

Efficacy of sprouted seed extracts of *Phaseolus aureus* on the corrosion inhibition of mild steel in 1M HCl

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ABSTRACT

Corrosion inhibitors play a major role in the cost effective control of corrosion. Because of the toxic nature and high cost of chemicals plant extracts are currently used as inhibitors. In the current study, efforts are taken to study the role of seed extracts of *Phaseolus aureus* on corrosion of mild steel in 1M HCl by weight loss method and potentiodynamic polarization technique. The Potentiodynamic polarization results reveal that the seed extract behaved like mixed type inhibitor. Maximum inhibition efficiency of *Phaseolus aureus* in 1M HCl was found to be 93%.

Keywords: Corrosion, *Phaseolus aureus*, HCl medium, mild steel.

INTRODUCTION

One of the methods to protect metals or alloys against corrosion is addition of species to the solution in contact with the surface in order to inhibit corrosion reaction and reduce the corrosion rate¹. The serious consequence of the corrosion process has become a problem of worldwide significance. Characterizing and solving corrosion problem is a challenging task. Natural oil extracted from Pennyroyal Mint was evaluated as corrosion inhibitor of steel in molar hydrochloric acid². The production of "Green" or low toxicity formulations has become the goal of most inhibitor developers. Extract of different parts of *Carica papaya* (seeds, leaves, heart wood and bark) were proved eco friendly corrosion inhibitors³. Numerous naturally occurring substances are evaluated as corrosion inhibitors, mainly due to their biodegradability and ecofriendliness. Hence the present study has been

undertaken to investigate the inhibitive action of seed extract of *Phaseolus aureus* in 1M HCl.

MATERIAL AND METHODS

Mild steel specimens of chemical composition C- 0.048% , Mn – 0.035% , silicon- 0.029% , S- 0.025% , Ni – 0.019% , Cr – 0.050% , Fe remainder were used for the entire study. For weight loss study MS specimens of size 1cm X 5 cm were used. MS specimens with an exposed area of 1 cm² were used for all electrochemical study. The specimens were mechanically polished, degreased, dried and stored in a dessicator.

Preparations of plant extract

25gms of dried and powdered sprouted seeds of *Phaseolus aureus* (SPA) were refluxed with 500 ml of 1 M HCl for 3 hours and kept overnight. The cooled extract was filtered and made up to 500ml (5% extract).

Weight loss measurement

The polished and weighed MS specimens were suspended in the corrosion medium (1M HCl) for various duration time such as ½ hr, 3 hrs, 6 hrs, 12 hrs, 24 hrs and 48 hrs and at various temperatures such as 308K, 318K, 328K, 338K with and without inhibitor in different concentration. Then the MS specimens were thoroughly washed with water, dried well and reweighed. The percentage of inhibition efficiency and (%IE), rate of corrosion were calculated.

Polarization techniques

Potentiodynamically the polarization curves were recorded using computerized solartron 1284Z for various concentrations of SPA extract in 1M HCl. The cell was constructed with three

electrodes in a beaker with Pt electrode as the counter electrode, a saturated calomel electrode as the reference electrode and MS as the working electrode with 1cm² working area. All the experiments were performed at room temperature.

RESULTS AND DISCUSSION

Effect of concentration

Values of percentage inhibition efficiency for the corrosion of MS in 1M HCl in the presence of various concentrations of the extract for different periods of immersion time are depicted in Table 1. The inhibition increases with concentration of the inhibitor for different periods of immersion Fig. 1. The IE increased proportionally with the concentration of the inhibitor.

Table 1: Variation of IE with time and temperature

Conc.of Theinhibitor (%)	Inhibition Efficiency (%)									
	Immersion Time (In Hours)						Temperature (° K)			
	0.5	3	6	12	24	48	318	328	338	348
0.1	82	85	90	93	96	90	88	88	65	49
0.2	84	88	91	93	97	94	90	89	73	89
0.3	87	89	92	94	97	94	91	93	79	91
0.4	87	89	92	95	97	95	93	93	80	92
0.5	88	90	93	95	98	95	93	94	80	92
0.6	89	91	93	95	98	95	94	94	80	93
0.7	90	92	95	96	98	96	94	94	81	93

Table 2: Variation of thermodynamic parameters with concentration

Conc. of the Inhibitor (%)	Activation Energy E _a =KJ/mol	Free energy of adsorption -ΔG=KJ/mol					Heat of adsorption ΔH=KJ/mol	Entropy change ΔS=J deg ⁻¹ mol ⁻¹
		308 K	318K	328 K	338 K	348K		
blank	44.73	-	-	-	-	-	-	
0.1	59.78	20.14	21.99	22.69	19.55	24.58	0.666	
0.2	50.80	18.79	20.66	21.15	18.63	23.24	-2.019	
0.3	51.87	18.24	20.12	21.41	18.40	22.32	-1.025	
0.4	52.17	17.68	19.93	20.74	17.73	21.68	-0.528	
0.5	51.62	17.28	19.48	20.50	17.17	21.14	-0.280	
0.6	50.84	17.02	19.22	20.09	16.76	21.00	-0.778	
0.7	47.03	17.07	19.23	19.76	16.44	20.77	-3.533	

In HCl medium the maximum efficiency (99.26%) was noticed with 0.7% concentration at 12hrs. This infers that there is a strong correlation between IE and concentration of the inhibitors and the enhanced IE at high concentration can be attributed to increase in surface area coverage of the inhibitor molecules on the mild steel surface.

Effect of immersion time

The results evaluated for the variation of weight loss with exposure time for the mild steel with and without inhibitor are presented in Table 1. From the table it can be seen that there is an increase in inhibition efficiency as the time of immersion increases which may attributed to the formations of strong inhibitor layer which prevents

the attack of acid on metal surface⁽⁵⁾.

Effect of temperature

Table 1 lists the IE of SPA in 1M HCl at different temperatures. From the Table it is noted that, as temperature increased the IE was found to increase Fig. 2.

The enhancement of IE at higher temperature may be due to

- Higher activation energy is available for adsorption at higher temperatures.
- Enhancement in the surface coverage at higher temperature by the inhibitor molecules on MS surface.

Table 3: Corrosion parameters of ms in 1m HCL in the presence of extract of SPA

S. No	C.R. (mpy)	b _a mV/dec	b _c mV/dec	I _{corr} (mA/cm ²)	IE(%)	E _{corr} mV/sec	Rp (Ω /cm ²)	IE(%)
1	2670.9	148.57	121.84	0.0058	-	-0.524	3.911	-
2	84.59	69.58	60.739	0.0001	86.47	-0.485	22.37	82.52
3	142.56	86.57	73.424	0.0003	94.66	-0.484	26.08	85.00
4	361.34	111.13	85.929	0.0007	97.24	-0.486	34.58	88.69

Adsorption Isotherm

In acid corrosion generally, it is assumed that inhibitors act through a process of adsorption on the metal surface⁶. An adsorption isotherm gives relationship between the coverage of an interface with an adsorbed species (the amount adsorbed) and the concentration of the species in solution. From the suitable adsorption isotherm plot, the free energy of adsorption of the inhibitor is obtained.

A plot of $\log \theta/1-\theta$ vs $\log C$ gives a straight line indicating that SPA under study obey Langmuir adsorption isotherm. This indicates that the main process of inhibition is adsorption. This may also infer that there is a molecular interaction among the adsorbed particles and the metal surface.

Thermodynamic and kinetic parameters

Thermodynamic parameter ΔG , ΔH and

ΔS for adsorption of inhibitor were calculated using the expression⁷ and listed in table 2. The free energy values are negative which shows a strong interaction of inhibitor molecules and a spontaneous adsorption of the inhibitor on the metal surface⁸. The values of ΔH and ΔS infer that the adsorption of SPA extract on MS is enthalpic and entropic controlled.

Energy of activation

Energy of activation (E_a) values has been evaluated from Arrhenius equation. In the presence of SPA extract the E_a values of inhibitor system are found be higher than the uninhibited system. The high E_a values indicate an efficient inhibiting action of the inhibitor⁹. Higher activation energy for the corrosion process in the presence of inhibitor leads to conclusion that probably the inhibitor is found to be adsorbed on the surface by specific adsorption process.

Electrochemical Measurements

Polarization Measurement is an important research tool in the investigation of a variety of electrochemical phenomena. Such measurements permit studies of the reaction mechanism and the kinetics of corrosion phenomena and the metal deposition. All electrochemical measurement, were made using a three electrode glass cell connected to a solartron 1284Z potentiostat controlled by a PC. The software package used was corrware. The corrosion kinetic parameters such as E_{corr} , I_{corr} , Tafel constant b_a , b_c are tabulated in Table 3.

A similar displacement of cathodic and anodic Tafel lines indicated that the inhibitor inhibited both the hydrogen evolution and the metal dissolution process. Thus this inhibitor acted as mixed type inhibitor⁹. Tafel slopes of b_a and b_c for MS in the presence of inhibitor change uniformly. This behaviour indicated the molecules are adsorbed on the both the anodic and cathodic sites acting as a mixed type of inhibitor. No significant change in E_{corr} values also supported mixed behaviour of the inhibitor.

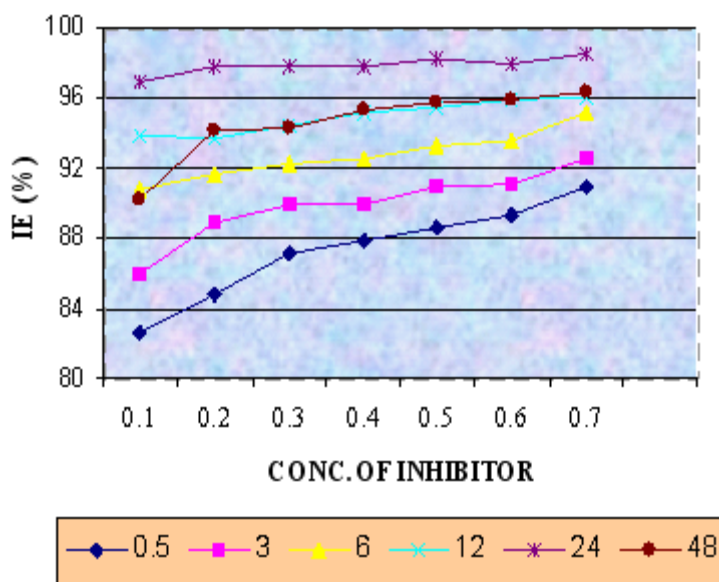


Fig. 1: Optimisation of time with IE

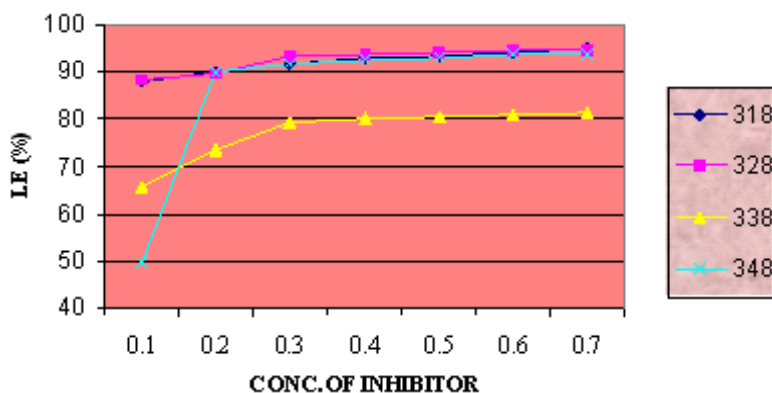


Fig. 2: Variation of IE at higher temperature

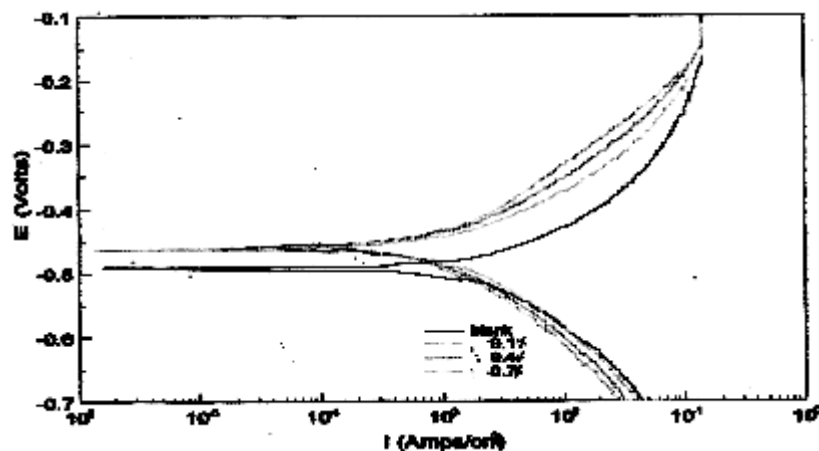


Fig. 3: Potentiodynamic polarisation curves for corrosion of mild steel (P.A. in 1M HCl)

Phytochemical constituents present in the SPA (Ref: Duke's phyto chemical database)

It has been observed that the adsorption of corrosion inhibitors depends mainly on certain phyto chemical properties of the molecule such as functional groups, steric factors, aromaticity, and electron density at the donor atoms and π orbital character of donating electrons. Alanine, alpha linolenic acid, arachidic acid, arginine, arsenic, ascarbic acid, ascorbigen, ash, aspartic acid, behenic acid, beta carotene, cadmium, calcium, carbohydrates, cerotic acid, chlorine, choline, copper, cystine, fat, fiber, folacin, glutamic acid, glycine, histidine, iodine, iron, isoleucine, lead, leucine, linoleic acid, lysine, manganese, mercury, sucrose, sulphur, thiamine, tryptophane, tyrosine, valine, vitamin B-6, water, zinc.

Mechanism

Based on the above observations the following probable adsorption model is suggested. When a metal steel piece is immersed in dilute solution of HCl containing amino acids, two kinds of species can adsorbed on its surface. If the metal surface is positively charged with respect to the solution, the chloride ions will first get adsorbed on the metal surface, which in turn will attract the protonated amino acid and protonated water molecule. So a close packed layer will form on the metal surface and preventing iron ions to enter the solution.

If the metal surface is negatively charged with respect to the solution, the protonated amino acids and protonated water molecule would be directly adsorbed on the metal surface. In modern practice the inhibitor is rarely used in the form of single compounds. A formulation of two or more inhibitor is usually employed. However the chemicals are too costly, hence considerations such as cost effectiveness, eco friendliness, and biodegradability, less toxic and easy availability are the main reasons to use plant materials as inhibitors.

In the present investigation sprouted seed extract of *Phaseolus aureus* was proved to be an excellent inhibitor in controlling corrosion of mild steel in 1M HCl.

CONCLUSION

In summary following conclusion have been drawn from the present investigation SPA extract behaves as an excellent inhibitor for the mild steel corrosion in 1M HCl. The SPA extract inhibited the corrosion of Mild steel in acid medium getting adsorbed on the MS surface obeyed the Langmuir adsorption isotherm. The SPA extract behaves as mixed type. Even at high temperatures also SPA extract is an effective corrosion inhibitor.

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