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Research Article

Corrosion Inhibition by Green Inhibitor: Sodium Metavanadate –Spirulina System

V. Sribharathy[1*] and Susai Rajendran[1,2]

[1]Corrosion Research Centre, Department of Chemistry, GTN Arts College, Dindigul, Tamil Nadu, India.
[2]Department of Chemistry, R.V.S. School of Engineering and Technology, Dindigul, Tami Nadu, India.

Abstract
The inhibition efficiency of sodium metavanadate in controlling corrosion of carbon steel in an aqueous solution containing 60 ppm of Cl^- has been evaluated by weight loss method. Sodium metavanadate (SMV) has good inhibition efficiency, 200 ppm of SMV has 98% inhibition efficiency (IE) 50 ppm of SMV has 48% (IE). The IE of the system improved by addition of various concentration of spirulina solution (0.5% aqueous solution) when 2 ml of spirulina solution is added to 50 ppm of SMV IE tremendously enhances from 48% to 98%. 't' test reveals that his enhancement is statistically significant. The protective film formed on the metal surface. It has been analyzed FTIR spectra and UV-visible spectra. The mechanistic aspects of corrosion inhibition have been investigated by electrochemical studies such as polarization studies and AC impedance spectra confirm the protective film formed on the metal surface.

Correspondence:
*V. Sribharathy, Corrosion Research Centre, Department of Chemistry, GTN Arts College, Dindigul – 624 005, Tamil Nadu, India.
Email: bharathy_chem@yahoo.co.in;
Contact: +91 9442034461.

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Introduction

Several inhibitors have been used to prevent corrosion of carbon steel in aqueous solution. Out of this environment friendly inhibitors have attracted several researchers. Natural products are non-toxic, bio-degradable, and readily available. Corrosion inhibition of steel by plant, extracts in acidic media has been reported [1,2] natural compounds as corrosion inhibitor for the industrial cooling systems have been studied [5]. Natural products such as caffeine [3,4],aqueous extracts of Rosemary leaves [6], zenthoxylum-alatum [7], lawsonia [8], henna [9], Rhizome (curcuma Longa L) powder [10], onion [11], Antrographis panizulata [12], carcia papaya extract [13], Hibiscus rosasinensis Linn [14], and beet root [15]. Corrosion behaviour of aluminium in the presence of aqueous extract of Hibiscus rosasinensis [16] has been studied. Corrosion behaviour of metals in artificial saliva in presence of spirulina powder has been studied [17]. The investigation of natural inhibitors is particularly interesting they are non expensive ecologically friendly acceptable and possesses no threat to the environment eater.

Experimental

Preparation of solution

An aqueous extract of spirulina was prepared by double distilled water, filtering the suspending impurities and making up to 500 mL and sodium meta vanadate was prepared by 1 g in 100 mL by double distilled water, sodium metavanadate was purchased from Sigma–Aldrich. The solutions were used as a corrosion inhibitor in the present study.

Preparation of specimens

Carbon steel specimens (0.0267% S, 0.06% P, 0.4% Mn, 0.16% C and the rest iron) of dimensions 1.0 cm x 4.0 cm × 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

Weight loss method

Carbon steel specimens were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the presence and absence of sodium metavanadate for one day. The weight of the specimens before and after immersion were determined using Shimadzu balance, model AY 62. The corrosion products were cleansed with Clarke's solution [18]. The inhibition efficiency (I.E.) was then calculated using the equation.

$$I.E\% = [1-(W_2/W_1)] \times 100\%$$

where W_1 = Corrosion rate in the absence of the inhibitor, W_2 = Corrosion rate in the presence of the inhibitor.

Surface Examination

The nature of the film formed on the surface of metal specimen was analyzed by FTIR spectroscopic study and UV-visible spectrum.

FTIR Spectra

In a Perkin – Elmer 1600 spectrophotometer the film formed on mild steel specimen were taken out and dried-up carefully removed, mixed thoroughly with KBr then made into pellets and the FTIR spectra were recorded.

UV-Visible spectra

The instrument UV Spetord S-100 Analytic Jena was used for recording UV-visible absorbance spectra.

Potentiodynamic polarization study

This study was carried out using CHI 660A electrochemical impedance analyzer model a three – electrode cell assembly was used. The working electrode was used as a rectangular specimen of mild steel with one face of the electrode of constant 1 cm^2 area exposed. A saturated calomel electrode (SCE) was used as reference electrode. A rectangular platinum foil was used as the counter electrodes. Polarization curves were recorded after doing *i*R compensation. The results such as Tafel slopes, I_{corr} and E_{corr} values were calculated. During the Polarization study, the scan rate (v/s) was 0.01; Hold time at Ef (s) was zero and quiet time (s) was 2.

AC impedance measurements

CHI 660A electrochemical impedance analyzer model was used to record AC impedance measurements. The cell set up was the same as that used for polarization measurements. In X-axis real part: (Z’) and Y-axis imaginary part: (Z”) of the cell impedance were measured in ohms for various frequencies. The R_t (charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated. AC Impedance spectra were recorded with initial E (v) = 0; High frequency (Hz) = $1x10^5$, Low frequency (Hz) = 1; Amplitude (v) = 0.05 and Quiet time (s) =2.

Result and Discussion

Analysis of weight loss method

Corrosion rates of carbon steel in an aqueous solution containing 60 ppm Cl^- in the absence ion presence of inhibitor obtained by weight loss method.

The inhibition efficiency is also given in this Table. It is observed that sodium metavanadate (SMV) has good inhibition efficiency. As the concentration of SMV increases the inhibition efficiency also increases 50 ppm of SMV has 48% IE 200 pm of SMV has 98% inhibition efficiency.

It is given in the **Table 1** that spirulina solution is not a very good inhibitor. It shows some inhibition efficiency. For example 2 ml of spirulina solution (0.5% aqueous solution) has only 25% inhibition efficiency. As the concentration of spirulina increases inhibition efficiency also increases. For 8 ml of spirulina solution has 42% inhibition efficiency.

Influence of spirulina solution on inhibition efficiency of SMV 50 ppm of SMV has 48% inhibition efficiency. Various concentrations of spirulina solution are added to improve the inhibition efficiency of SMV. It is interesting to observe the addition of various concentrations (2, 4, 6, 8 mL) of spirulina solution tremendously enhance the inhibition efficiency of SMV to a great extent. For example: when 2 ml of spirulina solution is added to 50 ppm of SMV, the inhibition efficiency increases from 48% to 98%. Similarly in the case with other concentration of spirulina solution (2 mL) has excellent inhibition efficiencies 98%.

Table 1 Corrosion rates of carbon steel in an aqueous solution containing 60 ppm of Cl^- in the absence or presence of inhibitors obtained by weight loss method. Immersion period: 1 day

Inhibitors: Sodium metavanadate (SMV) and spirulina solution

Cl^- ppm	SMV ppm	Spirulina Solution (mL)	CR (mm/y)	IE %
60	0	0	0.09	-
60	50	0	0.04	48
60	100	0	0.003	96
60	150	0	0.002	97
60	200	0	0.001	98
60	0	2	0.069	25
60	0	4	0.065	30
60	0	6	0.057	38
60	0	8	0.053	42
60	50	2	0.001	98
60	50	4	0.001	98
60	50	6	0.001	98
60	50	8	0.001	98

‘t’-test

Weight loss study reveals that when spirulina is added to SMV the inhibition efficiency increases tremendously to know whether it is statistically significant or not. ‘t’ test is applied [19-21].

It is observed from **Table 2** that the obtained t-value 50 is significant since it is greater than the critical t value of 2.447 for 6 degrees of freedom at 0.05 levels of significance. Hence, it is concluded that the influence of addition of various concentrations of spirulina solution on the inhibition efficiency of 50 ppm of SMV is statistically significant, where n = no of samples, M = mean of the sample.

Table 2 Distribution of t-value between the inhibition efficiency of SMV 50 ppm has 48% and various concentration SMV – Spirulina systems.

Category	n	M	t-value	Level of significant
SMV system	4	48	50	$p > 0.05$
SMV spirulina systems	4	98		

In order to know the influence of 200 ppm of SMV on the inhibition efficiency of various concentrations of spirulina statistically significant or not and the results are given in the **Table 3**.

Table 3 Distribution of t-value between the inhibition efficiency of SMV 50 ppm and various concentration of SMV – spirulina systems.

Category	n	M	S	t-value	Level of Significant
SMV system	4	33.75	6.56	58.09	p > 0.05
SMV spirulina systems	4	98	0		

It is observed from Table 3 that the obtained t-value 58.09 is significant, since it is greater than the critical t value of 2.447 for 6 degrees of freedom at 0.05 levels of significance. Hence, it is concluded that the influence of addition of 50 ppm of SMV solutions on the inhibition efficiency of various concentration spirulina solution is statistically significant.

Analysis of polarization curve

The potentiodynamic polarization curves of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- in the absence and presence of inhibitors are shown in the **Figure 1**.

The corrosion parameters are given in the **Table 4**. When carbon steel is immersed in an aqueous solution containing 60 ppm of Cl^-. The corrosion potential is -474 mV vs SCE (saturated calomel electrode). The corrosion current is 5.45×10^{-6} A/cm^2.

When 2 ml of spirulina 50 ppm of SMV is added to the above system, the corrosion potential shifts to the anodic side (-330 mV vs SCE). This suggests the formulation controls the anodic reaction predominately. In the presence of this inhibitor system the corrosion current decreases from 5.45×10^{-6} A/cm^2 to 0.355×10^{-6} A/cm^2. The LPR value increases from 9.19×10^3 ohm cm^2 to 165.5×10^3 ohm cm^2. This suggests that the inhibitive nature of the inhibitor system [22, 23].

Analysis of AC impedance

The AC impedance spectra carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- in the absence and presence of inhibitors are shown in the **Figure 2** (Nyquist plot) and **Figure 3** Bode plot. The AC impedance parameter such as charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in the **Table 5**. When carbon steel immersed in an aqueous solution containing 60 ppm Cl^-. Charger transfer resistance R_t is 1503 ohm cm^2 the double layer capacitance C_{dl} is 6.03×10^{-9} F/cm^2. The formulation consisting 2 ml of spirulina solution 200 ppm of SMV are added. R_t value increases and C_{dl} value decreases. This confirms that the protective film is formed on the metal surface. This decreases the corrosion rate of carbon steel and increases the inhibition efficiency [24].

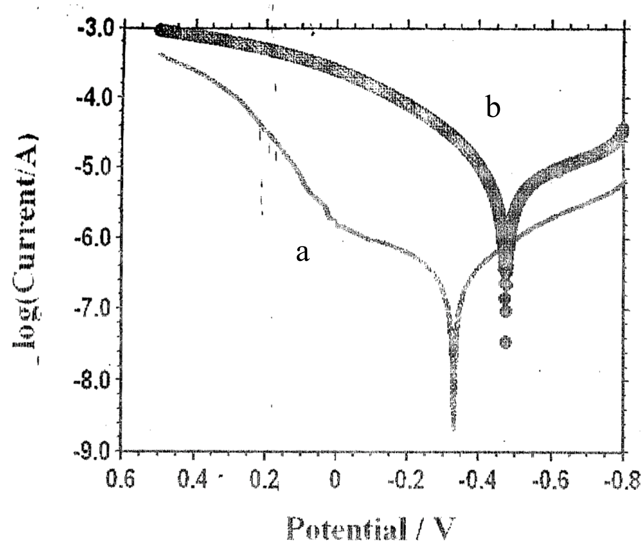

Figure 1 Polarization curves of carbon steel immersed in an aqueous solution containing a) 60 ppm Cl^-, b) 60 ppm Cl^- + 2 ml of spirulina + 200 ppm of SMV

Table 4 Corrosion parameter of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- in the absence and presence of inhibitors
Inhibitor: Sodium metavanadate and spirulina solution

Cl^- ppm	SMV ppm	Spiru-lina (mL)	$-E_{corr}$ mV vs SCE	b_c (mV/dec)	b_a (mV/dec)	LPR (ohm cm^2)	I_{corr} (A/cm^2)
60	0	0	474	334	175	9.19×10^3	5.45×10^{-6}
60	200	2	330	243	303	165.5×10^3	0.355×10^{-6}

Analysis of FTIR spectra

The FTIR spectrum (KBr) of pure SMV shows characteristic peak due to vanadate ion at 1385 cm^{-1}. Spirulina contains a mixture of amino acids and vitamin [25].

The FTIR spectrum of pure spirulina powder shows characteristic peaks at 1653 cm^{-1}, 1543 cm^{-1}, 1383 cm^{-1}, 1242 cm^{-1}, 1083 cm^{-1}, 1039 cm^{-1} (P-O).

The FTIR spectrum of protective film formed on the metal surface after immersion in an aqueous containing 60 ppm of Cl^- 200 ppm of SMV and 2 mL of spirulina due to metavanadate has shifted from 1385 cm^{-1} to 1383 cm^{-1}. This indicates that Fe^{2+} has coordinated through vanadate ion. The characteristic peak due to spirulina has shifted and appears at 1636 cm^{-1}, 1385 cm^{-1}, 965 cm^{-1}. These observation indicates that spirulina has coordinated with Fe^{2+} through polar groups such carboxylic group (1636 cm^{-1}) P–O (965 cm^{-1}), the stretching frequency due to C-N at 1636 cm^{-1}. This suggests that spirulina has coordinated through nitrogen atom also [26].

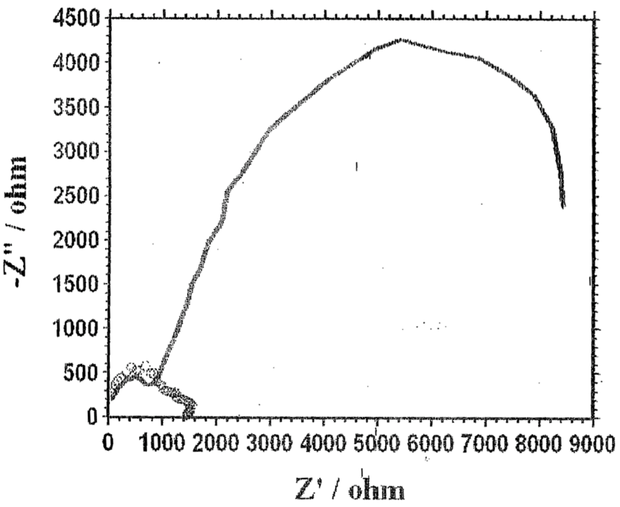

Figure 2 AC impedance spectra (Nyquist plot) of carbon steel immersed in an aqueous solution containing a) 60 ppm Cl^-, b) 60 ppm Cl^- + 2 mL of spirulina + 200 ppm SMV

Table 5 AC impedance parameter of carbon steel immersed in an aqueous solution containing 60 ppm of Cl^- in the absence and presence of inhibitors.

Cl^- ppm	SMV ppm	Spiru -lina (ml)	R_t (ohm cm^2)	C_{dl} (F/cm^2)	Impedance log (z/ohm)
60	0	0	1503	6.03×10^{-9}	3.162
60	200	2	8453	1.07×10^{-9}	3.925

UV-visible adsorption spectra

The UV-visible adsorption spectra were taken for various test solutions and aqueous solution of sodium metavanadate. The λ_{max} appears at 202 and 307 nm. The UV-visible adsorption spectrum of aqueous solution of spirulina showed λ_{max} at 205 and 314 nm. The UV-visible adsorption spectrum of aqueous solution containing SMV spirulina and Fe^{2+} has shown λ_{max} at 230 and 320 nm. This indicates that a complex is formed between Fe^{2+} and SMV and also with spirulina solution [27].

Mechanism of corrosion inhibition

Weight loss method reveals that the formulation consisting 2 ml of spirulina and 200 ppm of SMV offers 98% inhibition efficiency. Polarization study reveals that this formulation controls anodic reaction predominately. AC impedance spectrum reveals the protective film formed on the metal surface. FTIR spectra and UV-visible spectra reveal that the protective film consists of Fe^{2+}-SMV complex and Fe^{2+}-spirulina complex and produced on the anodic side of the metal surface. Then the anodic reaction of metal dissolution is controlled. This accounts for the inhibition efficiency of the system.

$$[Fe \dashrightarrow Fe^{2+} + 2e^-]$$

Conclusion

The present study leads to the following conclusion

1. Carbon steel immersed in aqueous solution containing 60 ppm Cl^-, formulation consisting 2 ml of spirulina and 200 ppm of SMV offers 98% inhibition efficiency
2. Polarization study reveals that the formulation controls anodic reaction predominantly.
3. AC impedance spectrum reveals the protective film formed on the metal surface.
4. FTIR spectra and UV-visible spectra reveal that the protective film consists of Fe^{2+}-SMV complex and Fe^{2+}- spirulina complex.

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