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RESEARCH ARTICLE

Curcumin Dye as Corrosion Inhibitor for Carbon Steel in Sea Water

V. JOHNSIRANI[a*], J. SATHIYABAMA[a], S. RAJENDRAN[a,b] and R. NAGALAKSHMI[c]

[a]P. G and Research Department of Chemistry, GTN Arts College, Dindigul-624005, Tamilnadu, India

[b]Department of Chemistry, RVS School of Engineering and Technology, Dindigul-624005, Tamilnadu, India

[c]Department of Chemistry, Arupadaiveedu Institute of Technology, Chennai, Tamilnadu, India

johnsirani15@gmail.com

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Abstract: The inhibition efficiency (IE) of an aqueous extract of the(*Curcuma longa* L.) plant material rhizome powder has been used as a corrosion inhibitor in controlling corrosion of carbon steel in sea water, by the weight-loss study, in the absence and presence of Zn^{2+}. The main constituent of this plant extract is curcumin. The results show that 93% IE is provided by binary system consisting of 10 mL of curcumin dye (CD) and 50 ppm of Zn^{2+}. Polarization study reveals that CD and Zn^{2+} system functions as mixed type inhibitor. The nature of the protective film formed on metal surface has been analysed by FTIR spectra.

Keywords: Corrosion inhibition, Curcumin, Seawater, FTIR.

Introduction

The extracts from plant leaves, roots and seeds have been studied and found to be cheap, environmental friendly and good corrosion inhibitors. Among the plants leaves extracts studied include opuntia extract[1], carica papaya (CP) and *Azadirachta Indica* (AI)[2], *Vernonia Amygdalina*[3], *Telfaria occidentalis*[4] and *Phyllanthus Amarus*[5]. In the present research work, an aqueous extract of the plant material rhizome powder has been taken as it is a good corrosion inhibitor for carbon steel in sea water. Turmeric has been used in India for hundreds of years and is a major part of Ayurvedic medicine. It was first used as a dye and then later for its possible medicinal properties[6]. Some research results show that there are compounds in turmeric with anti-fungal and anti-bacterial properties; however, curcumin is not one of them[7]. In another preliminary research example, curcumin is being studied for whether it alters the response to chemotherapy in patients with advanced bowel cancer[8], as found in a laboratory study[9]. Turmeric makes a poor fabric dye, as it is not very light fast. However, turmeric is commonly used in Indian and Bangladeshi clothing, such as saris and Buddhist monks' robes[10].

The present work is undertaken to evaluate the inhibition efficiency (IE) of curcumin dye (CD)-Zn^{2+} system in controlling corrosion of carbon steel immersed in sea water in the absence and presence of Zn^{2+} by weight loss method; to study the mechanism of corrosion inhibition by polarization study; to analyse the protective film by FTIR spectra and to propose the mechanism of corrosion inhibition based on the above results

Experimental

10 g of rhizome (*Curcuma longa* L.) powder was weighed and boiled with double distilled water. The yellow dye curcumin was filtered to remove suspending impurities and made up to 100 mL. The curcumin dye (CD) was used as corrosion inhibitor in the present study.

Preparation of specimen

Carbon steel specimens (0.02 6% S, 0.06% P, 0.4% Mn, 0.1% C and rest iron) of the dimensions 1.0x4.0x0.2 cm were polished to a mirror finish, degreased with trichloroethylene and used for the weight-loss method and surface examination studies.

Weight-loss method

Carbon steel specimens were immersed in 100 mL of the medium containing various concentrations of the inhibitor in the absence and presence of Zn^{2+} for 1day. The weights of the specimens before and after immersion were determined using a balance Shimadzu AY62 model. The corrosion IE was then calculated using the equation.

$$IE = 100\ [1-(W_2/W_1)]\ \%$$

Where W_1 is the weight loss value in the absence of inhibitor and W_2 is the weight loss value in the presence of inhibitor.

Polarization study

Polarization studies were carried out with a CHI-electrochemical workstation with impedance model 660A. A three electrode cell assembly was used. The working electrode was carbon steel. A saturated calomel electrode (SCE) was as the reference electrode and Platinum foil was used as the counter electrode.

Fourier transform infrared spectra

These spectra were recorded in a Perkin-Elmer-1600 spectrophotometer using KBr pellet. The FTIR spectrum of the protective film was recorded by carefully removing the film, mixing it with KBr and making the pellet.

Results and Discussion

Weight-loss method

The calculated inhibition efficiencies (IE) of curcumin dye in controlling the corrosion of carbon steel immersed in sea water both in the absence and presence of zinc ion have been tabulated in Table 1. The calculated values indicate the ability of curcumin dye to be a good corrosion inhibitor. The inhibition efficiency was found to be enhanced in the presence of zinc ion. The formulation consisting of 10 mL of CD and 50 ppm of Zn^{2+} offers 93% inhibition efficiency. That is, mixture of inhibitors shows better IE than the individual inhibitors[11].

Potentiodynamic polarization study

Polarization study has been used to detect the formation of protective film on the metal surface[12-13] . When a protective film is formed on the metal surface, the linear polarization resistance (LPR) increases and the corrosion current (I_{corr}) decreases. The potentiodynamic polarization curves of carbon steel immersed in various test solutions are shown in Figure 1. The corrosion parameters namely, corrosion potential (E_{corr}), Tafel slopes (b_c=cathodic; b_a=anodic), linear polarization resistance (LPR) and corrosion current (I_{corr}) are given in Table 2.

Table 1. The corrosion inhibition efficiencies and the corresponding corrosion rates (millimeter per year) of CD – Zn^{2+} system

Inhibitor CD, mL	Zn^{2+}, ppm					
	0		25		50	
	IE%	CR, mm/y	IE%	CR, mm/y	IE%	CR, mm/y
0	-	0.1576	16	0.1323	47	0.0835
2	48	0.0819	65	0.0551	80	0.0315
4	55	0.0709	71	0.0457	82	0.0283
6	60	0.0630	73	0.0425	85	0.0236
8	62	0.0598	75	0.0394	90	0.0157
10	63	0.0583	77	0.0362	93	0.0110

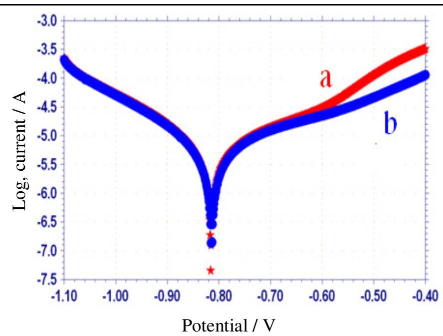


Figure 1. Polarization curves of carbon steel immersed in various test solutions, (a) sea water, (b) sea water + CD 10 mL + Zn^{2+} 50 ppm

Table 2. Potentiodynamic polarization curves of carbon steel immersed in various test solution

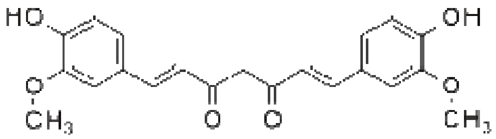
System	E_{corr} mV *vs.* SCE	b_c mV/decade	b_a mV/decade	LPR ohm cm^2	I_{corr} A/cm^2
Sea water	-816	157	239	$6.500x10^3$	$6.354x10^{-6}$
Sea water + 10 mL CD +50 ppm Zn^{2+}	-814	156	230	$7.354x10^3$	$5.502x10^{-6}$

When carbon steel was immersed in sea water, the corrosion potential was -816 mV *vs.* SCE. The formulation consisting of 10 mL of CD solution and 50 ppm of Zn^{2+} shifts the corrosion potential to -814 mV *vs.* SCE. The corrosion potential shift was very small. This suggests that the CD-Zn^{2+} formulation functions as a mixed inhibitor controlling the anodic reaction and cathodic reaction to the same extent.

The corrosion current value and LPR value for sea water were 6.354×10^{-6} A/cm^2 and $6.500x10^3$ ohm cm^2. For the formulation of CD (10 mL) and Zn^{2+} (50 ppm), the corrosion current value has decreased to $5.502x10^{-6}$ A/cm^2 and the LPR value has increased to $7.354x10^3$ ohm cm^2. This indicates that a protective film was formed on the metal surface. When a protective film was formed on the metal surface LPR value increases and corrosion current value decreases.

Analysis of FTIR spectra

The main constituent of rhizome powder is curcumin. The yellow colour of the extract is due to curcumin[14]. The structure of curcumin is shown in Scheme 1.



Scheme.1. Curcumin

The curcumin dye extract was evaporated to dryness to get a solid mass. Its FTIR spectrum is shown in Figure 2a. The –OH stretching frequency appears at 3408 cm^{-1}. The C=O stretching frequency appears at 171 cm^{-1}. The asymmetrical C-O-C stretching frequency of aryl alkyl ethers appears at 1224 cm^{-1}. The band at 1087 cm^{-1} corresponds to the symmetrical C-O-C stretching of alkyl aryl ether. Thus, curcumin was characterized by IR spectroscopy[15]. The FTIR spectrum of the protective film formed on the surface of the metal after immersed in the solution containing 50 ppm of Zn^{2+} and 10 mL of CD shown in Figure 2b. It is found that the -OH has shifted from 3408 cm^{-1} to 3400 cm^{-1}. The C=O stretching frequency has decreased from 1715 cm^{-1} to 1613 cm^{-1}. The asymmetrical C-O-C stretching frequency of alkyl aryl ether (1224 cm^{-1}) disappeared. The symmetrical C-O-C stretching of alkyl aryl ether (1087 cm^{-1}) disappeared. It was inferred that curcumin has coordinated with Fe^{2+} through the phenolic oxygen, ethereal oxygen, and carbonyl oxygen, resulting in the formation of the Fe^{2+} - curcumin complex on the anodic sites of the metal surface. The peak at 1360 cm^{-1} is due to Zn-O band. The peak at 3400 cm^{-1} is due to –OH stretching. Hence it is confirmed that $Zn(OH)_2$ is formed on the cathodic sites of the metal surface[16]. Thus, the FTIR spectral study leads to the conclusion that the protective film consists of the Fe^{2+}- curcumin complex[17] and $Zn(OH)_2$.

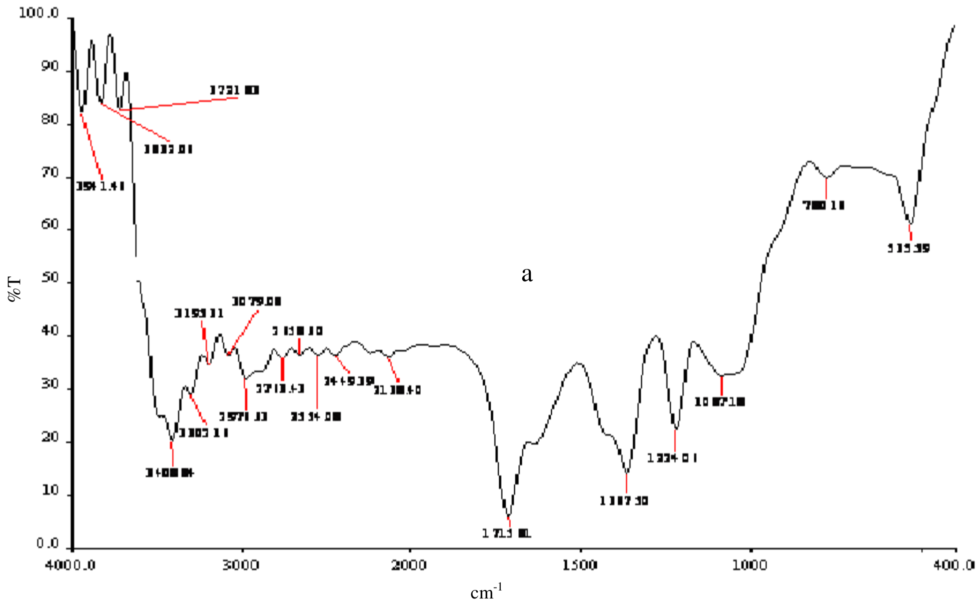


Figure 2a. FTIR spectrum of pure curcumin dye (dried solid mass, KBr)

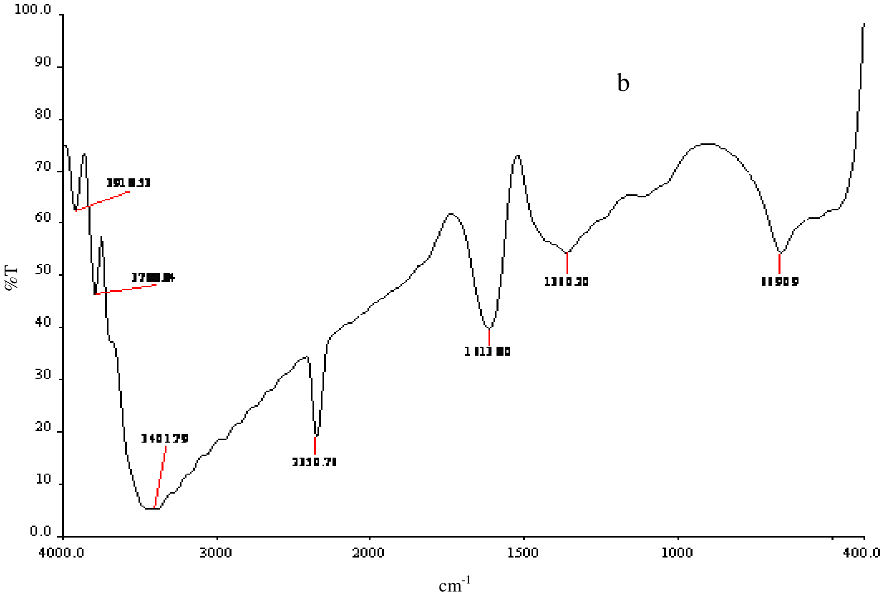


Figure 2b. FTIR spectrum of film formed on metal surface after immersion in sea water containing 10 mL of CD-50 ppm Zn^{2+}

Mechanism of corrosion inhibition

Weight loss method reveals that the formulation consisting of 10 mL of CD and 50 ppm of Zn^{2+} offers 93% IE to carbon steel immersed in sea water. Polarization study reveals that CD-Zn^{2+} system functions as a mixed inhibitor. FTIR spectra reveal that the protective film consists of Fe^{2+}-curcumin complex and $Zn(OH)_2$.

In order to explain the above facts in a holistic way, the following mechanism of corrosion inhibition is proposed. When the formulation consisting of sea water, curcumin dye and Zn^{2+} is prepared, there is formation of Zn^{2+} -curcumin complex in solution. When carbon steel is immersed in the solution, the Zn^{2+} - curcumin complex diffuses from the bulk of the solution towards the metal surface. - On the metal surface, Zn^{2+} - curcumin complex is converted into Fe^{2+} - curcumin complex.

Zn^{2+} is released

$$Zn^{2+}\text{ - curcumin} + Fe^{2+} \longrightarrow Fe^{2+}\text{ - curcumin} + Zn^{2+}$$

Conclusion

The present study leads to the following conclusions: The formulation consisting of 10 mL CD and 50 ppm Zn^{2+} has 93% inhibition efficiency to carbon steel immersed in sea water. Polarization study reveals that CD-Zn^{2+} system functions as a mixed inhibitor. FTIR spectra reveal that the protective film consists of Fe^{2+} - curcumin complex and $Zn(OH)_2$.

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