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Research Article

Allium Sativum (Garlic) Extract as Nontoxic Corrosion Inhibitor

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The inhibition efficiency (IE) of an aqueous extract of garlic in controlling corrosion of carbon steel in well water in the absence and presence of Zn^{2+} has been evaluated by mass-loss method. The formulation consisting of 2 mL of garlic extract and 25 ppm Zn^{2+} offers 70% inhibition efficiency to carbon steel immersed in well water. Polarization study reveals that this formulation controls the anodic reaction predominantly. FTIR spectra reveal that the protective film consists of Fe^{2+}-allicin complex and $Zn(OH)_2$.

1. Introduction

Environmental friendly inhibitors have attracted several researchers. Natural products are nontoxic, biodegradable, and readily available. They have been used widely as inhibitors. Natural products such as caffeine [1, 2] have been used as inhibitors. Corrosion inhibition of steel by plant extracts in acidic media has been reported [3, 4]. Scale inhibiting nature of plant extracts for various kinds of metals are summarized briefly [5]. Aqueous extract of Rosemary leaves [6], Zanthoxylum alatum [7], and *Lawsonia* [8] have been used to inhibit corrosion of metals. Corrosion inhibition of iron in hydrochloric acid solutions by naturally occurring henna has been investigated [9]. Corrosion inhibition of carbon steel in low chloride media by an aqueous extract of *Hibiscus rosasinensis Linn* has been evaluated [10]. Corrosion inhibition investigation of natural inhibitors is particularly interesting because they are nonexpensive, ecologically friendly, and possess no threat to the environment. The present work is undertaken:

(i) to evaluate the inhibition efficiency (IE) of an aqueous extract of garlic in controlling the corrosion of carbon steel in well water in the absence and presence of Zn^{2+}

(ii) to analyze the protective film formed on the carbon steel by FTIR spectra,

(iii) to understand the mechanistic aspects of corrosion inhibition by potentiodynamic polarization study,

(iv) and to propose a suitable mechanism for corrosion inhibition.

2. Experimental Procedure

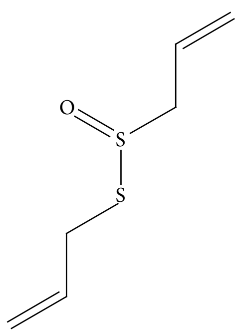
2.1. Preparation of Garlic Extract. An aqueous extract of garlic was prepared by grinding 20 g of garlic with double distilled water, filtering the impurities, and making up to 100 mL. The extract was used as corrosion inhibitor in the present study.

2.2. Preparation of Specimens. Carbon steel specimens (0.0267% S, 0.06% P, 0.4% Mn, 0.1% C, and the rest iron) of dimensions 1.0 cm × 4.0 cm × 0.2 cm were polished to a mirror finish and degreased with trichloroethylene.

2.3. Mass-Loss Method. Relevant data on the well water used in this study are given in Table 1. Carbon steel specimens in triplicate were immersed in 100 mL of well water containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for 3 days. The weight of the specimens before and after immersion was determined using Shimadzu balance, model AY 62. The corrosion products were cleansed

Table 1: Parameters of well water.

Parameter	Value
pH	8.6
Conductivity	2620 μmho/cm
TDS	1835 mg/L
Chloride	450
Sulphate	110
Total hardness	96



Scheme 1: Structure of allicin.

with Clarke's solution [11]. The inhibition efficiency (IE) was then calculated using the following equation:

$$IE = 100\left[1-\left(\frac{W_2}{W_1}\right)\right]\%, \quad (1)$$

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

2.4. Surface Examination. The carbon steel specimens were immersed in various test solutions for a period of 3 days, taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed by FTIR spectroscopic study.

2.5. Potentiodynamic Polarization. Polarization studies were carried out in an H&CH electrochemical work station impedance analyzer model CHI 660A. A three-electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was used as the reference electrode, and a rectangular platinum foil was used as the counter electrode.

2.6. FTIR Spectra. FTIR spectra were recorded in a Perkin-Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr, made into pellets, and FTIR spectra were recorded.

3. Results and Discussion

3.1. Analysis of Results of Mass-Loss Method. The corrosion rate (CR) of carbon steel immersed in well water (whose composition is given in Table 1) in the absence and presence of inhibitor systems is given in Table 2. The inhibition efficiencies are also given in the Table. It is seen from Table 2 that the aqueous extract of garlic is a good inhibitor to carbon steel in well water. 2 mL of garlic shows 50% IE. As concentration of garlic extract increases, IE also increases. That is, at higher concentrations, garlic accelerates corrosion inhibition [12, 13].

Table 2: Corrosion rate (CR) of carbon steel immersed in well water in the absence and presence of inhibitors and the inhibition efficiency (IE) obtained by mass-loss method. Immersion period: 3 days; inhibitor: garlic extract + Zn^{2+}.

	Zn^{2+}			
Garlic extract mL	0 (ppm)		25 (ppm)	
	CR (mdd)	IE %	CR (mdd)	IE %
0	22.42	—	17.94	20
2	11.21	50	6.73	70
4	7.17	68	4.48	80
6	2.24	90	1.79	92
8	1.35	94	0.90	96

3.1.1. Influence of Zn^{2+} on the Inhibition Efficiency of Garlic Extract. The influence of Zn^{2+} on the IE of garlic extract is given in Table 2. In the presence of Zn^{2+} (25 ppm), excellent inhibitive property is shown by garlic extract. For example, 2 mL of garlic extract accelerate corrosion of carbon steel (IE = 50%); 25 ppm of Zn^{2+} have 20% IE, but their combination has 70%.

3.2. Analysis of Polarization Curves. The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors are shown in Figures 1(a) and 1(b). The corrosion parameters are given in Table 3. When carbon steel is immersed in well water the corrosion potential is −704 mV versus SCE (saturated calomel electrode). The corrosion current is 2.600×10^{-6} A/cm^2. When 2 mL of garlic extract and 25 ppm of Zn^{2+} are added to the above system, the corrosion potential shifted to the anodic side (−690 mV versus SCE). This suggests that this formulation controls the anodic reaction predominantly. In the presence of the inhibitor system, the corrosion current decreases from 2.600×10^{-6} A/cm^2 to 2.353×10^{-6} A/cm^2. This suggests the inhibitive nature of this inhibitor system [14, 15].

3.3. Analysis of FTIR Spectra. The active principle in an aqueous extract of garlic is allicin. It consists of S=O and S group.

A few drops of an aqueous extract of garlic were dried on a glass plate. A solid mass was obtained. Its FTIR spectrum is shown Figure 2(a). Vinyl group appeared at 1026.28 cm^{-1}. S=O appeared at 1026 cm^{-1} and S at 1237.58 cm^{-1}. Thus the structure of allicin is confirmed by FTIR spectra (Scheme 1) [16]. The FTIR spectrum of complex prepared by mixing garlic extract and Zn^{2+} is shown in Figure 2(b). The band due to conjugated double bonds shifts from

TABLE 3: Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitors. Inhibitor system: garlic extract + Zn^{2+} system.

System	E_{corr} mV versus SCE	b_a (mV/decade)	b_c (mV/decade)	I_{corr} (A/cm^2)	LPR Ohm cm^2
Well water	−704	229.7	177.7	2.600×10^{-6}	16757.3
Garlic extract (2 mL) + Zn^{2+} (25 ppm)	−690	220.5	179.1	2.353×10^{-6}	17366.4

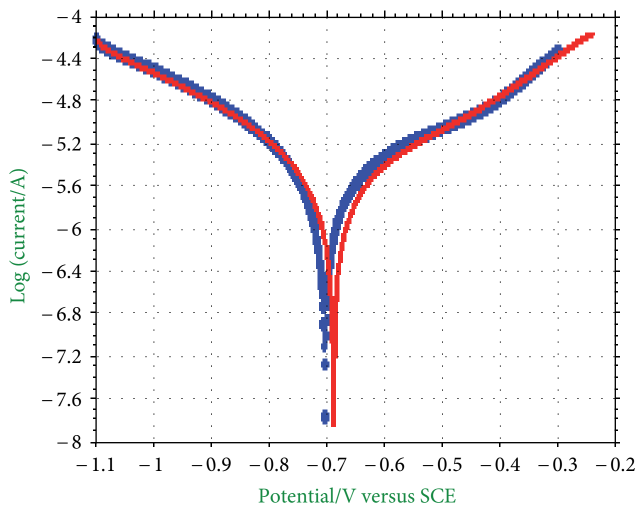


FIGURE 1: Polarization curves of carbon steel immersed in (a) well water and (b) well water +2 mL garlic extract +25 ppm of Zn^{2+}.

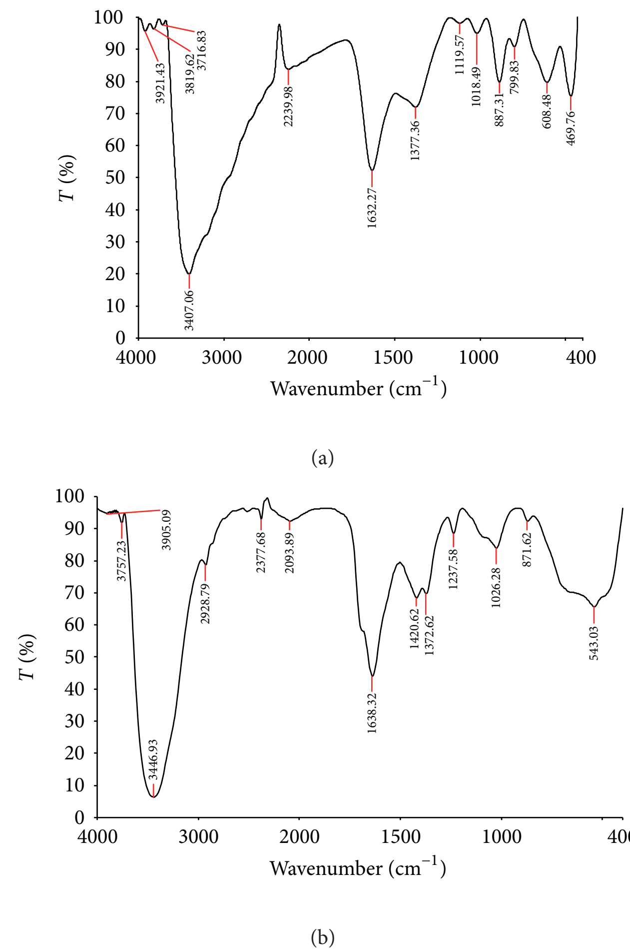


FIGURE 2: (a) FTIR spectra of solid mass obtained by evaporating the garlic extract. (b) FTIR spectra of film formed on surface of the carbon steel specimen after immersion in well water containing 2 mL of garlic extract and 25 ppm of Zn^{2+}.

3757.23 cm^{-1} to 3819.62 cm^{-1}. The band at 608.46 corresponds to Zn–O stretching. The OH stretching frequency appears at 3407.06 cm^{-1}. This confirms the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface [17–19]. Since there is complete coordination between Fe^{2+} and allicin, the band due to the formation of the complex gets vanished in the FTIR spectrum of the film formed on the surface of carbon steel by garlic extract (Figure 2(b)) [20, 21].

3.4. Mechanism of Corrosion Inhibition. Mass-loss study reveals that the formulation consisting of 2 mL of garlic extract +25 ppm of Zn^{2+} offers 70% IE to carbon steel immersed in well water. Polarization study reveals that this formulation controls the anodic reaction predominantly. FTIR spectra reveal that the protective film consists of Fe^{2+}-allicin complex and $Zn(OH)_2$. In order to explain the above facts in a holistic way, the following mechanism of corrosion inhibition is proposed.

(i) When the formulation consisting of well water, garlic extract, and Zn^{2+} is prepared, there is formation of Zn^{2+}-allicin complex in solution.

(ii) When carbon steel is immersed in the solution, the Zn^{2+}-allicin complex diffuses from the bulk of the solution towards the metal surface.

(iii) On the metal surface, Zn^{2+}-allicin complex is converted into Fe^{2+}-allicin complex. Zn^{2+} is released.

(iv) Zn^{2+}-allicin + Fe^{2+} $\rightarrow$ Fe^{2+}-allicin + Zn^{2+}.

(v) The released Zn^{2+} combines with OH^- to form $Zn(OH)_2$.

(vi) $Zn^{2+} + 2\,OH^- \rightarrow Zn(OH)_2$.

(vii) Thus, the protective film consists of Fe^{2+}-allicin complex and $Zn(OH)_2$.

4. Conclusions

The present study leads to the following conclusions:

(i) the formulation consisting of 2 mL garlic extract and 25 ppm of Zn^{2+} offers 70% inhibition efficiency to carbon steel immersed in well water;

(ii) polarization study reveals that this formulation controls the anodic reaction predominantly;

(iii) FTIR spectra reveal that the protective film consists of Fe^{2+}-allicin complex and $Zn(OH)_2$.

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