



# Carbon steel corrosion inhibition by combined effect of L- Methionine and ZnSO<sub>4</sub> in aqueous solution: Electrochemical, FTIR, and Statistical study

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**Abstract :** The corrosion and inhibition behaviors of carbon steel in the presence of L-Methionine and ZnSO<sub>4</sub> have been studied using gravimetric method and electrochemical techniques. Results obtained by various techniques are close to each other and maximum Inhibition efficiency is 93%. Synergistic parameters and Statistical study of “F” test suggest that a synergistic effect exists between L-Methionine and Zn<sup>2+</sup>. The protective film on the metal surface has been analyzed by FT – IR spectra. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from weight loss study, electrochemical study and surface analysis technique. The inhibitor L-Methionine -Zn<sup>2+</sup> system may find application in cooling water system.

**Keywords:** Carbon steel, L-Methionine, ZnSO<sub>4</sub>, synergistic effect, F-Test, FT-IR spectra

## 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<sup>1</sup>. Most of the organic compounds are not only expensive but also toxic to both human beings and environments<sup>2</sup> 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<sup>3-13</sup>. 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<sup>14-17</sup>. Eco-Friendly Inhibitor L-Cysteine-Zn<sup>2+</sup> System to control corrosion of carbon steel in Aqueous Medium<sup>6</sup>. The corrosion of SS 316L has been inhibited by glycine, leucine, valine, and arginine<sup>7</sup>. Sivakumar et al have used L-Histidine to prevent corrosion on carbon steel<sup>8</sup>. Cystein, glycine, glutamic acid, and glutathione have been used as corrosion inhibitor to prevent the corrosion of copper in HCl<sup>9</sup>. Amino acid such as DL-Phenylalanine has been used to prevent corrosion of carbon steel<sup>10</sup>. The corrosion of brass in O<sub>2</sub>-free NaOH has been prevented by methionine<sup>11</sup>. Sahaya Raja *et al* have used Glycine along with Zn<sup>2+</sup> to prevent corrosion of carbon steel in well water<sup>12</sup>. Synergistic and Antagonistic Effect of L – Alanine for carbon steel in aqueous medium has been investigated<sup>18</sup>. Prathipa et al was studied corrosion inhibition of carbon steel using green inhibitor (L-

Alanine)<sup>19</sup>. Arginine - Zn<sup>2+</sup> system has been used to inhibit corrosion of carbon steel<sup>13, 20</sup>. L – Alanine as inhibitor for carbon steel in well water was studied<sup>21</sup>.

## 2. Material and Methods:

**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<sup>2</sup>) X period of the immersion (days)] X (0.0365/ ρ). **Electrochemical and Impedance measurements** - Potentiodynamic polarization studies and AC Impedance measurements are carried out using CHI electrochemical impedance analyzer (model 660A). **Surface characterization studies- FTIR Spectra** were recorded in a Perkin – Elmer 1600 spectrophotometer. All solutions were prepared using well water collected from N.S.Nagar, Dindigul, Tamil Nadu, India. The study was carried out at room temperature (303K). The chosen environmental well water and its physicochemical parameters are given in **Table 1**.

**Table 1 Physico – chemical parameters of well water**

Parameters	Value
pH	8.0
Conductivity	1770 μmhos/cm
Total Dissolved Solids	1219 ppm
Total hardness	424 ppm
Total Alkalinity	396 ppm
Magnesium	69 ppm
Calcium	92 ppm
Sodium	174 ppm
Potassium	56 ppm
Chloride	669 ppm
Sulphate	217 ppm

## 3. Result and discussion

### 3.1 Analysis of the weight loss method

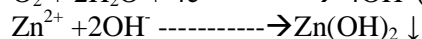
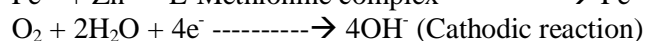
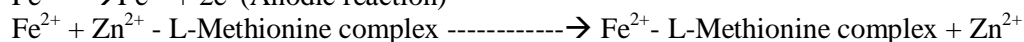
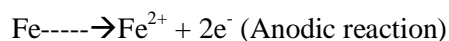
Corrosion rates (CR) of carbon steel immersed in well water in the absence and presence of inhibitor (L-Methionine) are given in **Table 2**. The inhibition efficiencies (IE) are also given in this table. It is observed that L-Methionine shows some inhibition efficiencies. 50 ppm of L-Methionine has 24 percent IE, as the concentration of L-Methionine increases, IE increases.

**Table.2: Corrosion rates (CR) of carbon steel immersed in well water in the presence and absence of inhibitor system at various concentrations and the inhibition efficiencies (IEs) obtained by weight loss method.**

L-Methionine ppm	Zn <sup>2+</sup> (0 ppm)		Zn <sup>2+</sup> (5 ppm)	
	IE %	CR (mm/y)	IE %	CR (mm/y)
0	--	0.1233	--	--
0	--	--	10	0.1110
50	24	0.0937	66	0.0419
100	31	0.0851	72	0.0345
150	38	0.0764	79	0.0259
200	47	0.0653	86	0.0172
250	59	0.0505	93	0.0086

### 3.2 .Influence of Zn<sup>2+</sup> on the inhibition efficiencies of L-Methionine

The influence of Zn<sup>2+</sup> on the inhibition efficiencies of L-Methionine is given in **Table 2**. It is observed that as the concentration of L-Methionine increases the IE increases. Similarly, for a given concentration of L-Methionine the IE increases as the concentration of Zn<sup>2+</sup> increases. It is also observed that a synergistic effect exists between L-Methionine and Zn<sup>2+</sup>. For example, 5 ppm of Zn<sup>2+</sup> has 10 percent IE; 250 ppm of L-Methionine has 59 percent IE. Interestingly their combination has a high IE, namely, 93 percent. In presence of Zn<sup>2+</sup> more amount of L-Methionine is transported towards the metal surface. Thus the anodic reaction and cathodic reaction are controlled effectively. This accounts for the synergistic effect existing between Zn<sup>2+</sup> and L-Methionine.



### 3.3 Synergism parameters (S<sub>I</sub>)

Synergism parameter (S<sub>I</sub>) have been used to know the synergistic effect existing between two inhibitors<sup>22-24</sup>. Synergism parameter (S<sub>I</sub>) can be calculated using the following relationship.

$$\text{Synergism parameters (S}_I) = 1 - \theta_{1+2} / (1 - \theta_1 \theta_2)$$

$$\text{Where } \theta_{1+2} = (\theta_1 + \theta_2) - (\theta_1 \theta_2),$$

$$\theta_1 = \text{Surface coverage by L-Methionine,}$$

$$\theta_2 = \text{Surface coverage by Zn}^{2+},$$

$$\theta_{1+2} = \text{Surface coverage by both L-Methionine and Zn}^{2+}$$

$$\theta = \text{surface coverage} = \text{IE}\% / 100$$

The synergism parameters of L-Methionine -Zn<sup>2+</sup> system are given in **Table 3**. For different concentrations of inhibitors, S<sub>I</sub> approaches 1 when no interaction between the inhibitor compounds exists. When S<sub>I</sub> > 1, it points to synergistic effects. In the case of S<sub>I</sub> < 1, it is an indication that the synergistic effect is not significant<sup>23</sup>. From **Table 3**, it is observed that value of synergism parameters (S<sub>I</sub>) calculated from surface coverage were found to be one and above. This indicates that the synergistic effect exists between L-Methionine and Zn<sup>2+</sup><sup>24</sup>. Thus, the enhancement of the inhibition efficiency caused by the addition of Zn<sup>2+</sup> ions to L-Methionine is due to the synergistic effect.

**Table 3: Inhibition efficiencies and synergism parameters for various concentrations of L-Methionine - Zn<sup>2+</sup> (5 ppm) system, when carbon steel is immersed in well water.**

L-Methionine ppm	Inhibition efficiency IE (%)	Surface Coverage $\theta^1$	Zn <sup>2+</sup> ppm	Inhibition efficiency IE (%)	Surface Coverage $\theta^2$	Combined IE % $I'_{1+2}$	Combined surface coverage $\theta'_{1+2}$	Synergism Parameters S <sub>I</sub>
50	24	0.24	5	10	0.10	66	0.66	<b>2.01</b>
100	31	0.31	5	10	0.10	72	0.72	<b>2.22</b>
150	38	0.38	5	10	0.10	79	0.79	<b>2.66</b>
200	47	0.47	5	10	0.10	86	0.86	<b>3.41</b>
250	59	0.59	5	10	0.10	93	0.93	<b>5.27</b>

### 3.4 'F'-test

To know whether the synergistic effect existing between L-Methionine and Zn<sup>2+</sup> is statistically significant or not, F-test was used<sup>19,22-24</sup>. The results are given in **Table 4**. It is observed that the calculated F-value 25.04 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-Methionine and Zn<sup>2+</sup> (5 ppm) is statistically significant. Therefore, it is concluded that the synergistic effect existing between L-Methionine and Zn<sup>2+</sup> (5 ppm) is statistically significant.

**Table 4: Distribution of F-Value between the inhibition efficiency of various concentration of L-Methionine (0ppm of Zn<sup>2+</sup>) and the inhibition efficiencies of L-Methionine in the presence of 5 ppm of Zn<sup>2+</sup>.**

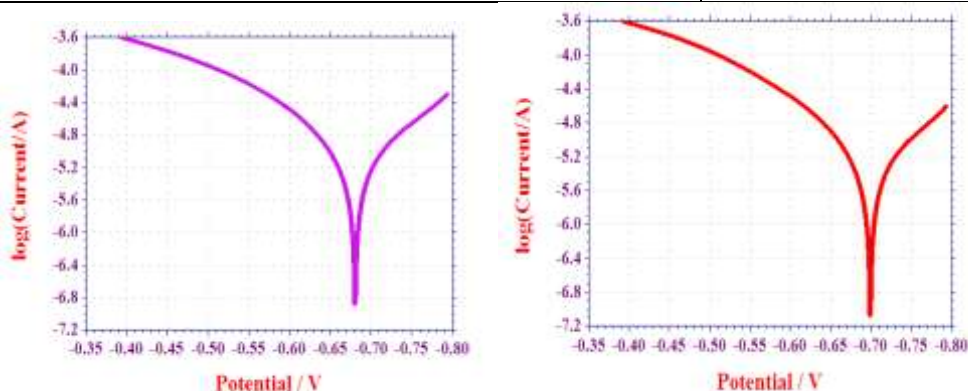
Source of variance	Sum of squares	Degrees of freedom	Mean square	F-value	Level of significance
Between the sample	760.5	1	760.5	< 0.05	25.04
Within the sample	243	8	30.3745		

### 3.5 Analysis of potentiodynamic polarization study

Polarization study has been used to confirm the formation of protective film formed on the metal surface during corrosion inhibition process<sup>6,8,10</sup>. If a protective film is formed on the metal surface, the corrosion current value ( $I_{corr}$ ) decreases. The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors are shown in **Fig-1**. The corrosion parameters are given in **Table 5**. When carbon steel was immersed in well water the corrosion potential was -680 mV vs SCE. When L-Methionine (250 ppm) and Zn<sup>2+</sup> (5 ppm) were added to the above system the corrosion potential shifted to -699 mV vs SCE. This suggests that a protective film is formed on the metal surface. Further the corrosion current decreases from  $8.476 \times 10^{-6}$  A/cm<sup>2</sup> to  $5.956 \times 10^{-6}$ . Thus polarization study confirms the formation of a protective film on the metal surface.

**Table 5: Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system obtained from potentiodynamic polarization study**

System	Tafel Results	
	$E_{corr}$ mV vs SCE	$I_{corr}$ A/cm <sup>2</sup>
Well water	-680	$8.476 \times 10^{-6}$
Well water+ L-Methionine (250ppm)+ Zn <sup>2+</sup> (5ppm)	-699	$5.956 \times 10^{-6}$



a) Well water (Blank)                      b) Well water + L- Methionine (250 ppm) + Zn<sup>2+</sup> (5 ppm)

**Fig 1: Polarization curves of carbon steel immersed in various test solutions**

a) Well water (Blank) ; b) Well water + L- Methionine (250 ppm) + Zn<sup>2+</sup> (5 ppm)

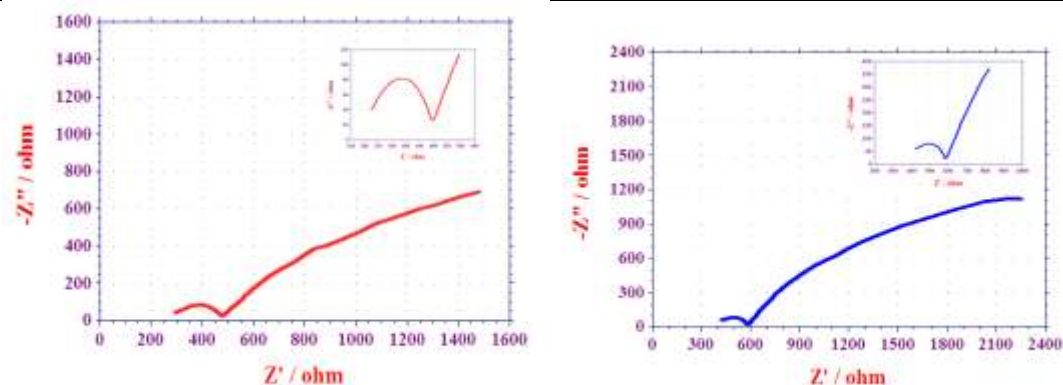
### 3.6 Analysis of AC Impedance spectra

AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective film on the metal surface<sup>11,13</sup>. If a protective film is formed on the metal surface, charge transfer resistance ( $R_t$ ) increases; double layer capacitance value ( $C_{dl}$ ) decreases. The AC impedance spectra of carbon steel immersed in well water in the absence and presence of inhibitors (L-Methionine -Zn<sup>2+</sup>) are shown in **Fig-2** (Nyquist plot). The AC impedance parameters namely charge transfer resistance ( $R_t$ ) and double layer

capacitance ( $C_{dl}$ ) derived from Nyquist plot are given in **Table 6**. It is observed that when the inhibitors (L-Methionine (250 ppm) +  $Zn^{2+}$  (5 ppm)) are added the charge transfer resistance ( $R_t$ ) increases from 1184  $\Omega\text{ cm}^2$  to 1830  $\Omega\text{ cm}^2$ . The  $C_{dl}$  value decreases from  $1.6297 \times 10^{-9}\text{ F/cm}^2$  to  $1.0544 \times 10^{-9}\text{ F/cm}^2$ . These results lead to the conclusion that a protective film is formed on the metal surface.

**Table 6: Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system obtained from AC impedance spectra.**

System	Nyquist plot	
	$R_t$ $\Omega\text{ cm}^2$	$C_{dl}$ $\text{F/cm}^2$
Well water	1184	$1.6297 \times 10^{-9}$
Well water+ L-Methionine (250ppm)+ $Zn^{2+}$ (5ppm)	1830	$1.0544 \times 10^{-9}$



a) Well water (Blank)    b) Well water + L- Methionine (250 ppm) +  $Zn^{2+}$  (5 ppm)

**Fig 2: AC impedance spectra of carbon steel immersed in various test solutions (Nyquist plots)**

a) Well water (Blank) ; b) Well water + L- Methionine (250 ppm) +  $Zn^{2+}$  (5 ppm)

## 4. Surface characterization study

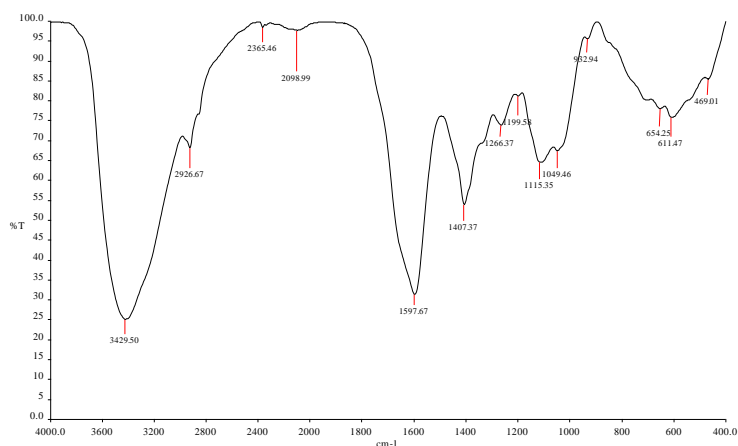
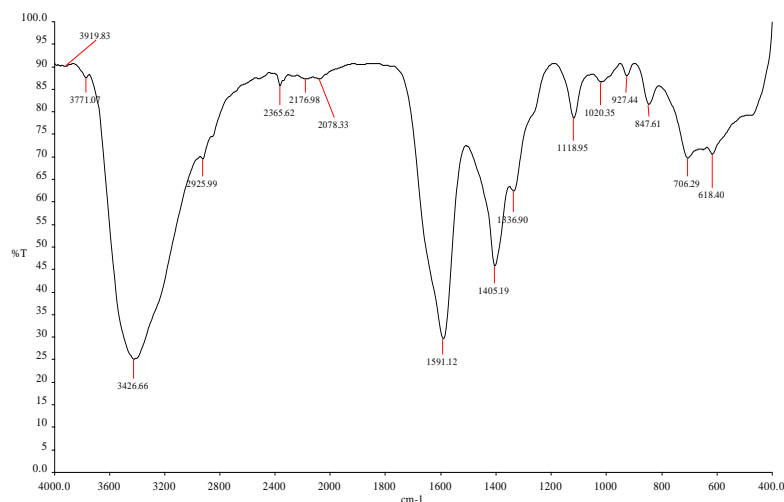
### 4.1 Analysis of FTIR spectra

Analysis of FTIR spectra are given the **Table 7**. FTIR spectra have been used to analyze the protective film formed on the metal surface<sup>19-25</sup>. The FTIR spectrum (KBr) of pure L-Methionine is shown in **Fig.3 (a)**. The C=O stretching frequency of carboxyl group appears at  $1598\text{ cm}^{-1}$ . The CN stretching frequency appears at  $1049\text{ cm}^{-1}$ . The SH stretching frequency appears at  $2365\text{ cm}^{-1}$ . The NH stretching frequency of the amine group appears at  $2926\text{ cm}^{-1}$ <sup>26-28</sup>. The FTIR spectrum of the film formed on the metal surface after immersion in the solution containing well water, 250 ppm of L-Methionine and 5 ppm  $Zn^{2+}$  is shown in **Fig.3 (b)**. The C=O stretching frequency has shifted from  $1598$  to  $1591\text{ cm}^{-1}$ . The CN stretching frequency has shifted from  $1049$  to  $1020\text{ cm}^{-1}$ . The NH stretching frequency has shifted from  $2926$  to  $2923\text{ cm}^{-1}$ . The SH stretching frequency has shifted from  $2365$  to  $2177\text{ cm}^{-1}$ . This observation suggests that L-Methionine has coordinated with  $Fe^{2+}$  through the oxygen atom of the carboxyl group, nitrogen atom of the amine group and the sulphur atom of the thiol group resulting in the formation of  $Fe^{2+}$  - L-Methionine complex on the metal surface. The peak at  $706\text{ cm}^{-1}$  corresponds to Zn-O stretching. The peak at  $3427\text{ cm}^{-1}$  is due to OH- stretching. This confirms that  $Zn(OH)_2$  is formed on the metal surface<sup>19</sup>. Thus the FTIR spectral study leads to the conclusion that the protective film consist of  $Fe^{2+}$ - L-Methionine complex and  $Zn(OH)_2$ .

**Table 7: Analysis of FTIR spectra**

Fourier transform infrared spectroscopy	
Functional group	Frequency (cm <sup>-1</sup> )
FTIR spectrum of pure L – Methionine	
C=O stretching	1598 cm <sup>-1</sup> .
CN stretching	1049 cm <sup>-1</sup> .
NH stretching	2926 cm <sup>-1</sup>
SH stretching	2365 cm <sup>-1</sup> .
FTIR spectrum of the film formed on the metal surface after immersion in the solution containing well water, 250 ppm of L-Methionine and 5 ppm Zn <sup>2+</sup>	

Functional group	Frequency (cm <sup>-1</sup> ) shifted from	Frequency (cm <sup>-1</sup> ) shifted to
C=O stretching	1598 cm <sup>-1</sup> .	1591 cm <sup>-1</sup>
CN stretching	1049 cm <sup>-1</sup>	1020 cm <sup>-1</sup>
NH stretching	2926 cm <sup>-1</sup>	2923 cm <sup>-1</sup> .
SH stretching	2365 cm <sup>-1</sup>	2177 cm <sup>-1</sup>
Zn – O stretching	706 cm <sup>-1</sup>	
OH- stretching	3427 cm <sup>-1</sup>	

**3(a) FTIR Spectra for Pure L- Methionine****3 (b) FTIR Spectra for Film formed on Metal Surface immersion in test solution containing 250ppm L Methionine + 5ppm Zn<sup>2+</sup>**

## 5. Mechanism of Corrosion inhibition

The results of the weight-loss study show that the formulation consisting of 250 ppm L-Methionine and 5 ppm of  $Zn^{2+}$  has 93% IE in controlling corrosion of carbon steel in well water. A synergistic effect exists between  $Zn^{2+}$  and L-Methionine. Polarization study reveals that this formulation functions as cathodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of  $Fe^{2+}$ - L-Methionine complex and  $Zn(OH)_2$ . In order to explain these facts the following mechanism of corrosion inhibition is proposed.

- When the solution containing well water, 5 ppm of  $Zn^{2+}$  and 250 ppm of L-Methionine is prepared, there is formulation of  $Zn^{2+}$  - L-Methionine complex in solution. When carbon steel is immersed in this solution, the  $Zn^{2+}$ - L-Methionine complex diffuses from the bulk of the solution towards metal surface.
- $Zn^{2+}$ - L-Methionine complex diffuses from the bulk solution to the surface of the metal and is converted into a  $Fe^{2+}$ - L-Methionine complex, which is more stable than  $Zn^{2+}$ - L-Methionine.
- On the metal surface  $Zn^{2+}$  - L-Methionine complex is converted in to  $Fe^{2+}$  - L-Methionine and  $Zn^{2+}$  is released.  

$$Zn^{2+} - L-Methionine + Fe^{2+} \text{ -----} > Fe^{2+} - L-Methionine + Zn^{2+}$$
- The released  $Zn^{2+}$  combines with  $OH^-$  to form  $Zn(OH)_2$ .  

$$Zn^{2+} + 2OH^- \text{ -----} > Zn(OH)_2 \quad \downarrow$$
- Thus the protective film consists of  $Fe^{2+}$ - L-Methionine complex and  $Zn(OH)_2$ .

## 6. Conclusion

Weight loss study reveals that the formation consisting of 250ppm of L-Methionine and 5ppm of  $Zn^{2+}$  has 93% inhibition efficiency, in controlling corrosion of carbon steel in well water. A Synergistic effect exists between  $Zn^{2+}$  and L-Methionine system. Statistical study of F-test revealed that the synergistic effect existing between L-Methionine and  $Zn^{2+}$  is statistically significant. Polarization study reveals that L-Methionine system function as cathodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectral study suggests that L-Methionine has coordinated with  $Fe^{2+}$  through the oxygen atom of the carboxyl group, nitrogen atom of the amine group and sulphur atom of the thiol group resulting in the formation of  $Fe^{2+}$ - L-Methionine complex and  $Zn(OH)_2$  is formed. Thus the FTIR spectral study leads to the conclusion that the protective film consist of  $Fe^{2+}$ - L-Methionine complex and  $Zn(OH)_2$  on the metal surface thereby inhibiting the corrosion of carbon steel, which is protective in nature.

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