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Inhibitory Action of Vasicinone and crude Adhatoda Vasica Leaves (AV) on the corrosion of Mild Steel in 1N HCl: A Comparative Study

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Abstract - Adhatoda vasica plant shows variety of medicinal uses in India and in many foreign countries. Likewise this plant material was utilized as corrosion inhibitor in various environment due to its eco-friendly nature. The inhibitive action of a crude extract of *Adhatoda vasica* leaves and isolated compound of Vasicinone on the corrosion of mild steel in 1N HCl has been studied by mass loss method. Based on the mass loss method electrochemical studies were performed at optimum concentration and the results were compared for both the inhibitors. The efficiency of these inhibitors was good and decreases by increasing the time. At an optimum concentration with different time intervals kinetic study was performed and it shows that inhibiton efficiency decrease with increase in time.

Keywords: **Kinetic study, Evolution, Tafel, capacitance, Nyquist plots**

I. INTRODUCTION

Electrochemical principle extensively used to determine the corrosion behavior of materials. Here the corrosion reaction can be represented by partial reactions such as metal oxidation and reduction of some reducible species of the environment both occurring simultaneously at an equal rate at the mixed potential of the reaction [1]. Corrosion reaction mainly occurs at the metal-environment interface. The electrochemical nature of corrosion can be illustrated by the corrosion of iron in hydrochloric acid. When the iron is dipped in acid a vigorous action occurs and as a result hydrogen gas is evolved and iron gets dissolved. Corrosion usually occurs due to the relative movement between a corrosive medium and the metal surface[2]. This type of corrosion is associated with systems where the corrosive fluid has high velocities. The relationship between current and potential for a corroding system in which anodic reaction is the metal dissolution reaction and the cathodic reaction is hydrogen evolution reaction can be derived by the application of electrochemical kinetic theory[3]. The inhibition of mild steel corrosion in aqueous solutions by ethyl acetate extract of *Uncaria Gambir* has been studied using different electrochemical and surface analysis. Inhibition was found to be highest at a concentration of 150 ppm in solutions with a pH of 5. The results showed that the ethyl acetate extract of Uncaria Gambir acts as a mixed-type inhibitor and could serve as an effective corrosion inhibitor on mild steel corrosion in aqueous solution [3,4]. It has been reported that the acid extract of *Solanum tuberosum* was tested as corrosion inhibitor for mild steel in 1M hydrochloric acid and sulphuric acid media using different techniques. Based on the studies the inhibition efficiency of ethanol extract of *Adhatoda vasica* leaves, isolated vasicine and vasicinone on mild steel corrosion in 1N HCl by weight loss and electrochemical methods.

II. MATERIALS AND METHODS

a. Collection of Plant Material and Authentication

Adhatoda vasica leaves were collected from Mecheri, Salem, Tamil Nadu, India, Latitude 11.832^{o} N and Longitude 77.9425^{o} E. Their authenticity was confirmed by Botanical Survey of India, Agriculture University, Coimbatore. The material was kept in shade dry for twenty days and grinded to power by using mixie.

b. Preparation of Ethanol Extract of *Adhatoda vasica* Leaves

The shaded an approximately 300 g of dry power of Adhatoda vasica leaves were taken in 500 ml plastic bottle with ethanol and shake in orbital shaker for one day at a room temperature Using Vacuum filtration process the filtrate were collected further it was concentrated under the reduced pressure using Rotary vacuum evaporator . A bulk of dark green crude was obtained from the ethanol extract of Adhatoda vasica leaves (48 g; 16 %) w/w [5].

c. Isolation of Vasicinone from Ethanol Extract of *Adhatoda Vasica* Leaves by Column

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Chromatography

After the preparation of crude sample an approximately 4 g of the fractionated crude 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). Using Chloroform and methanol eluent the column was performed. The vasicinone came out at 3% eluent as light brown solid (0.280 g, 8%) w/w, Its melting point 201^o C. whereas vasicine came out at 35% eluent as light brown solid (2.9 g; 72%) w/w. Its melting point 210^o C [6].

d. Materials Used For Corrosion Studies

The following materials were used for the corrosion studies

Mild Steel

Available mild steel specimens in the market of the following composition were used for the corrosion studies. Iron- 99.785%, Nickel-0.013%, Molybdenum-0.015%, Chromium- 0.041%, Sulphur-0.012%, Phosphorous-0.009%, Silicon-0.007%,Manganese-0.114% and Carbon-0.004%. Mild steel were subject to pickling process using concentrated sulphuric acid, Antimony (III) oxide and Tin (II) chloride dehydrated solution.

Acidic Solution

1N HCl: 1 N HCl solution was prepared by diluting 89 mL of 11.3 N AR-Grade HCl to 1000 mL using double distilled water.

Inhibitor Solutions

1000 ppm of the isolated vasicine, vasicinone and *Adhatoda vasica* extract (crude) solutions were prepared by dissolving 1gm of isolated vasicine, vasicinone and *Adhatoda vasica* extract in 30 mints respectively in one liter of 1 N HCl. This stock solution was diluted 800using 1 N HCl solution as optimum concentration.

e. Mass Loss method

Mild steel strips were cut into pieces of 5 × 1 cm^2 having the following percentage composition Iron- 99.785%, Nickel-0.013%, Molybdenum-0.015%, Chromium-0.041%, Sulphur-0.012%, Phosphorous-0.009%, Silicon-0.007%,Manganese-0.114% and Carbon-0.004%. Mild steel were subject to pickling process using Concentrated sulphuric acid, Antimony(III) oxide and Tin (II) chloride dehydrated solution. Using the following formula the weight loss was calculated.

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

$$\text{Inhibition efficiency IE\%} = \frac{W_U - W_I}{W_U} \times 100$$

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

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.

f. Electrochemical studies

Using conventional three electrode system electrochemical measurements were carried out. 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.

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). Impedance value were calculated using the following formula

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

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

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 vasicinone and crude extract of *Adhatoda vasica* 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. The plot of E Vs. log I was made from which corrosion current density, corrosion potential, anodic and cathodic Tafel slopes values were calculated.

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

III. RESULT AND DISCUSSION

a. Mass loss data:

The rate of corrosion and inhibiton effectiveness of mild steel in 1N HCl was performed in isolated compound of Vasicinone from ethanol extract of AV and crude extract of AV was given in **Figure I (a & b)**. This study was carried at a room temperature. It was observed from the graph that the rate of corr9osion decreases with increases

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in concentration of the inhibitors. The values of corrosion rate and inhibition efficiency in absence and presence of difference concentration of inhibitor used in 1N HCl solutions at 303K for one hour were given in Table 1.

Table-1. Comparison of mild steel in 1N HCl using isolated Vasicinone inhibitor and crude AV inhibitor

Concentrat-ion of the Inhibitor (PPM)	Corrosion Rate (mmpy)		InhibitonEfficiency (%)	
	Crude AV	Vasicinone	Crude AV	Vasicinone
Blank	38.52	37.21	---	---
100	36.24	30.10	77.56	80.16
200	33.45	24.85	79.21	82.89
300	30.28	23.13	81.49	83.03
400	28.74	19.84	82.97	84.02
500	25.42	17.32	83.64	86.26
600	21.65	15.12	85.10	87.01
700	19.75	12.98	87.33	89.23
800	16.48	11.85	89.31	91.25

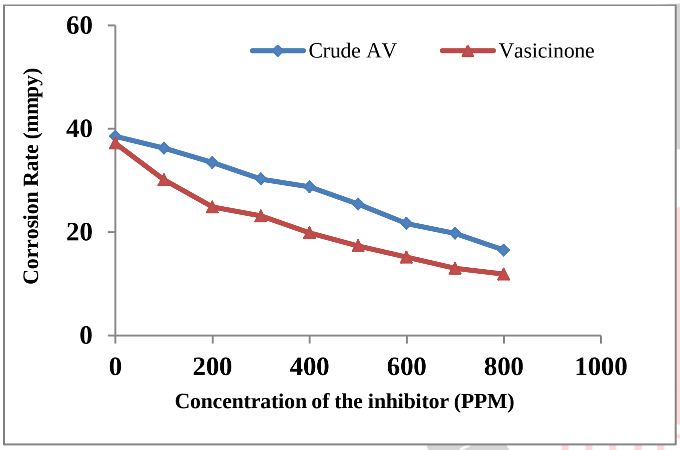

Figure-I (a) Comparison of Corrosion Rate of mild steel in 1N HCl using Vasicinone and Crude AV inhibitor

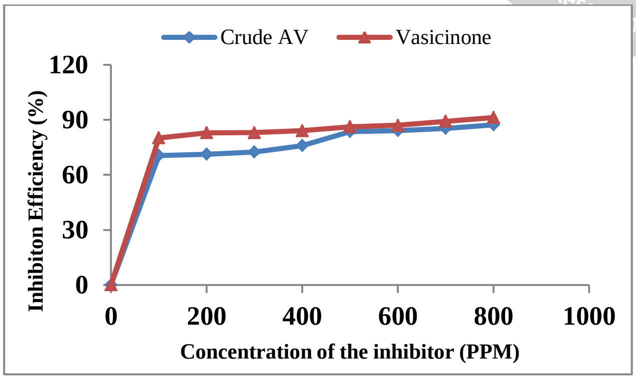

Figure-I (b) Comparison of Inhibition Efficiency of mild steel in 1N HCl using Vasicinone and Crude AV inhibitor

b. Comparison on Effect of immersion time for ethanol extract of *Adhatoda vasica* leaves and Vasicinone inhibitor at optimum concentration

The effect of immersion time from 1hr to 24 hrs was studied by using weight loss method and a graph obtained by considering time Vs. IE is shown in Figure-II

The inhibition efficiency of ethanol extract of *Adhatoda vasica* leaves and Vasicinone at an optimum concentration (800 ppm) for mild steel corrosion in 1 N HCl was shown in Table-II. It can be seen that the inhibition efficiency was found to be decreased in both inhibitors. But when comparing both inhibitors Vasicinone shows better inhibiton efficiency 95.03% at one hour [7].

Table-II Comparison of AV Crude and Vasicinone inhibitor on 1N HCl with an optimum concentration (800 ppm) at different time interval

System (800 ppm)	Inhibition efficiency (%) Time in (hr)								
	1	2	3	4	5	6	12	18	24
Conc. of Adhatoda vasica extract	92.00	91.14	90.03	89.00	88.02	87.55	85.97	84.61	83.51
Conc. of Vasicinone	95.03	94.71	93.63	92.83	92.56	90.92	89.72	88.21	86.75

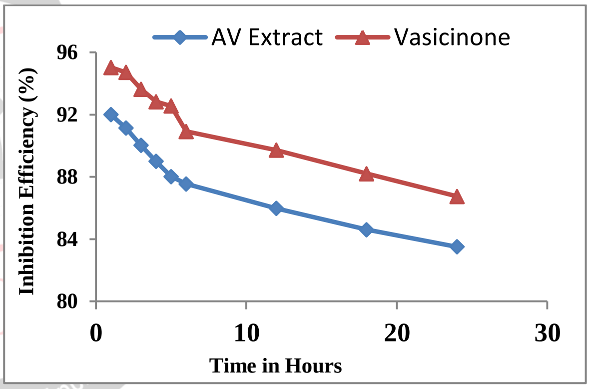

Figure-II Comparison of AV Crude and Vasicinone inhibitor on 1N HCl with an optimum concentration (800 ppm) at different time interval

c. Potentiodynamic Polarization Studies

The polarization curves for mild steel in 1N HCl (30 ± 1°C) without and with an optimum concentration of ethanol extract of *Adhatoda vasica* leaves and isolated material of Vasicinone are shown in Figure-II. The electrochemical parameters derived from the curves are given in Table-III. The E_{corr} values are shifted to more positive in the presence of *Adhatoda vasica* ethanol extract and Vasicinone. It is observed that the optimum concentration of both inhibitor has a little influence on values of anodic Tafel constant and appreciable influence on the values of cathodic Tafel constant, indicating that inhibitor may change the mechanism of cathodic reaction and may not affect the anodic dissolution mechanism[8].

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The appreciable increase in the cathodic Tafel values with increase in the *Adhatoda vasica* ethanol extract and Vasicinone concentration indicates that hydrogen evolution is suppressed due to the blockage of sites at the metal surface by the extract molecules[9]. This can be attributed to the formation of very closely adherent adsorbed film on the metal surface.

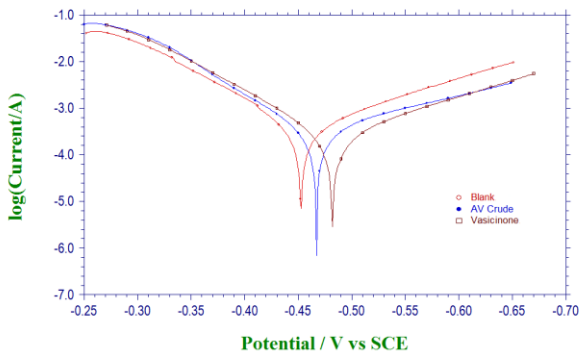

Figure-III Potentiodynamic polarization curves for mild steel in 1N HCl with an optimum concentration of AV Crude and Vasicinone inhibitor

Evidence exisited from patentiodyamic polarazation studies revealed that the adsorption over the mild steel surface by the inhibitors makes a physical barrier for the mass and charge transfer leading to the high degree of protection to the metal surface. From the mass loss data an optimum concentration was choosen 800 ppm for both the inhibitors. From the data it shows that both inhibitor were good in agrement of preventing mild steel, the maximum inhibiton efficiency 95.17% was observed from isolated compound Vasicinone.

Table-III Potentiodynamic polarization parameters for mild steel corrosion in 1N HCl with an optimum concentration of Crude AV extract and Vasicinone

Inhibitor used at optimum concentration (800ppm)	E_{corr} (mV)	Tafel slopes (mV/dec)		I_{corr} (μA/cm^{-2})	Inhibition efficiency (%)
		-βa	-βc		
Blank	-0.453	5.50	3.56	1550	-
Crude AV extract	-0.498	6.16	4.36	29.92	92.19
Isolated Vasicinone	-0.498	6.16	4.36	29.92	95.17

d. AC Impedance Studies

Impedance diagram obtained for the frequency range from 10 kHz to 0.01Hz with respect to the open circuit potential (OCP) of mild steel in 1N HCl with and without *Adhatoda vasica* ethanol extract and isolated compound Vasicinone are shown in Figure-IV. AC Impedance parameters derived from Nyquist plots were given in Table-IV. It is observed that the value of charge transfer resistance was found to be increased with increase in the concentration of inhibitors and the double layer capacitance (Cdl) values are decreased with increase in inhibitors concentration[10]. A significant charge transfer resistance is associated with slowly corroding systems. Also, improved inhibitor protection is associated with a decrease in metal capacitance. The decrease in double layer capacitance which resulted from a decrease in the local dielectric constant and the thickness of the electrical double layer confirmed that the active adsorption of inhibitors at the metal interface[11]. The optimum inhibition efficiency was found to be 92.26 % in 1N HCl for 800 ppm of *Adhatoda vasica* ethanol extract at 303 K. The inhibition efficiency obtained in AC impedance method is in good agreement with polarization and weight loss methods.

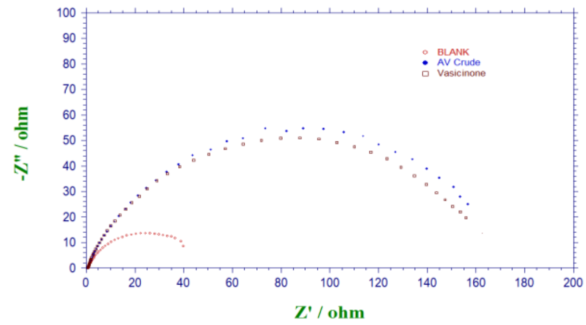

Figure-IV AC Impedance curves for mild steel in 1N HCl with an optimum concentration of Crude Av extract and Vasicinone inhibitor.

Table-III AC Impedance parameters mild steel in 1N HCl with an optimum concentration of Crude Av extract and Vasicinone inhibitor.

Inhibitor used at optimum concentration (800ppm)	R_{ct} (Ohm cm^2)	C_{dl} (μ F/cm^2)	Inhibition efficiency (%)
Blank	12	231.02	-
Crude AV extract	390	83.20	92.26
Isolated Vasicinone	320	81.36	95.26

IV. CONCLUSION

The ethanol extract of Crude *Adhatoda vasica* leaves and their isolated compounds vasicinone showed good performance as corrosion inhibitor in 1N HCl at 303 K. Due to the alkaloids present in the medium causes an insoluble protective film which suppresses the metal dissolution reaction. The Inhibitor Efficiency was decreased at the different time intervals. The maximum inhibition efficiency of *Adhatoda vasica* leaves and vasicinone were 89.31 % and 91.25% in mass loss data were calculated. Further the study was continued with different time intervals, by increasing in time from 1 hour to 24 Hours the efficiency of the inhibitor was decreased by increasing in time at 1N HCl at303K. Using electrochemical analysis like potentiodynamic polarization and AC impedance studies the efficiency of both the

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inhibitors were analysed at optimum concentration. The result shows a good agreement as per the mass loss data. From this study it was concluded that isolated material Vasicinone shows better inhibiton efficiency than ethanol extract of Crude AV leaves.

REFERENCE

[1] Abd El Rehim SS, Hassan HH & Amin MA, 'Corrosion inhibition of aluminium by 1,1(lauryl amido) propyl ammonium chloride in HCl solution', Mater. Chem. Phys., vol.70, pp. 64-72,2001.

[2] Abdel-Gaber A.M., Abd-El-Nabey. B.A., Abd-El-Nabey .I.M., Sidahmed, A.M., & El-Zayady, M.S, "Inhibitive action of some plant extracts on the corrosion of steel in acidic media", Corrosion Science, vol. 48, pp. 2765-2779,2006.

[3] Hazwan Hussin. M & Jain Kassim. M, "Electrochemical studies of mild steel corrosion inhibition in aqueous solution by Uncaria gambir extract", Journal of Physical Science, vol. 21, no.1, pp. 1-13, 2010.

[4] Pandian, Bothi Raja, Mathur Gopalakrishnan & Sethuraman "Solanum Tuberosum as an inhibitor of mild steel corrosion in acid media" Iranian Journal Chem. Chem. Eng. vol. 28, no. 1, pp. 77-84, 2009.

[5] Thailan.V, Kannan.K and Sivaperumal.G, "Effect of optimum concentration and temperature on inhibition of vasicine for mild steel corrosion in 1N hydrochloric acid", J. Chem. Pharm. Res., 7(8):975-986, 2015.

[6] Thailan.V, Kannan.K and Ganavel.G, "Isolation, characterization and inhibition effect of vasicine on mild steel corrosion in 1N HCl", J. Chem. Pharm. Res., 7(7):808-817,2015.

[7] Prabhu RA, Venkatesha VT & Shanbhag VA, 'Carmine and fast green as corrosion inhibitors for mild steel in hydrochloric acid solution', J. Iran. Chem. Soc., vol.6, pp. 353-363,2009.

[8] Ahmed Y Musa, 'Investigation of ethylenediaminetetra acetic acid as corrosion inhibitor for mild steel in 1M hydrochloric acid', Mod. Appl. Sci., vol. 3, pp. 91-94, 2009.

[9] Shyamala, M & Kasthuri, PK, 'The inhibitory action of the extracts of adhatoda avasica, eclipta alba and centella asiaticaon the corrosion of mild steel in hydrochloric acid medium a comparative study', International Journal of Corrosion, pp. 13, 2012.

[10] Mu GN, Li X & Li F, 'Synergistic inhibition between o-phenanthroline and chloride ion on cold rolled steel corrosion in phosphoric acid', Mater. Chem. Phys., vol. 86, pp. 59-68,2004.

[11] Oldham KB & Mansfeld F, 'Corrosion rate from polarization curves', Corros. Sci., vol.13, pp. 813-819,1973.

 DOI : 10.35291/2454-9150.2019.0384