Characterisation and Anti-Corrosion Behaviour of Isolated Vasicinone Compound on Mild Steel

V. Thailan

Department of Chemistry, Annapoorana Engineering College, Salem-636308, India

Corresponding author: E-mail: vthailan.2008@gmail.com

The availability of naturally occurring substances has been investigated as more efficient in prevention of corrosion. Due to the biodegradation, eco-friendliness, less expensive, not much of toxic and easy availability of naturally occurring material were used as corrosion inhibitors in the recent years. Based on these needs, this study is focused on the isolation, characterization and inhibition effect of vasicinone isolated from ethanolic exact of *Adhatoda vasica* leaves in 1N HCl. The isolated compound was analyzed using spectral studies and also it is subjected to various corrosion parameters such as weight loss method and electrochemical methods. The result reveals that isolated extract of vasicinone from ethanol extract of *Adhatoda vasica* leaves inhibits the mild steel material in an effective manner in 1N HCl medium. Further surface morphological studies were also confirmed that the compound shows better efficiency.

Keywords: Anti-Corrosion, *Adhatoda vasica* leaves, Vasicinone, Potentiodynamic polarization, AC impedance.

INTRODUCTION

Most of the metals do not occurs free in nature it may be in the form of sulphide or oxides. More energy is required to convert the metals into its purity but the nature does not allow them to be in a pure form as it is a spontaneous process [1,2]. Corrosion cause irreversible damage to structural materials through chemical or electrochemical reaction with their environment. Not only metals other materials like ceramics, plastics and concrete may also corroded [3]. In many industries, mild steel were used in construction of towers and boilers due to its ductile in nature, minimum cost, easy for construction and its easy convenience [4,5]. Usage of mild steel in industries for a long time may lead to severe corrosion and this may occurs during transportation of acid, descaling and due to the storage of acids. The heavy loss of metal when it is in contact with acids can be minimized by using inhibitors [6-8]. Several inorganic compounds such as chromates, phosphates, molybdates and a variety of organic compounds containing heteroatom having lone pair of electron like nitrogen, sulphur and oxygen are being used as corrosion inhibitors for mild steel [9-11]. Corrosion leads to loss the characteristics of the metal by direct and indirect losses due to corrosion process. By the direct loss of corrosion in developed countries it is estimated that 3 to 4 % of gross natural product (GNP) whereas in India it is roughly estimated that 2-3 % of gross natural product [12]. An inhibitor is a substance which decreases the rate of corrosion when it is added in a small concentration to an environment. Corrosion inhibitors are added to many systems, which include cleaning mats inside the acid containers, refrigeration process, refinery units, oil and gas production units, *etc*. [13]. Due to the vacant *d*-orbital in a metal atom and a donor-acceptor or π-electrons availability in an inhibitor is mainly decide the inhibition of corrosion process [14]. Literature survey shows that *Adhatoda vasica* aqueous extract used as a corrosion inhibitor by directly to the environment [15-17]. To our best of knowledge, no work is carried out on this novel vascinone compound extracted. Henceforth in this work, an isolated vasicinone phytochemical product prepared from ethonal extract of *Adhatoda vasica* leaves has been used as corrosion inhibitor in preventing mild steel in 1N HCl medium.

EXPERIMENTAL

Ethanolic extract of *Adhatoda vasica* leaves: About 300 g of shade dried podwer of *Adhatoda vasica* leaves was taken in 500 mL plastic bottle with ethanol (250 mL × 2) and subjected to shaking at room temperature using an orbital shaker for 24 h. Then the extract was filtered under vacuum and filtrate was

collected, the resulting filtrate was concentrated under the reduced pressure using rotary vacuum evaporator. A mass of dark green crude was obtained from the ethanolic extract of *Adhatoda vasica* leaves (yield: 48 g; 16 %, m.p.: 198-199 ºC).

Fractionation of ethanolic extract of *Adhatoda vasica* leaves: To a dark green crude mass (45 g) in 240 mL of 5 % acetic acid was added and heated at 60 ºC for 1 h, then the reaction mass was cooled and basifies by aqueous NH_3 to attain pH 9. The resulting aqueous layer extracted with chloroform. The organic layer was washed with water (3 × 150 mL) and saturated with NaCl (250 mL), dried on Na_2SO_4 and concentrated under reduced pressure. A mass of green crude was obtained from the above workup to yield 4.2 g (9 %).

TLC fingerprint profile: TLC fingerprint profile fractions of ethanolic extract of *Adhatoda vasica* leaves was developed in solvent system of chloroform:methanol (9:1) at 25 ºC. For TLC, precoated silica gel $60F_{254}$ TLC plates (E. Merck) were used. The ethanolic extract of *Adhatoda vasica* leaves was subjected to TLC plate and is spotted on TLC plate. The plate is developed in chloroform:methanol (9:1) solvent mixture system and dried. This dried TLC plate is kept in UV spectrum and four spots developed for the crude ethanolic extract of *Adhatoda vasica* leaves whereas for isolated vasicinone single spot was developed.

Isolation of vasicinone from ethanolic extract of *A. vasica* Leaves by column chromatography: Fractionated crude (4 g) was dissolved in 40 mL of dichloromethane and 12 g of 60-120 mesh silica-gel was added. The resulting slurry was pre-loaded in column (silica-gel 60-120 mesh). The column was performed by chloroform:methanol eluent. The vasicinone came out at 3 % eluent as light brown solid (yield: 0.280 g, 8 %, m.p.: 201 ºC).

Specimen preparation: Commercially available mild steel specimens of the following composition were used for the corrosion studies. 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 %.

Electrolyte solution: The 1N HCl were prepared by using AR grade hydrochloric acid and double distilled water.

Inhibitor solutions: A 1000 ppm of isolated vasicine, vasicinone and *Adhatoda vasica* extract (crude) solutions were prepared by dissolving 1 g of isolated vasicine, vasicinone and *Adhatoda vasica* extract in 30 min, respectively in 1 L of 1N HCl. This stock solution was diluted to 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 ppm using 1N HCl solution.

FT-IR analysis: The FT-IR spectra of isolated vasicine, vasicinone and ethanolic extract of *Adhatoda vasica* leaves (crude) were recorded on a Perkin-Elmer (Spectrum RX) in the range 4000-400 cm^{-1} using KBr pellets. The FT-IR spectrum also recorded for the mild steel specimen in 1N HCl without and with the inhibitors (vasicine, vasicinone and ethanolic extract of *Adhatoda vasica* leaves).

NMR analysis: ^1H NMR and ^{13}C NMR spectra of isolated vasicine, vasicinone compounds were recorded on a Bruker AC 300F (300 MHz) NMR spectrometer as using $CDCl_3$ as solvent and TMS as an internal standard.

Weight loss studies: Mild steel specimens were cut into a size of 5 cm × 1 cm × 0.1 cm for the weight loss measure-

ments. These mild steel specimens were pickled with pickling solution. The pickled specimens were washed, dried, polished with emery papers ranging from 110 to 410 grades and degreased with trichloroethylene [18]. After taking the initial weight, the specimens were stored in a vacuum desiccator. Each run of weight loss measurements were carried out in the glass vessel containing 100 mL test solution.

A clean weighed mild steel specimen was completely immersed by hanging from the glass rod using Teflon thread in the inhibitor solution [19]. After 1 h of immersion, the electrode was withdrawn, rinsed with doubly distilled water, washed with acetone, dried and weighed. This procedure was repeated for 1 h at 303 K.

Weight loss measurements were performed as per ASTM method described [20]. From the weight loss studies, corrosion rate, inhibition efficiency and surface coverage were calculated using the following equations:

Corrosion rate:

$$K = \frac{8.76 \times 10000 W}{ATD}$$

Inhibition efficiency:

$$IE\ (\%) = \frac{W_U - W_I}{W_U} \times 100$$

Surface coverage:

$$\theta = \frac{W_U - W_I}{W_U}$$

where T is a time of exposure in h, W is a weight loss of test specimen in g, A is an area of the test specimen in cm^2, D is the density of material in g cm^3 and W_U and W_I are the corrosion rates for mild steel in the absence and presence of inhibitor respectively at the same temperature.

Electrochemical measurements: Electrochemical measurements were carried out with conventional three electrode system. The working electrode was mild steel of 1 cm^2 area and the rest portions were covered with araldite. A rectangular platinum foil of 1 cm^2 was used as counter electrode and saturated calomel electrode (SCE) as a reference electrode. Measurements were performed using CH electrochemical analyzer Model CHI 608D/ E instrument.

Potentiodynamic polarization measurements: The potentiodynamic polarization measurements were carried out with the three-electrode system (working electrode, platinum electrode and saturated calomel electrode). The working electrode was polished with various grades of emery papers, washed with doubly distilled water and degreased with trichloroethylene. All the three electrodes were immersed in 1N HCl solution without and with inhibitors (isolated vasicine, vasicinone and ethanol extract of *Adhatoda vesica* leaves). The polarization measurements were carried out at ± 200 mV from the open circuit potential at a scan rate of 2 mV/s. Potentiodynamic polarization measurements were initiated about 30 min after the working electrode was immersed in the solution to stabilize the steady-state potential [21,22]. From the plot of E *versus* log I, corrosion current density, corrosion potential, anodic and cathodic Tafel slopes values were calculated. The inhibition efficiency of these systems was calculated using the following equation [23].

$$IE\ (\%) = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \times 100$$

where I_{corr} and $I_{corr(i)}$ are corrosion current density in the absence and presence of inhibitor, respectively.

AC Impedance studies: Impedance measurements were carried out with three electrode system. All the three electrodes were immersed in 1N HCl without and with the inhibitor. Open circuit potential was measured about 30 min after the immersion of working electrode to the test solution. The experiments were carried out in the frequency range of 10 kHz to 0.01 Hz using CH Electrochemical analyzer (Model CHI 608 D/E). The real and imaginary parts of the impedance were plotted in Nyquist plots. The solution resistance (R_s) and total resistance (R_t) were obtained from the low frequency and high-frequency intercepts on Z′ axis of Nyquist plot, respectively. The difference between R_t and R_s values give the charge transfer resistance R_{ct} value [24]. The C_{dl} values were obtained from the following equation:

$$C_{dl} = \frac{1}{2\pi f_{max} \times R_{ct}}$$

$$IE\ (\%) = \frac{R_{ct(i)} - R_{ct}}{R_{ct}} \times 100$$

where C_{dl} is double layer capacitance, R_{ct} is charge transfer resistance without inhibitor, f_{max} is frequency at Z″ value maximum and $R_{ct(i)}$ is charge transfer resistance in the presence of inhibitor.

SEM analysis: The mild steel specimens were immersed in 1N HCl solution without and with the inhibitor for 24 h. After 24 h of immersion, the specimens were taken out and dried. The morphology of mild steel surface was examined by scanning electron microscope (standard JEOL 6280 JXXA and LEO 435 VP model) [25].

RESULTS AND DISCUSSION

FT-IR analysis: The key FT-IR spectrum of mild steel in 1 N HCl with vasicinone is shown in Fig. 1 (Table-1). It is clearly confirmed that the above functional groups are present in the structure of vasicinone.

¹H NMR analysis: The chemical shift values clearly confirmed the structure of isolated vasicinone as shown in Fig. 2. The chemical shift value δ 5.22-5.27 (H-1) confirmed the

Fig. 1. FT-IR spectrum of mild steel in 1 N HCl with vasicinone
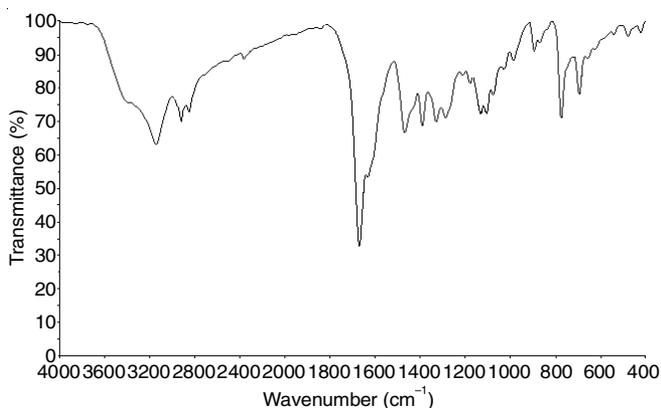
TABLE-1
KEY FT-IR SPECTRAL DATA OF ISOLATED VASICINONE

Peak values (cm⁻¹)	Possible groups
3158	OH group
2931	Stretching vibration C-H
1674	Due to stretching vibration of C=O
1469	C-N stretch
1124	C-O stretch
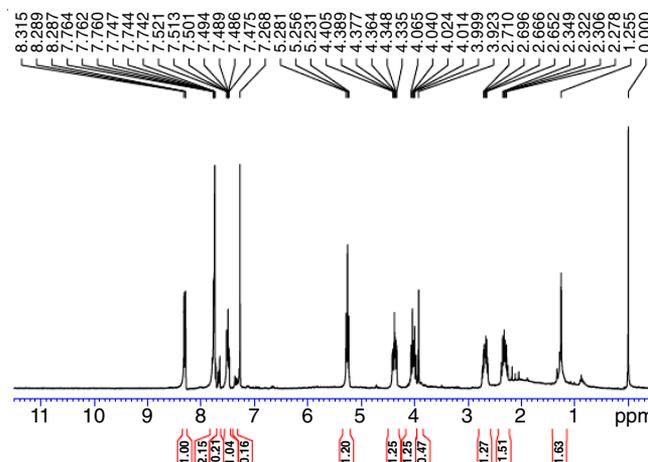
Fig. 2. ¹H NMR spectrum of vasicinone

four aliphatic proton attached with the different chemical environment and shows different δ chemical shift values for H-2 is observed δ 2.21-2.37 and 2.62-2.70 ppm. The chemical shift values for H-3 is observed at δ 3.98-4.05 and 4.32-4.41 ppm. The aromatic splitting pattern for ¹H NMR clearly observed between at δ 7.47-8.32 (H-4, H-5, H-6, H-7) ppm.

¹³C NMR analysis: The ¹³C NMR spectrum of vasicinone using CDCl₃ as solvent and TMS as internal standard is shown in Fig. 3. The assignment of peaks to various carbon environments are as follows, the singlet at 29.34 ppm is assigned to one carbon atom labeled as 2, singlet at 43.45 ppm is attributed to one carbon atom labeled as 3, singlet at 71.62 ppm (OH group) is referred to one carbon atom labeled as 1, singlet at 120.89 ppm is assigned to one carbon atom labeled as 10, singlet at 126.53 ppm is assigned to one carbon atom labeled as 5, singlet at126.58 ppm is assigned to one carbon atom labeled as 6, singlet at 126.93 ppm is assigned to one carbon atom labeled as 7, singlet 134.44 ppm is assigned to one carbon atom labeled as 8, singlet at 148.43 ppm is assigned to one carbon atom labeled as 9, singlet at 160.42 ppm (amide group)is assigned to one carbon atom labeled as 4, and singlet at 160.57 ppm (imine carbon C=N) is assigned to one carbon atom labeled as 11. All other aromatic region carbon is observed between 120.89 ppm to 148.43 ppm. It could be concluded from ¹³C NMR spectral data that the proposed structure of vasicinone is further confirmed [26].

LC-mass analysis: Mass spectra of an isolated vasicinone compound revealed a molecular ion peak at 203 *m/z* as shown in Fig. 4. The mass spectral fragmentation patterns as well as the molecular weight were observed. Standard vasicinone molecular weight 202, (M + 1 peak at 203), isolated vasicinone (molecular weight 202, M + 1 peak at 203) showed the molecular ion peak at 203.11 *m/z* which confirmed the presence and structure of isolated vsicinone.
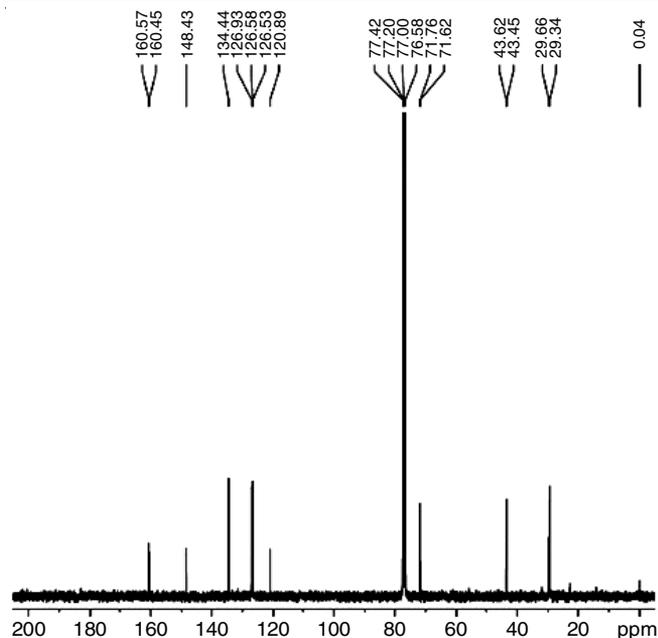
Fig. 3. ^{13}C NMR spectrum of vasicinone
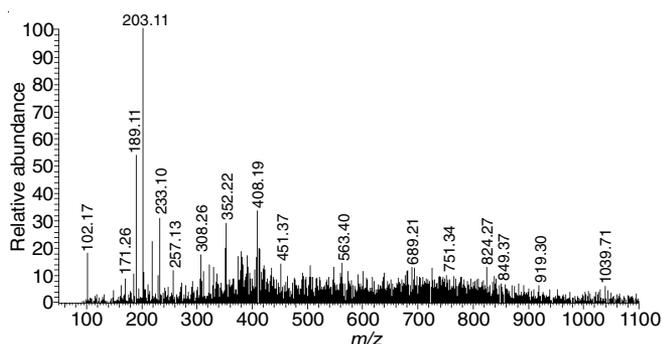
Fig. 4. LC-mass spectrum of vasicinone

was obtained at 800 ppm of an optimum concentration of vasicinone, which is due to the formation of a protective layer by the added vasicinone and then decresed even upto 1000 ppm.

Potentiodynamic polarization studies: The potentio-dynamic polarization curves for mild steel in 1N HCl without and with various concentrations of vasicinone are shown in Fig. 5. Anodic and cathodic Tafel slopes and inhibition efficiency (IE) for the corrosion of mild steel in 1N HCl at 303 K in the absence and presence of different concentrations of vasicinone are given in Table-3. Polarization studies revealed that corrosion current density (I_{corr}) markedly decreased with the addition of vasicinone and the corrosion potential shifts to less negative values upon the addition of vasicinone [27]. It was observed that the inhibition efficiency was found to be increased with an increase in the concentration of vasicinone from 100 ppm to 800 ppm and then decreased even upto 1000 ppm. The highest inhibition efficiency of 95.12 % was observed for an optimum concentration of 800 ppm [28].

Fig. 5. Potentiodynamic polarization curves for mild steel in 1 N HCl with vasicinone

Weight loss studies: Various corrosion parameters such as corrosion rate (CR), inhibition efficiency (IE) and surface coverage were obtained from weight loss method for mild steel in 1N HCl without and with the various concentrations of vasicinone ranging from 100 ppm to 1000 ppm at 303 K are given in Table-2. The inhibition efficiency was found to be increased with an increase in concentration of isolated vasicinone and then decreases. The maximum inhibition efficiency 95.25 %

TABLE-2
WEIGHT LOSS PARAMETERS OF ISOLATED VASICINONE ON MILD STEEL CORROSION IN 1 N HCl

Conc. of vasicinone (ppm)	Rate of corrosion (mmpy)	Surface coverage (θ)	Inhibition efficiency (%)
Blank	31.21	–	–
100	3.10	0.8516	85.16
200	2.85	0.8689	86.89
300	2.13	0.8703	87.03
400	1.84	0.8902	89.02
500	1.32	0.9026	90.26
600	1.12	o.9101	91.01
700	0.98	0.9323	93.23
800	0.85	0.9525	95.25
900	0.94	0.9389	93.89
1000	0.95	0.9186	91.86

TABLE-3
POTENTIODYNAMIC POLARIZATION PARAMETERS FOR MILD STEEL IN 1 N HCl WITH VASICINONE AT 303 K

Conc. of vasicinone (ppm)	E_{corr} (mV)	Tafel slopes (mV/dec)		I_{corr} (µA/cm^{-2})	Inhibition efficiency (%)
		-βa	-βc		
Blank	-0.450	5.50	3.56	1550	–
100	-0.461	5.77	3.97	93.88	84.14
200	-0.469	5.84	4.04	89.43	85.19
300	-0.477	6.00	4.20	88.09	86.23
400	-0.482	6.01	4.21	81.99	87.02
500	-0.483	6.06	4.26	75.02	88.26
600	-0.484	6.09	4.29	62.40	90.01
700	-0.488	6.11	4.31	58.11	92.23
800	-0.501	6.16	4.36	29.92	95.12
900	-0.490	6.19	4.39	31.77	93.19
1000	-0.485	6.22	4.42	40.82	91.76

AC impedance studies: Impedance diagrams obtained for the frequency range from 10 kHz to 0.01 Hz with respect to the open circuit potential of mild steel in 1 N HCl in the absence and the presence of inhibitor under study are shown in Fig. 6. Impedance parameters derived from Nyquist plots are given in Table-4. It is observed that the value of charge transfer resistance (R_{ct}) was found to be increased with increase in concen-
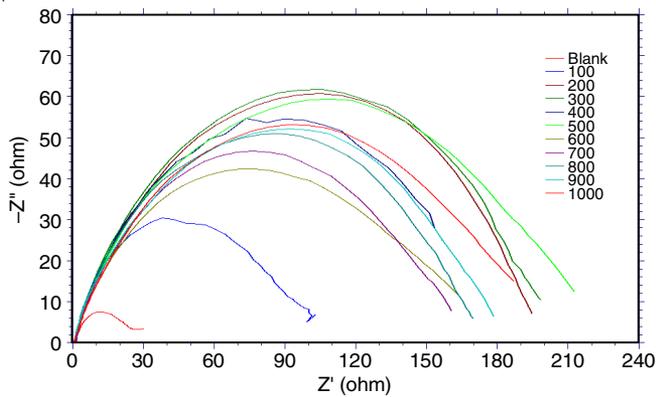
Fig. 6. AC impedance curves for mild steel in 1 N HCl with vasicinone

TABLE-4
AC IMPEDANCE PARAMETERS FOR MILD
STEEL IN 1 N HCl WITH VASICINONE AT 303 K

Conc. of vasicinone (ppm)	R_{ct} (Ohm cm^2)	C_{dl} (µF/cm^2)	Inhibition efficiency (%)
Blank	13	231.02	–
100	65	177.31	85.31
200	71	166.15	86.00
300	76	154.74	87.64
400	80	121.10	88.70
500	85	116.72	89.83
600	95	112.58	91.87
700	100	90.83	93.89
800	135	83.21	95.01
900	120	87.52	92.03
1000	105	93.41	91.64

tration of vasicinone and the double layer capacitance (C_{dl}) values are decreased with increase in inhibitor concentration [29]. A significant charge transfer resistance is associated with slowly corroding systems. In addition, improved inhibitor protection is associated with a decrease in metal capacitance.

A decrease in double layer capacitance, which resulted from a decrease in the local dielectric constant and the thickness of electrical double layer confirmed that vasicinone was adsorbed at the metal interface. The semi-circular 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. The maximum inhibition efficiency was found to be 95.01 % in 1N HCl for an optimum concentration of 800 ppm of vasicinone at 303 K. The inhibition efficiency obtained in AC impedance method is in good agreement with polarization and weight loss methods [30].

SEM analysis: Polished mild steel specimens immersed in 1N HCl in the absence and presence of vasicinone for 24 h at 303 K. SEM were examined at the magnification of 2000X by JEOL scanning electron microscope. The SEM micrographs (Fig. 7) revealed that the surface was strongly damaged owing to corrosion in the absence of inhibitor. But in the presence of inhibitor, there is much less damage on the surface due to the adsorption of the inhibitor on mild steel surface.

Conclusions

Based on the above studies, it was concluded as:
• Isolated vasicinone from ethanolic extract of *Adhatoda vasica* leaveswere characterized and its structure was confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR and LC-mass analysis.
• The weight loss studies indicated that the corrosion rate was found to be decreased with the addition of isolated vasicinone when compared with uninhibited system. The inhibition efficiency of vasicinone was found to be increased by increasing concentration.
• After 800 ppm, there is decrease in inhibiton efficiency. It shows that 800 ppm will be an optimum temperatue on weight loss measurment.
• The polarization measurements revealed that i_{corr} values were found to be decreased with the addition of vasicinone. It is also found that this inhibitor act as mixed type inhibitor.
• The polarization measurements revealed that i_{corr} values were found to be decreased with the addition of vasicinone, which indicated that these inhibitors are acted as mixed type inhibitors.
• SEM analysis confirms that the inhibition of corrosion of mild steel is through adsorption of *Adhatoda vasica* leaves ethanol extract, vasicine and vasicinone on the surface of mild steel and these studies also supplement the results of weight loss and electrochemical techniques.
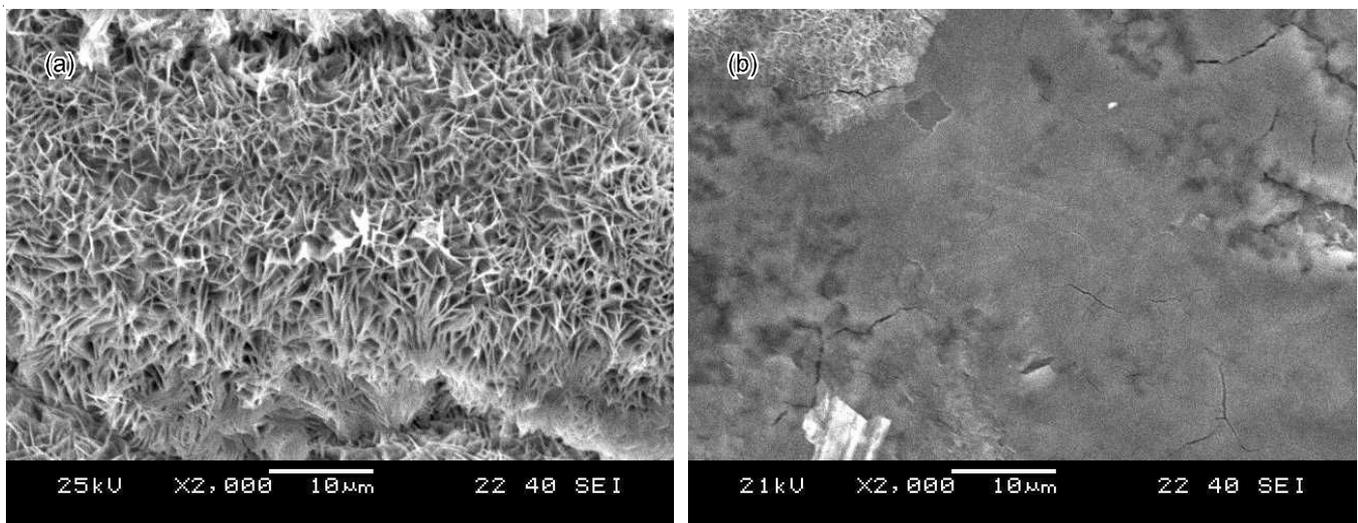
Fig. 7. SEM micrograph of mild steel in 1 N HCl without (a) and with vasicinone inhibitor (b)

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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