Effect of *Plectranthus amboinicus (*Indian borage*)* on the corrosion of carbon steel in well water

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ABSTRACT

Corrosion inhibition effect of plectranthus amboinicus on carbon steel in well water. The inhibition effect of plectranthus Amboinicus leaves extract on the corrosion of carbon steel was studied by weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy and a surface study like scanning electron microscope (SEM). The potentiodynamic polarization studies reveal that the extract behaves as a mixed type inhibitor. The effect of temperature on the inhibition of corrosion was also studied. Activation energy (Ea), enthalpy (ΔH) and heat of adsorption (Qads) were calculated thermodynamically.

Keywords: **PDP, EIS, Langmuir isotherm, SEM, Thermodynamic parameters**

1. INTRODUCTION

An inhibitor is a substance (or a combination of substances) added in a very low concentration to treat the surface of a metal that is exposed to a corrosive environment that terminates or diminishes the corrosion of a metal. These are also known as site blocking elements, blocking species or adsorption site blockers, due to their adsorptive properties **[1].**The expansion of high atomic weight natural mixes, for example, surfactants to battle erosion of carbon steel has discovered wide application in numerous fields. It has been accounted for that these mixes have high restraint efficiencies for steel consumption [2-4]. Erosion is the moderate and constant annihilation of a metal or combination by the climate. Corrosion is the cancer of metals due to thermodynamic instability. Metals and alloys are generally used as fabrication or construction materials. In the event that the metal or compound structures are not appropriately kept up, they weaken gradually by the activity of barometrical gases, dampness and different synthetic substances. Due to low cost, availability etc., steel is considered in wide area of practical applications such as water pipelines, cooling water systems, RO water, and boilers. Carbon steel finds a lot of application in industries like metal finishing, boiler scale removal, pickling baths, etc. Carbon steel rusts when in contact with any aqueous medium. The utilization of inhibitors is probably the best strategy for securing metals against consumption. Corrosion is a chemical or electrochemical process in nature with four components which include: anode, cathode, electrolyte and some direct electrical connection between the anode and cathode. The adsorbed inhibitor at that point demonstrations to slow consumption measure by either: expanding the anodic or cathodic polarization conduct or decreasing the development or dispersion of particles to the metallic surface. Consumption inhibitors are utilized to forestall the

impact of erosion in such cases. The majority of well-known inhibitors are organic compounds containing heteroatom, such as O, N, S and multiple bonds [5]

2. EXPERIMENTAL

The *Plectranthus amboinicus* leaves extract (PA) were collected and cut into small pieces and they were dried in an air oven at 70°C for 1h. They were ground well into powder. From this, 20g of the sample was refluxed with in 100ml distilled water for 1h. The refluxed solution was filtered carefully and the filtrates were heated on water bath to evaporate fully the moisture content to get the dried inhibitor sample **[6].** The inhibitor concentrations of 200, 400, 600 and 800 were prepared using well water.

2.1 WEIGHT LOSS MEASUREMENTS

Weight loss measurements were carried out as described elsewhere **[7].**Carbon steel specimens were immersed in 100ml of inhibited and uninhibited solutions for 1 hrs at 30°C. The corrosion rate (mmpy), inhibition efficiency **[8]**,surface coverage **[9].** Were calculated using the following equations, Corrosion Rate (mmpy) = $\frac{\mathbf{kW}}{\mathbf{ATD}}$

Where, K = 87.6×10^4 (constant), W = weight loss (mg), A = area (cm), T = time (h) and D = density in (g/cm^3)

Inhibition Efficiency (%) = $W_B - W_I / W_B \times 100$[5]. Where, W_B and W_I are weight loss per unit time in the absence and presence of PA

$$\mathbf{Surface\,Coverage}(\theta) = \frac{W_B - W_1}{W_B}$$

Where, W_B is the weight loss in the absence of the extract, W_1 is the weight loss in the presence of the extract. The information was tried graphically for fitting a reasonable isotherm. The Langmuir adsorption isotherm is given by:

$$C/\theta = 1/K_{ads} + C$$

Where, C is the concentration of the inhibitor, K_{ads} is the equilibrium constant and θ is degree of the surface coverage by the inhibitor. Langmuir adsorption isotherm is best applicable at 303K. This confirms that the adsorption behaviour of the inhibitor is strongly influenced by temperatures. A plot of C/θ vs. C at various temperatures is shown figure (Fig.2). The resulting parallel lines at 303K confirm that inhibition was due to the adsorption of PA on the metal surface **[10].**

3. RESULTS AND DISCUSSION

The percentage of inhibition efficiency (IE %) of the extract from weight loss method at different concentrations of *Plectranthus amboinicus* leaves extract *(PA)* at 303K are shown in the table (Table 1 and in the figure (Fig. 1).

Table - 1

Effect of time on inhibition efficiency of PA

Conc. of inhibitor (ppm)	Time (h)			
	IE%			
	1	3	5	10
200	71.9	63.9	59.2	54.0
400	86.4	88.7	85.0	70.4
600	90.7	92.4	90.9	81.9
800	92.4	93.5	94.1	90.6

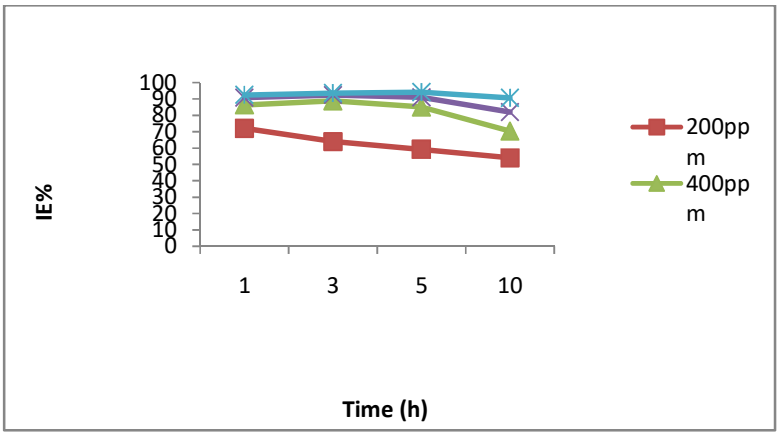


Figure – 1: Influence of immersion time of PA on the inhibition efficiency of carbon steel in well water

3.1 Langmuir adsorption isotherm

Straight lines are observed in the graph (Fig. 2). The linearity indicates that adsorption of inhibitors on the metal surface obeys Langmuir Adsorption isotherm. The deviation of the slopes from unity indicates that there is attraction or repulsion in the adsorbed layer of inhibitor on the carbon steel surface**.**

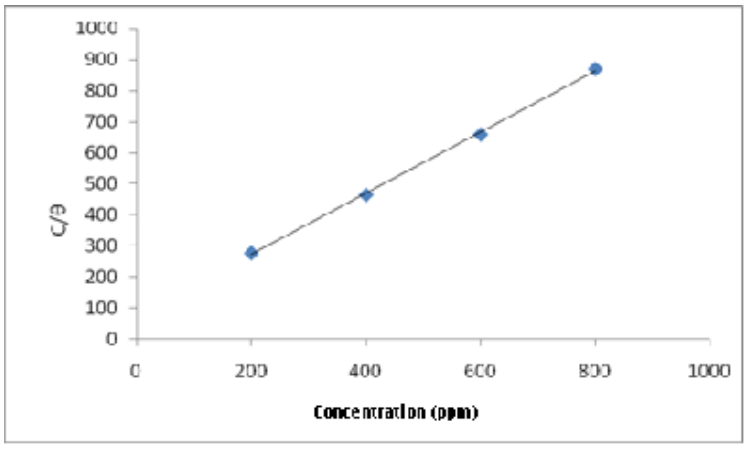


Figure – 2: Langmuir adsorption isotherm of PA at 303K

The percentage of inhibition efficiency (IE %) of the extract from weight loss method at different concentrations and different temparature of *Plectranthusamboinicus*leaves extract *(PA)* are shown in the table (Table 2 and in the figure (Fig. 3).

Table-2
Effect of temperature on inhibition efficiency of PA

Conc. of inhibitor (ppm)	Temperature (K)		
	IE%		
	303	323	343
200	71.9	46.6	32.8
400	86.4	71.9	51.9
600	90.7	84.3	82.7
800	92.4	88.0	85.8

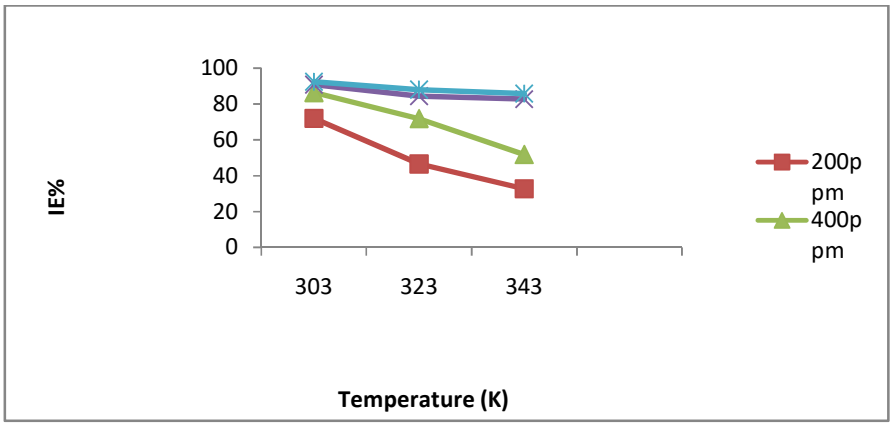


Figure – 3: Influence of various temperature of PA on the inhibition efficiency of carbon steel in well water

3.2 KINETIC AND THERMODYNAMIC PARAMETERS

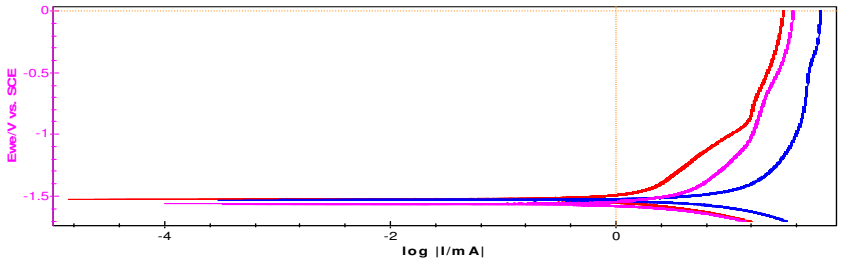
Thermodynamic parameters for the adsorption of PA
On carbon steel [*Temperature range 303K -323K]*
Table-3

Conc. Of inhibitor (ppm)	E_a ($kJmol^{-1}$)	ΔH ($kJmol^{-1}$)	Q_{ads} ($kJmol^{-1}$)
Blank	49.17	46.57	-
200	75.38	72.78	-43.94
400	78.78	76.18	-29.59
600	70.30	67.69	-24.08
800	67.92	65.32	-20.73

The energy of activation, E_a and enthalpy, ΔH values calculated for the corrosion processes in The Absence and Presence of the Inhibitor Are Given in the Table (Table 3). The E_a and ΔH Values for the corrosion processes, in the presence of inhibitors are higher (more positive) than those of the blank. Higher the values of E_a and ΔH, less spontaneous are the corrosion processes i.e. corrosion is decreased in the presence of inhibitors. The negative values of heat of adsorption (Q_{ads}) prove that the adsorption of the inhibitors on the metal surface is a spontaneous process

3.3 ELECTROCHEMICAL STUDIES AND ANALYSIS OF SEM IMAGES

The Potentiodynamic Polarization Curves (Tafel plots) for the blank, 400 and 800ppm concentration of PA are given in Figures (Fig.6 & 4) the corrosion potential values remain nearly unaltered. The trends in the variations in the anodic and cathodic slopes also indicate that PA actsas mixed type of inhibitor.



Blue: Blank; Pink: 400 ppm; Red: 800 ppm
Figure - 4: Polarization study (Tafel plot) for blank and PA

The AC impedance Nyquist graphs are given in Figures (Fig.4). The Nyquist data are given in the (Table-4). From the Nyquist data it can be seen that there is an increase in the charge transfer resistance or polarization resistance (R_{ct}) values and decrease in double layer capacitance (C_{dl}) values in presence of inhibitors, indicating that there is a stable adsorption layer formed on the carbon metal surface. The resistance values obtained from the Bode plots of blank and inhibited systems [Fig.6, 7, &8]. The genuine part (Z) and fanciful root(Z') at the cell impedance were estimated in ohms at different frequencies .The values of charge transfer resistance R_t and the double layer capacitance C_{dl} **[11]**were calculated.

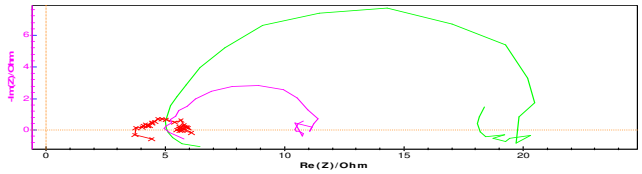
$R_t = (R_s + R_t)-R_s$

Where, R_s = Solution resistance

$C_{dl} = 1/2\pi R_t f_{max}$

Where

f_{max} = Maximum frequency



Red: Blank; Pink: 400 ppm; Green: 800 ppm

Figure – 5: Impedance study (Nyquist plot) of blank and PA

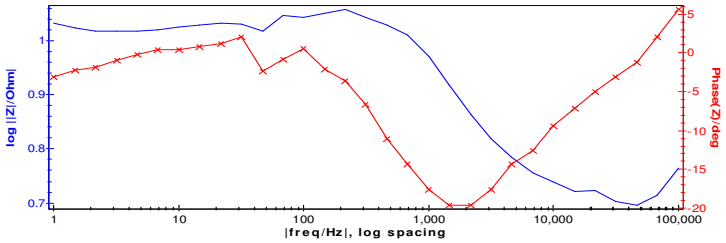


Figure – 6: Bode plot for blank

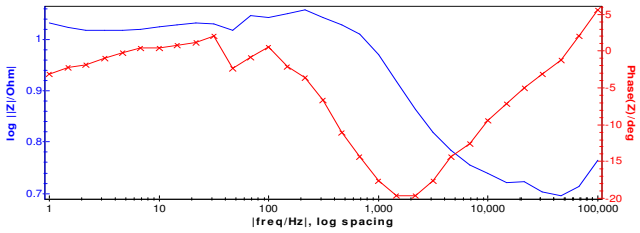


Figure – 7: Bode plot of PA (400ppm)

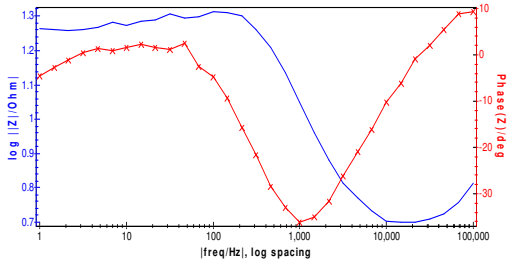


Figure – 8: Bode plot of PA (800ppm)

Table – 4
Data from electrochemical studies

Inhibitor (ppm)	Tafel plot				Nyquist plot		Bode plot
	E_{corr} (mV)	I_{corr} (mA)	β_a (mV)/dec	β_c (mV)/dec	R_{ct} (ohm)	C_{dl} (µF)	Z (ohm)
Blank	-1535.452	7022.972	406.7	246.7	1.796	130.1	0.775
400(PA)	-1568.349	2430.812	449.0	175.8	5.455	19.88	1.03
800(PA)	-1515.523	1463.839	526.4	180.1	13.83	24.71	1.26

3.4Analysis of SEM images

Surface examination of the carbon steel specimens was made using the Scanning Electron Microscope images Figures (Fig. 9 to 11). The SEM studies showed that the inhibited carbon steel surface was found smoother than the uninhibited surface due to the formation of protective film on the inhibited carbon steel surface SEM technique provides a pictorial representation of the surface. To understand the nature of the surface film in the presence and absence of inhibitors and the extent of corrosion products of carbon steel the SEM micrographs of the surface are examined.

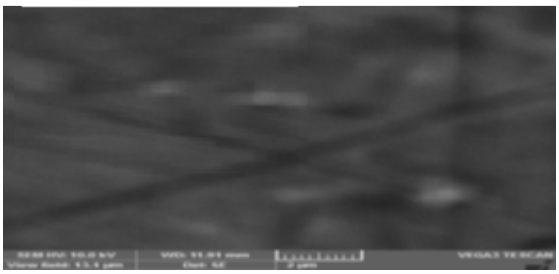


Figure – 9: SEM image of carbon steelimmersedin well water (pure metal)

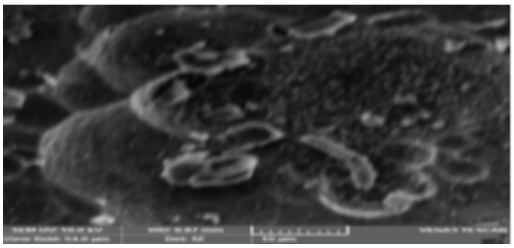


Figure – 10: SEM image of carbon steel immersed in well water (blank)

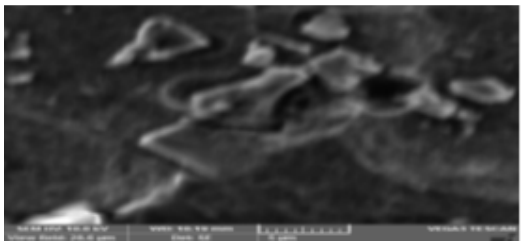


Figure – 11: SEM image of carbon steel immersed in well water for PA

CONCLUSION

The corrosion inhibition of carbon steel by using *Plectranthus amboinicus* leaves extract in well water. When PA is used as inhibitor, it has a maximum of 88.7% IE for 3h duration at 303K of 400ppm concentration. When PA is used as inhibitor, it has a maximum of 92.4% IE for 1h duration at 303K of 800ppm concentration. The effect of immersion period on the IE was also studied and discussed. The effect of temperature on the IE was evaluated from which E_a and ΔH for the corrosion process was justified. Q_{ads} values are negative in sign indicating the spontaneous of adsorption of the inhibitors on the carbon steel surface. Polarization studies

reveal that PA acts as mixed type of inhibitor. SEM and impedance studies confirmed the formation of adsorption layer of the complexes of the inhibitors on the metal surface.

REFERENCES

[1] *E. Protopopofft and P.Marcus, "Electrochemistry and materials science of cathodic hydrogen absorption", J.ElectrochemSoc ,vol.94, no. 21,(**1995**) pp. 374-389*

[2] *A. M.Al-Sabagh,M. A.Migahed, MRSC, "Reactivity of polyester aliphatic amine surfactants as corrosion inhibitors for carbon steel in formation water(deep well water)", vol. 48, no. 4, **(2006)**, pp.813-828.*

[3] *M.Elachour,M.S. Hajji, S.Kertit, E.M. Essassi, M.Salem, and R.Coudert, "Some surfactants in the series of 2-(alkyldimethylammonio) alkanol bromides as inhibitors of the corrosion of iron in acid chloride solution", Corrosion Science, vol. 37, no. 3, **(1995)**, pp.381-389.*

[4] *E.EssassiM.Elachouri, M.S. Hajji, M.Salem, S.Kertit, J. Aride, and R.Coudert,"Some non-ionic surfactants as inhibitors of the corrosion of iron in acid chloride solutions", Corrosion Science,, vol. 52, no. 2, **(1996)**, pp.103-108.*

[5] *Bothi Raja, MathurGopalakrishnanSethuraman,"Inhibitive effect of black pepper extract on the sulphuric acid corrosion of mild steel", Mater.Lett.vol. 62, no. 2977, **(2008)**.*

[6] *Olusegun K Abiola, JOE Otaigbe, OJ Kio, GossipiumhirsutumL.,"Extracts as green corrosion inhibitor for aluminium in NaOHsolution",Corrosion Science,vol. 51, no. 8, **(2009)**, pp. 1879-1881.*

[7] *T.Gowrani, K.Parameswari, A.Selvaraj, and A.Subramania,"The influence of benzoyl hydrazine and some of its substituents on corrosion inhibition of carbon steel in sulphuric acid solution", Anti-Corros.Methods Mater,vol. 62, no. 2977, **(2008)**.*

[8] *K.LakshmiPrabha, ShameelaRajam, B.R.Venkatraman,"The effect of aeglemarmelos leaves extract on corrosion inhibition of aluminium in alkaline solution, Der ChemicaSinica, vol. 3, no. 1, **(2012)**, pp. 114-123.*

[9] *HariharaputhranmR.Subramanian, A.AntonyA.A.Sankar, P.M.Gopalan, A.Vasudevan, T., and S.V.Iyer,"Influence of substituent groups on performance of N-Benzylidine phenylamine-N-oxide as corrosion inhibitor of mild steel in acidic solutions", British Corrosion Journal, vol. 33, no. 3, **(1998)**, pp. 214-218.*

[10] *P.Kalaivani, P.HillaiArasu, S.Rajendaren,"Inhibition Performance on the Surface of aluminium in alkaline medium", Int.JChem Tech Res,vol. 5, no.4, **(2013)**, pp. 1714-1723.*