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# *Dodonaea viscosa* (L.) Leaves extract as acid Corrosion inhibitor for mild Steel – A Green approach

**S. Leelavathi, R. Rajalakshmi**
*Department of Chemistry, Avinashilingam Institute for Home science and Higher education for Women, University, Coimbatore-641043, Tamil nadu, India.*

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* Corresponding Author: Email: rajivardhan@gmail.com, leelasubu@gmail.com

## Abstract

There is a growing trend to utilize plant extracts and pharmaceutical compounds as corrosion inhibitors. The inhibitive performance of extract of *Dodonaea viscosa* Leaves (DVLE) on the corrosion of mild steel in 1M HCl and 0.5M $H_2SO_4$ were studied using mass loss and electro chemical measurements. Characterization of DVLE was carried out using GC-MS and FT-IR spectroscopy. Results confirmed that the extract of *Dodonaea viscosa* Leaves (DVLE) acts as an effective corrosion inhibitor in the acid environment. The inhibition efficiency increased with increase in concentration of the inhibitor and decreased with temperature. Thermodynamic parameters revealed that the inhibition is through spontaneous adsorption of inhibitors onto the metal surface. Potentiodynamic polarization and electrochemical impedance studies confirmed that the system follows mixed mode of inhibition. Adsorbed film of inhibitor at metal /solution interface has been confirmed using reflectance Fourier transform infrared spectroscopy. Surface analysis by UV, FTIR and SEM confirmed the formation of protective layer on the mild steel (MS) surface. Efforts were also taken to propose a suitable mechanism for the inhibition.

*Keywords:* Mild steel, *Dodonaea viscosa* Leaves, corrosion inhibition, electrochemical measurements.

## 1. Introduction

The use of mild steel as construction material in industrial sectors has become a great challenge for corrosion engineers or scientists nowadays. In practice, most of the acidic industrial applications such as refining crude oil, acid pickling, industrial cleaning, acid descaling, oil–well acid in oil recovery and petrochemical processes use mild steel as their material. Corrosion is an electrochemical process by which metallic surfaces react with their environment causing the metal to lose its material properties due to surface deterioration [1-2]. The use of inhibitors is one of the most practical methods for protection metal against corrosion, especially in acidic media [3]**.** As acidic media, hydrochloric acid (HCl) and sulphuric acid ($H_2SO_4$) are often used as industrial acid cleaners and pickling acids. Large numbers of organic compounds revealed that N, S and O containing organic compounds acted as promising inhibitors. However, most of these compounds are not only expensive, but also toxic to living beings. It is needless to point out the importance of cheap and safe inhibitors for corrosion of mild steel.

So, considerable efforts are made to select corrosion inhibitors which are environmentally safe, readily available and of relatively low cost. Literature shows a growing trend in the use of natural products known as non-toxic compounds, called also green inhibitors, as corrosion inhibitors. Available literature has shown that naturally occurring plant leaves such as *Azadirachta indica* leaves, *Murraya koenigii* leaves, *Ervatamia coronaria* leaves, *Ananas comosus* leaves, *Purpurea* leaves, *Olive* leaves [4-9] have been reported to inhibit the corrosion of metals in acidic media. Our research team has also investigated several plant extracts for corrosion inhibition studies which include sprouted seeds of *Phaseolus aureus*, *Cocos nucifera* Shell, seed extract of *Cyamopsis tetragonoloba, Petiole Extract of cocos nucifera, staminate flower extract of Cocos nucifera and leaf sheath extract of Cocos nucifera* [10-15]. So far no studies were reported using *Dodonaea viscosa* leaves as corrosion inhibitors for metals. Therefore, the present article is concerned with corrosion inhibition studies using *Dodonaea viscosa* leaves extract (DVLE) on mild steel in acidic medium using Mass loss and electrochemical measurements. Dodonaea viscosa Linn. is an evergreen woody perennial and drought tolerant shrub, indigenous and wide spread throughout the tropics belonging to family Sapindaceae [16]. *Dodonaea viscosa* is also commonly known as “hopbush”. The aim of this study is to investigate the inhibitive effect of *Dodonaea viscosa* leaves extract (DVLE) as a cheap, nontoxic, readily available and novel corrosion inhibitor for the corrosion of mild steel in 1M HCl and 0.5 $H_2SO_4$.

## 2. Experimental

### *2.1. Sample Preparation*

The mild steel samples were obtained from a locally available industrial Fe-C steel with very low concentration of carbon. A large sheet of cold rolled mild steel coupons with a chemical composition of carbon 0.13%, manganese 0.23%, silicon 0.03%, phosphorus 0.03%, sulphur 0.016%, chromium 0.022%, nickel 0.012% and iron 99.95% was utilized for the present study. The mild steel samples, with an active surface of 1cm x 5cm were used for Mass loss measurements and 1cm x 1cm specimen for electrochemical measurements. The mild steel samples were mechanically polished, degreased, washed in double distilled water and dried in warm air. Mass loss experiments and electrochemical measurements were done according to ASTM G1-03 [17].

### *2.2. Inhibitor preparation*

*Dodonaea viscosa* leaves were collected from the farm near velliangiri hills, Coimbatore district, Tamilnadu. Fresh leaves were cut in to small pieces and shade dried. *Dodonaea viscosa* leaves were authenticated by Botanical Survey of India, Coimbatore, Tamilnadu. The voucher specimen was stored in the pest proof container in Botany department of our University.

The extract was prepared by refluxing 25 gms of powdered *Dodonaea viscosa* leaves in 1M HCl for 3 h and kept overnight for cooling. The cooled extract were filtered and made up to 500ml with 1M HCl acid to get 5%v/v extract of the inhibitor. Similar procedure was adopted in 0.5M $H_2SO_4$ and 5%v/v extract in 0.5M $H_2SO_4$ was also prepared. Concentration of DVLE is expressed in %v/v [18]. Phytochemical screening of the *Dodonaea viscosa* Leaves extract was carried out using standard procedure. [19]

### *2.3. Mass loss measurements*

Mass loss measurements were carried out using a Denver balance. The specimens were immersed in beaker containing 100 ml acid solution without and with different concentrations of DVLE using glass hooks and rods for a predetermined time period at room temperature. At higher temperatures, a constant immersion period of ½ h was selected and studies were conducted for various concentrations of inhibitors. In order to get good reproducibility, experiments were carried out in triplicate. At the end of exposure period, specimens were cleaned according to ASTM G-81 and the weight recorded. The average mass loss of three parallel mild steel specimens was obtained. The test specimens were removed and then washed with de-ionised water, dried and reweighed.

The experiments were performed for various parameters such as:

- Concentration variation (0.1%v/v,0.2%v/v,0.3%v/v, 0.4%v/v, 0.5%v/v, 0.6%v/v, 0.7%v/v and 0.8%v/v)
- Different time intervals (1/2h, 1 h, 3 h, 6 h,12h and 24h)
- Temperature variation (308K, 318K, 328K, 338K, 348K and 358K)

The percentage inhibition efficiency was calculated from,

$$\text{IE (\%)} = CR_{blank} - CR_{inhibited} / CR_{blank} \times 100 \qquad (1)$$

Where $CR_{blank}$ and $CR_{inhibited}$ are corrosion rate of mild steel in blank and inhibited solutions.

### *2.4. Electrochemical measurements*

Electrochemical studies were carried out using conventional three electrode cell with larger area platinum foil as counter electrode and saturated calomel electrode (SCE) as reference electrode. Solartron electrochemical analyser (model 1280 B) interfaced with an IBM computer was used for measurements [20]. The polarization studies were made after the specimen attained a steady state potential. The polarization was carried out using a Corrware software from a cathodic potential of -0.2 V to an anodic potential of +0.2 V with respect to the corrosion potential at a sweep rate of 0.5 mV/s. E versus log I curves were plotted. The linear TAFEL segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities. The corrosion inhibition efficiency was evaluated from the measured $i_{corr}$ values using the relationship:

$$\text{IE (\%)} = i_{corr} - i'_{corr} / I_{corr}{}^{o} \times 100 \qquad (2)$$

where $i_{corr}$ and $i'_{corr}$ are the corrosion current densities without and with the addition of various concentrations of the inhibitor, respectively. For linear polarization measurements a sweep from -0.02 to +0.02 V versus open circuit potential at a sweep rate of 0.5 mV/s was used. The polarization resistance, $R_p$, is obtained as the slope of the ‘‘h versus i’’ curve at the vicinity of corrosion potential Ecorr. This DC method of perturbation yields Rp which includes the solution resistance $R_s$. The inhibition efficiencies were evaluated from the polarization resistance, $R_p$ values as

$$\text{IE\%} = R_p' - R_p / R_p' \times 100 \qquad (3)$$

where $R_p$ and $R_p'$ are the polarization resistances without and with the addition of inhibitors, respectively. Z plot software was used for data acquisition and analysis of interfacial impedance. AC signals of 10 mV amplitude and a frequency spectrum from 100 KHz to 0.01 Hz was impressed and the Nyquist representations of the impedance data were analysed with Zview software. The charge transfer resistance Rct is obtained as the diameter of the semi circle of Nyquist curve. By doing so, in this AC method of perturbation, the contributions from the solution resistance are eliminated. The inhibition efficiency was evaluated from the measured charge transfer resistance $R_{ct}$ values as

$$\text{IE\%} = R_{ct}' - R_{ct} / R_{ct}' \times 100 \qquad (4)$$

where $R_{ct}$ and $R_{ct}$' are the charge transfer resistance values in the absence and presence of inhibitors, respectively. The interfacial double layer capacitance $C_{dl}$ is obtained from the frequency of the point having maximum imaginary component (i.e. the point corresponding to the top of the semi circle) as

$$C_{dl} = 1/\ 2\pi f_{max}\, R_{ct} \qquad (5)$$

where ‘‘$f_{max}$’’ corresponds to the frequency having maximum imaginary component.

### *2.5. Surface analytical techniques*

Mild steel specimens were immersed in the solution without inhibitor as well as in the solution containing optimum concentration of inhibitor separately for 3 h. Then, the specimens were removed and rinsed with running water quickly. After washing, specimens were dried and finally analyzed using SEM, UV and FT-IR techniques.

## 3. Results and discussion

### *3.1 Characterization of DVLE*

GC-MS and FTIR techniques were followed to characterize the DVLE extract.

### *3.1.1 GC-MS Technique*

Gas chromatography (GC)–mass spectroscopy (MS) spectra of crude plant extract is shown in Figure.1. The GC/MS analysis detected all organic species quantitatively. Each peak area in the chromatogram was proportional to the amount of the organic compound(s) forming that peak. Structural assignment of GC retention data of compounds is based on spectral matching with NIST library (National Institute of Standards and Technology). It can be observed that the DVLE consists of 6 major compounds. The peaks belong to the flavonoids -5,5''-Diethynyl-2,2':6',2''-terpyridine, Benzene acetic acid, 3,4-tris[(trimethylsilyl)oxy] trimethylsilyl ester, 4,5-Bis(p-bromophenoxy)-1,2-dicyanobenzene and Dimethylsilylcarbodiimide**.** Since retention time of majority of compounds is close to each other and it is very difficult to separate them, the DVLE was used as such for corrosion inhibition studies.

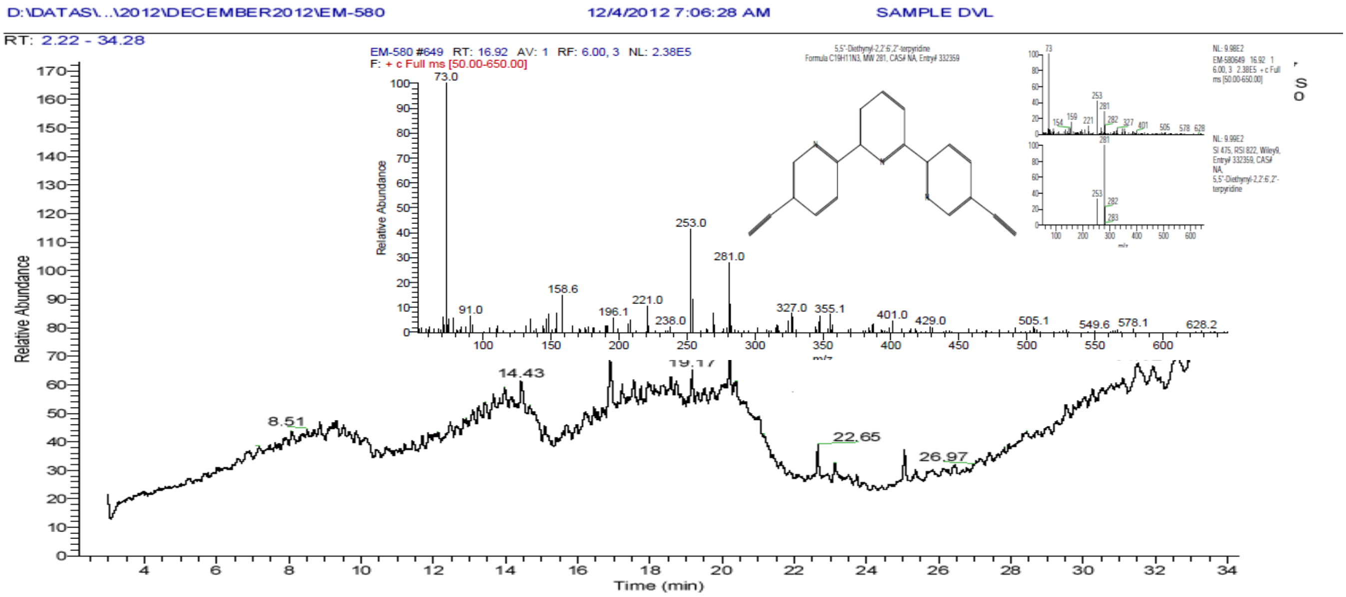


**Figure 1**: GC-MS for DVLE

### *3.1.2 FT-IR Technique*

Few drops of crude plant extract of DVLE were mixed with KBr. A solid mass was made into pellets. Its FT-IR spectrum is shown in Figures 2. A broad peak at 3337cm$^{-1}$ is attributed to polymeric O-H group, the frequency at 2848cm$^{-1}$ corresponds to C-H stretching frequency and the the peak at 1629cm$^{-1}$ has been assigned to C=O. The presence of the functional groups C-N and C-O-C in DVLE extract is confirmed from the bands at 1273 cm$^{-1}$, C-H bending frequency is noted at 1373cm$^{-1}$ .A notable band at 1015cm$^{-1}$ can be assigned to C-O stretching Aromatic ring present in the extract reflected the band appeared at 666cm$^{-1}$. Similar spectral information for biologically active c-alkylated flavonoids from *Dodonaea viscosa* was also reported by Akhtar Muhammad *et al*., (2012) [21]. They have isolated the following c-alkylated flavonoids such as 5,7 –Dihydroxy -3’-(4’’-acetoxy -3’’methylbutyl)-3,6,4’-trimethoxyflavone, and 5,7 –Dihydroxy -3’-(3-hydroxymethylbutyl)-3,6,4’-trimethoxyflavone from the arial parts of *Dodonaea viscosa*. From the FTIR studies and the reported phytochemical constituents by Akhtar Muhammad *et al*., (2012) it is confirmed that flavonoids are the main components present in DVLE.

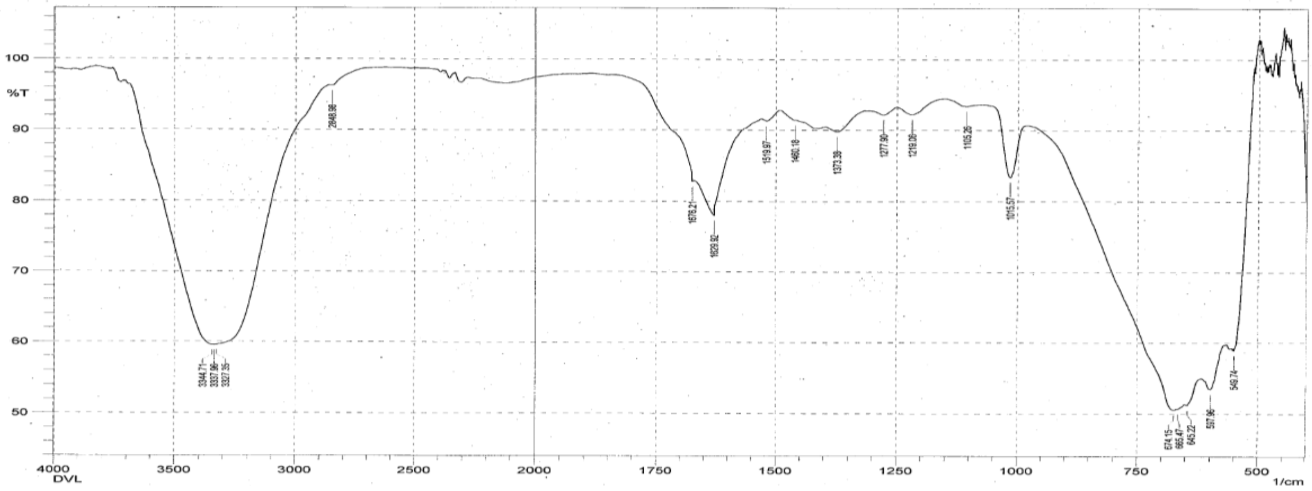


**Figure 2**: FTIR spectrum for DVLE

### *3.2. Mass loss measurements*

### *3.2.1. Effect of concentration*

The Mass loss method of monitoring corrosion rate is useful because of its simple application and reliability [22]. Inhibition efficiencies of mild steel with different concentrations of *Dodonaea viscosa* leaves extract in 1M HCl and 0.5M $H_2SO_4$ solutions at room temperature at different periods of immersion are presented in table 1. From the table, corrosion rate decreases noticeably with an increase in DVLE concentration, i.e. the corrosion inhibition enhances with the inhibitor concentration. This behavior is due to the fact that the adsorption and coverage of the inhibitor on the mild steel surface increase with the inhibitor concentration [23]. Maximum Inhibition efficiency of DVLE at 0.8%v/v concentration was found to be 95.41% in 1M HCl and 91.04% in 0.5M $H_2SO_4$ at 3h immersion. At any given inhibitor concentration, the corrosion rate in 0.5 M $H_2SO_4$ is comparatively higher than that in 1M HCl solution hence inhibition efficiency is higher for the investigated inhibitor in 1M HCl. The high inhibitive performance of DVLE suggests a higher bonding ability of inhibitor on to mild steel surface. Similar observations were reported by Ahmed et al., 2010 [24].

### *3.2.2. Effect of immersion time*

In order to assess the stability of adsorbed inhibitor film at mild steel/ acid solution interface with time, mass loss measurements were performed in both acid media in absence and presence of inhibitors at various concentrations for ½ h -24 h immersion time at 35°C. From table 1 it was noticed that a maximum inhibition efficiency of 95.4% and 91.0% was observed for 3h of immersion period for 1M HCl and 0.5M $H_2SO_4$ respectively. Immersion studies reveal that as the time of immersion increased from 1/2 h to 3 h the inhibition efficiency also increased from 85.9% to 95.4%. After 3 h there is a slight decline in the inhibition efficiency at 6 h yielding 93.6% and then stabilized at 24 h (81.6%). This may be explained due to increase of adsorbed of inhibitor molecules on MS surface with time. Prolonged immersion may result in desorption of the extract from mild steel surface [25]. Shriver et al explained that decrease in inhibition for long period of immersion can be attributed to the depletion of available inhibitor molecules in the solution due to chelate formation between iron and the inhibitor ligands [26]. The stabilization of the inhibition efficiency at 24 h proves that DVLE is a promising inhibitor for MS in 1M HCl and 0.5M $H_2SO_4$ at various time of immersion.

### *3.2.3. Effect of Temperature*

To evaluate the adsorption of DVLE in both acid media and activation parameters of the corrosion process of mild steel in acidic media, mass loss measurements were investigated in the range of temperature 308–358 K, and the results are depicted in Figure 3, As the temperature rises from 308 K to 328 K, inhibition efficiency was found to increase from 85.9% to 94.3% in 0.5M $H_2SO_4$ and 79.1% to 88.3% in 1M HCl at maximum concentration of 0.8%v/v. Further rise in temperature, decreased the IE but at higher concentration affording 81.6% in 1M HCl and 84.5% in 0.5M $H_2SO_4$. These observations established the effectiveness of DVLE in reducing corrosion of mild steel in the temperature range of 308K to 338K in 1M HCl and in 0.5M $H_2SO_4$.

**Table1:** Inhibition efficiency as a function of immersion time and concentration of DVLE in 1M HCl and 0.5M $H_2SO_4$

| **S.No** | **C (%v/v)** | **Inhibition Efficiency (%) for various Immersion Time in HCl (h)** | | | | | | **Inhibition Efficiency (%) for various Immersion Time in $H_2SO_4$ (h)** | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | **0.5** | **1** | **3** | **6** | **12** | **24** | **0.5** | **1** | **3** | **6** | **12** | **24** |
| 1 | 0.1 | 50.00 | 66.86 | 52.45 | 76.82 | 72.53 | 58.44 | 51.39 | 37.64 | 72.31 | 60.02 | 75.39 | 61.18 |
| 2 | 0.2 | 71.88 | 79.25 | 68.22 | 81.20 | 79.19 | 66.24 | 56.94 | 49.81 | 82.34 | 73.89 | 79.29 | 71.22 |
| 3 | 0.3 | 78.12 | 81.84 | 76.91 | 83.15 | 40.74 | 71.92 | 66.67 | 58.17 | 86.49 | 78.01 | 80.75 | 74.27 |
| 4 | 0.4 | 79.69 | 85.01 | 81.63 | 83.89 | 84.22 | 75.10 | 68.06 | 61.22 | 87.96 | 81.04 | 82.64 | 78.09 |
| 5 | 0.5 | 81.25 | 87.03 | 83.49 | 84.49 | 82.00 | 78.89 | 72.22 | 66.54 | 88.23 | 84.98 | 84.86 | 80.56 |
| 6 | 0.6 | 82.81 | 92.51 | 87.09 | 88.27 | 86.32 | 79.55 | 73.61 | 71.86 | 89.70 | 86.07 | 86.05 | 81.11 |
| 7 | 0.7 | 84.38 | 93.95 | 94.29 | 89.56 | 87.49 | 80.06 | 76.39 | 77.95 | 90.50 | 89.58 | 89.51 | 81.86 |
| 8 | 0.8 | 85.94 | 94.20 | 95.41 | 93.64 | 86.67 | 81.62 | 79.17 | 81.75 | 91.04 | 90.01 | 90.59 | 84.54 |

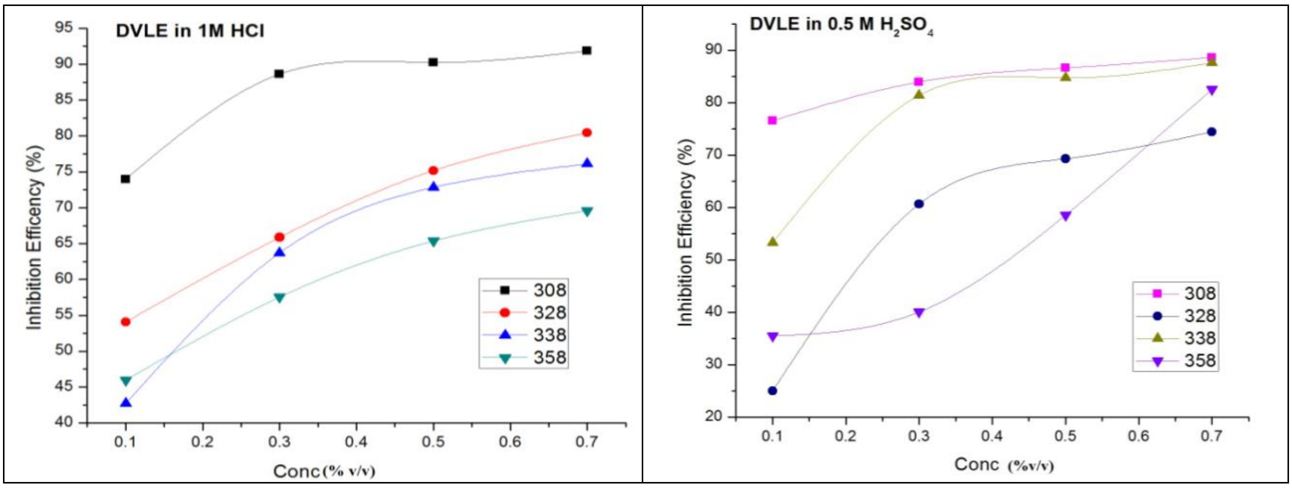


**Figure 3**: Variation of inhibition efficiency with concentration at various temperature

This may be explained as follows. Adsorption and desorption of inhibitor molecules continuously occur at the metal surface and the equilibrium exists between these two processes at a particular temperature. With the increase of temperature, the equilibrium between adsorption and desorption process is shifted leading to a higher desorption rate than adsorption until equilibrium is again established at a different value of equilibrium constant. It explains the lower inhibition efficiency at higher temperature [27]. Values of inhibition efficiency with temperature indicate that the adsorption of DVLE on mild steel surface is physical at low temperature and at higher temperature; chemical adsorption may also take place. This is evidenced from inhibition efficiency values of DVLE in 1M HCl (81.6 % at 358 K) and in 0.5M $H_2SO_4$ (84.5 % at 358 K).

### *3.3 Adsorption Considerations*

Surface coverage data play an important role in assessment of inhibitor characteristics and are useful for fitting experimental data into adsorption isotherms which give an insight into the inhibition mechanism. Addition of inhibitor molecules adsorb on the metal surface and interaction between them can be described by adsorption isotherms [28]. DVLE obeys Langmuir and Temkin adsorption isotherms by giving a straight line for a plot of log C versus log ($\theta$/1-$\theta$) log and log C versus $\theta$, respectively. These straight lines obtained reveal that the main process of inhibition is adsorption. It can also be explained that the increase in inhibition efficiency with increase in extract concentration is an indication of an increase in the number of components of the extract adsorbed over the mild steel surface blocking the active sites, in which direct acid attacks proceed and protect the metal from corrosion, while the decrease in inhibition efficiency with temperature rise is suggestive of electrostatic interaction (physical adsorption) of the phytochemical constituents of the extract on mild steel surface forming a protective layer and shielding the metal from corrosion. Increase in inhibition efficiency up to particular temperature and after that decrease in inhibition efficiency followed by increase in inhibition efficiency at higher temperature indicate that physical adsorption as well as chemical adsorption operate on the system.

### *3.3.1. Langmuir Isotherm*

Langmuir adsorption isotherm can be expressed according to Equation (6) [29],

$$C / \theta \quad = 1/K + C \qquad (6)$$

Where C is the concentration of the inhibitor, K is the adsorption equilibrium constant and θ is degree of surface coverage of the inhibitor. Taking logarithm of both sides of Equation (6) yields Equation (7).

$$\text{Log } (C/ \theta) = \log C - \log K \qquad (7)$$

A plot of log (θ/1- θ) against log C is linear as shown in Fig. 4. Parameters of Langmuir isotherm are presented in Table 2.

| Acid media (Temperature -328 K) | Langmuir | | Temkin | |
|---|---|---|---|---|
| | $R^2$ | Slope | $R^2$ | Slope |
| 1M HCl | 0.973 | 0.645 | 0.986 | 0.317 |
| $0.5H_2SO_4$ | 0.961 | 1.068 | 0.959 | 0.565 |

**Table 2:** Correlation coefficients deduced from Langmuir and Temkin isotherm for mild steel in 1 M HCl and 0.5M $H_2SO_4$ in the presence of DVLE

The $R^2$ values and slope are very close to unity, indicating strong adherence to Langmuir adsorption isotherm [30]. The application of Langmuir isotherm to the adsorption of extract of *Dodonea viscosa* on surface of mild steel indicates that there is no interaction between the adsorbate and adsorbent [31].

### *3.3.2. Temkin Isotherm*

According to Temkin adsorption isotherm, the degree of surface coverage (θ) is related to inhibitor concentration (C) according to Equation (8)

$$\text{Exp } (-2a\theta) = KC \qquad (8)$$

Where K is the adsorption equilibrium constant and a, is the attractive parameter. Rearranging and taking logarithm of both sides of Equation (8), Equation (9) is obtained.

$$\theta = -2.303 \log K/ 2a - 2.303 \log C /2a \qquad (9)$$

Plots of θ against log C as shown in Figure 4 gave a linear relationship indicating that Temkin adsorption isotherm was obeyed. Temkin adsorption parameters are recorded in Table 2.

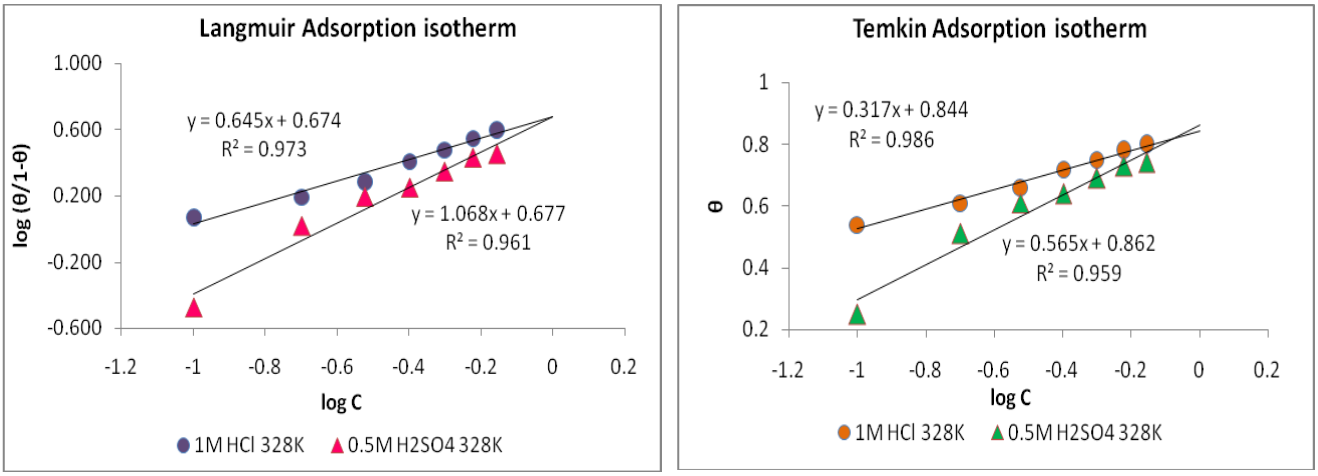


**Figure 4:** Langmuir and temkin adsorption isotherm in presence of DVLE in both acid media

### *3.4 Activation Energy*

The apparent activation for the corrosion process is calculated from Arrhenius type plot according to the following equation:

$$W = k \exp - E_a / RT \qquad (10)$$

Where $E_a$ is the apparent activation corrosion energy, R is the universal gas constant, k is the Arrhenius pre-exponential constant and T is the absolute temperature. Arrhenius plots for the corrosion rate of mild steel are given in Table 3. The value of apparent activation energy $E_a$ of hydrogen evolution reaction for 1M HCl without an inhibitor (55 $kJmol^{-1}$) agrees well with literature data on $E_a$ for steel in sulphuric acid [32]. In the presence of DVLE,

the process of metal dissolution is characterized by activation energy which is more than that in the 1M HCl (Table 2). The addition of inhibitor modified the values of $E_a$; this modification may be attributed to the change in the mechanism of the corrosion process in the presence of adsorbed inhibitor molecules [33]. A decrease in inhibition efficiency with rise in temperature with analogous increase in corrosion activation energy in the presence of inhibitor compared to its absence is frequently interpreted as being suggestive of formation of an adsorption film of a physical nature [34, 35].
The lower value of the $E_a$ was attributed by Hoar and Holliday [36] to a slow rate of inhibitor adsorption with a resultant closer approach to equilibrium during the experiments at the higher temperature. But, Riggs and Hurd [37] explained that the decrease in activation energy of corrosion at higher levels of inhibition arises from a shift of the net corrosion reaction from that on the uncovered part on the metal surface to the covered one. Schmid and Huang [38] found that organic molecules inhibit both the anodic and cathodic partial reactions on the electrode surface and a parallel reaction takes place on the covered area, but that the reaction rate on the covered area is substantially less than on the uncovered area [39].

### *3.5 Thermodynamic parameters:*

From the temperature study results, thermodynamic parameters such as ΔG, ΔH and ΔS were calculated. Values of -ΔG, ΔH and ΔS were obtained at different temperature for various concentration of DVLE is presented in table 3.
The negative values of free energy of adsorption ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface [40]. Generally the values of ΔG up to $-20KJmol^{-1}$ are consistent with electrostatic interaction between charged molecules and a charged metal and the process indicates physical adsorption, while those more negative than $-40KJmol^{-1}$ involves charge sharing or transfer from the inhibitor molecules to the metal surface to from a co-ordinate type of bond that indicates chemical adsorption [41]. In the present study, the values of ΔG vary from -15.2 to -19.4 in 1M HCl and -15.5 to -22.9 in 0.5M $H_2SO_4$ which indicate that DVLE functions by physically adsorbing onto the surface of the metal**.** Physisorption is a result of electrostatic attraction between charged metal surface and charged species in the bulk of the solution. Adsorption of negatively charged species is facilitated if the metal surface is positively charged. Positively charged species can also protect the positively charged metal surface acting with a negatively charged intermediate, such as acid anions adsorbed on the metal surface [42].

**Table 3:** Kinetic and thermodynamic parameters of mild steel in the presence DVLE in both acid media.

| **S.NO** | **Conc (% v/v)** | **$E_a$ kJ/mol** | **Free energy of adsorption -ΔG (kJ/mol)** | | | | | | **-ΔS kJ/mol** | **ΔH kJ/mol** |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | **308K** | **318K** | **328K** | **338K** | **348K** | **358K** | | |
| 1. | Blank HCl | 55 | - | - | - | - | - | - | 28 | 14 |
| 2. | 0.1 | 58 | 17.18 | 19.44 | 17.59 | 17.35 | 17.48 | 17.25 | 30 | 13 |
| 3. | 0.2 | 66 | 17.80 | 18.68 | 20.08 | 17.52 | 15.75 | 16.80 | 34 | 13 |
| 4. | 0.3 | 58 | 17.62 | 17.86 | 19.46 | 19.07 | 15.98 | 17.80 | 30 | 12 |
| 5. | 0.4 | 59 | 17.13 | 17.26 | 19.33 | 18.69 | 15.56 | 17.26 | 30 | 12 |
| 6. | 0.5 | 58 | 16.82 | 16.96 | 19.06 | 18.62 | 15.17 | 17.15 | 30 | 12 |
| 7. | 0.6 | 58 | 16.63 | 16.78 | 18.89 | 18.31 | 15.06 | 17.01 | 30 | 12 |
| 8. | 0.7 | 59 | 16.53 | 16.92 | 18.87 | 18.12 | 15.30 | 16.69 | 30 | 12 |
| 9. | 0.8 | 57 | 16.50 | 16.87 | 19.03 | 18.38 | 15.26 | 17.07 | 29 | 12 |
| | | | | | | | | | | |
| 1. | Blank $H_2SO_4$ | 64 | - | - | - | - | - | - | 33 | 13 |
| 2. | 0.1 | 70 | 17.61 | 16.70 | 21.22 | 20.31 | 22.98 | 21.66 | 36 | 14 |
| 3. | 0.2 | 72 | 16.41 | 16.18 | 20.91 | 20.14 | 21.61 | 20.94 | 37 | 15 |
| 4. | 0.3 | 72 | 16.43 | 16.00 | 20.67 | 19.64 | 20.70 | 20.19 | 38 | 15 |
| 5. | 0.4 | 71 | 15.85 | 15.58 | 20.24 | 19.36 | 20.24 | 19.96 | 37 | 14 |
| 6. | 0.5 | 69 | 15.79 | 15.60 | 19.71 | 19.52 | 20.07 | 19.74 | 36 | 14 |
| 7. | 0.6 | 62 | 15.51 | 15.78 | 19.62 | 19.25 | 19.81 | 19.31 | 32 | 13 |
| 8. | 0.7 | 61 | 15.49 | 16.23 | 19.44 | 19.75 | 20.31 | 18.99 | 31 | 13 |
| 9. | 0.8 | 60 | 15.56 | 16.50 | 19.25 | 19.50 | 20.27 | 19.17 | 31 | 12 |

However physical adsorption was the major contributor while chemisorption only slightly contributed to the adsorption mechanism judging from the decrease in percentage of inhibition efficiency with increase in temperature [24]. In the current investigation, values of ΔG and effect of temperature on the mild steel corrosion in the presence of DVLE in 1M HCl and 0.5M $H_2SO_4$ support the physical as well as chemical adsorption process on mild steel surface. The values of ΔH and ΔS were obtained from the equation (11).

$$\Delta G = \Delta H - T\Delta S \qquad (11)$$

The entropy of adsorption (ΔS) and enthalpy of adsorption (ΔH) are calculated from the plot of ΔG Vs T. ΔS and ΔH were obtained from the slope and intercept respectively. DVLE in both acidic media, the positive value of the enthalpies reflects the endothermic nature of the mild steel dissolution process meaning that dissolution of steel is difficult [43, 44]. The values of entropy of adsorption are negative. The negative values of entropies (ΔS) in the presence of DVLE in both acidic media reflect that the inhibitor molecules, freely moving in the bulk solution were adsorbed in an orderly fashion onto the mild steel surface. This implies that the activation complex in the rate determining step represents an association rather than a dissolution step, meaning that a decrease in disordering takes place on moving from reactants to the activated complex [45].The change of ΔH and ΔS with concentration of the inhibitor suggests that the process is enthalpic and entropic controlled [46].

### *3.6 Potentiodynamic polarization studies*

The potentiodynamic polarization curves of mild steel in 1M HCl and 0.5M $H_2SO_4$ with the addition of various concentrations of DVLE is shown in Fig. 5. As seen from the figure-5 addition of DVLE extracts affects both anodic dissolution of steel and cathodic reduction reactions indicating that the extracts could be classified as mixed type inhibitor. The corrosion kinetic parameters such as corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), anodic Tafel slope ($b_a$) and cathodic Tafel slope ($b_c$) deduced from the curves for 1M HCl and 0.5M $H_2SO_4$ are given in Table-4. The increase in concentration of the inhibitor decreases the $I_{corr}$ values. The addition of DVLE on acid corrosion of mild steel in both investigated acid media, do not show any appreciable shift in $E_{corr}$ values which imply that the analyzed DVLE acts as mixed type inhibitor and influences both metal dissolution and hydrogen evolution. However the variation in the values of both $b_a$ and $b_c$ suggest the mixed nature of the inhibitors. Polarization resistance values ($R_p$) obtained from the LPR method showed an increase in value from 5.27 ohm/cm$^2$ for that of blank to 27.45 ohm/cm$^2$ for the addition of the highest concentration of DVLE in 1M HCl and from 4.04 ohm/cm$^2$ for that of blank to 15.52 ohm/cm$^2$ for the addition of the highest concentration of DVLE in 0.5M $H_2SO_4$. Maximum IE using $I_{corr}$ values in 1M HCl and in 0.5M $H_2SO_4$was found to be 89.8% and 75.3% respectively.

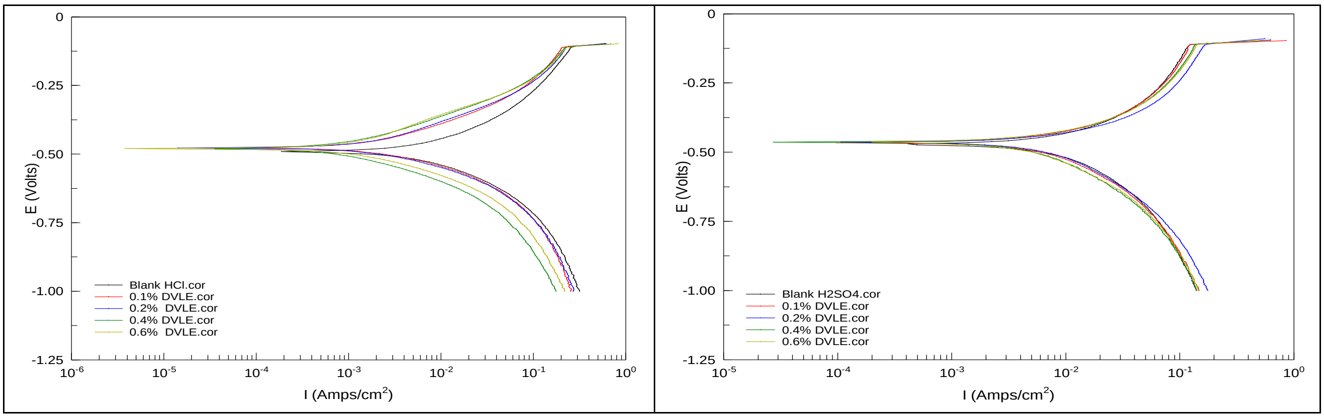


**Figure 5:** Potentiodynamic polarization curves for mild steel in 1 M HCl and in 0.5M $H_2SO_4$ in absence and presence of DVLE inhibitor

### *3.7 Electrochemical impedance measurements (EIS):*

The effect of DVLE concentration on the impedance behavior of mild steel in 1M HCl and 0.5M $H_2SO_4$ is presented in the form of Nyquist plots in Fig.6. The curves show a similar type of Nyquist plots for mild steel in the presence of various concentrations of DVLE. Values of impedance parameters of mild steel in both acid media are presented in Table 4.

As it can be seen from table 4, the $R_{ct}$ values increased with increasing concentration of the inhibitor indicating charge transfer process mainly controlling the corrosion of the steel. Deviations from perfect circular shape are often referred to the frequency dispersion of interfacial impedance which arises due to the roughness and other inhomogeneities of the surface [47, 48]. As seen from Table 4, the $R_{ct}$ values of inhibited substrates increased with the concentration of inhibitors. On the other hand, the values of $C_{dl}$ are decreased with increase in inhibitor concentration which is most probably is due to the decrease in local dielectric constant and/or increase in thickness of the electrical double layer, which imply that DVLE acts via adsorption at the metal/solution interface [49,50]. The inhibition efficiencies calculated from EIS showed good agreement with the results obtained from polarization methods.

**Table 4**: Electrochemical Potentiodynamic polarization and Impedance studies of mild steel in the presence of DVLE in 1M HCl and 0.5M $H_2SO_4$

| **Conc (% v/v)** | **-$E_{corr}$ mV/ SCE** | **$I_{corr}$ $A/cm^2$** | **$b_a$ mV/ dec** | **$b_c$ mV/ dec** | **IE (%)** | **$R_p$ Ohm/ $cm^2$** | **IE (%)** | **$R_{ct}$ ohm $cm^2$** | **IE (%)** | **$C_{dl}$ (µ $Fcm^{-2}$)** | **θ** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Blank HCl | 489 | 0.0059 | 72.6 | 130.9 | - | 5.27 | - | 19.34 | - | 117.9 | |
| 0.1 | 473 | 0.0025 | 85.4 | 147.5 | 57.6 | 13.91 | 55.7 | 33.97 | 43.0 | 39.8 | 0.662 |
| 0.2 | 477 | 0.0021 | 92.3 | 154.7 | 64.4 | 14.02 | 59.5 | 35.27 | 45.1 | 32.6 | 0.723 |
| 0.3 | 473 | 0.0019 | 63.4 | 126.2 | 67.8 | 14.11 | 62.6 | 39.65 | 51.2 | 29.5 | 0.750 |
| 0.4 | 480 | 0.0017 | 88.9 | 166.4 | 71.1 | 20.39 | 74.1 | 92.55 | 79.1 | 25.2 | 0.786 |
| 0.5 | 480 | 0.0016 | 97.2 | 176.8 | 72.8 | 21.14 | 75.0 | 127.2 | 84.8 | 21.5 | 0.818 |
| 0.6 | 486 | 0.0015 | 89.5 | 182.1 | 75.4 | 21.35 | 75.3 | 177.4 | 89.1 | 20.4 | 0.827 |
| | | | | | | | | | | | |
| Blank $H_2SO_4$ | 472 | 0.0192 | 87.7 | 154.7 | - | 4.04 | - | 6.48 | - | 140.2 | |
| 0.1 | 466 | 0.0139 | 63.5 | 179.2 | 27.2 | 8.12 | 50.3 | 7.26 | 10.8 | 83.9 | 0.402 |
| 0.2 | 465 | 0.0120 | 77.4 | 190.2 | 37.4 | 9.89 | 59.1 | 11.46 | 43.5 | 78.2 | 0.442 |
| 0.3 | 464 | 0.0107 | 95.8 | 186.4 | 44.4 | 10.13 | 60.1 | 14.59 | 55.6 | 65.4 | 0.534 |
| 0.4 | 464 | 0.0104 | 72.1 | 160.2 | 45.9 | 11.49 | 64.8 | 16.04 | 59.6 | 35.3 | 0.748 |
| 0.5 | 462 | 0.0058 | 69.4 | 172.9 | 69.7 | 12.61 | 67.9 | 21.65 | 70.0 | 34.9 | 0.751 |
| 0.6 | 467 | 0.0057 | 75.2 | 135.7 | 70.1 | 13.60 | 70.3 | 27.14 | 76.1 | 32.7 | 0.767 |

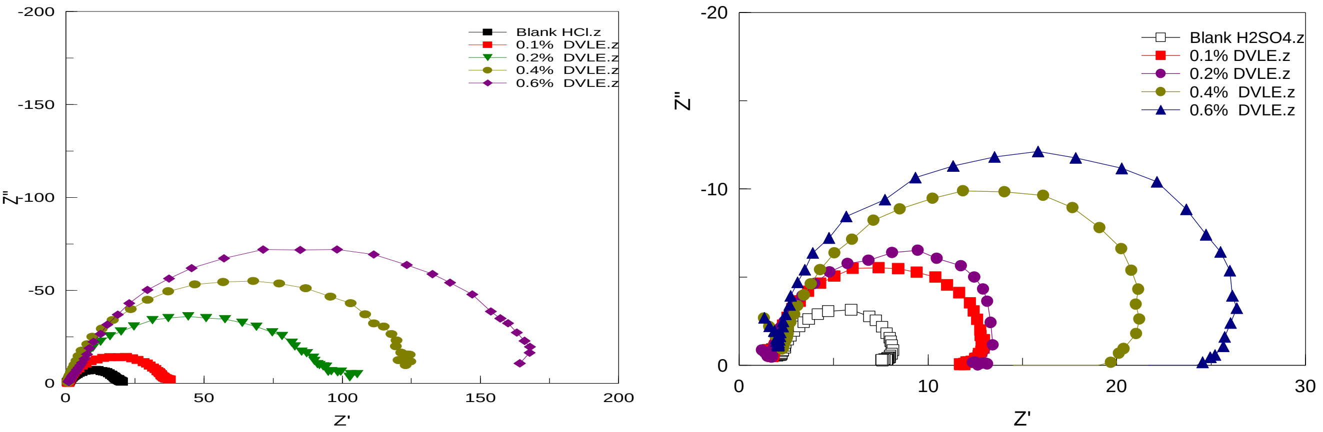


**Figure 6**: Nyquist plots for mild steel in 1M HCl and in 0.5M $H_2SO_4$ in absence and presence of different concentration of DVLE

### *3.8 Comparison of IE of DVLE in both acid media using various techniques*

The inhibitive ability of DVLE in 1M HCl is greater than that in 0.5M $H_2SO_4$ which implies that the adsorption of inhibitor could be influenced by the nature of anions in acidic solutions. It is well known that $Cl^-$ ions have stronger tendency to adsorb than do $SO_4^{2-}$ ions [51] and the electrostatic influence on the inhibitor adsorption may be the reason for an increased protective effect in halide containing solution [52]. Moreover the lesser interference of $SO_4^{2-}$ ions with the adsorbed protonated cations may lead to lower adsorption [53-54]. So the adsorption of DVLE on steel surface in 1M HCl solution is stronger than that in 0.5M $H_2SO_4$ solution, which leads to higher inhibition performance in HCl than that in $H_2SO_4$. It is graphically represented in the figure 7.

### *3.9 Surface analysis*

#### *3.9.1 SEM Analysis*

The SEM images were recorded to establish the interaction of inhibitor molecules with metal surface. Fig. 8 represents the SEM images of plain mild steel, mild steel immersed in 1M HCl, mild steel immersed in the presence of DVLE in 1M HCl and 0.5M $H_2SO_4$.

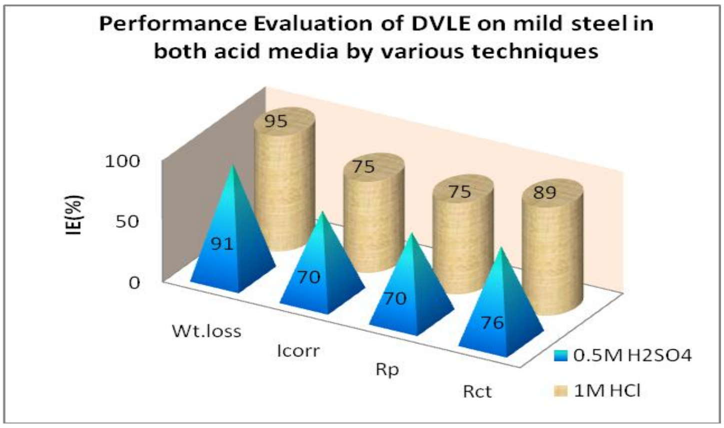


**Figure 7:** Performance evaluation plot by various techniques

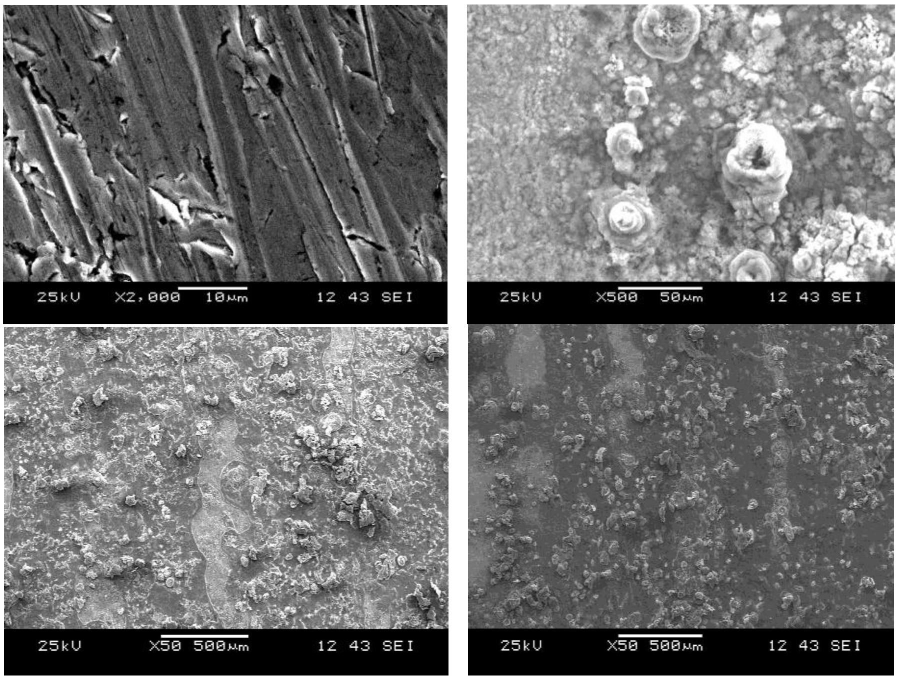


**Figure 8**: SEM micrograph of (a) Plain mild steel, (b) mild steel immersed in acid, (c) mild steel immersed in the presence of DVLE in 1M HCl and(d) mild steel immersed in the presence of DVLE in 0.5M $H_2SO_4$

The SEM images revealed that the mild steel specimen immersed in inhibited solution is in better condition having a smooth surface while the metal surface immersed in blank acid solutions is rough covered with corrosion products and appeared like full of pits and cavities [55]. Result shows that the phytochemical constituents present in the DVLE form a protective layer of the mild steel specimen and thereby reduce the corrosion rate.

### *3.9.2. UV-Visible Spectroscopy*

Corrosion inhibition of mild steel in acidic solution by *Dodonaea Viscosa* leaves extract can be explained on the basis of molecular adsorption. *It* contains many organic components as per information provided in literature [16]. It is quite complex to separate every compound present in the extract. In order to confirm the possibility of the formation of DVLE-Fe complex, UV-Visible absorption spectra obtained for crude plant extract is shown in figure 9 and spectrum of mild steel immersed for 6 h, in solution containing 1M HCl with 0.7%v/v concentration of DVLE is depicted figure 10. The electronic absorption spectra of DVLE crude extract display a main visible band at 268nm. From Figure10 it was noted that the absorption spectra shifted to 329 nm. Change in position of the absorption maximum and or change in the value of absorbance indicate the formation of a complex between two species in solution [56]. On the basis of this fact, it can be concluded that the phytochemical components present in the *Dodonaea Viscosa* leaves extract were adsorbed on the mild steel surface.

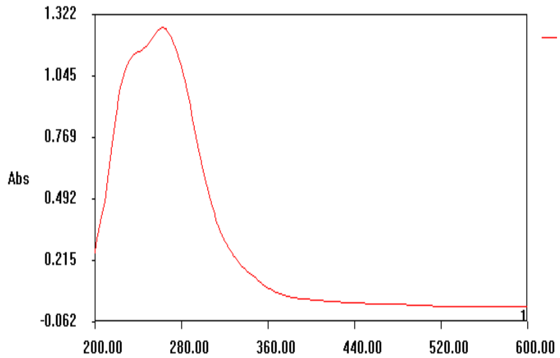


**Figure 9**: UV-Visible spectrum of crude DVLE

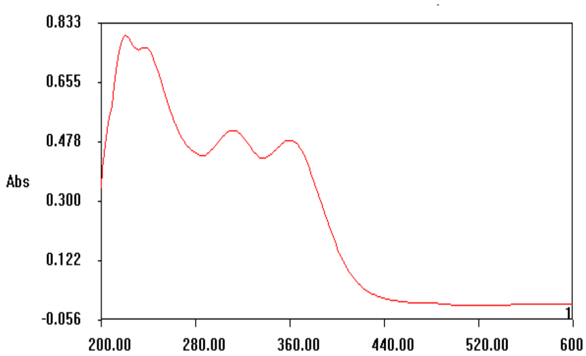


**Figure 10**: UV-Visible spectrum of corrodent solution containing 0.7%v/v DVLE

### *3.9.3 FT-IR Analysis*

Figures 11 a and b represent the IR spectrum of *Dodonea Viscosa* leaves extract (crude) and that of the corrosion product of mild steel when the extract containing maximum concentration of %v/v DVLE was used as an inhibitor. From table 5 , it was found that O-H stretch at 3337.96cm$^{-1}$ was shifted to 3350.50cm$^{-1}$ and the C=O stretch at 1629.92cm$^{-1}$ was shifted to 1703.22cm$^{-1}$ indicating that there is interaction between the inhibitor and mild steel surface [57].The band at 450cm$^{-1}$ to700cm$^{-1}$ probably originates mainly from $\gamma$-$Fe_2O_3$ (685.7cm$^{-1}$). Other functional groups were missing suggesting that the adsorption of the inhibitor on the surface of mild steel might have occurred through the missing bonds [58].

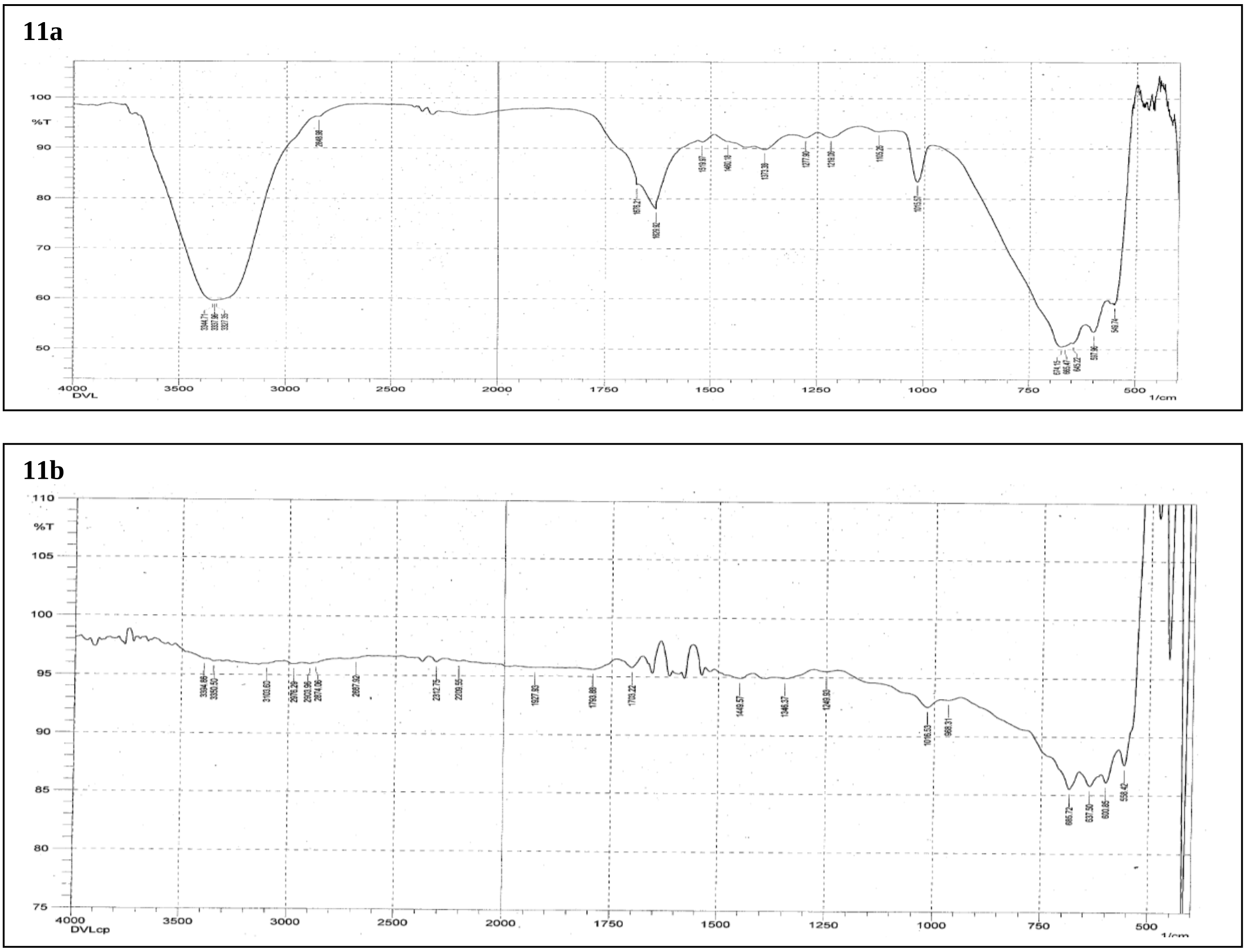


**Figure 11**: a .FTIR spectrum of crude DVLE b. FTIR spectrum of corrosion product with DVLE

| **Pure Extract** | | **Corrosion Product** | |
|---|---|---|---|
| **Frequency (cm$^{-1}$)** | **Assignment** | **Frequency (cm$^{-1}$)** | **Assignment** |
| 3337.96 | O-H Stretch, free hydroxyl | 3350.50 | N-H stretch |
| 2848.98 | C-H stretch | 1703.22 | C=O Stretch |
| 1629.92 | C=C Stretch, C=O Stretch | 685.7 | $\gamma$ -$Fe_2O_3$ |
| 1519.97 | N-O asymmetric stretch | | |
| 1373.38 | C-H rock | | |
| 1219.06 | C-O-C | | |
| 1015.57 | C-O Stretch | | |
| 665.47 | C-H “oop” | | |

**Table 5.** Frequencies of IR absorption by the corrosion product and *Dodonea viscosa* leaves extract

## 4. Mechanism of Inhibition

Phytochemical screening of *Dodonaea viscosa* Leaves were carried out using standard procedure [19] and listed in the table 6.

| Phytochemical component | Flavonoids | Alkaloids | Tannins | Saponins | Anthraquinones | Coumarin |
|---|---|---|---|---|---|---|
| *Dodonaea viscosa* Leaves | + | - | + | + | - | + |

**Table 6:** Phytochemical screening of *Dodonaea viscosa* Leaves.

In aqueous acidic solutions, main constituents exist either as neutral molecules or as protonated molecules (cations). The inhibitors may adsorb on the metal/acid solution interface by one and/or more of the following ways:

- Electrostatic interaction of protonated molecules with already adsorbed chloride ions,
- Donor-acceptor interactions between the p-electrons of aromatic ring and vacant d orbital of surface iron atoms,
- Interaction between unshared electron pairs of hetero atoms and vacant d orbital of iron surface atoms.

It is often not possible to assign a single general mechanism of action to an inhibitor, because the mechanism may change with experimental conditions. Thus, the predominant mechanism of action of an inhibitor in acidic solutions may vary with factors such as concentration of the extracts, the nature of the anion of the acid, the presence of other species in the solution, the extent of reaction to form secondary inhibitors and the nature of the metal [59]. In the present situation two modes of adsorption could be considered:

i. The neutral DVLE may adsorb onto the metal surface via the chemisorption mechanism, involving the displacement of water molecules from the metal surface and sharing electrons between the O atoms and Fe. The DVLE molecules can also adsorb on the metal surface on the basis of donor-acceptor interactions between $\pi$-electrons of aromatic ring and vacant d-orbitals of Fe.
ii. The protonated DVLE may adsorb through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. In other words, there may be a synergism between $Cl^-$ and DVLE, which improves the inhibitive capability of the inhibitor.

When protonated DVLE is adsorbed on metal surface, a coordinate bond may be formed by partial transference of electrons from polar atoms (O atoms) to the metal surface. In addition, owing to lone-pair electrons of O atom in DVLE or protonated DVLE may combine with freshly generated $Fe^{2+}$ ions on steel surface forming metal inhibitor complexes:

$Fe \rightarrow Fe^{2+} + 2e^-$

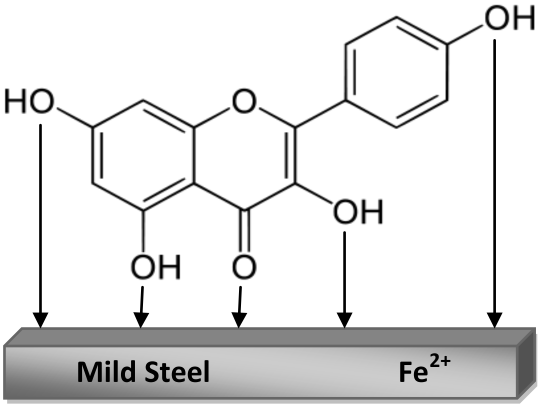
$DVLE + Fe^{2+} \leftrightarrow [DVLE\text{-}Fe]^{2+}$

$[DVLEH_x]^{x+} + Fe^{2+} \leftrightarrow [DVLEH_x\text{-}Fe]^{(2+x)+}$

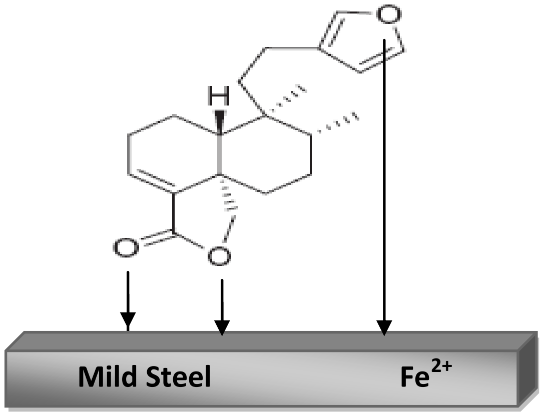
Similar type of mechanism was also proposed by Xiang-Hong Li *et al.*, (2010) [60]. These complexes might be adsorbed onto steel surface by vander Waals force to form a protective film to prevent mild steel from corrosion.

The main constituents of the extract are santin, kaempferol 3-methyl ether, hautriwaic lactone, vanillic acid, pinocembrin,etc., Notable among them are depicted below

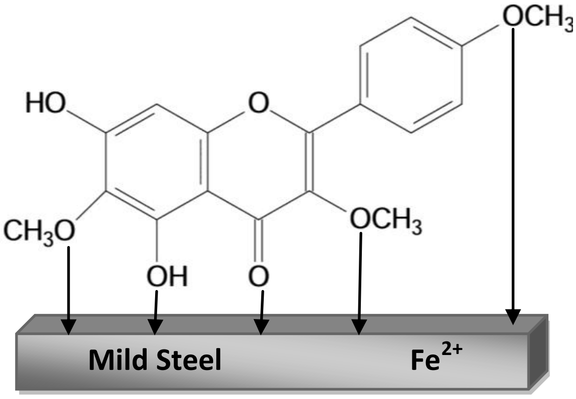
**Kaempferol**



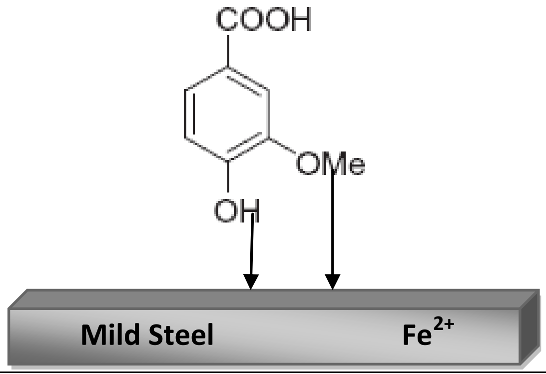
**Hautriwaic lactone**



**Santin**



**Vanillic acid**



The effective performance of the inhibitor may also be due to the large size of the phytochemical constituents of the plant extract cover a wider area of the metal surface thus minimising the corrosion.

## Conclusion

1. The results obtained from present study showed that DVLE is a good inhibitor and acted as a mixed-type inhibitor in both 1 M HCl and $H_2SO_4$.
2. Adsorption of DVLE on mild steel surface was found to obey Langmuir and Temkin adsorption isotherms.
3. The negative free energy of adsorption indicates strong and spontaneous adsorption of the DVLE on the mild steel surface.
4. The presence of the DVLE increases the activation energy ($E_a$) of the corrosion process.
5. Potentiodynamic polarization studies show that the inhibitor system affects both the anodic and cathodic tafel slopes which suggest that the inhibitors functioned via a mixed inhibition mechanism.
6. FTIR spectra clearly reveal that the phytochemical constituents adsorbed on the mild steel surface.
7. SEM micrographs revealed that corrosion inhibition is due to the adsorption of DVLE at mild steel/acid solution interface
8. Environmentally acceptable inhibitors are always preferred over non toxic organic inhibitors.

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