CORROSION INHIBITION OF MILD STEEL IN WELL WATER BY AN AQUEOUS EXTRACT OF ADHATODA VASICA (JUSTICIA ADHATODA) LEAVES

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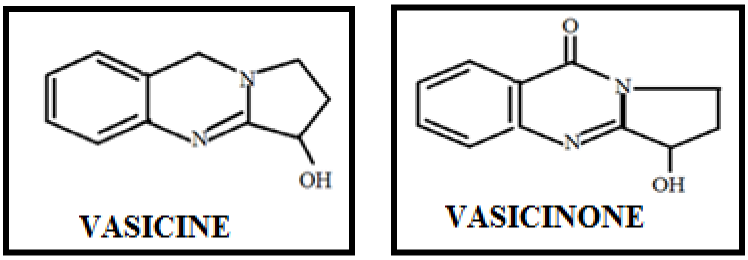
Abstract : The corrosion inhibition efficiency of an aqueous extract of adhatoda vasica leaves in controlling corrosion of mild steel immersed in well water has been evaluated by weight loss method. The mechanistic aspects of corrosion inhibition have been evaluated by electrochemical studies such as potentiodynamic polarization study and alternating current impedance spectra. The protective film formed on the metal surface has been analyzed by Fourier transforms infrared spectra, UV-visible absorption spectra and Fluorescence spectra. 10 mL of the inhibitor offers good corrosion inhibition efficiency. It is an environmentally friendly inhibitor.

Key words: corrosion inhibition, Justicia adhatoda leaves, mild steel, green inhibitor.

I. INTRODUCTION

Corrosion cannot be prevented but it can be controlled. Many methods are adapted to control corrosion. One of the methods is using inhibitors. Inhibitors are substances when added into the corrosive environment in small concentration; it will control the corrosion by forming the protective film on the metal surface. Plant products such as leaves, barks, seeds, and flowers, roots have been used as corrosion inhibitors. Plant products are environmental friendly, easily available, low cost, non-toxic, and biodegradable [1-4]. Hence plants are widely used as corrosion inhibitors. The active principle in the plant materials is responsible for the formation of metal-inhibitor complex. The hetero atoms like N, O, S, P which is present in the active principle of the plant material forms the metal- inhibitor complex through their lone pair of electrons [5], [6]. Adhatoda vasica leaves have a long history of traditional medicine use. The chemical examination of adhatoda vasica revealed to contain alkaloids, glycosides, phenolic components and sterols in which the major constituents identified are the two alkaloids: vasicine ($C_{11}H_{12}N_2O$) and vasicinone ($C_{11}H_{10}N_2O_2$). The structures of the molecules are shown in Scheme- 1 [7].



Scheme 2: The structure of vasicine and vasicinone.

II. MATERIALS AND METHODS

2.1 Preparation of specimens

Mild steel specimens of dimensions 1.0 x 4.0 x 0.2 cm were polished to mirror finish, degreased with trichloroethylene and used for the weight loss method and for surface examination studies.

2.2 Preparation of Inhibitor solution

Adhatoda vasica leaves were dried well in the absence of sunlight. 10 g of adhatoda vasica leaves was taken, boiled with distilled water. It was cooled to room temperature, filtered and the filtrate was made up to 100 mL. The extract was used as corrosion inhibitor in the present study.

2.3 Weight loss method

Three mild steel specimens were immersed in 100 mL of well water in various concentrations of the inhibitor (aqueous extract of adhatoda vasica leaves) for a period of 1 day. The weight of the specimen before and after immersion was determined using Shimadzu balance AY62.Inhibition efficiency (IE) was calculated from the relationship

$$IE = \frac{W_1 - W_2}{W_1} \times 100\ \% \qquad \text{Eq. (1)}$$

W1 =corrosion rate in the absence of inhibitor, and W_2 = corrosion rate in the presence of the inhibitor.

2.4 Potentiodynamic polarization study

Polarization study was carried out in an H and CH electrochemical work station Impedance Analyzer Model CHI 660A provided with iR compensation facility, using a three electrode cell assembly. Mild steel was used as working electrode, platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. After having done iR compensation, polarization study was carried out at a sweep rate of 0.01 V/Sec. The corrosion parameters such as linear polarization resistance (LPR), corrosion potential E_{corr}, corrosion current I_{corr} and Tafel slopes (b_a and b_c) were measured.

2.5 Alternating current impedance spectra

AC impedance spectra were recorded in the same instrument used for polarization study, using the same type of three electrode cell assembly. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. The charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values were calculated.

2.6 FTIR spectra

FTIR study was carried out with a Perkin- Elmer 1600 spectrophotometer. The protective film was removed from the metal surface, mixed with KBr and made into pellet. The pellet was used for FTIR study. A few drops of an aqueous extract of inhibitor were dried on a glass plate. A solid mass obtained and it was mixed with KBr and made into pellet.

2.7 UV absorption spectra

UV spectroscopy is an important tool in analytical chemistry. The other name of UV (Ultra-Violet) spectroscopy is Electronic spectroscopy as it involves the promotion of the electrons from the ground state to the higher energy state or excited state.

III. RESULTS AND DISCUSSIONS

The inhibition of corrosion of mild steel in well water by an aqueous extract of adhatoda vasica leaves has been investigated by the following methods.

3.1 Weight loss method

The inhibition efficiency of an aqueous extract of adhatoda vasica leaves in controlling corrosion of mild steel in well water has been evaluated by weight loss method [8-12]. The results are summarized in Table 1.

Table 1: Corrosion inhibition efficiency of adhatoda vasica leaves extract in controlling corrosion of mild steel in well water.

Volume of adhatoda vasica leaves extract mL	Corrosion rate (CR) mdd	IE%
0	32.68	-
2	17.64	46
4	14.05	57
6	9.80	70
8	6.2	81
10	2.61	92

It is observed from the Table 1 that as the concentration of adhatoda vasica leaves extract increases, the corrosion inhibition efficiency also increases. The active principle of adhatoda vasica leaves extract, namely vasicine, vasicinone has coordinated with Fe^{2+} on the metal surface and forms a protective film consisting of Fe^{2+}- vasicine or Fe^{2+} - vasicinone complex. Thus the anodic reaction of metal dissolution is prevented.

3.2 Polarization study

Polarization study is useful in confirming the formation of protective film formed on the metal surface [13-17]. If a protective film is formed, the linear polarization resistance increases and the corrosion current value decreases. The polarization curves of mild steel immersed in various test solutions are shown in Figure 1.

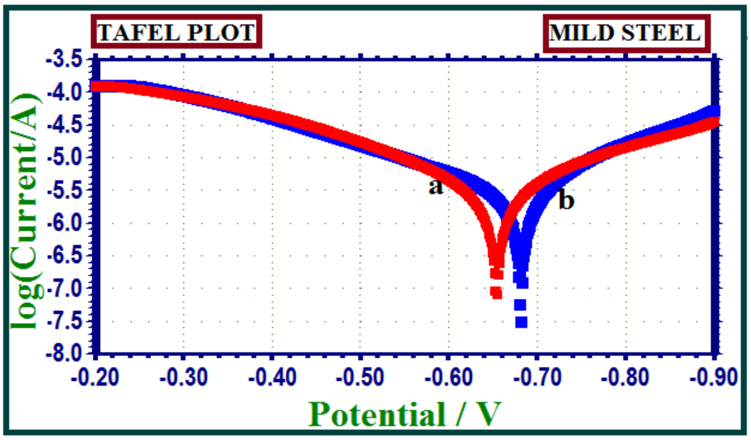


Figure1: Polarization curves of mild steel immersed in various test solutions (a) Well water (b) Well water + 10 mL of adhatoda vasica leaves extract

The corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), linear polarization resistance (LPR) and Tafel slopes (b_c=cathodic; b_a= anodic) are given in Table 2.

Table 2: Corrosion parameters of mild steel immersed in well water in the absence and presence of an aqueous extract of adhatoda vasica leaves.

S.No	System	E_{corr} mV vs SCE	I_{corr} A/cm^2	LPR ohm cm^2	b_c mV/decade	b_a mV/decade
1.	Well water	-654	9.447×10^{-6}	4022.1	181.6	168.4
2.	Well water + Adhatoda leaves extract	-682	3.61×10^{-6}	11108.3	155.9	225.8

It is observed from Table 2, when mild steel is immersed in well water, the corrosion potential is -654 mV vs SCE. The corrosion current is 9.447×10^{-6} A/cm^2. The LPR value is 4022.1 ohm cm^2. In the presence of inhibitor, the corrosion potential is shifted from -654 to -682 mV vs SCE. This is an cathodic shift. It suggests that the anodic reaction is controlled predominantly. The LPR value increases from 4022.1 to 11108.3 ohm cm^2. The corrosion current decreases from 9.447×10^{-6} to 3.61×10^{-6} A/ cm^2.These observations confirm that a protective film is formed on the metal surface. This controls the corrosion of metal.

3.3 AC impedance spectra

Impedance spectroscopy is a non- destructive technique. It is an alternating current technique. AC impedance spectra are useful in confirming the formation of protective film formed on the metal surface [18-22]. If a protective film is formed on the metal surface, the charge transfer resistance (R_t) value increases; double layer capacitance value (C_{dl}) decreases and the impedance [log (z/ ohm)] value increases. The AC impedance spectra of mild steel immersed in well water in presence of inhibitor system are shown in Figure 2 and Figure 3. The Nyquist plots are shown in Figure 2.The Bode plots are shown in Figure (3a, 3b). The corrosion parameters, namely, R_t, C_{dl} and impedance values are given in Table 3.

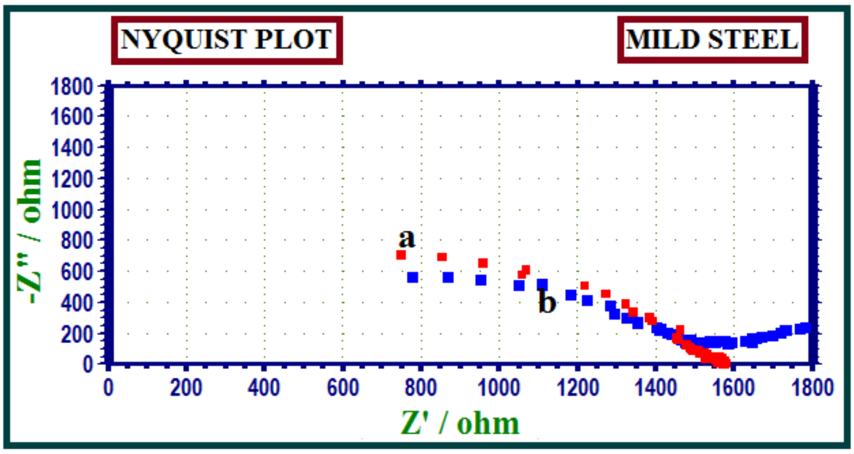


Figure 2: AC impedance spectra of mild steel immersed in various test solution (Nyquist Plot) a) Well water b) Well water + 10 mL of adhatoda vasica leaves extract

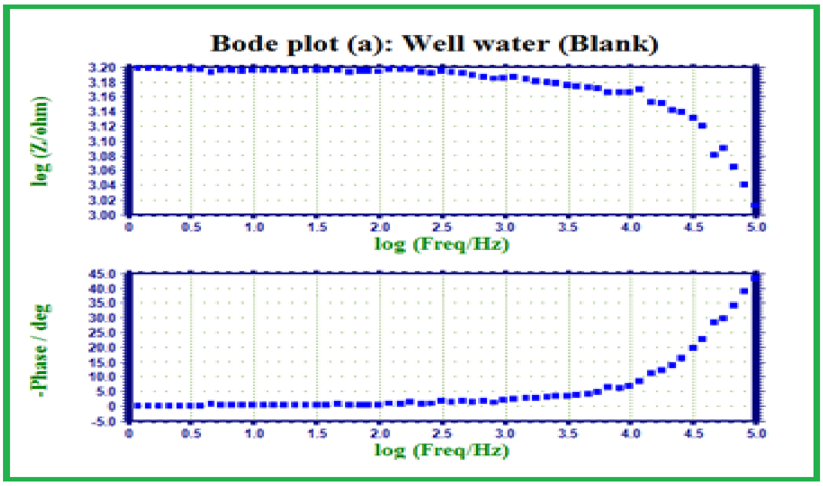


Figure 3a: AC impedance spectra of mild steel immersed in well water (Bode Plot)

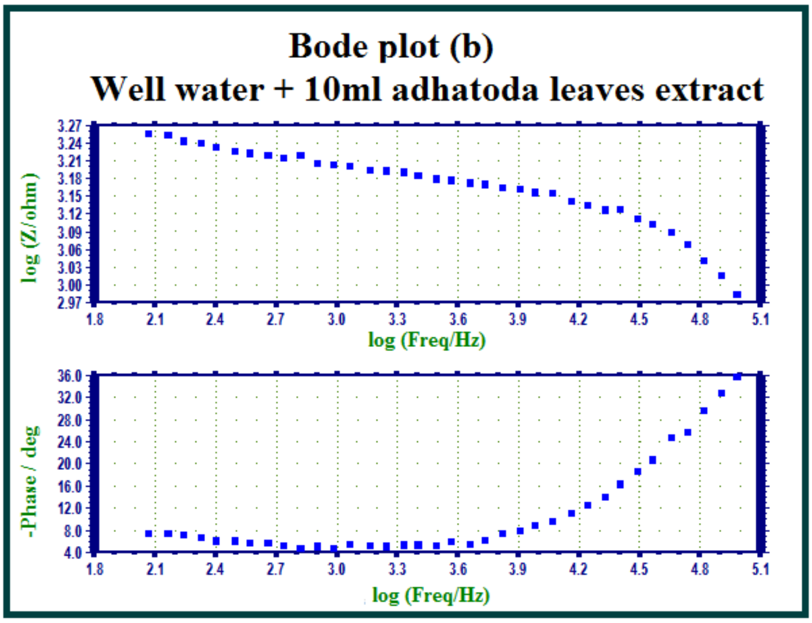


Figure 3b: AC impedance spectra of mild steel immersed in well water + 10 mL of adhatoda vasica leaves extract (Bode Plot)

Table 3: Corrosion parameters of mild steel immersed in well water in presence of adhatoda vasica leaves extract obtained from AC impedance spectra

System	Nyquist plot		Bode plot
	R_t ohm cm^2	C_{dl} F cm^{-2}	Impedance log (z/ohm)
Well water (blank)	286.7	17.739 x 10^{-9}	2.721
Well water + 10 mL of adhatoda vasica leaves extract	921	5.428 x10^{-9}	3.201

It is observed from the Table 3 that when mild steel is immersed in well water, the charge transfer resistance is 286.7 ohm cm^2. The double layer capacitance is 17.739 x 10^{-9} F cm^{-2}.The impedance value is 2.721. In the presence of inhibitor (10 mL of adhatoda vasica leaves extract), The charge transfer resistance value (R_t) increases from 286.7 ohm cm^2 to 921 ohm cm^2.The double layer capacitance value (C_{dl}) decreases from 17.739 x 10^{-9} F cm^{-2} to 5.428 x10^{-9} F cm^{-2}. The impedance log (z/ohm) increases from 2.721 to 3.201.These observations confirm that a protective film is formed on the metal surface. This prevents the transfer of electrons from the metal to the solution medium. Thus corrosion of mild steel is prevented.

3.4 UV-Visible absorption spectra

UV-visible absorption study has been widely used in corrosion inhibition studies [23-26]. The UV-visible absorption spectrum of an aqueous extract of adhatoda vasica leaves is shown in Figure 4a. A Peak appears at 436 nm. The UV-visible absorption spectrum of an aqueous solution containing extract of adhatoda vasica leaves, Fe^{2+} ($FeSO_4.7H_2O$ solution freshly prepared) is shown in Figure 4b. A peak appears at 444 nm. There is shift in the position of the peak. There is change in absorbance value also. This confirms the formation of complex in the solution. This probably consists of Fe^{2+}- vasicine or Fe^{2+} -vasicinone complex in solution.

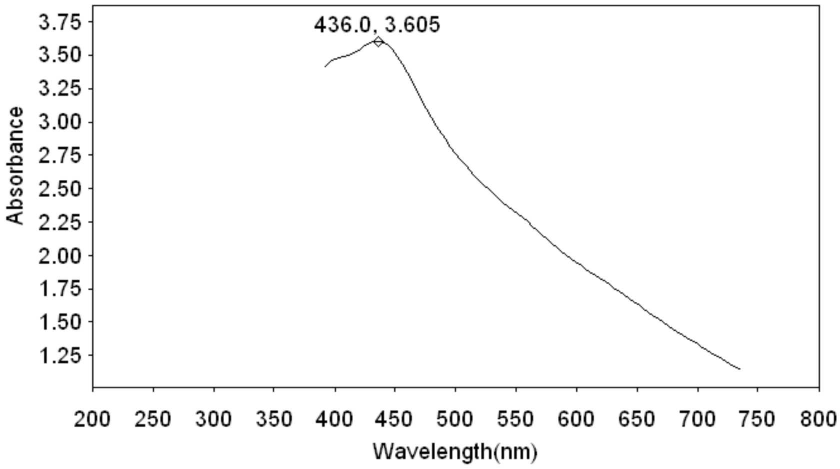


Figure 4a: UV-visible spectrum of adhatoda vasica leaves extract

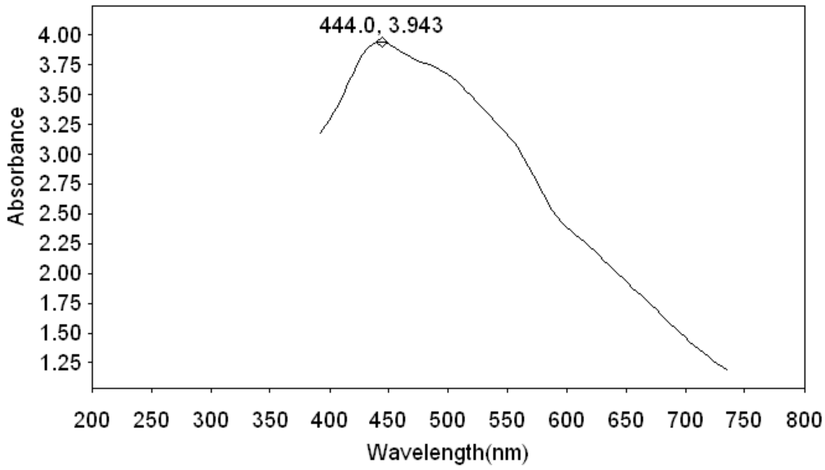
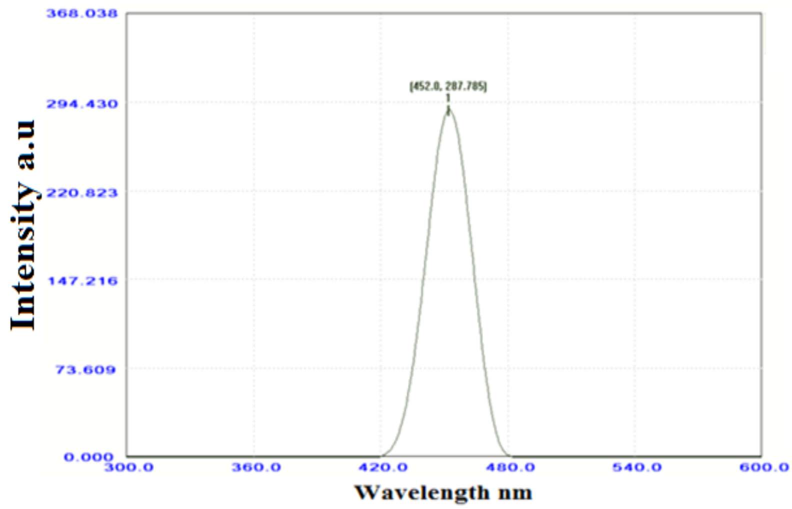


Figure 4b: UV-visible spectrum of adhatoda vasica leaves extract + Fe^{2+} ion

3.5 Fluorescence spectra

Fluorescence spectra have been used in corrosion inhibition study by many researchers [27].The fluorescence spectrum (λ_{ex} = 300 nm) of a solution containing Fe^{2+} and aqueous extract of adhatoda vasica leaves is shown in Figure 5a. A peak appears at 452 nm.This peak corresponds to Fe^{2+}- vasicine or Fe^{2+} - vasicinone complex in solution. The fluorescence spectrum (λ_{ex}=300 nm) of the film formed on the metal surface after immersion in the solution consisting of well water and adhatoda vasica leaves extract is shown in Figure 5b. A peak appears at 456.5 nm. This peak matches with the peak of Fe^{2+}- vasicine or Fe^{2+} - vasicinone complex. Thus it is confirmed that the protective film consists of Fe^{2+}- vasicine or Fe^{2+} - vasicinone complex formed on the metal surface. It is observed that the intensity of the fluorescence spectrum in metal is lower (6.039) than the intensity of the fluorescence spectrum formed in solution (287.785).This can be explained by the fact that in the solid state (protective film) the electronic transition is restricted than in solution. So the intensity of fluorescence spectrum of the protective film decreases.



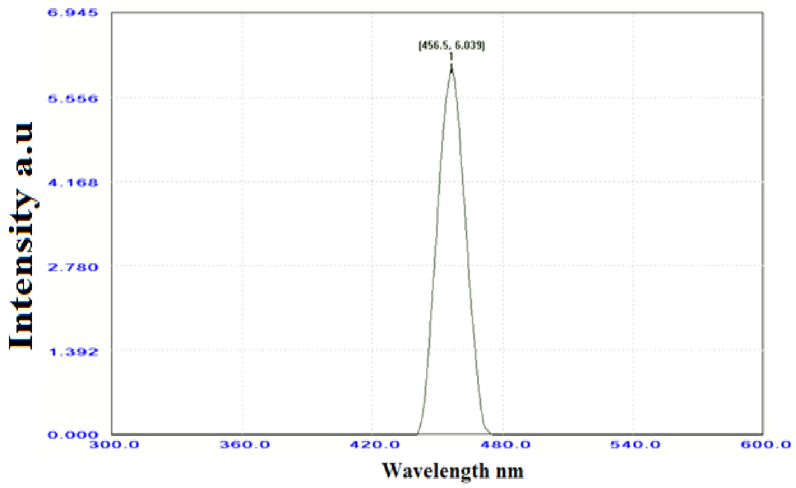


Figure 5: Fluorescence spectra λ_{ex} = 300 nm (a) Fe^{2+} + adhatoda vasica leaves extract (b) Film formed on metal surface after immersion in the solution containing 10 mL of adhatoda vasica leaves extract

3.6 FTIR spectra

FTIR spectra have been used in corrosion inhibition study to analyze the protective film formed on the metal surface [28-32]. A few drops of an aqueous extract of adhatoda vasica leaves were dried on a glass plate. A solid mass was obtained. Its FTIR spectrum (KBr) is shown in Figure 6a. The OH stretching frequency appears at 3402.03 cm^{-1}.The stretching frequency of C=O appears at 1624.95 cm^{-1}. The C=C stretching frequency appears at 1515.53 cm^{-1}.The stretching frequency of C-N appears at 1242.04 cm^{-1}. Thus the structure of the active principle of adhatoda vasica leaves extract namely vasicine and vasicinone is confirmed by FTIR spectrum.

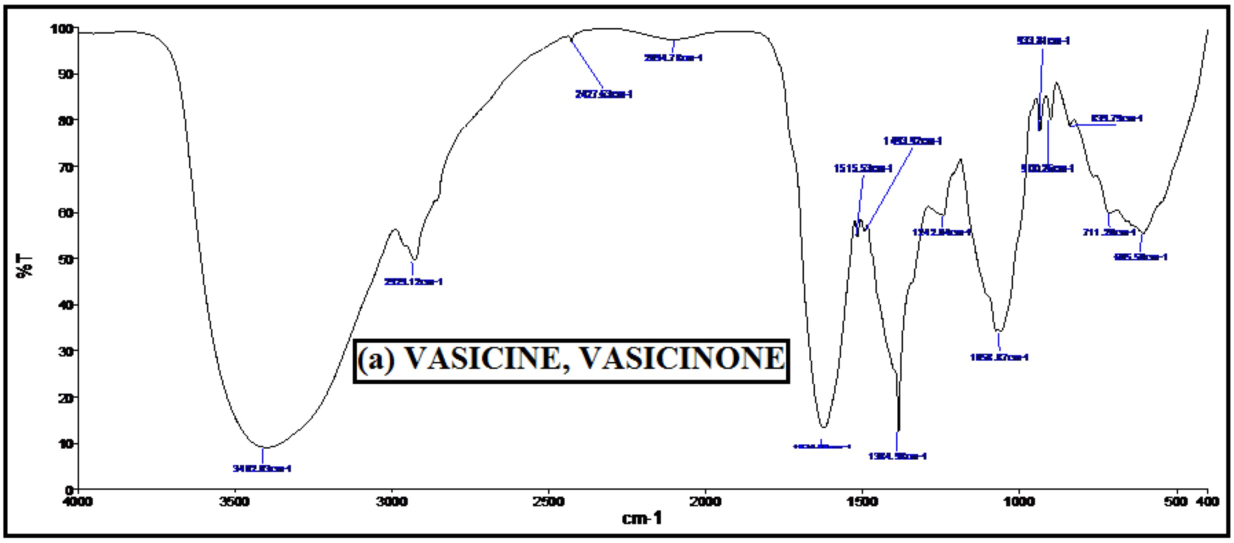


Figure 6a: FTIR Spectrum: adhatoda vasica leaves extract evaporated to dryness (Vasicine,vasicinone)

The FTIR spectrum of the protective film formed on the metal surface after immersion in the solution containing well water and inhibitor solution is shown in Figure 6b. It is observed that the stretching frequency of OH group has shifted from 3402.03 cm^{-1} to 3373.23 cm^{-1}. The stretching frequency of C=O has shifted from 1624.95 cm^{-1} to 1630.33 cm^{-1}.The stretching frequency of C=C has shifted from 1515.53 cm^{-1} to 1570.64 cm^{-1}. The stretching frequency of C-N has shifted from 1242.04 cm^{-1} to 1274.44 cm^{-1}. The stretching frequency of various functional groups is given in Table 4. Thus it is observed that vasicine or vasicinone has coordinated with Fe^{2+} through oxygen atom, nitrogen atom of vasicine or vasicinone. It is confirmed that the protective film is Fe^{2+}- vasicine or Fe^{2+} - vasicinone complex.

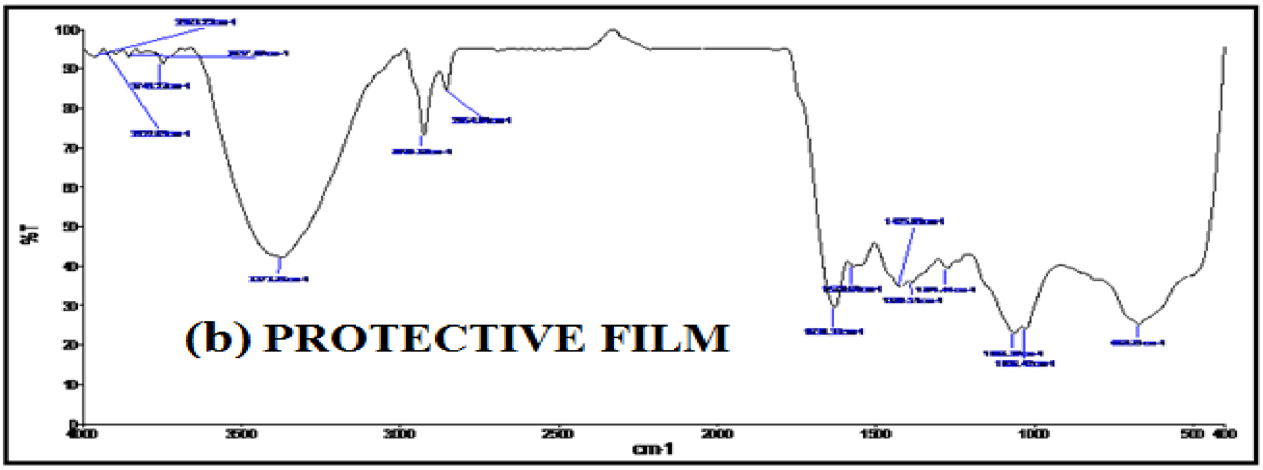


Figure 6b: FTIR Spectrum: Film formed on metal surface after immersion in the solution containing 10 mL aqueous extract of adhatoda vasica leaves.

Table 4: The stretching frequency of various functional groups

Functional groups	Stretching frequency cm^{-1}	
	Vasicine and vasicinone	**Protective film**
OH	3402.03	3373.23
C=O	1624.95	1630.33
C=C	1515.53	1570.64
C-N	1242.04	1274.44

IV. CONCLUSION

The inhibition efficiency of adhatoda leaves extract in controlling corrosion of mild steel in well water has been evaluated by weight loss method. As the concentration of inhibitor increases, inhibition efficiency increases. Polarisation study and AC impedance spectra reveal that a protective film is formed on metal surface. UV absorption spectra and FTIR spectra confirm the protective film consists of Fe^{2+}- vasicine or Fe^{2+} - vasicinone complex. Adhatoda leaves extract can be used as eco-friendly alternative inhibitor to protect mild steel from corrosion.

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