



CORROSION INHIBITION OF MILD STEEL BY AN AQUEOUS EXTRACT OF ALLIUM SATIVUM

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ABSTRACT

The inhibition efficiency of allium sativum extract (garlic extract) in controlling corrosion of mild steel, immersed in well water has been evaluated by weight loss method. Weight loss study reveals that the formulation consisting 10 mL of garlic extract has 90% inhibition efficiency. The mechanistic aspects of corrosion inhibition have been evaluated by polarization study and AC impedance spectra. FTIR spectra reveal that the protective film consists of Fe²⁺-allicin complex. This is confirmed by UV- visible absorption spectra.

KEYWORDS: corrosion inhibition, mild steel, allium sativum extract, green inhibitor.

INTRODUCTION

Corrosion is the destructive attacks of a metal by chemical and electrochemical reaction with the environment.^[1] There are many methods are available to control corrosion. One of the methods is by using inhibitors. Corrosion inhibitor is a chemical substance. So if we add the suitable inhibitor in the corroding medium in maximum concentration, the corrosion rate of metal will decrease considerably.^[2] Even though the inhibition properties of ATMP and HEDP along with zinc have been extensively studied, it is now being phased out because of its carcinogenic properties.^[3] Plant extracts are viewed as environmentally friendly and ecologically acceptable inhibitors. Plant products are low cost, easily available and non-conventional source of materials. The extracts from their leaves, barks, seeds, fruits and roots comprise of mixture of organic compounds containing nitrogen, sulphur and oxygen atoms.^[4] The list of works done on the use of plants extract as corrosion inhibitors are endless, to mention but few are extract of fenu greek seeds and leaves,^[5] L. Dopa,^[6] Azardirecta indica,^[7] Emilia Sonchifolia and Vitex Doniana,^[8] adhatoda vasica,^[9] Phyllanthus amarus extracts.^[10] Rajendran et al., have extensively used extracts of plant materials as corrosion inhibitors.^[11-20] They have used an aqueous extract of beet root,^[11] Hyacinth Leaves,^[12] phyllanthus amarus,^[13] extract of banana peel,^[14] henna (Lawsonia

inermis) extract,^[15,16] spirulina powder,^[17] caffeine,^[18,19] Cuminum cyminum extracts.^[20]

In the present work garlic extract (GE) has been taken as a corrosion inhibitor of mild steel in well water. The corrosion inhibition property of garlic extract was studied by weight loss method, electrochemical studies, FTIR spectra and UV spectra.

The active principle of garlic is allicin.^[21] It has polar groups such as S, O which coordinate with mild steel metal surface and forming protective film and thereby controls corrosion. The structure of allicin is shown in Fig .1.

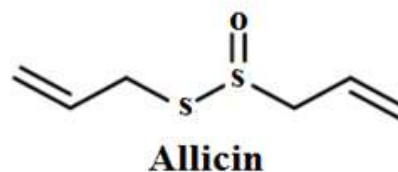


Fig. 1: Structure of allicin.

MATERIALS AND METHODS

Preparation of specimens

Mild steel specimens of dimensions 1.0 x 4.0 x 0.2 cm were polished to mirror finish, degreased with

trichloroethylene and used for the weight loss method and for surface examination studies.

Inhibitor solution

Garlic is dried well in the absence of sunlight. 10 gm of garlic is taken, boiled with distilled water. The solution is filtered and the filtrate is made up to 100 mL. This is used as corrosion inhibitor in the present study.

Weight loss method

Three mild steel specimens were immersed in 100 mL of well water in various concentrations of the inhibitor (aqueous extract of garlic) for a period of 1 day. The weight of the specimen before and after immersion was determined using Shimadzu balance AY62. Inhibition efficiency (IE) was calculated from the relationship

$$IE = \frac{W_1 - W_2}{W_1} \times 100\%$$

W_1 = corrosion rate in the absence of inhibitor, and W_2 = corrosion rate in the presence of the inhibitor.

Potentiodynamic polarization study

Polarization study was carried out in an H and CH electrochemical work station Impedance Analyzer Model CHI 660A provided with iR compensation facility, using a three electrode cell assembly. Mild steel was used as working electrode, platinum as counter electrode and saturated calomel electrode (SCE) as reference electrode. After having done iR compensation, polarization study was carried out at a sweep rate of 0.01 V/Sec. The corrosion parameters such as linear polarization resistance (LPR), corrosion potential E_{corr} , corrosion current I_{corr} and Tafel slopes (b_a and b_c) were measured.

Alternating current impedance spectra

AC impedance spectra were recorded in the same instrument used for polarization study, using the same type of three electrode cell assembly. The real part (Z') and imaginary part (Z'') of the cell impedance were measured in ohms for various frequencies. The charge transfer resistance (R_t) and double layer capacitance (C_{dl}) values were calculated.

FTIR spectra

FTIR study was carried out with a Perkin- Elmer 1600 spectrophotometer. The protective film was removed from the metal surface, mixed with KBr and made into pellet

UV absorption spectra

UV spectroscopy is an important tool in analytical chemistry. The other name of UV (Ultra-Violet) spectroscopy is Electronic spectroscopy as it involves the promotion of the electrons from the ground state to the higher energy or excited state.

RESULTS AND DISCUSSION

Analysis of results of the weight loss method

The inhibition efficiency of an aqueous extract of garlic extract in controlling corrosion of mild steel in well water has been evaluated by weight loss method. The results are summarized in Table 1.

Table 1: Corrosion inhibition efficiency of garlic extract in controlling corrosion of mild steel in well water.

Volume of garlic Extract mL	Corrosion rate (CR) MDD	IE%
0	32.68	-
2	17.9	45
4	14.37	56
6	10.45	68
8	6.53	80
10	3.26	90

It is observed from the Table 1 that as the concentration of garlic extract increases, the corrosion inhibition efficiency also increases. The active principle of garlic extract, namely allicin has coordinated with Fe^{2+} on the metal surface and forms a protective film consisting of Fe^{2+} -allicin complex. Thus the anodic reaction of metal dissolution is prevented.

Analysis of potentiodynamic polarization curves

Polarization study is useful in confirming the formation of protective film formed on the metal surface.^[22,23] The polarization resistance R_p is inversely proportional to the rate of corrosion expressed as the equivalent corrosion current density I_{corr} . If a protective film is formed, the linear polarization resistance increases and the corrosion current value will decrease. The polarization curves of mild steel immersed in various test solutions are shown in Fig. 2.

The corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), linear polarization resistance (LPR), and Tafel slopes (b_c =cathodic; b_a =anodic) are given in Table 2.

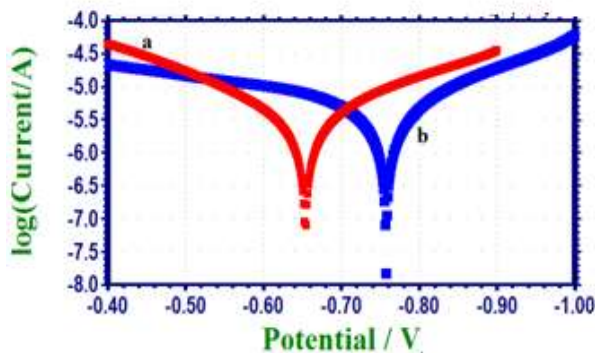


Fig. 2: Polarization curves of mild steel immersed in various test solutions. (a) Well water (b) Well water + 10 ml of garlic extract.

Table 2: Corrosion parameters of mild steel immersed in well water in the absence and presence of an aqueous extract of garlic.

S.No	System	E_{corr} mV vs SCE	I_{corr} A/cm ²	LPR ohm cm ²	b_c mV/decade	b_a mV/decade
1.	Well water	-654	9.447×10^{-6}	4022.1	181.6	168.4
2.	Well water + Garlic extract	-758	4.397×10^{-6}	10291.2	170.2	267.8

It is observed from the Table 2 that when mild steel is immersed in well water, the corrosion potential is -654 mV vs SCE. The corrosion current is 9.447×10^{-6} A/cm². The LPR value is 4022.1 ohm cm².

In the presence of inhibitor, the corrosion potential is shifted from -654 to -758 mV vs SCE. This is a cathodic shift. It suggests that the cathodic reaction is controlled predominantly. The LPR value increases from 4022.1 to 10291.2 ohm cm². The corrosion current decreases from 9.447×10^{-6} to 4.397×10^{-6} ohm cm². These observations confirm that a protective film is formed on the metal surface. This controls the corrosion of metal.

AC Impedance spectra

AC impedance spectra [Electro chemical impedance spectra] have been used to confirm the formation of protective film on the metal surface. If a protective film is formed on the metal surface, the charge transfer resistance (R_t) value increases; double layer capacitance value (C_{dl}) decreases and the impedance [$\log(z/\text{ohm})$] value increases. The AC impedance spectra of carbon steel immersed in well water, in presence of inhibitor system (GE) are shown in Figs. 4 to 6. The Nyquist plots are shown in Fig 4. The Bode plots are shown in Figs. 5 and 6. The corrosion parameters, namely, R_t , C_{dl} and Impedance [$\log(Z/\text{ohm})$] values are given in Table 3.

Table 3: Corrosion parameters of carbon steel immersed in well water in presence of GE system obtained from AC impedance spectra.

System	Nyquist plot		Bode plot
	R_t ohm cm ²	C_{dl} F cm ⁻²	Impedance log (z/ohm)
Well water (blank)	286.7	17.739×10^{-9}	2.721
Well water + 10 ml of garlic extract	753.5	6.635×10^{-9}	2.94

GE=Garlic extract

When the inhibitor [GE] is added to well water, the R_t value increases from 286.7 to 753.5 ohm cm²; the C_{dl} value decreases from 17.739×10^{-9} to 6.635×10^{-9} F/cm² and the impedance value $\log(Z/\text{ohm})$ increases from 2.721 to 2.94. These results lead to the conclusion that a protective film is formed on the metal surface.

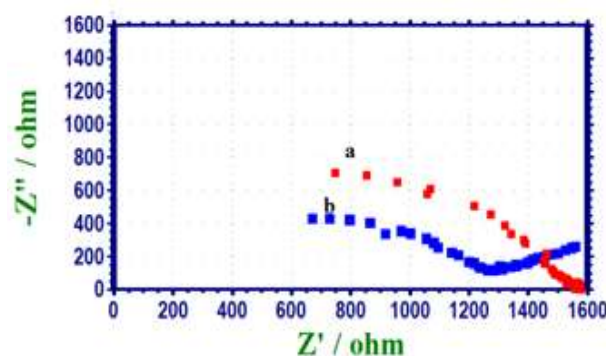


Fig. 3: AC impedance spectra of mild steel immersed in various test solution (Nyquist Plot); a) well water; b) well water + 10 ml of garlic extract.

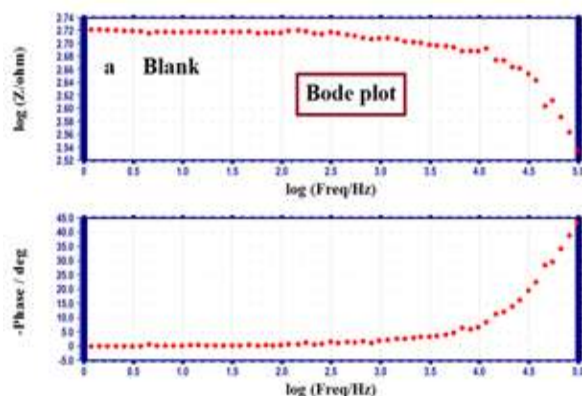


Fig. 4: AC impedance spectra of mild steel immersed in well water (Bode Plot).

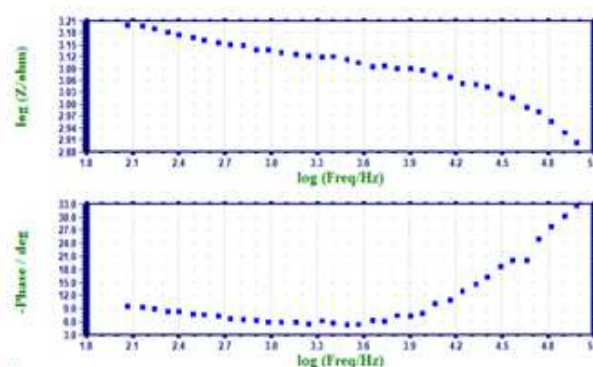


Fig. 5: AC impedance spectra of mild steel immersed in well water + 10 mL of GE extract.

Analysis of FTIR spectra

The term "infrared" generally refers to any electromagnetic radiation falling in the region from 4000-400 cm⁻¹. FTIR spectrum is used in many applications such as reduction of waste, improvement of product quality and reduction of environmental pollution.^[24,25]

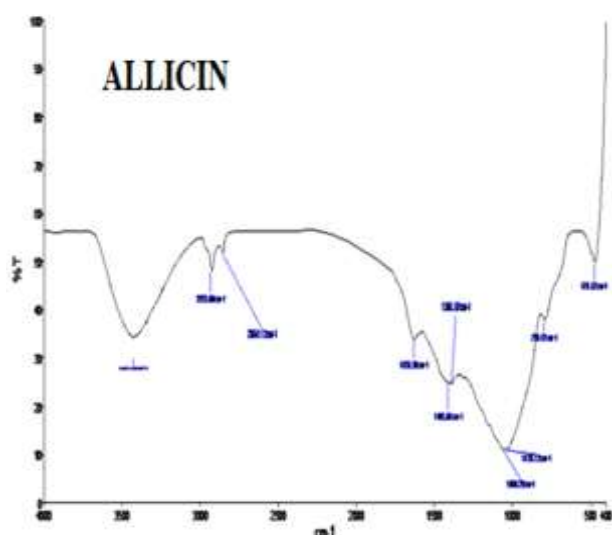


Fig. 6: FTIR Spectrum: garlic extract evaporated to dryness (allicin).

FTIR spectra have been used in corrosion inhibition study to analyze the protective film formed on the metal surface. A few drops of an aqueous extract of garlic were dried on a glass plate. A solid mass is obtained. Its FTIR spectrum (KBr) is shown in Fig. 6. The OH stretching frequency appears at 3421.48 cm^{-1} . The stretching frequency of S=O appears at 1038.12 cm^{-1} . The $\text{CH}_2\text{-S}$ stretching frequency appears at 1405.8 cm^{-1} . The stretching frequency of -C=CH appears at 1060.29 cm^{-1} . Thus the structures of the active principle of garlic extract namely allicin Fig. 1 is confirmed by FTIR spectrum.

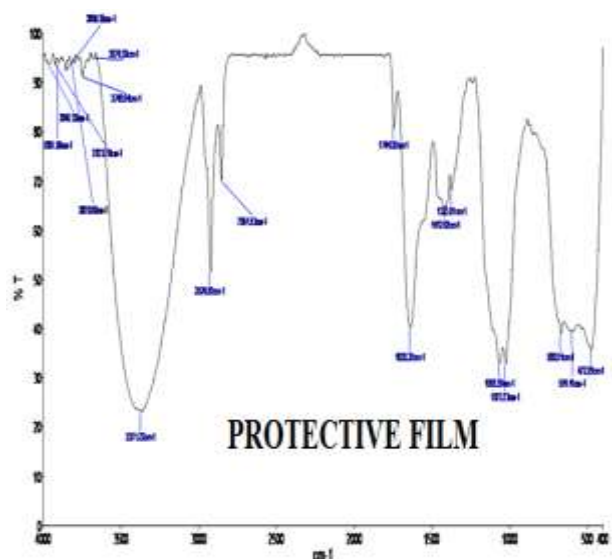


Fig. 7: FTIR Spectrum: Film formed on metal surface after immersion in the solution containing 10 ml aqueous extract of garlic.

The FTIR spectrum of the protective film formed on the metal surface after immersion in the solution containing well water and inhibitor solution is shown in Fig. 7. It is observed that the stretching frequency of OH group has

shifted from 3421.48 cm^{-1} to 3371.22 cm^{-1} . The stretching frequency of S=O has shifted from 1038.12 cm^{-1} to 1023.23 cm^{-1} . The stretching frequency of $\text{CH}_2\text{-S}$ has shifted from 1405.8 cm^{-1} to 1412.43 cm^{-1} . The stretching frequency of -C=CH has shifted from 1060.29 cm^{-1} to 1063.90 cm^{-1} . Thus it is observed that allicin has coordinated with Fe^{2+} through oxygen atom, sulphur atom of allicin. It is confirmed that the protective film is Fe^{2+} -allicin complex.

Table 4: The stretching frequency of various functional groups.

Functional groups	Stretching frequency cm^{-1}	
	Allicin	Protective film
OH	3421.48	3371.22
S=O	1038.12	1023.23
$\text{CH}_2\text{-S}$	1405.8	1412.43
-C=CH	1060.29	1063.90

Analysis of UV- visible absorption spectrum

UV- Visible absorption spectrum of an aqueous extract of garlic is shown in Fig.8. A peak appears at 320, 380 nm. This is due to the absorption spectrum of allicin, which is the active ingredients present in the aqueous extract of garlic. UV-Visible absorption spectrum of an aqueous solution containing garlic extract and Fe^{2+} ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) is shown in Fig.9. A peak appears at 296, 380 nm. The 320 nm peak has disappeared and a new peak appears at 296nm. This indicates that this peak is due to Fe^{2+} - allicin complex formed in solution.

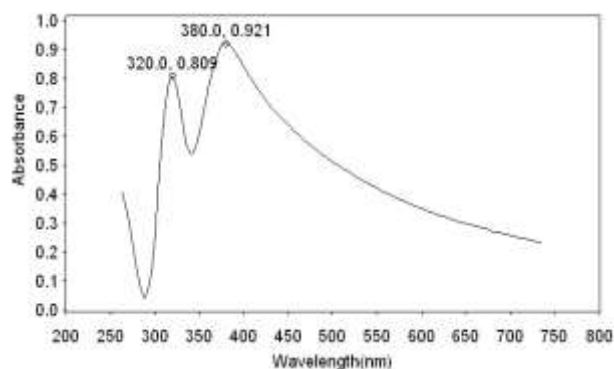


Fig. 8: UV-visible absorption spectrum of an aqueous solution of garlic.

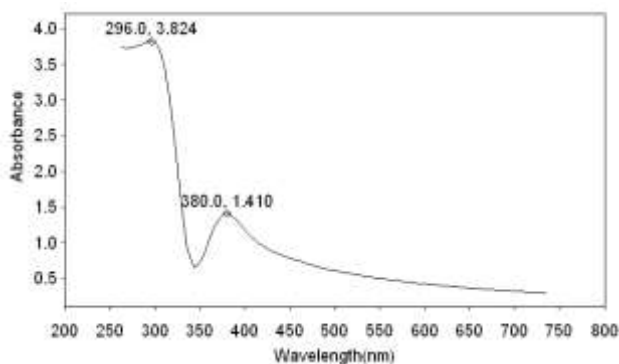


Fig. 9: UV-visible absorption spectrum of an aqueous solution of garlic + Fe^{2+} .

CONCLUSION

- Garlic is a non-toxic, environmentally friendly inhibitor.
- It controls mild steel corrosion effectively.
- 10 ml of inhibitor offers 90% inhibition efficiency.
- Polarization study shows that garlic extract acts as cathodic inhibitor and protective film is formed on the metal surface.
- FTIR confirms that the protective film consists of Fe^{2+} -allicin complex.

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