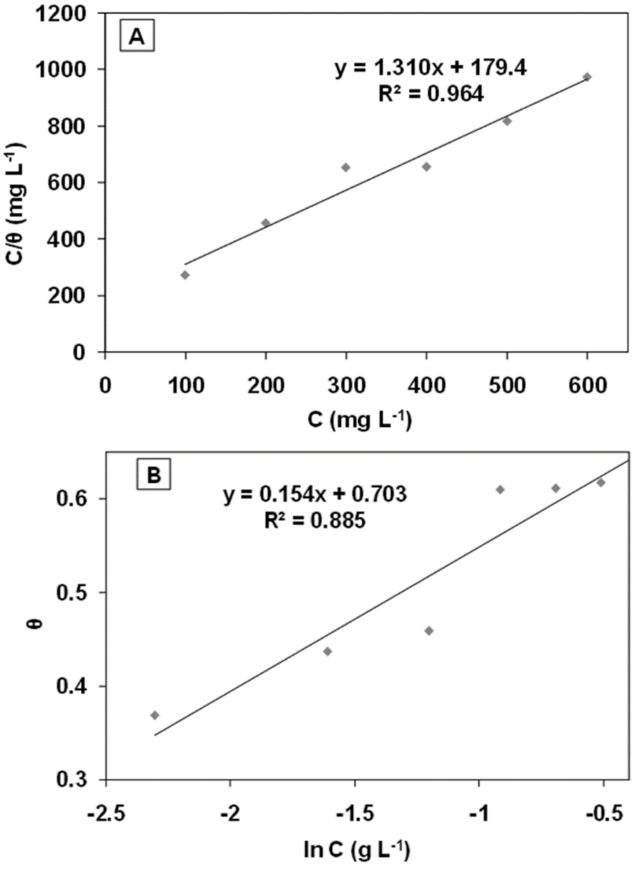

Fig. 6 — Plots for mild steel in 0.1N HNO_3 in the presence of 500 ppm inhibitor (A) Langmuir isotherm and (B) Temkin isotherm.

$$\theta = \frac{-\ln k_{\mathrm{ads}}}{2a} - \frac{\ln C}{2a} \qquad \ldots (8)$$

In the above equation, k_{ads} is the adsorption equilibrium constant and a is the attractive parameter. From Fig. 6(B), the plot of θ versus ln$C$ yields a straight line with correlation coefficient of 0.8854 and slope of 0.1548.

The standard free energy of adsorption ($\Delta G^0_{\mathrm{ads}}$) of inhibitor on mild steel surface can be evaluated from the following equation 9[28]:

$$\Delta G^0_{\mathrm{ads}} = -RT \ln(K_{\mathrm{ads}} \times \rho_w) \qquad \ldots (9)$$

where, R is universal gas constant, T is the absolute temperature in K, ρ_{w} is the density of water in g/L. The negative value of $\Delta G^0_{\mathrm{ads}}$ indicates spontaneous adsorption of the inhibitor molecule on the mild steel surface and a strong interaction between inhibitor molecules and metal surface is formed. $\Delta G^0_{\mathrm{ads}}$ calculated for Langmuir adsorption isotherm was -21.37 kJ/mol. The value of $\Delta G^0_{\mathrm{ads}}$ for Temkin adsorption isotherm was -28.38 kJ/ mol. The threshold value between chemical and physical adsorption processes of $\Delta G^0_{\mathrm{ads}}$ is considered to be -40 kJ/mol. A $\Delta G^0_{\mathrm{ads}}$ value up to -20 kJ/ mol is considered to be physisorption and more negative than -40 kJ/ mol is chemisorption[31]. The data for this present system obey the Langmuir isotherm to higher percentage hence for the present system $\Delta G^0_{\mathrm{ads}}$ values are closer to -21 kJ/mol can be considered as physical adsorption.

Inhibition mechanism

In most of the studies of inhibition, the formation of donor-acceptor surface complexes between the vacant d-orbital of metal and pi-electrons of inhibitor were postulated for hydrochloric and sulphuric acid medium. According to the mechanism of inhibition, the first action of inhibitor in acid media is the adsorption on the metal surface. Extract of *M. koenigii* has murrafoline-I, pyrayafoline-D and mahabinine-A as its main constituents which has large number of aromatic rings. The availability of pi-electrons to get bonded to the vacant d-orbital of Fe is increased because the constituent molecules contain aromatic rings (pi-electrons) and electron releasing groups attached to these aromatic rings[25]. Due to large size of constituent molecules of *M. koenigii* extract, it forms a protective layer over the surface of steel, thereby retarding the corrosion and thus increases the performance.

Conclusion

The present study shows that *M. Koenigii* extract function as an efficient corrosion inhibitor in 0.1N HNO_3. The weight loss measurement studies show that in the absence of inhibitor, the corrosion rate or dissolution rate of mild steel in the acidic solution increases with increase in nitric acid concentration and addition of inhibitor reduces the dissolution rate of mild steel in the nitric acid medium. Due to protective layer formation over the specimen of mild steel surface, corrosion rate decreases with increase in time period of immersion of the specimen in the nitric acid medium. Inhibition efficiency increases with inhibitor concentration but decreases with rise in temperature.

It has been also found that the inhibition efficiency increases with immersion period. SEM analysis reveals that in the presence of inhibitor, surface pits reduced due to the formation of protective film on the mild steel surface. Thermodynamic studies showed the endothermic nature of the solution process indicating that inhibition efficiencies decrease with increase in temperature.

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