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CORROSION INHIBITION STUDY OF CITRUS AURANTIUM BARK (LEMON) POWDER AS GREEN INHIBITOR FOR MILD STEEL IN SULPHURIC ACID

AJAY N. PATEL, P. Y. DAVE AND G. M. MALIK
Department of Chemistry, Navyug science college, Surat.
Email: ajayupi_patel@yahoo.co.in, gmmalik2010@gmail.com

ABSTRACT

In this study, we report the study of the inhibition effect of Citrus aurantium bark powder on corrosion of mild steel in sulphuric acid using weight loss measurements and electrochemical techniques. The inhibitor efficiency of Citrus aurantium bark powder extract was found uniform for 24 h. Experimental results revealed that inhibition efficiency (I.E %) increased with increasing inhibitor concentration. As temperatures increased, percentage of inhibition decreases. Experimental results revealed that inhibition efficiency (I.E %) increased with increasing inhibitor concentration. The inhibitive and adsorptive characteristics of ethanol extract of Citrus aurantium bark powder for the corrosion of mild steel (MS) in 0.05 M H_2SO_4 ***solutions have been studied using following methods for monitoring corrosion. Ethanol extract of Citrus aurantium bark powder is a good adsorption inhibitor for the corrosion of mild steel in*** H_2SO_4.

The methods used were weight loss, effect of temperature, polarization and Electrochemical Impedance Spectroscopic (EIS). The inhibition efficiency(I.E.) increases with inhibitor concentration. The adsorption study of these compounds of mild steel surface found to obey Citrus aurantium bark powder adsorption isotherm. The value of free energy of adsorption (ΔG^0_{ads} ***), heat of adsorption (*** Q_{ads} ***), energy of activation (*** E_a ***), enthalpy of adsorption(*** ΔH^0_{ads} ***) and entropy of adsorption (*** ΔS^0_{ads} ***) were calculated. Present study indicates that Citrus aurantium bark powder extract is a good inhibitor for the corrosion of Mild steel in sulphuric acid medium.***

Keywords : Mild steel-1, Sulphuric acid-2, Citrus aurantium bark powder-3, corrosion-4, inhibition effect-5.

INTRODUCTION

Metals undergo corrosion in the presence of oxygen and moisture and involve two electrochemical reactions. Oxidation occurs at anodic site and reduction occurs at cathodic site. Corrosion inhibitors reduce or prevent these reactions, they are adsorbed on the metal surface and act by forming barrier to oxygen, moisture and some of the inhibitors facilitate formation of passive film on the metal surface. The corrosion and inhibition behaviors of mild steel in sulfuric acid in the presence of *Citrus auran*tium bark extract have been studied using the electrochemical methods. It was found that the inhibition efficiency increased with Citrus aurantium bark extract concentration. The inhibition efficiency of *Citrus aurantium* bark was found to vary with concentration, temperature and immersion time. Good inhibition efficiency I.E.% was recorded in acid solution. The inhibition efficiency was found to be more than 90% in 0.05 M H_2SO_4 solution of 1 gm/Lit. inhibitor concentration. The adsorption study of these compounds on mild steel surface found to obey Temkin's adsorption isotherm. The potentiodynamic polarization results showed that the compound studied was mixed type inhibitor.

METHODOLOGY

Metal specimen and surface pretreatment: Rectangular specimens of the size 4.4 x 2.0 x 0.2 cm having an area of 0.2011sq. dm. of mild steel with small hole of 0.5 cm diameter near the upper edge, were used for the determination of corrosion rate. The specimens were cleaned by washing with distilled water, degreased by acetone for 1-2 minutes, then dried in warm air by air drier several times and are preserve in desiccators till use.

Preparation of extract: *Citrus aurantium* bark were collected in oven and dried at 50°C, dried leaves were ground to powder form. 10.0 g of the powder was digested in 100 ml of alcohol. Filter the solution and evaporate it in room temperature.

The powder was used to prepare various concentrations as the inhibitor.

Weight loss measurements: In this method, the mild steel specimen having an area of approximately 0.2011 sq.dm. were each suspended and completely immersed in 230 ml of sulphuric acid solution with different concentration like 0.05M, 0.1M and 0.5M solution without and with different concentration of *Citrus aurantium* bark for 24 hrs immersed period. After the test specimen washed with distilled water followed by acetone and dried with air dryer and reweighed. From the weight loss data, corrosion rate (CR) was calculated.

Surface coverage values are very useful in explaining the adsorption characteristics. The inhibition efficiency (η%) and degree of surface coverage (θ) at each concentration of inhibitors was calculated by comparing the corrosion loss in the absence (W_u) and presence of inhibitor (W_i) using the relationships:

$$\eta\% = \frac{W_u - W_i}{W_i} \times 100 \qquad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

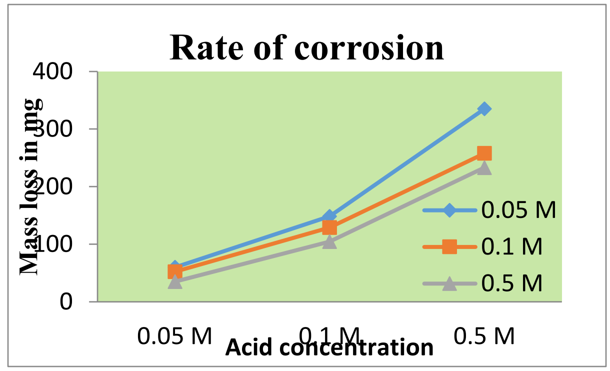


Figure 1: Corrosion rate of mild steel in **0.05 M H_2SO_4** in absence and presence of *Citrus aurantium* bark root for an immersion period of 24 h**.**

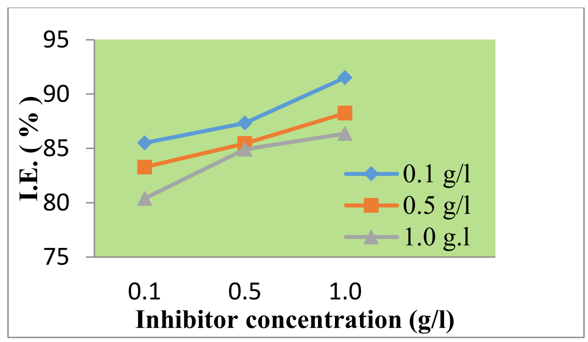


Figure 2: Rate of Inhibition efficiency of Mild steel in **0.05 M H_2SO_4** in absence and presence of *Citrus aurantium* bark root for an immersion period of 24 h**.**

Table-1: Effect of acid H_2SO_4 concentration on corrosion loss (CL) and inhibition efficiency (IE) of mild steel containing *Citrus aurantium bark* as inhibitor

Inhibitor conc.	Inhibitor	Time (h)							
		6h		12 h		18 h		24 h	
		mg dm^{-2} d^{-1}	I.E %	mg dm^{-2} d^{-1}	I.E %	mg dm^{-2} d^{-1}	I.E %	mg dm^{-2} d^{-1}	I.E %
1.0 gm/Lit	Blank	0.108	-	0.213	-	0.343	-	0.427	-
	Citrus aurantium	0.021	77.78	0.044	79.34	0.065	81.05	0.078	84.31

Table: 2 Inhibition efficiency (I E) of mild steel in different concentration of acid.
Immersion period: 24h. Effective specimen area: $0.2011 dm^2$

		Acid concentration					
		0.05 M		**0.1 M**		**0.5 M**	
Inhibitors	**Inhibitor Conc. (gm/Lit.)**	Mass loss (mg/dm^2)	I E (%)	Mass loss (mg/dm^2)	I E (%)	Mass loss (mg/dm^2)	I E (%)
Blank	-	413.19	-	887.45	-	1709.22	-
Citrus aurantium bark	0.1	58.89	85.51	148.42	83.28	335.13	80.39
	0.5	52.29	87.34	129.22	85.44	257.77	84.92
	1.0	35.06	91.51	104.38	88.24	233.22	86.36

Table: 3 Corrosion rate (Log ρ) of mild steel in **0.05 M H_2SO_4** in absence and presence of *Citrus aurantium* bark root for an immersion period of 24 h**.**

Inhibitor Conc. (gm/Lit)	**C.R (ρ)**	**Log ρ**	**I E (%)**	**Surface coverage (θ)**	**1-θ**	**Log (θ/1–θ)**
Blank	413.19	2.6161	-	-	-	-
0.1 gm/Lit	58.89	1.7774	85.51	0.8551	0.1449	0.7708
0.5 gm/Lit	52.29	1.7184	87.34	0.8734	0.1266	0.8390
1.0 gm/Lit	35.06	1.5448	91.51	0.9151	0.0849	1.0328

Table : 4 Corrosion rate (Log ρ) of mild steel in **0.1 M H_2SO_4** in absence and presence of *Citrus aurantium* bark root for an immersion period of 24 h**.**

Inhibitor Conc. (gm/Lit)	**C.R (ρ)**	**Log ρ**	**I E (%)**	**Surface coverage (θ)**	**1-θ**	**Log (θ/1–θ)**
Blank	887.45	2.9481	-			
0.1 gm/Lit	148.42	2.1715	83.28	0.8328	0.1642	0.6972
0.5 gm/Lit	129.22	2.1113	85.44	0.8544	0.1456	0.7685
1.0 gm/Lit	104.38	2.0186	88.24	0.8824	0.1176	0.8752

Table: 5 Corrosion rate (Log ρ) of mild steel in **0.5 M H_2SO_4** in absence and presence of *Citrus aurantium bark* root for an immersion period of 24 h**.**

Inhibitor Conc. (gm/Lit)	C R (ρ)	Log ρ	I E (%)	Surface coverage (θ)	1-θ	Log (θ/1–θ)
Blank	1709.22	3.2328	-	-	-	-
0.1 gm/Lit	335.13	2.5252	80.39	0.8039	0.1961	0.6128
0.5 gm/Lit	257.77	2.4112	84.92	0.8492	0.1508	0.7506
1.0 gm/Lit	233.22	2.3678	86.36	0.8636	0.1364	0.8013

OBSERVATION

Effect of temperature:

To study the effect of temperature on corrosion rate, the specimens was immersed in 230 mL in 0.05 M, 0.1 M, 0.5 M concentration of acid, with and without inhibitor at solution temperatures of 313, 323 and 333 K for a period of 2 hours.

Energy of activation (Ea) was calculated from the slopes of log ρ versus 1/T

(ρ = corrosion rate, T = absolute temperature) and also with the help of Arrhenius equation.

$$\log \frac{\rho_2}{\rho_1} = \frac{Ea}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad \ldots\ldots\ldots\ldots (2)$$

where ρ_1 and ρ_2 are the corrosion rate at temperature T_1 and T_2 respectively.

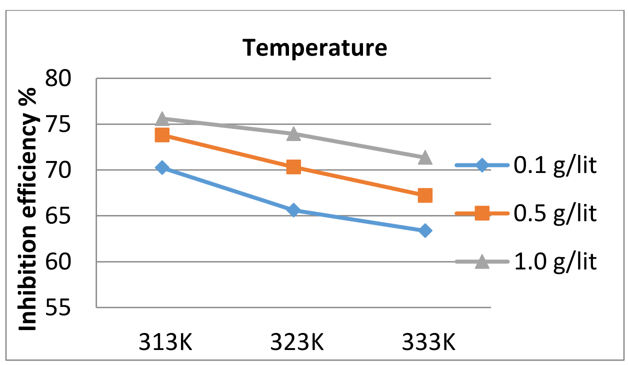
The values of the free energy of adsorption (ΔG^0_{ads}) were calculated with slope of the following equation.

$$\log C = \log\left(\frac{\theta}{1-\theta}\right) - \log B \quad \ldots\ldots\ldots\ldots (3)$$

where $\log B = -1.74 - \left(\frac{\Delta G^0_{ads}}{2.303RT}\right)$ and C is the inhibitor concentration. The values of heat of adsorption (Q_{ads}) calculated by the following equation.

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{T_1T_2}{T_2 - T_1} \quad \ldots\ldots\ldots\ldots (4)$$

Figure 3: Effect of temperature on corrosion rate



Effect of temperature on IE (%) for mild steel corrosion in 0.05 M H_2SO_4 at different inhibitor concentration of *Citrus aurantium* bark extract for immersion period of 2 h**.**

Effect of temperature on IE (%) for mild steel corrosion in 0.05 M H_2SO_4 at different inhibitor concentration of *Citrus aurantium* bark extract for immersion period of 2 h**.**

It was found that the value of Ea for inhibited system was higher than that of uninhibited system. It indicate that the inhibitors are more effective at lower temperature.

→ The enthalpy of adsorption (ΔH^0 ads) were calculated by using the equation.

$$\Delta H^0_{ads} = Ea - RT \; (R = 8.314) \ldots\ldots\ldots\ldots. (5)$$

Where, Ea is activation energy at absolute temperature T in Kelvin and R is the gas constant.

→ The entropy of adsorption (ΔS^0 ads) were calculated by using the equation.

$$\Delta S^0_{ads} = (\Delta H^0_{ads} - \Delta G^0_{ads}) / T \; \ldots. (6)$$

Table 6: Indicated that the value of I E% at difference temperature.

Inhibitor Concentration	Temperature K 313K C R mg/dm²	313K I E %	323K C R mg/dm²	323K I E %	333K C R mg/dm²	333K I E %	(Ea) from equation (kJ/Mol)	(Ea) from Plot (kJ/Mol)
Blank	217.87	-	299.43	-	412.21	-	27.66	33.07
0.1 gm/Lit	68.14	68.72	101.23	66.19	159.38	61.34	36.94	42.19
0.5 gm/Lit	56.08	74.26	89.43	70.13	135.04	67.24	38.05	42.37
1.0 gm/Lit	51.38	76.42	81.28	72.86	119.32	71.05	36.45	39.88

Polarization measurement

In the electrochemical cell Mild steel specimens having an area of 0.2011 sq.dm. was used as a working electrode, Ag / AgCl electrode as a reference electrode and platinum electrode as an auxiliary electrode and allowed to established a steady-state open circuit potential (OCP) for approximately 15 min. Polarization curves were plotted with potential against log current density

Electrochemical Impedance spectroscopy measurement (EIS) :

The typical Nyquist plots of Mild steel in the absence and presence of *Citrus aurantium* bark extract in 0.05M sulphuric acid solution was presented in figure. From the figure it was observed that the diameter of the semicircle increases in the case of inhibited acid solution, indicated an increase in corrosion resistance of system.

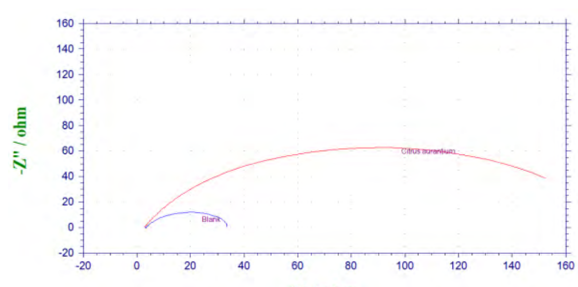


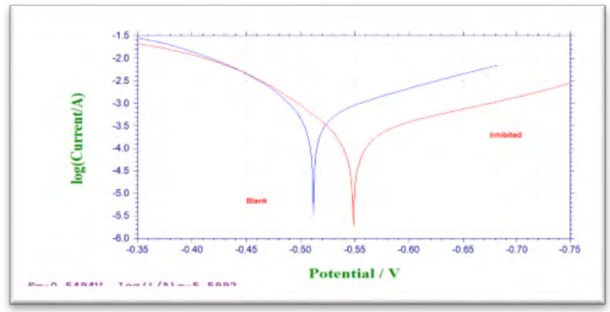
Figure 4: Nyquist plots of Mild steel in the absence and presence of *Citrus aurantium* bark

Tafel plot : Cathodic and anodic polarization curves give cathodic and anodic Tafel lines correspondingly. This technique is used to measure the corrosion current(i_{corr}) so that the corrosion rate can be calculated. A Tafel plot can yield i_{corr} directly or it can yield the Tafel constants (βa and βc). The Tafel constants can then be used with the R_p value of calculate i_{corr}.

The inhibition efficiency IE (%) was evaluated from the Potentiodynamic polarization data of corrosion current density (i_{corr}) by the following formula.

$$\text{IE}(\%) = \frac{i_{corr}\,(\text{uninhi}) - i_{corr}\,(\text{inhi})}{i_{corr}\,(\text{uninhi})} \times 100 \quad ..(7)$$

Where , $i_{corr\ (uninhi)}$ and $i_{corr\ (inhi)}$ are corrosion current densities of metal in the absence and presence of inhibitors respectively.



The double layer capacitance (Cdl) was calculated from the equation as below.

$$\text{Cdl} = \frac{1}{2\pi\,\text{fmax Rct}} \quad \ldots\ldots\ldots\ldots.(8)$$

Where , f_{max} is the frequency at which the imaginary component of the impedance is maximum.

Table 7: Impedance parameters for corrosion of Mild steel in 0.05M sulphuric acid in the absence and presence of *Citrus aurantium* bark extract.

System	R_{ct} (Ω cm^2)	C_{dl} (μF/cm^2)	Inhibition efficiency (I.E %)	
			By EIS Method	By Mass Loss Method
Blank	30	44.2097	-	-
Citrus aurantium bark bark	149	1.7228	87.54 %	96.10 %

RESULTS AND DISCUSSION:

Weight loss studies

The values of inhibition efficiency (I.E %) and the corrosion rate (CR) obtained from the weight loss method at different concentrations of H_2SO_4 given in table-1.

Effect of temperature

The effect of temperature was studied in 0.05 M H_2SO_4 containing 1.0 gm/Lit. of inhibitor concentration at 313, 323 and 333 K temperature. The results showed corrosion loss increased with increase in temperature. Inhibition efficiency of inhibitors decreased with the rise in temperature.

Potential measurement

In 0.05 M H_2SO_4 the potential shifted to the negative direction from its initial value.
On addition of 1.0 g/lit of the inhibitor *Citrus aurantium* bark in 0.05 M H_2SO_4 the initial value of the OCP (open circuit potential) increased and settled at about within 5 minutes.

Polarization measurements

Anodic and cathodic polarization curves for mild steel in 0.05 M H_2SO_4 at 1.0 gm/Lit inhibitor concentration in the presence of inhibitors are shown in figure-1. The value of the corrosion potential with inhibitors were found more positive than without inhibitors as shown in figure-2. The semicircular nature of the plots indicates that the corrosion of mild steel is mainly controlled by charge transfer process.

Table 8: Potentiodynamic data and inhibition efficiency I.E (%) for mild steel in 0.05 M sulphuric acid at 1.0 g/l *Citrus aurantium* bark extract inhibitor.

System	E_{corr} (mV)	i_{corr} (μA)	Tafel Slop			Inhibition efficiency (I.E %)	
			Anodic +βa	Cathodic -βc	β (mV)	By Polarization Method	By Mass Loss Method
Blank	-0.548	85.6×10^{-4}	9.182	4.519	1.3167	-	-
Citrus aurantium bark	-0.567	17.6×10^{-4}	8.865	4.635	1.3233	86.45	91.51

CONCLUSION

Citrus aurantium bark was found as good eco-friendly inhibitor for the corrosion control of mild steel in H_2SO_4 solution. The inhibition efficiency increases with increase in *Citrus aurantium* bark concentration. *Citrus aurantium* bark adsorbed on metal surface follows Langmuir adsorption isotherm. Tafel plot indicates *Citrus aurantium* bark acts as a mixed type inhibitor.

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