Isolation, characterization and inhibition effect of vasicine on mild steel corrosion in 1N HCl

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ABSTRACT

Vasicine compound is the principal alkaloid found in Adhatoda vasica which belong to the family of anthracite, contains vasicine, vasicinone and deoxyvasicine .The alkaloid present in the plant gives expectorant activity, antispasmodic, antiseptic and anthelmintic properties, but not uses as corrosion inhibitor. Hence, in the present study mainly focused on the isolation ,characterization and inhibition effect of vasicine alkaloid from adhatoda vasica. Alkaloids are extracted with ethanol, quantified and identified by reactions and proved using TLC, HPLC, FT-IR and H^{1}NMR and used as corrosion inhibitor. The inhibition of vasicine on mild steel corrosion in 1 N HCl was carried out by weight loss, polarization and impedance methods. Weight loss studies indicated that the inhibition efficiency was found to be increased with increase in the concentration of inhibitor. Polarization studies revealed that the inhibitor act as mixed type inhibitor. AC impedance method indicated that the charge transfer resistance was found to be increased with increase in concentration. The adsorption of inhibitor follows Langmuir adsorption isotherm to gain information about the inhibitive action mechanism. The optimum inhibition efficiency 99 % was obtained for 800 ppm of vaccine at 303 K

Keywords: Vasicine, TLC, HPLC, and FT-IR, Electrochemical methods and SEM
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INTRODUCTION

Adhatoda vasica is one of the most remarkable traditional medicinal shrubs in India. It is well known for its use in respiratory ailments. In traditional medicine system of India this plant is considered like a mother to doctors. The leaves of the plant are valued for containing bronchodilator alkaloids, mainly vasicine, quinazoline, vasicinone, deoxyvasicine[1]. Vasicine has antioxidant and anti-inflammatory activity [2,3,9] and it is a valuable antispasmodic, antiseptic and anthelmintic plant [4,15]. The roots also contained various alkaloids. Vasicine is the most important active compound of this medicinal plant. It is a quinazoline type alkaloid [5]. It is an optically active molecule in its natural condition but, gets racemized when isolated vasicine. Adhatoda vasica is the principal source of this vasicine compound. This plant has been used in India for more than 2000 years [3].

Mild steel is the material of choice because it is widely used in pipes, tanks, and in various chemical companies due to its characteristics. Hydrochloric acid medium is used for pickling mild steel material [10]. About 90% of pickling problems can be solved efficiently and extensively by introducing appropriate pickling inhibitor treatment of respiratory activity [6,18]. The majority of well-known inhibitors are organic compounds containing hetero atoms, such as O, N, S and multiple bonds [12]. In this study, isolation of vasicine from extract of Adhatoda vasica and characterization of isolated vasicine by TLC, HPLC, and H^{1}NMR and corrosion inhibition effect of vasicine on mild steel corrosion in 1N hydrochloric acid was investigated by electrochemical methods like polarization method, impedance technique and SEM analysis [2,3]. Literature survey revealed that Adhatoda vasica extract has been directly used as corrosion inhibitor [5]. But the vascine isolated from Adhatoda vasica is not used as corrosion

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Inhibitor. This paper reveals that the corrosion inhibition effect of the above compound vasicine isolated from adthoda vasica on mild steel in 1 N hydrochloric acid

EXPERIMENTAL SECTION

2. Experimental Procedure
2.1 Preparation of Specimens
Mild steel specimens are cut into a size of 5 cm x 1 cm having the following percentage of composition. The surfaces of the specimens are polished with various grades of emery papers ranging from 1/0 to 4/0. Further, the metal decreased with trichloroethylene then dried and stored in a vacuum desiccator containing silica-gel [8,].

2.2 Preparation of Working Electrode
Mild steel specimens of composition Fe = 99.686, Ni =0.013, Mo = 0.015, Cr = 0.043, S = 0.014, P = 0.009, Si= 0.007, Mn= 0.196, and C = 0.017 with exposed area of 1 cm^2 are used as working electrode. The specimens are cleaned according to the ASTM standard [7,19]. Experiments are carried out using this working electrode in 1 N HCl solution at room temperature.

2.3 Preparation of Solution
1N HCl solution is prepared   by adding 83.33 ml of 12N AR Grade HCl in 1000 ml of double distilled water

2.4 Preparation of Inhibitor
2.4.1 Collection of Plant Material and Authentication
Adhatoda vasica leaves are collected from the village of Mecheri, Salem- Tamil Nadu, India, Latitude - 11°8366065 and Longitude -77°9413891.

2.4.2 Isolation of Vasicine from Adhatoda vasica leaves extract
Adhatoda vasica leaves are dried under the shadow for 15 days and then the leaves are powdered into medium size particles. The powdered material is taken in 500 ml plastic bottle with 200 ml ethanol [4]. The resulting materials are kept into orbital shaker and shaking for 16 hrs and concentrated under reduced pressure using Rotary vacuum evaporator. Some black leaf precipitate is formed when the crude is acidified for 2 minutes [17]. Then the aqueous solution is basified using NaHCO$_3$ and extracted with chloroform and di-ether to remove non-polar impurities [4, 5, 38]. The isolated vasicine is confirmed by TLC and HPLC. The Structure of this compound is confirmed with FT-IR and H[1]NMR .

2.4.3. Isolation of Vasicine by Thin Layer and Column Chromatography (TLC)
The extract is subjected to TLC plate with crude Adhatoda vasica and isolated vasicine are dissolved in ethyl acetate separately and it is spotted on TLC plate. The plate is developed in ethyl acetate: methanol (9:1) solvent mixture system and it is dried. This dried TLC plate is kept in UV spectrum and various spots are observed [13]. There were four spots developed for the crude Adhatoda vasica. Where as isolated vasicine was only one spot was developed. The crude product was purified by 60-120 silica Column and the vasicine was isolated as light brown solid. vasicine which is confirmed by using characterization techniques such as   HPLC, FT-IR and H[1] NMR.

2.4.4 HPLC (High Performance Liquid Chromatography) analysis
The standard stock solution of vasicine for HPLC analysis   was prepared. The HPLC analysis were carried out at 25°C on a LC-10AT liquid ethanol at 1000 μg mL^{-1}. Chromatograph equipped with a Phenomenex RP$_{18}$ column (250x4.60 mm , 5 μm) with a Phenomenex guard column (4x2 mm , 5 μm). The samples are injected using 10 mg/ml. The mobile phase consist of methanol: phosphate buffer (70:30) and the separation was performed by using isocratic elution at a flow rate of 1 mL min^{-1}. The chromatograms were run for 15 min. Photodiode array detector is used at 280 nm for detection. The data is processed on a LC Gradient absorption of maximum vasicine compound[13,14].

2.5. *Spectral analysis of vasicine* (FT-IR and NMR)
2.5.1 FT-IR and NMR *analysis*
The FT-IR spectra are recorded in JASCO FT-IR 430 spectometer in KBr pellet. The ^{1}HNMR spectra are recorded on 400MHz NMR spectrometer using CDCl$_3$ as solvent and TMS as internal standard.

2.6   Weight Loss studies.
The initial weight of specimens was noted and were immersed in the experimental solution (in triplicate-3) with the help of glass hooks in the beaker containing 100 ml test solution for 1h of immersion time at 30 ^{0}c and the electrode was rinsed with double distilled water and washed with trichlorethane,dried and weighed. The final weight

of the specimens were noted. From the initial and final weights corrosion rate, inhibition efficiency (%), and surface coverage of isolated compound were calculated using the formula

Corrosion rate (mmpy) = KW/AT D   (1)

Where, K = 8.76×10^4 (constant),W is weight loss in g, A is area in cm^2, t is time in hours and D is density in gm/cm3 (7.86)

Inhibition Efficiency (%) = Wu – Wi / Wu x100   (2)

Surface coverage (θ)   =   Wu – Wi / Wu   (3)

Where, u and i are corrosion rates in the absence and presence of the inhibitor.

2.7 Polarization Studies
The polarization measurements were made to three-electrode cell assembly with working electrode as mild steel, platinum electrode and the reference electrode as calomel electrode, Mild steel of 1 cm^2 area used as the working electrode. These electrodes are immersed in 100 ml of 1N HCl in the absence and presence of inhibitors. CH electrochemical analyzer Model CHI 608 D/E .The inhibition efficiency was calculated [4, 5] The percentage inhibition efficiency (IE%) from the polarization measurements was calculated using the following equation [11]

$$IE\% = \frac{I^o corr - i^i corr}{i^o corr} \times 100$$ (4)

Where $i^o corr$ and $i^i corr$ are the corrosion and current density values without and with the inhibitor

2.8 Electrochemical Impedance Method.
The electrochemical AC-impedance measurements of steady state OCP (open circuit potential) in the frequency range of 10 kHz to 0.1 kHz were carrid out usig CH electrochemical analyzer Model CHI 608 D/E. Three-electrode cell get-together as such used for potentiodynamic polarization studies. Electrochemical measurements were carried about 30 min immersion of three-electrode cell assembly to attain steady-state potential. From the plot, the charge transfer resistance (Rct) was found out. The charge transfer resistance (*Rct*) was calculated and the double layer capacitance calculated using the following equation

Cdl=1/2πmax Rct   (5)

Where Cdl is double layer capacitance, and Rct is charge transfer resistance Cdl is double layer capacitance, and Rct is charge transfer resistance

The percentage inhibition efficiency (IE%) from the electrochemical impedance measurements was calculated using the following equation [12,16]

$$IE\ (\%) = \frac{Rct(0) - Rct(w)}{Rct(0)} \times 100$$ (6)

Where Rct(o) and Rct(w) are the values of charge transfer resistance in absence and presence of the inhibitor respectively.

2.9 Surface Analysis by Scanning electron microscope (SEM)
Surface of mild steel specimens in 1N HCl without and with the isolated compound immersed for 24 h at 303K was studied using JEOL-Scanning electron microscope (SEM) with the magnification of 2000x specimens[6].

RESULTS AND DISCUSSION

3.1 High-Performance Liquid Chromatography method (HPLC)
The HPLC analysis was performed using a UV detector without considering the peak purity which may result in pure peak identification of vasicine. Also, there was no baseline separation of peaks in the reported procedures. Here, we have tried   a number of solvent systems in different compositions resulting in optimum methanol:

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phosphate to give baseline separation of peaks of vasicine compound and was eluted for Retention times 30 min .The data was processed on an LC Gradient for the absorption of maximum compound vasicine 92.5% pure as shown in Fig.1
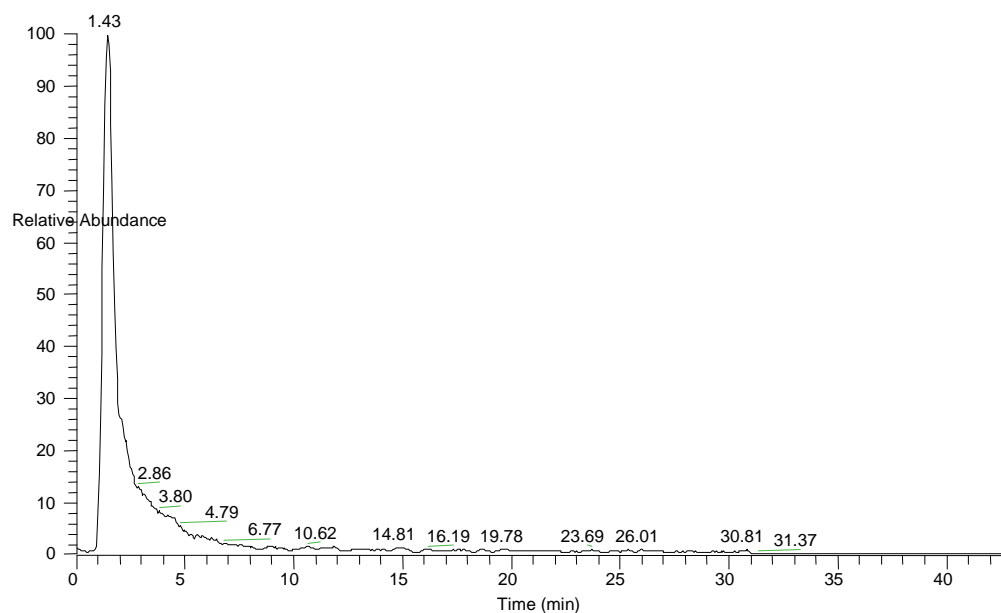

Fig. 1 HPLC chromatogram of Isolate vasicine

3.2 FT-IR spectral data analysis

The FT-IR spectrum of mild in 1 N HCl with vaccine is shown in Fig.2. The FT-IR spectral data are shown in table-1. The assignments of speak appeared in various region of FT-IR spectrum to the functional groups present in the vascine as followes [21]. The FT-IR spectrum vascine showed the characteristic absorption at 1363 cm^{-1} (due to CN bond), 1649, 1516,1746 cm^{-1} (due to stretching vibration of C-O), 2992 cm^{-1} (due to stretching vibration C-H Asymmetric) ,2712 cm^{-1} (due to stretching vibration C-H symmetric),3709 cm^{-1} (due to stretching vibration of OH group) [20,22,37].

Table-1 FT-IR spectral data of isolated vasicine

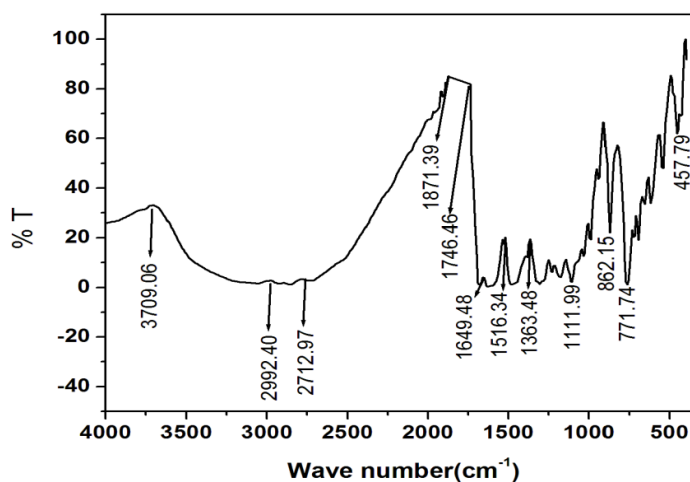| Peak values (cm^{-1})	Possible groups
3709	OH group
2992	stretching vibration C-H Asymmetric
2712	C-H symmetric stretch
1649,1516, 1746	due to stretching vibration of C -O
1363	C-N stretch

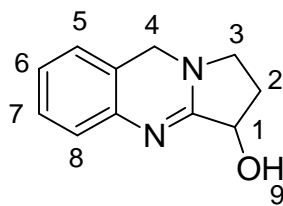**Fig.2 FT-IR spectrum of mild steel in 1 N HCl with vasincine**

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3.3 H¹NMR spectral analysis

Fig.3 The structure of vasicine

The proton NMR chemical shift value for vaisine was shown in table 2. The chemical shift values clearly confirm the structure of isolated vasicine. The chemical shift value δ 4.45(triplet,1H) confirm the proton which is attached with OH.Two multiplet at δ 1.70-2.26 clearly shows that proton which is attached alcohol carbon. The tertiary nitrogen attached protons show the chemical shift value at δ 3.11-3.30 and 4.53.The aromatic region protons show the chemical shift value at δ 6.88-7.11.
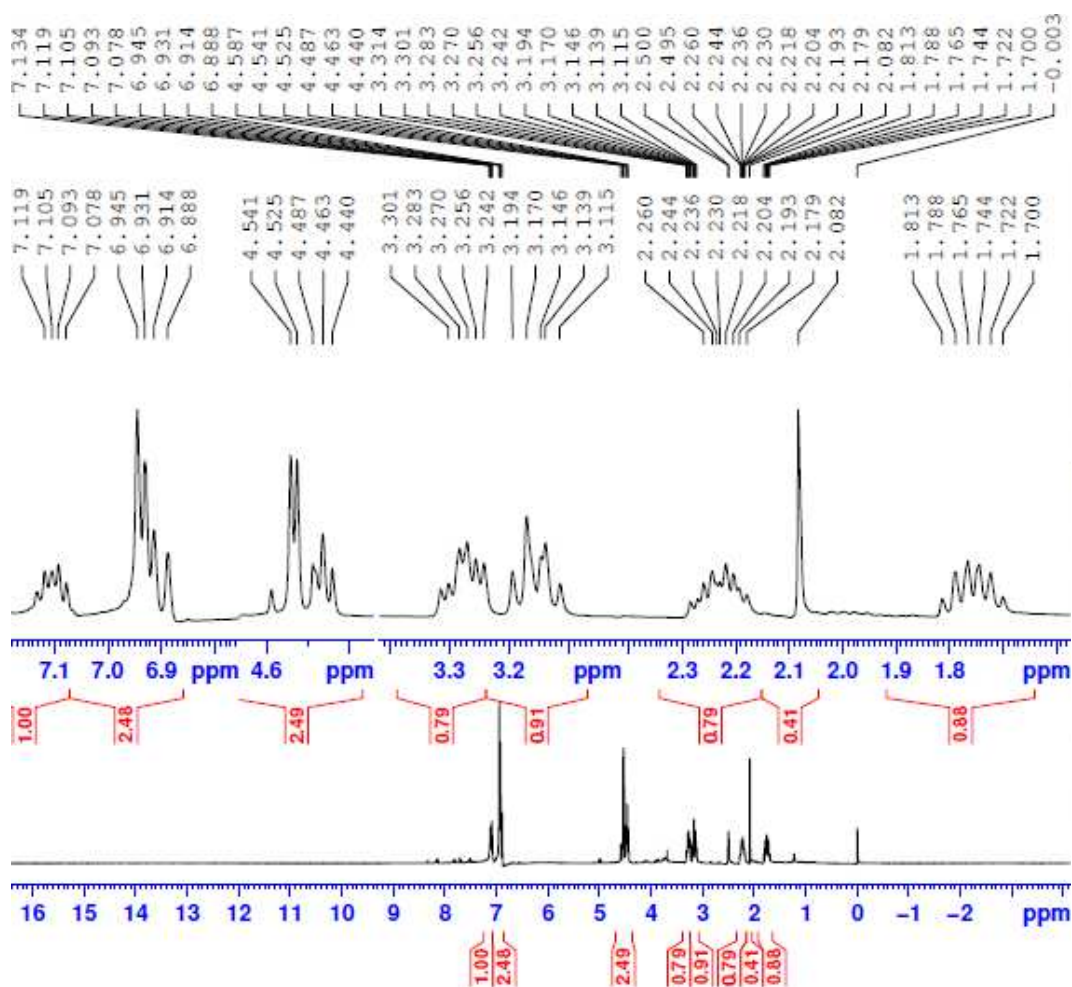

Fig.4 H¹ NMR spectrum of vasicine

Table -2 The proton NMR chemical shift value for vaisine

| Sl.No	Chemical shift value δ	Splitting pattern	No. of hydrogen	Proton numbered
1.	1.70-1.81	Multiplet	1	2
3.	2.17-2.26	Multiplet	1	2
4.	3.11-3.19	Quartet	1	3
5.	3.24-3.30	Triplet of doublet	1	3
6	4.45	Triplet	1	1(OH attached)
7.	4.53	Doublet	2	4
8.	6.88-7.11	Multiplet	4	5,6,7,8(Aromatic)

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3.4 Weight Loss studies.

The various corrosion parameters such as corrosion rate (CR), inhibition efficiency (IE), and surface coverage were obtained from weight loss method for mild steel 1N hydrochloric acid without and with of various concentrations of the vasicine compound ranging from 100 ppm to 1000 ppm at 303K and listed in Table 3. It can be seen from the Table-3 that the inhibition efficiency was found to be increased with an increase in cocentration of isolated vasicine and then decreses. The maximum inhibition efficiency 99.25 % was obtained at 800 ppm of vasicine which is due to the formation of a protective layer by the added vasicine and then decresed even upto 1000 ppm.

Table-3 Inhibition efficiency of isolated vasicine on mild steel corrosion in 1N HCl at 303 K by Weight Loss Studies

Conc. Vasicine(ppm)	Rate of corrosion(mmpy)	Sureface coverage(θ)	Inhibitor efficience(%)
Blank	29.67	-	-
100	2.89	0.9217	92.17
200	1.99	0.9389	93.89
300	1.83	0.9401	94.01
400	1.60	0.9501	95.01
500	1.51	0.9525	95.25
600	1.42	o.9601	96.01
700	0.98	0.9723	97.23
800	0.75	0.9925	99.25
900	0.93	0.9889	98.89
1000	0.96	0.9786	97.86

3.5 Potentiodynamic Polarization Studies

The Potentiodynamic Polarization curves for mild steel in 1 N HCl without and with various concentrations of vasicine are shown in Figure-5. The anodic and cathodic Tafel slopes and inhibition efficiency (IE) for the corrosion of mild steel in 1N HCl at room temperature in the absence and presence of different concentrations of the vasicine are given in Table-4. Polarization studies revealed that the corrosion current density (I_{corr}) markedly decreased with the addition of vasicine and the corrosion potential shifts to less negative values upon the addition of the vasicine . Moreover, the values of anodic and cathodic. Tafel slopes [23,24] are slightly changed indicating that this behavior reflects the vasicine ability to inhibit the corrosion of mild steel in 1N HCl solution of vasicine and the adsorption of vasicine molecule on both anodic and cathodic [25]. It was observed that the inhibition efficiency was found to be incresed with an increase in the concentration of vasicine from 100 ppm to 800 ppm and then decreased even up to1000 ppm. The optimum inhibition efficiency of 99.69% was observed for 800 ppm. The corrosion behavior of mild steel in 1N HCl with vasicine observed by weight loss method is confirmed by polarization studies.
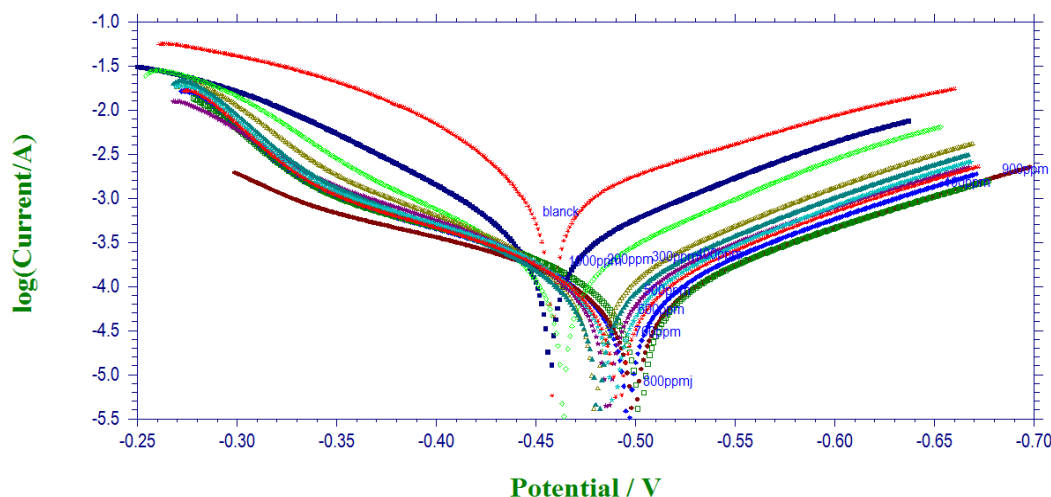
Fig.5 Potentiodynamic Polarization curves for mild steel in 1 N HCl with vasicine

3.6 Electrochemical AC Impedance Method.

Impedance diagram obtained for the frequency range from 10 kHz to 0.01Hz with respect to the open circuit potential of mild steel in 1 N HCl in the presence and the absence of inhibitor under study are shown in Fig.6 Impedance parameters derived from Nyquist plots were given in table-5. It is observed that the value of charge transfer resistance (Rct) was found to be increased with increase in concentration of vasicine and the double layer capacitance (Cdl) values are decreased with increase in inhibitor concentration. A significant charge transfer resistance is associated with slowly corroding systems [26]. In addition, improved inhibitor protection is associated

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with a decrease in metal capacitance[27].The decrease in double layer capacitance which resulted from a decrease in the local dielectric constant and an in the thickness of the electrical double layer, confirmed vasicine as active adsorption at the metal interface [28].The semicircular appearance of impedance diagram indicates that the corrosion of mild steel is mainly controlled by a charge transfer between the inhibitor molecule and mild steel surface [29]. The optimum inhibition efficiency was found to be 98.23 % in 1N HCl for 800 ppm of vasicine at 303 K. Inhibition efficiency obtained in AC impedance method is in good agreement with polarization and weight loss methods.

Table-4 Potentiodynamic Polarization parameters for mild steel in 1 N HCl with vasicine at 303K

Cncentraction of vasicine (ppm)	E_{corr} (mV)	Tafel slopes (Mv/dec)		I_{corr} (A/cm^2)	Inhibition efficiency (%)
		ba	Bc		
Blank	-0.459	5.50	3.56	1550	-
100	-0.460	5.77	3.97	93.88	93.94
200	-0.4625	5.84	4.04	89.43	94.23
300	-0.477	6.00	4.20	88.09	94.32
400	-0.482	6.01	4.21	81.99	94.71
500	-0.483	6.06	4.26	75.02	95.91
600	-0.484	6.09	4.29	62.40	95.15
700	-0.488	6.11	4.31	58.11	96.16
800	-0.494	6.16	4.36	29.92	99.69
900	-0.498	6.19	4.39	31.77	98.33
1000	-0502	6.22	4.42	40.82	97.95

Table-5 Electrochemical AC Impedance parameters for mild steel in 1 N HCl with vasicine at 303 K

Concentration vasicine (ppm)	$R_{ct (Ohm\ cm^2)}$	$C_{dl\ (F/cm^2)}$	Inhibition efficiency (%)
Blank	12	231.02	-
100	211	177.31	94.31
200	240	166.15	95.00
300	275	154.74	96.64
400	350	121.10	96.70
500	364	116.72	96.83
600	371	112.58	96.87
700	376	90.83	96.89
800	389	83.21	98.23
900	383	87.52	98.03
1000	380	93.41	97.54
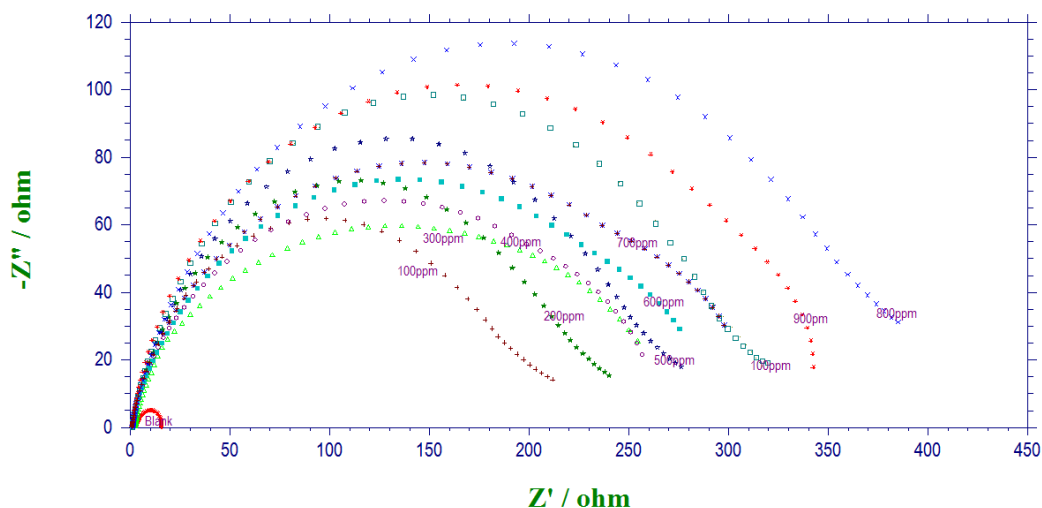
Fig.6 AC Impedance curves for mild steel in 1N HCl with vasicine

3.7. Adsorption isotherms
Basic information on the interaction between the inhibitor and mild steel surface coverage (θ) are investigated by the adsorption isotherms with different concentrations of vasicine compound in 1N HCl at 303K have been used to explain the best isotherm to determine the adsorption process. The value of the surface coverage (θ) was calculated using the relationship [19,32]

θ = [IE%] /100   (7)

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These values to various isotherm including Temkin, El-Awady, Frumkin, Freundlich, Flory-Huggins and Langmuir to fit.

The best fit was obtained with Langmuir isotherm as suggested by the plot between C/ θ and C (Fig -7) and the linear correlation coefficient of the fitted data was close to 1,indicating   that the adsorption of the inhibitor molecules obey the Langmuir's adsorption isotherm as expressed by relationship [33]

$$[C/ \theta] = C + [1/K_{ads}] \tag{8}$$

Where C is the inhibitor concentration and K_{ads} is the equilibrium constant for adsorption, desorption process of the inhibitor molecules on the metal surface K_{ads} values were calculated from the intercept of the plot for the adsorption process.

The adsorption and the standard free energy (Δgo ads) is related to equilibrium constant K_{ads} by the following equation [34]

$$K (ads) = [1/55.5] \exp [-\Delta g_o (ads)/RT] \tag{9}$$

Where the value 55.5 in the above equation is the molar concentration of water in solution in mol/L and the negative sign of Δg_o ads indicated that adsorption of the vasicine compound was spontaneous process [30]. The adsorption of the vasicine can be presented as a substitution adsorption process between the organic molecules in aqueous solution (Org aq) and the water molecules (H2O ads) on the metallic surface [35].

$$Org (aq) + x. H2O(ads) \quad \leftrightarrow Org (ads) +x. H2O(aq) \tag{10}$$

Where x is the number of water molecules displaced by one molecule of the vasicine compound and x is assumed to be independent of coverage or charge on the electrode. Since the adsorption of the vasicine on the metal surface is conforming to Langmuir isotherm, there is no interactive or repulsive force between the adsorbed molecules on the metal surface [31].

Table-6 Langmuir adsorption isotherm for adsorption of vasicine on mild steel in   1N HCl

Conc.vasicine (ppm)	Rate of corrosion(mmpy)	Surface coverage(θ)	C/ θ	Inhibitor efficiency(%)
Blank	29.67	-	-	-
100	2.89	0.9217	108.4951	92.17
200	1.99	0.9389	213.0152	93.89
300	1.83	0.9401	319.1149	94.01
400	1.60	0.9501	412.0083	95.25
500	1.42	0.9512	525.6518	96.12
600	1.51	0.9612	624.2197	96.01
700	0.98	0.9723	719.9424	97.23
800	0.75	0.9923	806.2078	99.25
900	0.93	0.9889	910.1021	98.89
1000	0.96	0.9786	1021.868	97.86

3.8 Surface Examination Studies (SEM)
Surface analysis was carried out by SEM technique in order to evaluate the surface condition of the mild steel in contact with 1N HCl acid solution. Surface image morphology of mild steel specimens in the presence and absence of different concentrations of the isolated vasicine compound immersed for 24 hr at 30^0 C was studied using JEOL-Scanning electron microscope (SEM) with the magnification of 2000x specimens[24]. In the presence of the inhibitor, the micrographs show no evidence of pitting but shows a smooth surface. This result is due to the adsorption of vasicine compound around the pits. This passive film block the active site present on the mild steel surface there by retarded the corrosion process
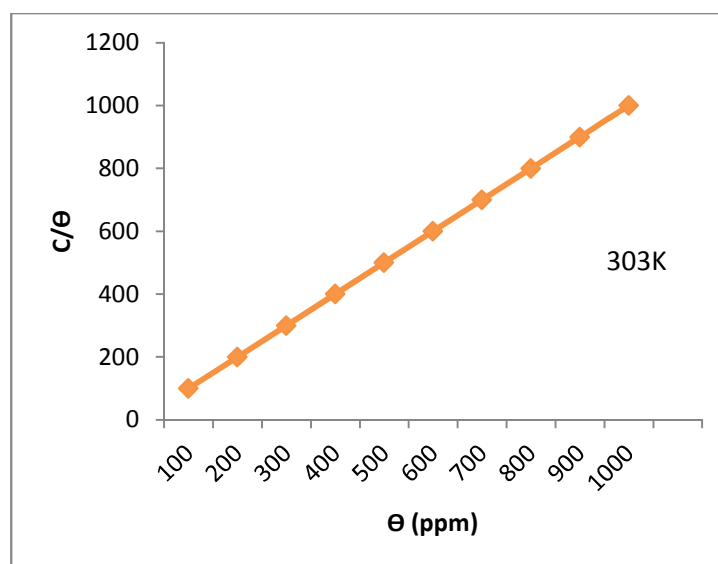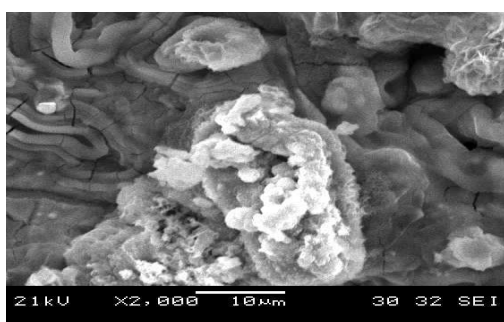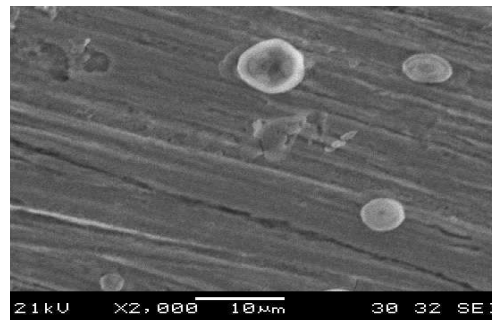
Fig .7 Langmuir adsorption isotherm for adsorption of vasicine on mild steel in 1N HCl

| (a) | (b) |

Fig. 8 (a) SEM   Micrograph on mild steel in 1N HCl (b) SEM   Micrograph on mild steel in 1N HCl with vasicine

CONCLUSION

The following conclusion were made from the studies.
- The isolated vasicine compound was conformed by TLC, HPLC, FT-IR, and H^{1}NMR spectral analysis.
- Isolated vasicine acts as efficient corrosion inhibitor on mild steel in 1N hydrochloric acid.
- The use of isolated vasicine as corrosion inhibitor is environmentally safe, less toxic, and eco-friendly
- Inhibition efficiency obtained in Electrochemical AC impedance analysis was in good agreement with potentiodynamic polarization analysis, showed that the examined vasicine acted as a mixed type inhibitor.
- Corrosion rates on mild steel in 1N HCl acid decreased with increasing concentration of vasicine up to 800 ppm in all the studies.
- The optimum inhibition efficiency 99% of vasicine was observed with respect to inhibitor up to 800 ppm in all the cases
- The adsorption of vasicine was consistent with the Langmuir adsorption isotherm

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