



Electrochemical Study and Spectroscopic Methods Used for Analyzing Protective Film Formed By L-Alanine on Carbon Steel in Well Water: A Green Approach

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ABSTRACT

The corrosion inhibition of carbon steel (CS) using the “green” inhibitor, L-alanine (L-Ala) was investigated. This study was conducted at pH 7.6. The effect caused by Zn^{2+} additive also was investigated. The study was done over a range of concentrations. Gravimetric method and electrochemical methods were applied. It was found that the L-alanine acts as a good inhibitor at pH 7.6. The inhibition efficiency increases with increasing L-Ala concentrations. The addition of Zn^{2+} to L-alanine significantly increased the inhibition efficiency. Tafel results indicated that decrease the corrosion current (I_{corr}) value. The influence of biocide SDS on the inhibition efficiency of L-alanine – Zn^{2+} system has been investigated. Also it is evident that at minimum concentration of biocides added to the inhibitor system, 100 % biocidal efficiency is noticed. The protective film formed on the metal surface has been analyzed by UV-visible, Fluorescence and FT-IR spectra. It is found that the protective film consists of Fe^{2+} - L-alanine complex and $\text{Zn}(\text{OH})_2$.

1. Introduction

Carbon steel finds a lot of application in industries like metal finishing, boiler scale removal, pickling baths etc. It gets rusted when it comes in contact with any aqueous medium. The use of inhibitors is one of the best methods for protecting metals against corrosion. Corrosion is a chemical or electrochemical process in nature with four components are: an anode, a cathode, an electrolyte and some direct electrical connection between the anode and cathode, the adsorbed inhibitor then acts to slow corrosion process by either: 1. Increasing the anodic or cathodic polarization behaviour; 2. Reducing the movement or diffusion of ions to the metallic surface. Corrosion inhibitors are used to prevent the effect of corrosion in such cases. The majority of well-known inhibitors are organic compounds containing heteroatom, such as O, N, S and multiple bonds [1]. Most of the organic compounds are not only expensive but also toxic to both human beings and environments [2] and therefore the use of hazardous chemical inhibitors is totally reduced because of environmental regulations. It is better to look for environmentally safe inhibitors. Many researchers investigated the inhibition effect of environment friendly inhibitors like amino acids on metal corrosion [3-13]. This is due to the fact that amino acids are non-toxic, biodegradable, relatively cheap, and completely soluble in aqueous media and produced with high purity at low cost. Various amino acids have been used to inhibit the corrosion of metals and alloys [3-13]. Eco-Friendly Inhibitor L-cysteine- Zn^{2+} System to control corrosion of carbon steel in Aqueous Medium [6]. The corrosion of SS 316L has been inhibited by glycine, leucine, valine, and arginine [7]. Sivakumar et al have used L-histidine to prevent corrosion on carbon steel [8]. Cystein, glycine, glutamic acid, and glutathione have been used as corrosion inhibitor to prevent the corrosion of copper in HCl [9]. Amino acid such as DL-phenylalanine has been used to prevent corrosion of carbon steel [10]. The corrosion of brass in O_2 -free NaOH has been prevented by methionine [11]. Sahaya Raja et al have used Glycine along with Zn^{2+} to prevent corrosion of carbon steel in well water [12]. Arginine - Zn^{2+} system has been used to inhibit corrosion of carbon steel [13]. The

environmental friendly L- alanine (Fig. 1) is chosen as the corrosion inhibitor for this present work. The aim of this research is to investigate the Inhibitive Effect of L- alanine. For this purpose the electrochemical studies such as potentiodynamic polarization and AC-impedance spectroscopy. Surface film studies such as UV-visible, Fluorescence and FT-IR spectra have been used in this present work.

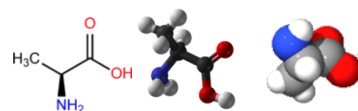


Fig.1 Various structural views of L – alanine

2. Experimental Methods

2.1 Determination of Corrosion Rate

All the weight of the carbon steel specimens before and after corrosion was carried out using Shimadzu Balance-AY62. Corrosion rates were calculated using the following relationship. Corrosion Rate (mm/y) = [loss in weight (mg) X 1000 / surface area of the specimen (dm^2) X period of the immersion (days)] X (0.0365/ ρ).

2.2 Electrochemical and Impedance Measurements

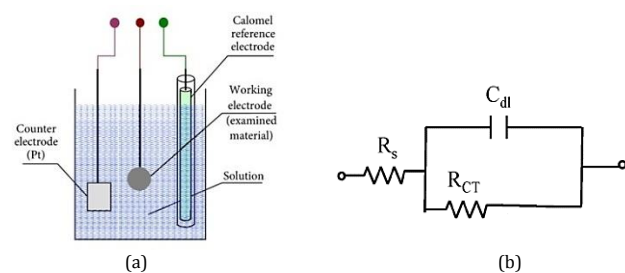
Potentiodynamic polarization studies and AC Impedance measurements are carried out using CHI electrochemical impedance analyzer (model 660A) is shown in scheme 1.

2.3 Characterisation Studies

UV- Visible absorption spectra of solutions were recorded in a UV spectra S-100 Analytic Jena spectrophotometer. FTIR Spectra were recorded in a Perkin – Elmer 1600 spectrophotometer. Fluorescence spectra of solutions and also the films formed on the metal surface were recorded using Jasco F – 6300 spectrofluorometer.

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Scheme 1 a) Circuit diagram of three – electrode assembly;
b) Equivalent circuit diagram: R_s is solution resistance, R_{CT} is charge transfer resistance, C_{dl} is double layer capacitance

3. Results and Discussion

3.1 Analysis of the Weight Loss Method

The inhibition efficiencies of the L-alanine- Zn^{2+} systems as a function of concentrations of L-alanine are shown in Fig. 2. It is observed that as the concentration of L-alanine increases the IE increases. Similarly, for a given concentration of L-alanine the IE increases as the concentration of Zn^{2+} increases. For example 250 ppm of L-alanine has 47 percent IE. Interestingly their combination (5 ppm of Zn^{2+} and 250 ppm L-alanine) has a high IE, namely, 83 percent. In presence of Zn^{2+} more amount of L-alanine is transported towards the metal surface. On the metal surface Fe^{2+} -L-alanine complex is formed on the anodic sites of the metal surface. Thus the anodic reaction is controlled. The cathodic reaction is the generation of OH^- , which is controlled by the formation of $Zn(OH)_2$ on the cathodic sites of the metal surface. Thus the anodic reaction and cathodic reaction are controlled effectively.

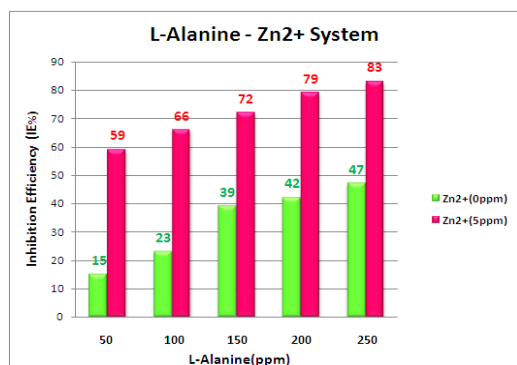


Fig. 2 The inhibition efficiencies (IEs) of carbon steel immersed in various test solutions

3.2 Synergism Parameters (S_i)

Synergism parameter (S_i) have been used to know the synergistic effect existing between two inhibitors [14-16]. Synergism parameter (S_i) can be calculated using the following relationship.

$$\text{Synergism parameters } (S_i) = 1 - \theta_{1+2} / 1 - \theta_{1+2}$$

Where	θ_{1+2}	=	$(\theta_1 + \theta_2) - (\theta_1\theta_2)$,
	θ_1	=	Surface coverage by L-alanine,
	θ_2	=	Surface coverage by Zn^{2+} ,
	θ_{1+2}	=	Surface coverage by both L-alanine and Zn^{2+}
	θ	=	Surface coverage = IE%/100

Table 1 Inhibition efficiencies and synergism parameters for various concentrations of L-Ala- Zn^{2+} (5 ppm) system, when carbon steel is immersed in well water.

L-alanine ppm	Inhibition efficiency IE (%)	Surface Coverage θ_1	Zn ²⁺ ppm	Inhibition efficiency IE (%)	Surface Coverage θ_2	Combined IE % θ_{1+2}	Combined surface coverage θ_{1+2}	Synergism Parameters S_i
50	15	0.15	5	8	0.08	59	0.59	1.91
100	23	0.23	5	8	0.08	66	0.66	2.08
150	39	0.39	5	8	0.08	72	0.72	2.00
200	42	0.42	5	8	0.08	79	0.79	2.54
250	47	0.47	5	8	0.08	83	0.83	2.87

The synergism parameters of L-alanine- Zn^{2+} system are given in Table 1 and shown in the Fig. 3. For different concentrations of inhibitors, S_i approaches 1 when no interaction between the inhibitor compounds exists. When $S_i > 1$, it points to synergistic effects. In the case of $S_i < 1$, it is an indication that the synergistic effect is not significant [15]. From Table 1, it is observed that value of synergism parameters (S_i) calculated from surface coverage were found to be one and above. This indicates that the synergistic effect exists between L-alanine and Zn^{2+} [16]. Thus, the enhancement of the inhibition efficiency caused by the addition of Zn^{2+} ions to L-alanine is due to the synergistic effect.

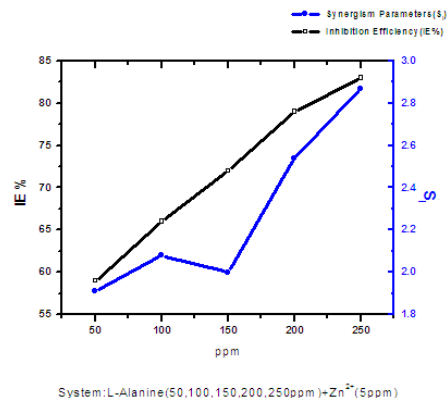


Fig. 3 Inhibition efficiencies and synergism parameters for various concentrations of L-Ala- Zn^{2+} (5 ppm) system

3.3 Analysis of Tafel Plot and Nyquist Plot

Tafel plot and Nyquist plot have been used to confirm the formation of protective film formed on the metal surface during corrosion inhibition process [6, 8, 10, 11, 13] are shown in Fig. 4. Tafel plot - It is observed when carbon steel was immersed in the presence of L-alanine (250 ppm) and Zn^{2+} (5 ppm) the corrosion potential has shifted from -673 mV vs SCE to -656 mV vs SCE. This indicates that a film is formed on the anodic sites of the metal surface. The corrosion current decreases from 5.980×10^{-7} A/cm² to 2.832×10^{-7} A/cm². Thus polarization study confirms the formation of a protective film on the metal surface. Nyquist plot - It is observed that when the inhibitors (L-alanine (250 ppm) + Zn^{2+} (5 ppm)) are added into the carbon steel immersed in well water the charge transfer resistance (R_c) increases from $1199 \Omega \text{ cm}^2$ to $11478 \Omega \text{ cm}^2$. The C_{dl} value decreases from 3.8832×10^{-9} F/cm² to 4.0560×10^{-10} F/cm².

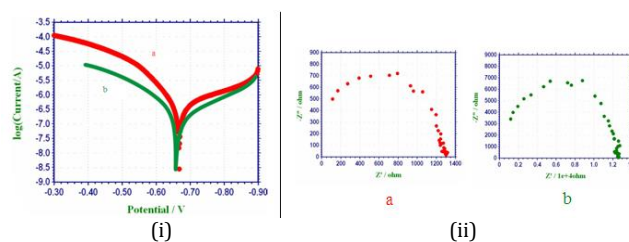


Fig. 4 i) Tafel Plot and ii) Nyquist plot - a) well water and b) well water+L-alanine (250 ppm)+ Zn^{2+} (5 ppm)

3.4 F'-Test

To know whether the synergistic effect existing between L-alanine and Zn^{2+} is statistically significant or not, F-test was used [17]. The results are given in Table 2. It is observed that the calculated F-value 27.42 is greater than the table value 5.32 for 8 degrees of freedom at 0.05 level of significance. Hence it is concluded that the synergistic effect existing between L-alanine and Zn^{2+} (5 ppm) is statistically significant. Therefore, it is concluded that the synergistic effect existing between L-alanine and Zn^{2+} (5 ppm) is statistically significant.

Table 2 Distribution of F-Value between the inhibition efficiency of various concentration of L-alanine (0 ppm of Zn^{2+}) and the inhibition efficiencies of L-alanine in the presence of 5 ppm of Zn^{2+} .

Source of variance	Sum of squares	Degrees of freedom	Mean square	F-value	Level of significance
Between the sample	761	1	761	27.42	p > 0.05
Within the sample	222	8	27.75		

3.5 Influence of Immersion Period on the Inhibition Efficiency of the L-alanine (250 ppm) - Zn²⁺ (5 ppm) System

The influence of immersion period on the IE of L-alanine - Zn²⁺ system is given in Table 3 and shown in the Fig. 5. It is observed that as the immersion period increases the IE decreases. This indicates that the protective film formed on the metal surface is unable to withstand the continuous attack of corrosive ions such as Cl⁻ ion (700 ppm) present in well water. There is a competition between the formation of FeCl₂ (and also FeCl₃) and Fe-L-alanine complex (on the anodic sites of the metal surface). A perusal of the results suggests that the formation of FeCl₂ is favoured when compared with the formation of Fe-L-alanine complex [18,19]. Similar observations have been made by Selvaraj et al [18], while studying corrosion inhibition, using glycine and also by Rajendran et al.[19], while investigating corrosion inhibition by sodium dodecyl sulphate.

Table 3 Influence of immersion period on the inhibition efficiency of the L-alanine (250 ppm) - Zn²⁺ (5 ppm) system (pH=7.6)

System	Immersion period (days)			
	3	5	7	10
Well water CR mm/y	0.0514	0.0537	0.0565	0.0607
Well water + L - alanine (250 ppm) + Zn ²⁺ (5 ppm) CR mm/y	0.0149	0.0204	0.0252	0.0315
IE %	71	62	55	48

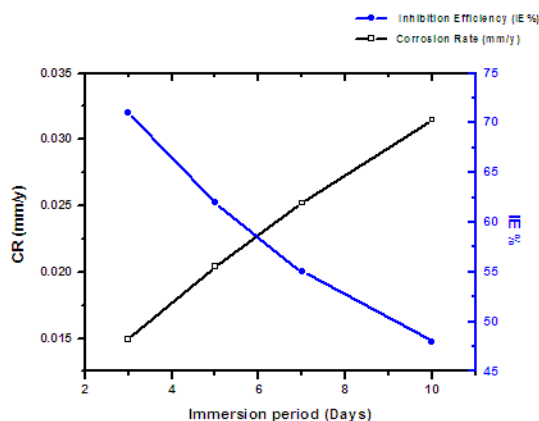


Fig. 5 Influence of immersion period Variations

3.6 Influence of pH on the IE Efficiency of L-alanine-Zn²⁺ System

The influence of pH on the IE of L-alanine-Zn²⁺ system is given in the Table 4 and shown in the Fig. 6. It is observed that at low pH (pH = 3 dilute sulphuric acid) the IE is low (38%). This decrease in IE is due to the fact that the protective film formed on the metal surface is broken by the attack of H⁺ ions. At pH 7.6 the IE is 80%. Further increase in pH of the solution lowers IE substantially. Experimental results suggest that the amount of Zn²⁺ available to transport L-alanine towards the metal surface decreases at high pH. This may be due to the fact that zinc ions in the bulk of the solution are precipitated as zinc hydroxide [20].

Table 4 Influence of various pH on the inhibition efficiency of the L-alanine (250 ppm) - Zn²⁺ (5 ppm) system

System	Variation of pH		
	3	7	11
Well water CR mm/y	0.0700	0.0460	0.0649
Well water + L-alanine (250 ppm) + Zn ²⁺ (5 ppm) CR mm/y	0.0434	0.00920	0.0344
IE %	38	80	47

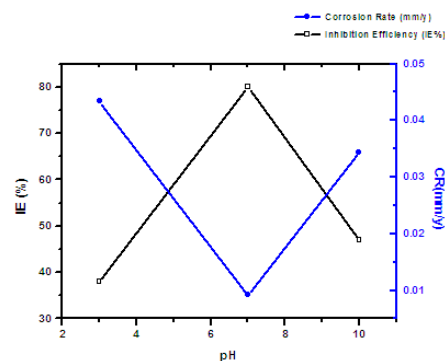


Fig. 6 Influence of pH Variations

3.7 Analysis of UV-Visible Absorption Spectra

Analysis of UV-visible absorption spectra are given in the Table 5. The UV-visible absorption spectra of an aqueous solution containing L-alanine is shown in Fig. 7a. A peak appears at 242 nm, when Fe²⁺ (FeSO₄·7H₂O) is added, a peak appears at 288 nm and there is an increase in intensity is shown in the Fig.7b. This indicates that a complex in solution is formed between L-alanine - Fe²⁺ [21,22].

Table 5 Analysis of UV-visible absorption spectra

System	Wavelength (nm)	Absorbance
L-alanine	242	2.4232
L-alanine + FeSO ₄ ·7H ₂ O	288	2.8427

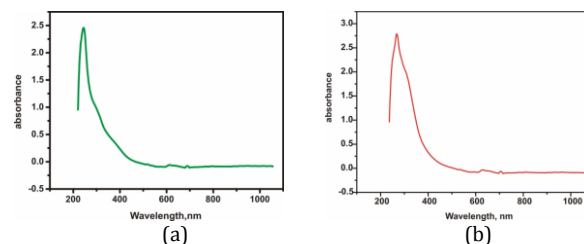


Fig. 7 a) UV-absorption spectra of solution containing L -alanine, (b) L-alanine + Fe²⁺ complex in solution

3.8 Analysis of the Fluorescence Spectra

Analysis of the fluorescence spectra are given in Table 6. Fluorescence spectra have been used to detect the presence of Fe²⁺-inhibitor complex formed on the metal surface [23-25]. The emission spectrum (λ_{ex} = 280 nm) of the Fe²⁺-L-alanine complex solution, prepared by mixing an aqueous solution of Fe²⁺ (prepared freshly from FeSO₄·7H₂O) and L-alanine, is shown in Fig. 8a. A peak appears at 337 nm. The emission spectrum (λ_{ex} = 280 nm) of the film formed on the metal surface after immersion in the solution containing, 250 ppm L-alanine and 5 ppm of Zn²⁺ is shown in Fig. 8b. A peak appears at 333 nm. This indicates that the film present on the metal surface consist of Fe²⁺-L-alanine complex. The slight variation in the position of the peak is due to the fact that the Fe²⁺-L-alanine complex is entailed in Zn(OH)₂ present on the metal surface. Further, the increase in intensity of the peak is due to the fact that the metal surface, after the formation of the protective film is very bright, the film is very thin and there is enhancement in the intensity of the peak [24]. The number of peak obtained is only one. Hence it is inferred that the complex is of somewhat highly symmetric in nature [25].

Table 6 Analysis of the Fluorescence spectra

Fluorescence spectra (λ _{ex} = 280nm)		
System	Wavelength (nm)	Intensity (a.u)
Fe ²⁺ -L-alanine complex in solution	337	83.2
Protective film formed on the surface of carbon steel after immersion in the solution containing 250 ppm of L-alanine and 5 ppm of Zn ²⁺	333	265.7

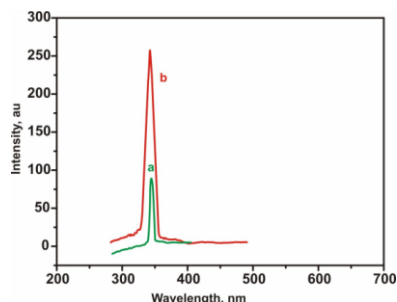


Fig. 8 Fluorescence spectra a) Fe^{2+} - L-alanine complex in solution; b) Protective film formed on the surface of carbon steel after immersion in the solution containing 250 ppm of L-alanine and 5 ppm of Zn^{2+}

3.9 Analysis of FTIR Spectra

Analysis of FTIR spectra are given in Table 7. FTIR spectra have been used to analyze the protective film formed on the metal surface [26-30]. The FTIR spectrum (KBr) of pure L-alanine is shown in Fig. 9a. The C=O stretching frequency of carboxyl group appears at 1571 cm^{-1} . The CN stretching frequency appears at 1127 cm^{-1} . The NH stretching frequency of the amine group appears at 3090 cm^{-1} [27-29]. The FTIR spectrum of the film formed on the metal surface after immersion in the solution containing well water, 250 ppm of L-alanine and 5 ppm Zn^{2+} is shown in Fig. 9b. The C=O stretching frequency has shifted from 1571 to 1592 cm^{-1} . The CN stretching frequency has shifted from 1127 to 1202 cm^{-1} . The NH stretching frequency has shifted from 3047 to 3271 cm^{-1} . This observation suggests that L-alanine has coordinated with Fe^{2+} through the oxygen atom of the carboxyl group and nitrogen atom of the amine group resulting in the formation of Fe^{2+} -L-alanine complex on the anodic sites of the metal surface. The peak at 580 cm^{-1} corresponds to Zn-O stretching. The peak at 3524 cm^{-1} is due to OH- stretching. This confirms that $\text{Zn}(\text{OH})_2$ is formed on the cathodic sites of metal surface [30]. Thus the FTIR spectral study leads to the conclusion that the protective film consist of Fe^{2+} -L-alanine complex and $\text{Zn}(\text{OH})_2$.

Table 7 Analysis of FTIR spectra

Functional group	Frequency (cm ⁻¹)	
FTIR spectrum of pure L – alanine		
C=O stretching	1571 cm ⁻¹	
CN stretching	1127 cm ⁻¹ .	
NH stretching	3047cm ⁻¹	
FTIR spectrum of the film formed on the metal surface after immersion in the solution containing well water, 250 ppm of L-alanine and 5 ppm Zn ²⁺		
Functional group	Frequency (cm ⁻¹) shifted from	Frequency (cm ⁻¹) shifted to
C=O stretching	1571 cm ⁻¹	1592 cm ⁻¹
CN stretching	1127 cm ⁻¹ .	1202 cm ⁻¹
NH stretching	3047 cm ⁻¹	3271 cm ⁻¹
Zn – O stretching		580 cm ⁻¹
OH- stretching		3524 cm ⁻¹

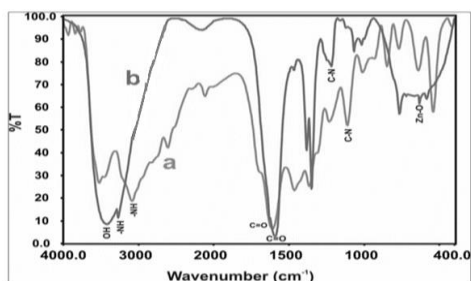


Fig. 9 FTIR spectra a) Pure L-alanine; b) Film formed on the metal surface after immersion in well water + L-alanine (250 ppm) + Zn^{2+} (5 ppm)

3.10 Influence of Sodium dodecyl Sulfate (SDS) on the Corrosion Inhibition Efficiency of the L-alanine - Zn^{2+} System (pH = 7.6)

SDS is an anionic surfactant. It is a biocide [31, 32]. The corrosion IE and biocidal efficiency of the L-alanine- Zn^{2+} - SDS system are given in the Table 8 and shown in the Fig. 10. When carbon steel was immersed in well water (in the absence of inhibitor), the number of colony forming units per mL is 10.72×10^3 . Various concentrations of SDS (50, 100, 150, 200 and 250) ppm were added to the L-alanine (250 ppm) - Zn^{2+} (5 ppm) system. The corrosion IE and the biocidal efficiency were calculated. The formulation

consisting of 250 ppm of L-alanine and 5 ppm Zn^{2+} has 83% corrosion IE and 13.5% biocidal efficiency. When 50 ppm of SDS is added to the L-alanine- Zn^{2+} system, the IE increases from 83% to 89% the biocidal efficiency increased from 13.5% to 60.6%. It is observed that the formulation consisting of 250 ppm L-alanine; 5 ppm of Zn^{2+} and 150 ppm of SDS has 98% corrosion IE and 100% biocidal efficiency.

Table 8 Influence of SDS on the corrosion inhibition on efficiency of the L-alanine (250 ppm) + Zn^{2+} (5 ppm) system (pH=7.6)

L-alanine ppm	Zn^{2+} ppm	SDS ppm	CR mm/y	IE %	Colony forming units/mL	Biocidal Efficiency (BE) %
0	0	0	0.0473	--	10.72×10^3	--
250	5	0	0.0080	83	9.27×10^3	13.5
250	5	50	0.0052	89	4.22×10^3	60.6
250	5	100	0.0024	95	0.26×10^3	97.6
250	5	150	0.0009	98	Nil	100
250	5	200	0.0009	98	Nil	100
250	5	250	0.0009	98	Nil	100

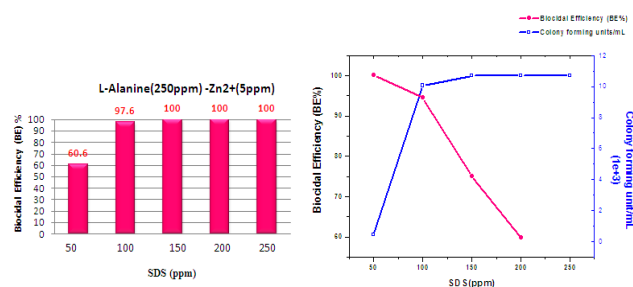


Fig. 10 Influence of SDS on the corrosion inhibition on efficiency of the L-alanine (250 ppm) + Zn^{2+} (5 ppm) system

4. Conclusion

Weight loss study reveals that the formation consisting of 250ppm of L-alanine and 5 ppm of Zn^{2+} has 83% inhibition efficiency, in controlling corrosion of carbon steel in well water. A synergistic effect exists between Zn^{2+} and L-alanine system. Statistical study of F-test revealed that the synergistic effect existing between L-alanine and Zn^{2+} is statistically significant. When immersion period increases the IE decreases in the L-alanine- Zn^{2+} system. This indicates that the protective film formed on the metal surface is unable to withstand the continuous attack of corrosive ions such as Cl^- ion present in well water and it is observed that at low pH the IE is low. This decrease in IE is due to the fact that the protective film formed on the metal surface is broken by the attack of H^+ ions. Further increase in pH of the solution lowers IE substantially. Experimental results suggest that the amount of Zn^{2+} available to transport L-alanine towards the metal surface decreases at high pH. This may be due to the fact that zinc ions in the bulk of the solution are precipitated as zinc hydroxide. Polarization study reveals that L-alanine system function as anodic inhibitors. AC impedance spectra reveal that a protective film is formed on the metal surface. UV-visible absorption spectra indicate that a complex in solution is formed between L-alanine- Fe^{2+} . Fluorescence spectra indicates that the film present on the metal surface consist of Fe^{2+} -L-alanine complex and $\text{Zn}(\text{OH})_2$. FTIR spectral study suggests that L-alanine has coordinated with Fe^{2+} through the oxygen atom of the carboxyl group and nitrogen atom of the amine group resulting in the formation of Fe^{2+} -L-alanine complex on the anodic sites of the metal surface and $\text{Zn}(\text{OH})_2$ is formed on the cathodic sites of metal surface. Thus the FTIR spectral study leads to the conclusion that the protective film consist of Fe^{2+} - L-alanine complex and $\text{Zn}(\text{OH})_2$. The effective synergistic formulation with 50 ppm of SDS has 98 % corrosion inhibition efficiency and 100% biocidal efficiency.

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