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ORIGINAL ARTICLE **OPEN ACCESS**

Eco-friendly Corrosion Inhibitors: Inhibitive Action of Ethanol Extracts of *Adathoda vasica* leaves for the Corrosion of Mild Steel in HCl solution

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ABSTRACT
This study is mainly focused on using natural inhibitors due to being easily available and eco-friendly to nature. The inhibitive action of ethanol extracts of vasicine and vasicinone from Adathoda vasica leaves (AVL) on mild steel (MS) in 1N HCl was studied and analysed using various experimental techniques like mass loss data, Kinetic parameters and electrochemical analysis. The rate of corrosion is prominent with a rise in temperature for the uninhibited HCl solution than the inhibited solution suggesting that the vasicine and vasicinone were absorbed on MS at all temperatures studied ranging from (303-353K) at optimum concentration. Comparing the result at 353K vasicine and vasicinone shows 90.57% and 86.17 % inhibition efficiency. Based on the kinetic study the efficiency of the inhibitor was studied at different intervals of time in which the efficiency of both inhibitor vasicine and vascinone isolated from ethanol extract of AVL decreased from 1 hour to 24 hours. Electrochemical studies like Potentiodynamic polarization and AC Impedance results also confirmed the above studies.
Keywords: *Kinetic, AC impedance, vasicine, vasicinone, Polarization*

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INTRODUCTION

In a corrosion process oxidation of metal takes place by replacing a pure metal with metal oxide. Due to the nature of the surroundings, a chemical or electrochemical reaction may occur which makes the metal lose its weight. Physical damage occurs in metal in such a way as erosion, corrosive wear or fretting-corrosion due to the action of chemical or electrochemical reaction [1, 2]. Not only metals may get corrode other materials such as PVC, ceramics and concrete may also be corroded due to the environment [3]. Many organic and Inorganic based inhibitors were identified and reported. Now a day natural products are utilized for the prevention of corrosion due to their easy availability and eco-friendly nature [4-6]. In the presence and absence of *Allamanda blanchetti* corrosion inhibitor was studied and reported in 1N citric acid and 1 N H2SO4 solution at room temperature using mild steel material [7]. Various natural product corrosion inhibitors such as extraction of *Andrographis paniculata, Thespesia populnea, Mangifera indica, Datura metal, Mentha pulgeium, Sesbania grandiflora seeds, Ficus benghalensis bark, Psidium gerajan*ra (bark) and *Callistemos* (leaves), *Canavalia ensiformis* etc were studied as a corrosion inhibitor in the prevention of mild steel [8-9]. Due to being eco-friendly and possess no hazard to the environment natural products are used as corrosion inhibitors in corrosion prevention studies. Therefore in my investigation, an isolated compound of vasicine and vasicinone obtained from ethanol extract of AVL were immersed in 1N HCl at a different temperature at optimum concentration were studied and reported.

MATERIAL AND METHOD

Specimen Preparation

Mild steel (MS) specimens were collected and cut into 5cm x1cm coupons and punched a number and put a hole at the top of the specimen according to ASTM procedure [10]. MS specimen has the following

weight percentage composition Fe-99.686%, Ni-0.013%, Mo-0.015%, Cr-0.043%, S-0.014%, P-0.009%, Si-0.07%, Mn-0.196% and C-0.017%. The coupons were degreased acetone.

For electrochemical analysis, MS plate 1 cm x 1 cm x 0.3 cm dimensions were cut and one face of the conductor was masked with Araldite, to expose an area of $1cm^2$. The surface of the electrodes was polished effectively on the emery papers of different grades 400-1200 grit and then degreased with acetone [11].

Solution Preparation

89mL of 11.3 N Analytical Grade HCl solutions were diluted in 1000 ml of double distilled water to prepare 1N HCl. Inhibitor solution 1000ppm was prepared by dissolving 1g of an isolated compound of Vasicine and Vasicinone extract from AVL respectively in one litre of 1N HCl. From the stock solution and different concentrations of the inhibitor, the solution was prepared.

Mass Loss Data

After the pickling process is over the specimens were cleaned and dried in a desiccator and initial weights were taken. All run of weight loss measurements was carried out in the glass vessel containing 100 mL test solution. After one hr of immersion, the electrode was withdrawn, rinsed with doubly distilled water, washed with acetone, dried and weighed. This procedure was repeated for 1 hr over the temperature range of 303 K to 353 K. According to ASTM procedure and formulae the mass loss data and efficiency were calculated

$$\text{Rate of Corrosion} K = \frac{8.76 \times 10000\, W}{ATD}$$

$$\text{Efficiency of the inhibitor } IE\% = \frac{W_U - W_I}{W_U} \times 100$$

$$\text{Surface coverage } \theta = \frac{W_U - W_I}{W_U}$$

Where T is the time of exposure in hours, W is the weight loss of the 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 a conventional three electrode system. The working electrode was MS. A rectangular platinum foil of 1 cm^2 was used as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. Measurements were performed using CH electrochemical analyzer Model CHI 608D/ E instrument. Tafel slope values have calculated the usage of polarization measurements which are accomplished at ± 200 mV from the open circuit capacity at a test charge of 2 mV/s. This examination turned into performed after 30mins immersion of the running electrode dipped within the take a look at the answer for consistent state capacity. From the anodic and cathodic Tafel slopes values a graph is plotted between E Vs. Log I and the efficiency was calculated with the use of those formulae

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

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

Similarly, an AC impedance study was carried out in the frequency range of 10 kHz to 0.01 Hz. 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 the Z' axis of the Nyquist plot respectively. The difference between R_t and R_s values gives the charge transfer resistance R_{ct} value. The C_{dl} values were obtained from the 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.

RESULT AND DISCUSSION

Effect of Temperature

The rate of corrosion and inhibition efficiency for moderate steel corrosion in 1N HCl from 303 K to 353 K with a top of the line awareness (800 ppm) of an isolated compound of vasicine and vasicinone of ethanol extract of *Adhatoda vasica* leaves are proven in Figure-1 and2. The corrosion rate and inhibition performance at 800 ppm with temperature increasing from 303K to 353K are given in Table -1. The

corrosion rate turned into determined to be accelerated in each of the inhibitors which shows that there is a not unusual increase in weight reduction as the temperature accelerated from 303K to 353 K and the inhibition efficiency in vasicine was found to be decreased slightly from 99.03% to 90.57% whereas in vasicinone the range differs from 95.16% to 86.17%. But both the inhibitors were able to withstand even at 353 K. This is the general rule guiding the rate of chemical reactions which says that chemical reaction increases with increasing temperature.

Table-1 Effect of temperature at an optimum concentration (800 ppm) of vasicine and vasicinone on corrosion of mild steel in 1 N HCl by weight loss method

Name of the Inhibitor	Temperature	Rate of Corrosion (mmpy)	Inhibition Efficiency (%)
Vasicine	303	0.75	99.03
	313	1.56	97.46
	323	2.01	95.81
	333	2.24	94.43
	343	3.31	92.76
	353	4.12	90.57
Vasicinone	303	0.81	95.16
	313	1.81	93.34
	323	2.10	91.21
	333	2.64	89.33
	343	3.71	87.56
	353	4.31	86.17

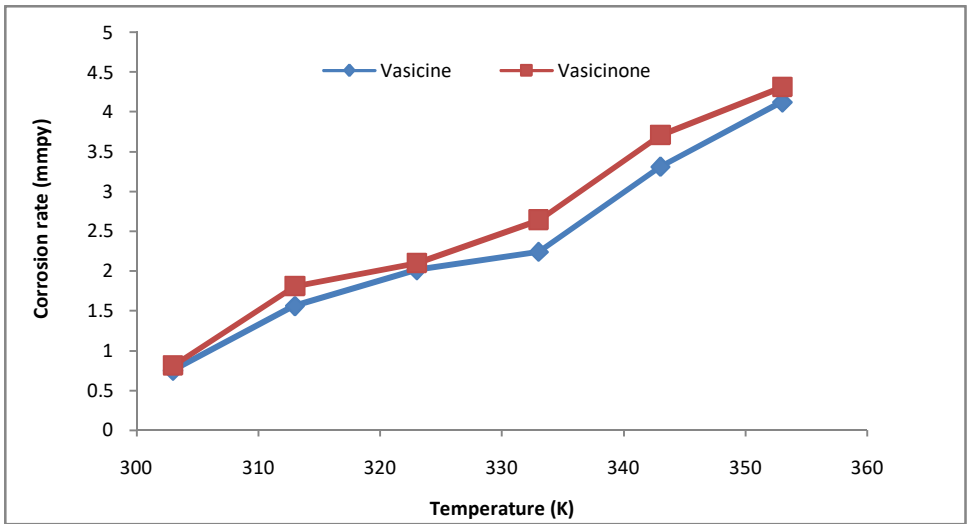

Figure-1 Effect of temperature on corrosion rate for mild steel in 1N HCl with an optimum concentration (800 ppm) of vasicinone and vasicinone at different temperatures

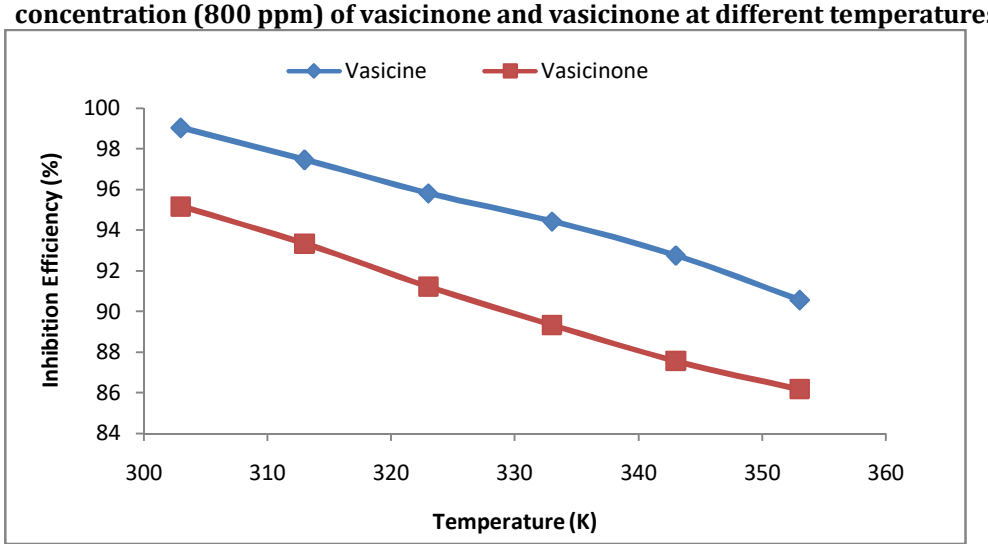

Figure-2 Effect of temperature on Inhibition Efficiency of mild steel in 1N HCl with an optimum concentration (800 ppm) of vasicinone and vasicinone at different temperatures

Effect of immersion time

The effect of kinetic study by immersing the MS specimen in vasicine and vasicinone inhibitor at different time intervals from 1 hr to 24 hr. The inhibition efficiency was found to be decreased from 95.03 % to 83.75 %. The effect of immersion time on inhibition efficiency of mild steel in 1N HCl at 303K in the presence of an optimum concentration (800 ppm) of vasicinoneis given in Table- 2 and the graphical representationis shown in Figure- 3. Though 83.75 % inhibition efficiency was obtained for 24 hr of immersion time, the maximum inhibition efficiency was found to be 95.03% for 1 hr. It was found that vasicinone acted as a good corrosion inhibitor for mild steel in 1N HCl at an optimum concentration of 800 ppm for1 hr at 303 K.

Table-2: Effect of immersion time on inhibition efficiency for mild steel in 1N HCl with an optimum concentration (800 ppm) of vasicine and vasicinone at 303 K

System	Inhibition Efficiency (%)								
	Time (hr)								
	1	2	3	4	5	6	12	18	24
800ppm of vasicine	99.03	98.14	97.03	96.00	95.36	94.75	92.97	92.01	91.51
800 ppm of vasicinone	95.03	93.71	91.63	89.83	88.56	87.92	85.72	84.21	83.75

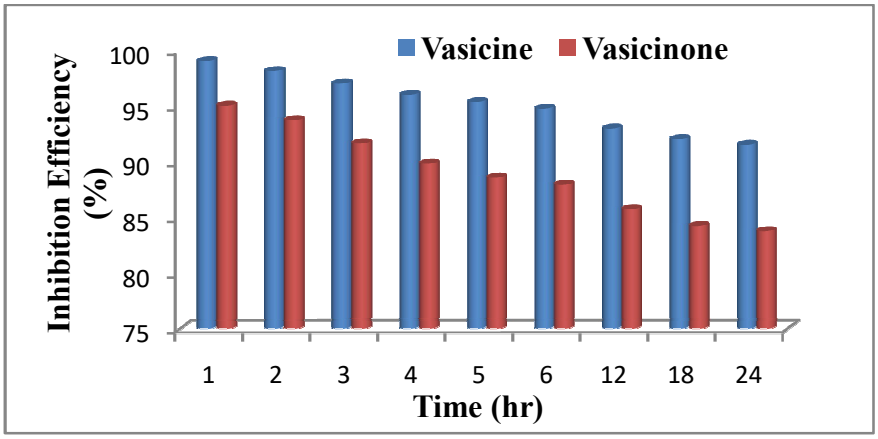

Figure- 3 Effect of immersion time on inhibition efficiency for mild steelin1N HCl with an optimum concentration (800 ppm) of vasicine and vasicinone at 303 K

Electrochemical Studies

Potentiodynamic Polarization Studies

The polarization curves for mild steel in 1N HCl (30 ± 1◦C) without and with an optimum concentration of vasicine and vasicinone are shown in Figure -4. The electrochemical parameters derived from the curves are given in Table 3. The E_{corr} values are shifted to more positive in the presence of both the inhibitors. It is observed that the optimum concentration of both the inhibitors has a little influence on the values of the anodic Tafel constant and appreciable influence on the values of the cathodic Tafel constant, indicating that inhibitors may change the mechanism of the cathodic reaction and may not affect the anodic dissolution mechanism[13].The appreciable increase in the cathodic Tafel values with an increase in thevasicine and vasicinone concentration indicates that hydrogen evolution is suppressed due to the blockage of sites at the metal surface by the vasicine and vasicinone molecule.

Table-3 Potentiodynamic polarization parameters for mild steel in 1 N HCl with Vasicine and Vascinone at 303K

Conc. of Inhibitors (ppm)	E_{corr} (mV)	Tafel slopes (mV/dec)		I_{corr} ($\mu A/cm^{-2}$)	Inhibition efficiency (%)
		-βa	-βc		
Blank	-0.410	5.50	3.56	15.50	-
800(vasicine)	-0.478	6.16	4.36	29.92	99.67
800(vasicinone)	-0.461	5.80	4.21	26.53	95.63

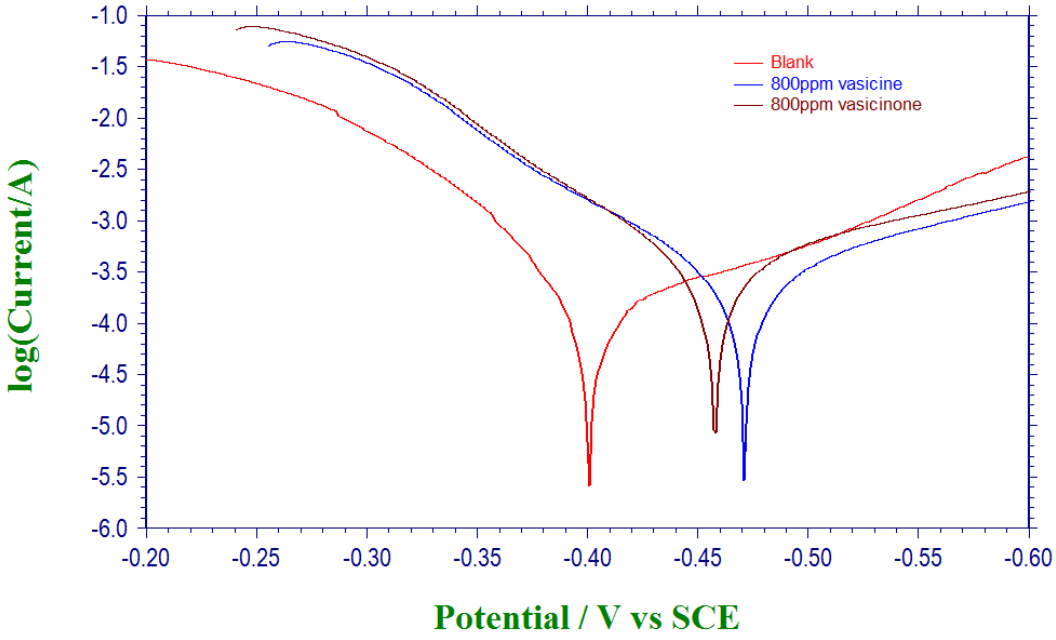

Figure-4 Potentiodynamic polarization curves for mild steel in 1N HCl with vasicine and vasicinone.

This canbe attributed to the formation of the very closely adherent adsorbed film on the metal surface. Supplementary evidenceshows that the adsorption of vasicine molecules on the metal surface makes a physicalbarrier for the mass charge transfer leading to a high degree of protection to the metal surface. The maximum inhibition efficiency was found in vasicine at 99.67% when compared with vasicinone which shows 95.63%.

AC Impedance Study

The impedance diagram obtained for the frequency range from 10 kHz to 0.01Hz concerning the OCP potential of mild steel in 1N HCl without and with an optimum concentration (800 ppm) of vasicine and vasicinone is shown in Figure5.

Table-4 AC Impedance parameters for mild steel in 1 N HCl with vasicine and vasicinone at 303 K

Conc. of Inhibitors(ppm)	R_{ct} (Ohm cm^2)	C_{dl} (µF/cm^2)	Inhibition efficiency (%)
Blank	12	231.02	-
800(vasicine)	390	85.37	99.15
800(vasicinone)	320	83.20	95.26

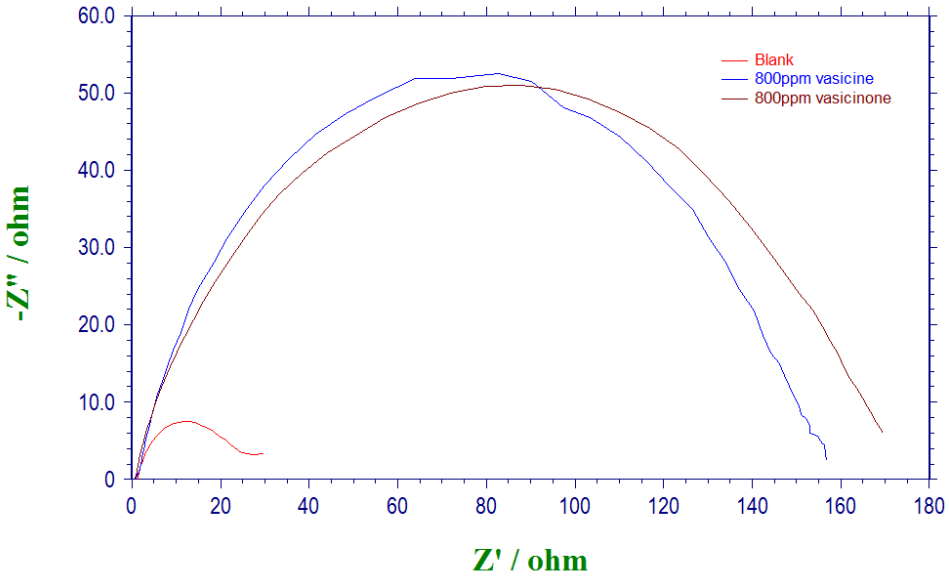

Figure-5 AC Impedance curves for mild steel in 1N HCl with vasicineand vasicinone inhibitors at 303K

AC Impedance parameters derived from Nyquist plots were given in Table four. It is discovered that the price of price switch resistance was discovered to be improved with an increase in the concentration of vasicine and the double layer capacitance (Cdl) values are reduced with an increase in inhibitor awareness. The decrease in double layer capacitance resulted from a lower within the nearby dielectric constant and the thickness of the electric double layer which showed that the vasicine became adsorbed on the metal interface. The semicircular appearance of the impedance diagram shows that the corrosion of moderate steel is managed by a fee switch among the inhibitor molecule and the slight metallic floor. The most inhibition efficiency was located to be 99.15 % in 1N HCl for a most excellent concentration of 800 ppm of vaccine at 303 K whereas in Vascinone it indicates 95.26%. The Inhibition efficiency acquired inside the AC impedance method is in desirable settlement with polarization and weight loss techniques.

CONCLUSION

The study deals with the isolation of vasicine and vasicinone extracted from *Adhatoda vasica* leaves. The inhibition effect on mild steel corrosion in 1 N HCl by weight loss method was studied at different temperatures further the kinetic study was performed at a different time interval. Electrochemical studies such as polarization and AC impedance methods were performed at optimum concentration and the results were compared with the weight loss method. Based on the above report on the weight loss method temperature varies from (303-353K), 99.03% of inhibition efficiency was shown by vasicine whereas 95.16% of inhibition efficiency was revealed by vasicinone at 303K. Both the inhibitors show better efficiency but in comparison, vasicine shows better results than vasicinone. These results were confirmed from kinetic parameter and electrochemical studies such as potentiodynamic polarization and AC impedance study.

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CONFLICT OF INTEREST

The corresponding author states that there is no conflict of interest.

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