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## Inhibition of corrosion of carbon steel in well water by arginine-Zn<sup>2+</sup> system

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### Abstract

The environmental friendly inhibitor system arginine-Zn<sup>2+</sup>, has been investigated by weight-loss method. A synergistic effect exists between arginine and Zn<sup>2+</sup> system. The formulation consisting of 250 ppm of arginine and 5 ppm of Zn<sup>2+</sup> offers good inhibition efficiency of 98 %. Polarization study reveals that this formulation functions as an anodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. The FTIR spectral study leads to the conclusion that the Fe<sup>2+</sup>-DL-arginine complex, formed on anodic sites of the metal surface, controls the anodic reaction. Zn(OH)<sub>2</sub> formed on the cathodic sites of the metal surface controls the cathodic reaction. The surface morphology and the roughness of the metal surface were analyzed with Atomic Force Microscope. A suitable mechanism of corrosion inhibition is proposed based on the results obtained from weight loss study and surface analysis technique.

### Keywords

Carbon steel; arginine; corrosion inhibition; synergistic effect; SEM; AFM.

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### Introduction

The principles and practices of corrosion inhibition have begun in recent years to take into account the health and safety considerations. The use of hazardous chemicals has been restricted to no contact with the environment. Hence, there is a search for non-toxic, eco-friendly corrosion inhibitors. The use of inhibitors is one of the most practical methods to protect metals from corrosion. Corrosion inhibitor is a chemical substance which, when added to the corrosive environment at an optimum concentration, significantly decreases the corrosion rate of metals (or) alloys. Unfortunately, many common corrosion inhibitors are highly toxic and health-hazardable, such as

chromates [1], nitrite [2] aromatic heterocyclic compounds [3] etc. Therefore, it is better to look for environmentally safe inhibitors [4-6]. Some researchers investigated the inhibition effect of environment friendly inhibitors like amino acids on metal corrosion [6-13]. 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. The environmental friendly arginine is chosen as the corrosion inhibitor for this present work. The literature presents some studies involving amino acids having the ability to prevent the corrosion of iron [14], steel [15-17], aluminum [18,19], nickel [20] and copper [21-25]. The electrochemical studies such as polarization and AC impedance spectra [26-30] and cyclic voltammetry [19] have been studied by using amino acids. The adsorption of amino acids on carbon steel in acidic environment has been investigated by Akiyama *et al.* [31].

## Experimental

### Preparation of specimens

Carbon steel specimens (0.0267 % S, 0.067 % P, 0.4 % Mn, 0.1 % C and the rest iron) of the dimensions 1.0 cm × 4.0 cm × 0.2 cm were polished to mirror finish and degreased with trichloroethylene and as such used for weight-loss method and surface examination studies.

### Weight - 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 and various concentrations of arginine in the presence and absence of Zn<sup>2+</sup> (as ZnSO<sub>4</sub>×7H<sub>2</sub>O) for a period of seven days. The corrosion products were cleaned with Clarke's solution [32]. The weight of the specimens before and after immersion was determined using Shimadzu balance AY62. The corrosion inhibition efficiency (*IE*) was calculated using the equation (1).

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

where  $W_1$  is the corrosion rate in the absence of the inhibitor and  $W_2$  is the corrosion rate in the presence of inhibitor. From the weight loss, the corrosion rate ( $\text{mm year}^{-1}$ ) was calculated using the equation (2):

$$CR = \frac{LW}{A t 0.0365 \rho^{-1}} \quad (2)$$

where  $CR$  is corrosion rate in  $\text{mm year}^{-1}$ ;  $LW$  is the weight loss in mg;  $A$  is surface area of the specimen in  $\text{dm}^2$ ;  $t$  is period of immersion in days and  $\rho$  is density of the metal in  $\text{g cm}^{-2}$  (7.86).

### Potentiodynamic polarization study

Potentiostatic polarization studies were carried out using a CHI electrochemical impedance analyzer, model 660 A. A three-electrode cell assembly was used. The working electrode was a rectangular specimen of carbon steel with one face of the electrode ( $1 \text{ cm}^2$  area) exposed and the rest shielded with red lacquer. A saturated calomel electrode (SCE) was used as the reference electrode and a rectangular platinum foil was used as the counter electrode. Polarization curves were recorded using  $iR$  compensation. The results, such as Tafel slopes, and  $I_{\text{corr}}$ ,  $E_{\text{corr}}$  and linear polarization resistance (LPR) values were calculated. During the polarization study, the scan rate was  $0.01 \text{ V s}^{-1}$ ; hold time at  $E_f$  was 0 s and quiet time was 2 s.

### AC impedance measurements

A CHI electrochemical impedance analyzer (model 660A) was used for AC impedance measurements. A time interval of 5 to 10 minutes was given for the system to attain its open circuit potential. The real part  $Z'$  and the imaginary part  $Z''$  of the cell impedance were measured in ohms at various frequencies. The values of the charge transfer resistance  $R_t$ , double layer capacitance  $C_{dl}$  and impedance value were calculated.

$$R_t = (R_s + R_t) - R_s \quad (3)$$

where  $R_s$  = solution resistance

$$C_{dl} = \frac{1}{2} \pi R_t f_{max} \quad (4)$$

where  $f_{max}$  = maximum frequency

AC impedance spectra were recorded with initial  $E = 0$  V; high frequency =  $10^5$  Hz; low frequency = 10 Hz; amplitude = 0.005 V; and quiet time = 2 s.

### FTIR spectra

The structure of arginine is shown in Fig.1. The carbon steel specimens immersed in various test solutions for seven days were taken out and dried. The film formed on the metal surface was carefully removed and thoroughly mixed with KBr, so as to make it uniform throughout. The FTIR spectra were recorded in a Perkin-Elmer 1600 spectrophotometer.

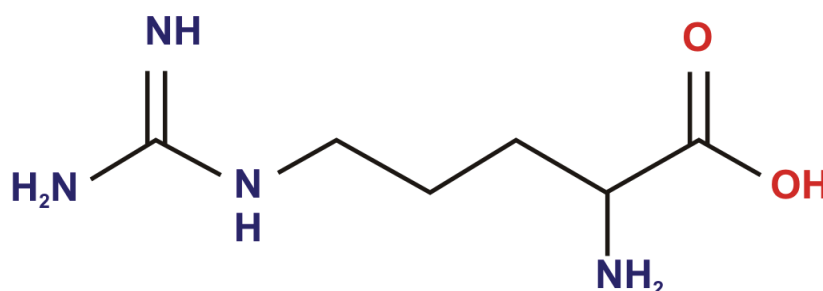


Figure1. Structure of DL-arginine

### Scanning electron microscopy (SEM analysis)

SEM provides a pictorial representation of the surface. It helps to understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of carbon steel. The scanning electron microscopy photographs were recorded at various magnifications using Hitachi scanning electron microscopy machine S-3000 H.

### Atomic force microscopy

Atomic force microscope (AFM) is an exciting new technique that allows surface to be imaged at higher resolutions and accuracies than ever before [33-35]. The microscope used for the present study was VEECO, Lab incorporation. Polished specimens, prior to the initiation of all corrosion experiments, were examined through an optical microscope to find out any surface defects such as pits or noticeable irregularities like cracks, etc. Only those specimens, which had a smooth pit free surface, were subjected to AFM examination. The protective films formed on the carbon steel specimens after immersion in the inhibitor systems for different time durations were examined for a scanned area of  $05 \times 05 \mu\text{m}$  at a scan rate of  $6.68 \mu\text{m s}^{-1}$ . The two dimensional and three-dimensional topography of surface film gave various roughness parameters of the film.

## Results and Discussion

### Analysis of the weight loss method

Corrosion rates (CR) of carbon steel immersed in well water in the absence and presence of inhibitor (DL-arginine) are given in Tables 1 to 3. The inhibition efficiencies (IE) are also given in these Tables. The corrosion rates of the DL-arginine - Zn<sup>2+</sup> systems as a function of concentrations of DL-arginine are shown in Fig.2.

**Table 1.** 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 (IE) obtained by weight loss method. Inhibitor system: DL-arginine – Zn<sup>2+</sup> (amount of Zn<sup>2+</sup> = 0 ppm); Immersion period: 7 days; pH 8

| Amount of DL-arginine, ppm | CR mm year <sup>-1</sup> | IE / % |
|----------------------------|--------------------------|--------|
| 0                          | 0.0874                   | --     |
| 50                         | 0.0455                   | 48     |
| 100                        | 0.0472                   | 46     |
| 150                        | 0.0525                   | 40     |
| 200                        | 0.0533                   | 39     |
| 250                        | 0.0577                   | 34     |

**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 (IE) obtained by weight loss method. Inhibitor system: DL-arginine – Zn<sup>2+</sup> (amount of Zn<sup>2+</sup> = 5 ppm); Immersion period: 7 days; pH 8

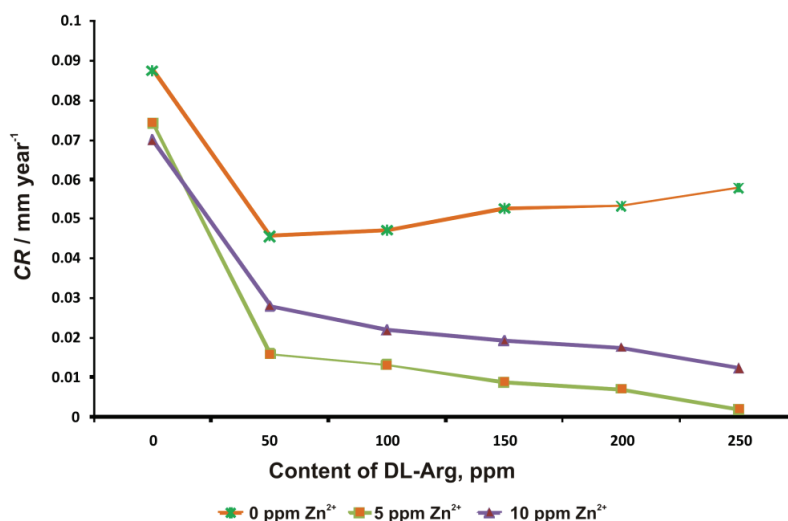
| Amount of DL-arginine, ppm | CR mm year <sup>-1</sup> | IE / % |
|----------------------------|--------------------------|--------|
| 0                          | 0.0743                   | 15     |
| 50                         | 0.0157                   | 82     |
| 100                        | 0.0131                   | 85     |
| 150                        | 0.0087                   | 90     |
| 200                        | 0.0069                   | 92     |
| 250                        | 0.001748                 | 98     |

**Table 3 :** 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 (IE) obtained by weight loss method. Inhibitor system: DL-arginine – Zn<sup>2+</sup> (amount of Zn<sup>2+</sup> = 10 ppm); Immersion period: 7 days; pH 8

| Amount of DL-arginine, ppm | CR mm year <sup>-1</sup> | IE / % |
|----------------------------|--------------------------|--------|
| 0                          | 0.0699                   | 20     |
| 50                         | 0.0280                   | 68     |
| 100                        | 0.0218                   | 75     |
| 150                        | 0.0192                   | 78     |
| 200                        | 0.0175                   | 80     |
| 250                        | 0.0122                   | 86     |

It is observed from Table 1 that DL-arginine shows some inhibition efficiencies. 50 ppm of DL-arginine has 48 percent IE. As the concentration of DL-arginine increases, the IE decreases. This is due to the fact that as the concentration of DL-arginine increases, the protective film (probably

iron DL-arginine complex) formed on the metal surface diffuses into solution. That is, the system goes from passive region to active region [36].

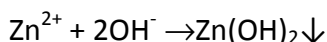
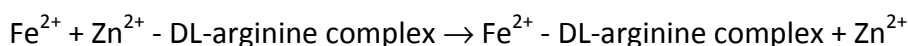
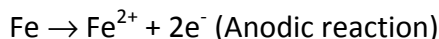


**Figure 2.** Corrosion rates of carbon steel immersed in various test solutions

#### Influence of Zn<sup>2+</sup> on the inhibition efficiencies of DL-arginine

The influence of Zn<sup>2+</sup> on the inhibition efficiencies of DL-arginine is given in Tables 2 and 3. It is observed that as the concentration of DL-arginine increases the IE increases. Similarly, for a given concentration of DL-arginine the IE increases as the concentration of Zn<sup>2+</sup> increases. It is also observed that a synergistic effect exists between DL-arginine and Zn<sup>2+</sup>. For example, 5 ppm of Zn<sup>2+</sup> has 15 percent IE; 250 ppm of DL-arginine has 34 percent IE. Interestingly their combination has a high IE, namely, 98 percent.

In the presence of Zn<sup>2+</sup> more amount of DL-arginine is transported towards the metal surface. This is due to fact that when Zn<sup>2+</sup> is added to the environment, Zn<sup>2+</sup>- DL-arginine complex is formed, it diffuses towards metal surface. On the metal surface, iron-amino acid complex is formed and Zn<sup>2+</sup> is released. This combines with OH<sup>-</sup> to give insoluble Zn(OH)<sub>2</sub> formed on cathodic sites which is controlled the cathodic reaction. On the metal surface Fe-DL-arginine complex is formed on the anodic sites of the metal surface and anodic reaction is controlled. Thus, the anodic reaction and cathodic reaction are controlled effectively. This accounts for the synergistic effect existing between Zn<sup>2+</sup> and DL-arginine.



#### Analysis of potentiodynamic polarization study (pH = 8)

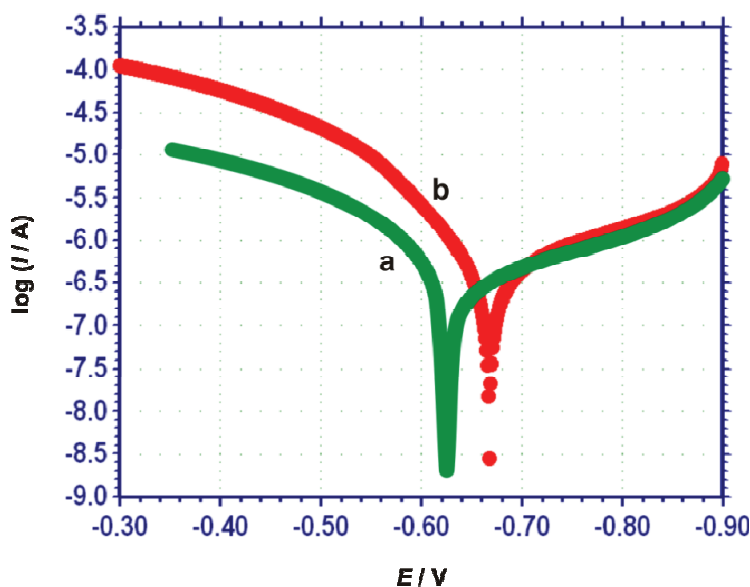
Polarization study was used to confirm the formation of protective film formed on the metal surface during corrosion inhibition process [37-42]. If a protective film is formed on the metal surface, the linear polarization resistances value (LPR) increases and the corrosion current value ( $I_{\text{corr}}$ ) decreases.

The potentiodynamic polarization curves of carbon steel immersed in well water in the absence and presence of inhibitors are shown in Fig. 3 and the corrosion parameters are given in Table 4. When

carbon steel was immersed in well water the corrosion potential was -668 mV vs SCE. When DL-arginine (250 ppm) and Zn<sup>2+</sup> (5 ppm) were added to the above system, the corrosion potential shifted to the noble side, i.e. to -626 mV vs SCE. This indicates that a film is formed on anodic sites of the metal surface. This film controls the anodic reaction of metal dissolution by forming Fe<sup>2+</sup>-DL-arginine complex on the anodic sites of the metal surface. The formation of protective film on the metal surface is further supported by the fact that the anodic Tafel slope (*b<sub>a</sub>*) increases from 104 to 173 mV.

**Table 4 :** Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system obtained from potentiodynamic polarization study

| System   | <i>E<sub>corr</sub></i><br>mV vs. SCE | <i>b<sub>c</sub></i><br>mV decade <sup>-1</sup> | <i>b<sub>a</sub></i><br>mV decade <sup>-1</sup> | <i>I<sub>corr</sub></i><br>A cm <sup>-2</sup> | LPR<br>Ω cm <sup>2</sup> |
|--|---------------------------------------|---|---|---|--------------------------|
| Well water   | -668                                  | 268   | 104   | 5.775 x 10 <sup>-7</sup>                      | 5.630 x 10 <sup>4</sup>  |
| Well water + DL-Arg (250 ppm) + Zn <sup>2+</sup> (5 ppm) | -626                                  | 128   | 173   | 5.125 x 10 <sup>-7</sup>                      | 6.253 x 10 <sup>4</sup>  |



**Figure 3.** Polarization curves of mild steel immersed in various test solutions: (a) well water + DL-arginine (250 ppm) + Zn<sup>2+</sup> (5 ppm); (b) well water (blank)

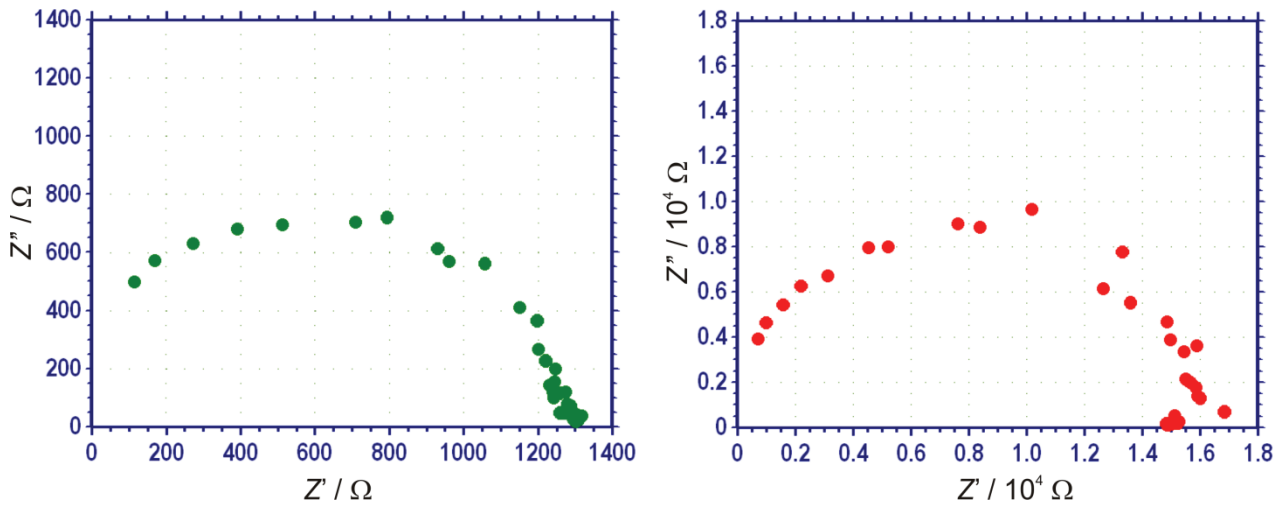
Further, the LPR value increases from 5.630×10<sup>4</sup> ohm cm<sup>2</sup> to 6.253×10<sup>4</sup> ohm cm<sup>2</sup>; the corrosion current decreases from 5.775×10<sup>-7</sup> A cm<sup>-2</sup> to 5.125×10<sup>-7</sup> A cm<sup>-2</sup>. Thus, polarization study confirms the formation of a protective film on the metal surface.

*Analysis of AC impedance spectra*

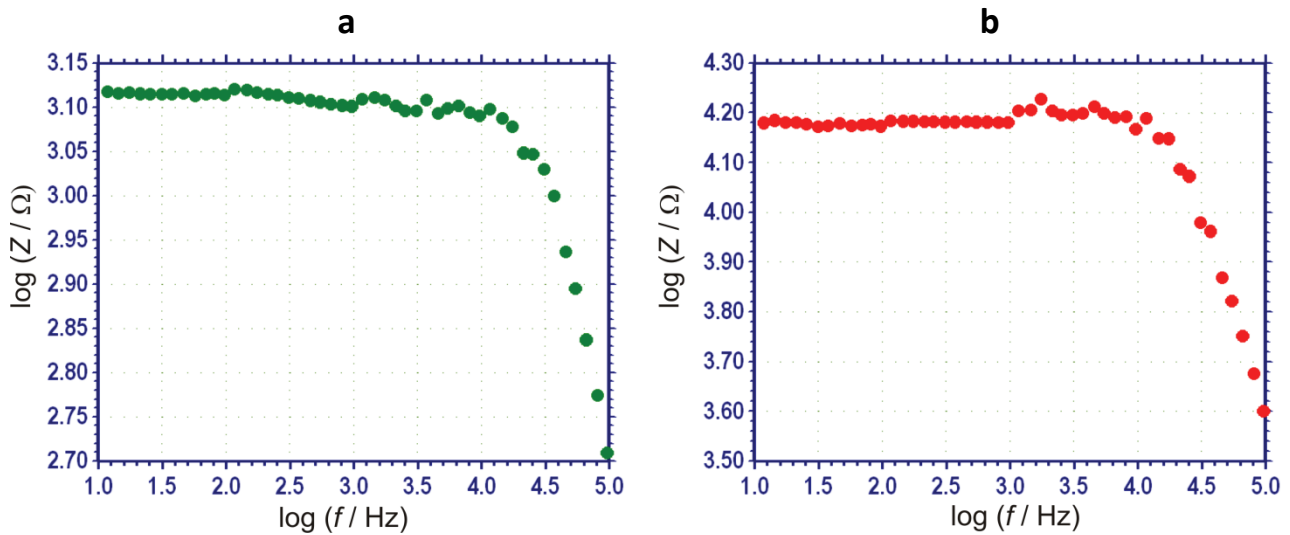
AC impedance spectra (electrochemical impedance spectra) have been used to confirm the formation of a protective film on the metal surface [43-45]. If a protective film is formed on the metal surface, charge transfer resistance (*R<sub>t</sub>*) increases; double layer capacitance value (*C<sub>dl</sub>*) decreases and the impedance log (*Z/Ω*) value increases. The AC impedance spectra of carbon steel immersed in well water in the absence and presence of inhibitors (DL-arginine-Zn<sup>2+</sup>) are shown in Figs. 4a and 4b (Nyquist plots) and Figs. 5a and 5b and Figs. 6a and 6b (Bode plots). The AC impedance parameters namely charge transfer resistance (*R<sub>t</sub>*) and double layer capacitance (*C<sub>dl</sub>*) derived from Nyquist plots are given in Table 5. The impedance log (*Z/Ω*) values derived from Bode plots are also given in Table 5.

**a**

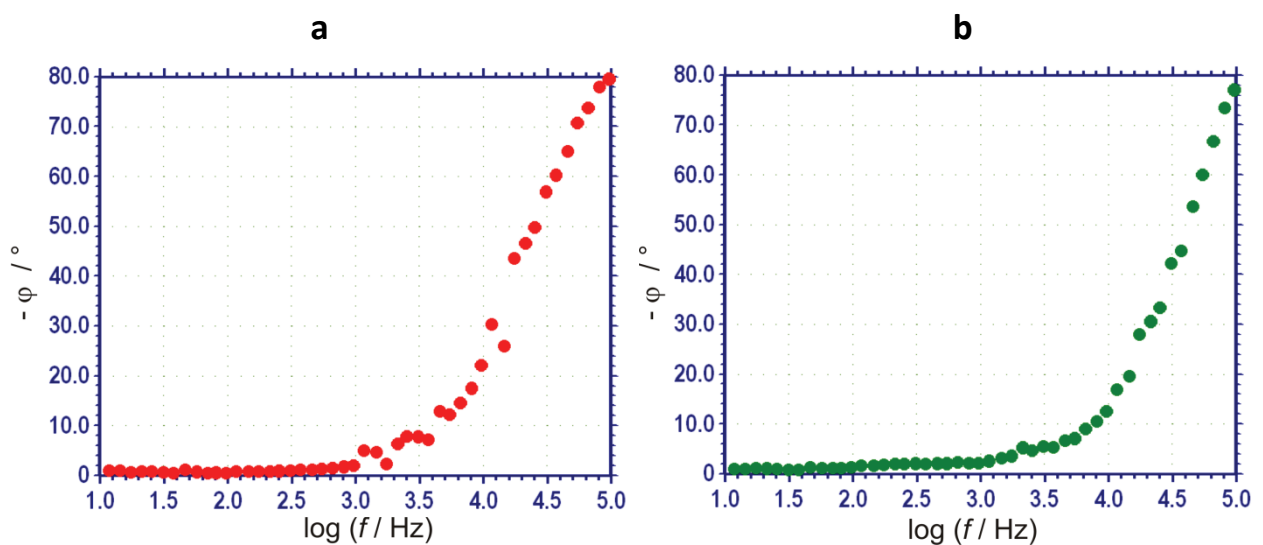
**b**



**Figure 4.** AC impedance spectra of carbon steel immersed in various test solution (Nyquist plot) (pH 8): **a)** well water (blank); **b)** well water + DL-arginine (250 ppm) + Zn<sup>2+</sup> (5 ppm)



**Figure 5.** AC impedance spectra of carbon steel immersed in various test solution (Bode plot) (pH 8): **a)** well water (blank); **b)** well water + DL-arginine (250 ppm) + Zn<sup>2+</sup> (5 ppm)



**Figure 6.** AC impedance spectra of carbon steel immersed in various test solution (Phase – Bode plot) (pH 8): **a)** well water (blank); **b)** well water + DL-arginine (250 ppm) + Zn<sup>2+</sup> (5 ppm)

**Table 5.** Corrosion parameters of carbon steel immersed in well water in the absence and presence of inhibitor system obtained from AC impedance spectra (pH 8).

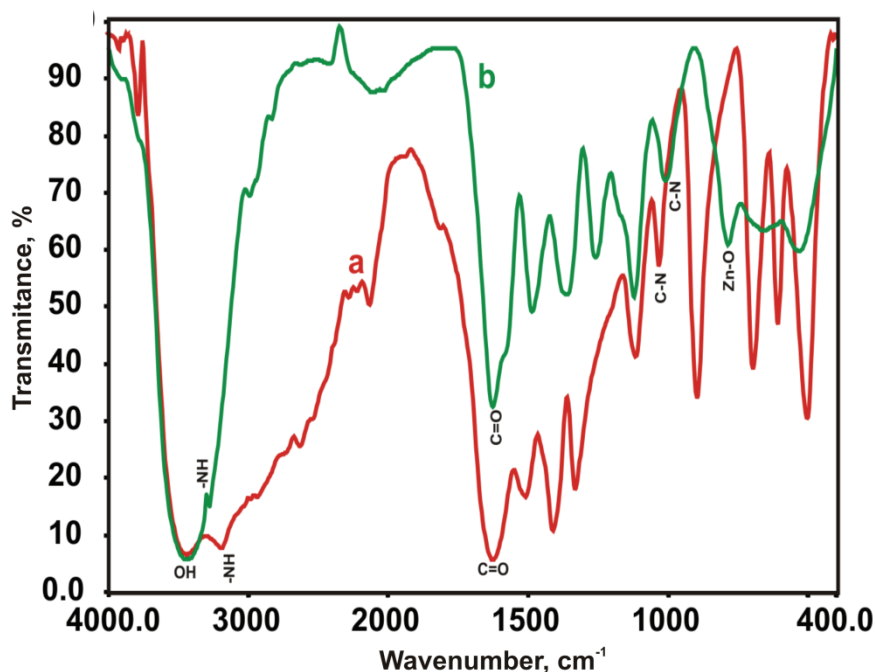
| System  | Nyquist plot                |                             | Bode plot          |
|---|-----------------------------|-----------------------------|--------------------|
|   | $R_t / \Omega \text{ cm}^2$ | $C_{dl} / \text{F cm}^{-2}$ | $\log(Z / \Omega)$ |
| Well water  | 1212                        | $3.8424 \times 10^{-9}$     | 3.120              |
| Well water + DL-arginine (250 ppm) + Zn <sup>2+</sup> (5 ppm) | 16240                       | $3.1373 \times 10^{-10}$    | 4.181              |

It is observed that when the inhibitors [DL-arginine (250 ppm) + Zn<sup>2+</sup> (5 ppm)] are added, the charge transfer resistance ( $R_t$ ) increase from 1212  $\Omega \text{ cm}^2$  to 16240  $\Omega \text{ cm}^2$ . The  $C_{dl}$  value decreases from  $3.8424 \times 10^{-9}$  to  $3.1373 \times 10^{-10}$  F  $\text{cm}^{-2}$ . The impedance value  $\log(Z/\Omega)$  increases from 3.120 to 4.181. These results lead to the conclusion that a protective film is formed on the metal surface.

It is observed that weight loss study gives very high  $IE$ . But this is not the case with the electrochemical studies. This may be explained by the fact that weight loss study is the result of 7 days whereas electrochemical studies are an instantaneous study. Similar observations were already reported [37-45].

#### Analysis of FTIR spectra

FTIR spectra have been used to analyze the protective film formed on the metal surface [39,46-53]. The FTIR spectrum (KBr) of pure DL-arginine is shown in Fig. 7a. The C=O stretching frequency of carboxyl group appears at 1610  $\text{cm}^{-1}$ . The CN stretching frequency appears at 1098  $\text{cm}^{-1}$ . The NH stretching frequency of the amine group appears at 3182  $\text{cm}^{-1}$ .



**Figure 7.** FTIR spectra of: **a)** pure DL-arginine; **b)** film formed on the metal surface after immersion in well water + DL-arginine (250 ppm) + Zn<sup>2+</sup> (5 ppm)

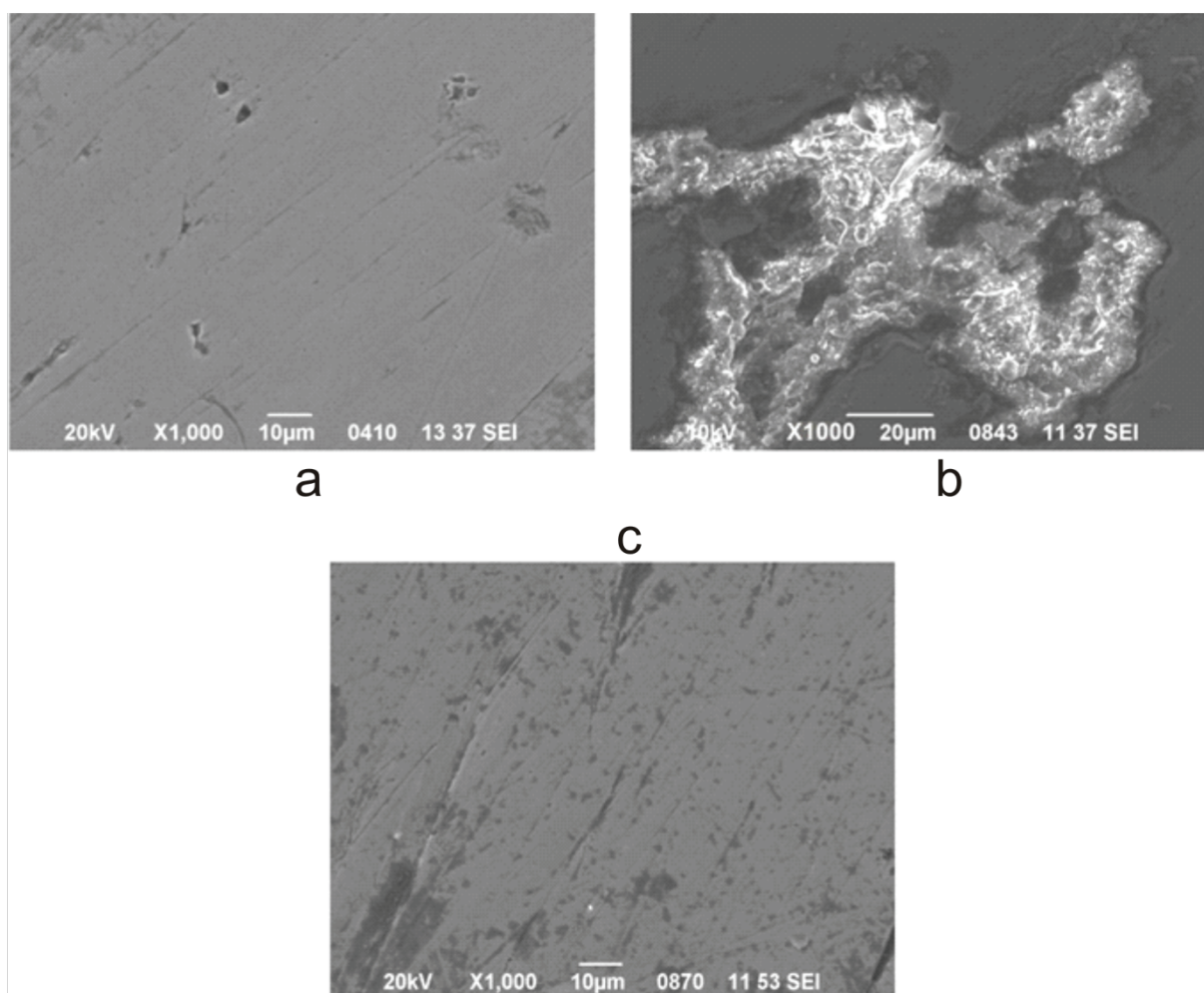
The FTIR spectrum of the film formed on the metal surface after immersion in the solution containing well water, 250 ppm of DL-arginine and 5 ppm Zn<sup>2+</sup> is shown in Fig.7b. The C=O stretching frequency has shifted from 1610 to 1619  $\text{cm}^{-1}$ . The CN stretching frequency has shifted from 1098 to 1005  $\text{cm}^{-1}$ . The NH stretching frequency has shifted from 3182 to 3285  $\text{cm}^{-1}$ . This observation suggests that DL-arginine has coordinated with Fe<sup>2+</sup> through the oxygen atom of the carboxyl group and nitrogen atom of the amine group resulting in the formation of Fe<sup>2+</sup>-DL-argi-

nine complex on the anodic sites of the metal surface. The peak at  $788\text{ cm}^{-1}$  corresponds to Zn-O stretching. The peak at  $3442\text{ cm}^{-1}$  is due to  $\text{OH}^-$  stretching. This confirms that  $\text{Zn}(\text{OH})_2$  is formed on the cathodic sites of metal surface [46,51-53]. Thus the FTIR spectral study leads to the conclusion that the protective film consists of  $\text{Fe}^{2+}$ -DL-arginine complex and  $\text{Zn}(\text{OH})_2$ .

#### SEM Analysis of Metal Surface

SEM provides a pictorial representation of the surface. This helps to understand the nature of the surface film in the absence and presence of inhibitors and the extent of corrosion of carbon steel. The SEM micrographs of the surface are examined [54-56]. The SEM images of different magnification (500 x, 1000 x) of carbon steel specimen immersed in well water for 7 days in the absence and presence of inhibitor system are shown in Figs. 8a and 8b and 8c respectively.

The SEM micrographs of polished carbon steel surface (control) in Figs. 8a and 8b show the smooth surface of the metal. This shows the absence of any corrosion products (or) inhibitor complex formed on the metal surface.



**Figure 8.** SEM analysis of: **a)** Carbon steel (Control); **b)** Carbon steel immersed in well water (Blank); **c)** Carbon steel immersed in well water + 250 ppm of DL-arginine + 5 ppm of  $\text{Zn}^{2+}$

The SEM micrographs of carbon steel surface immersed in well water (Figs. 8b) show the roughness of the metal surface which indicates the highly corroded area of carbon steel in well water. However, Figs. 8c indicate that in the presence of inhibitor (250 ppm DL-arginine and 5 ppm  $\text{Zn}^{2+}$ ) the rate of corrosion is suppressed, as can be seen from the decrease of corroded areas. The metal surface is almost free from corrosion due to the formation of an insoluble complex on the

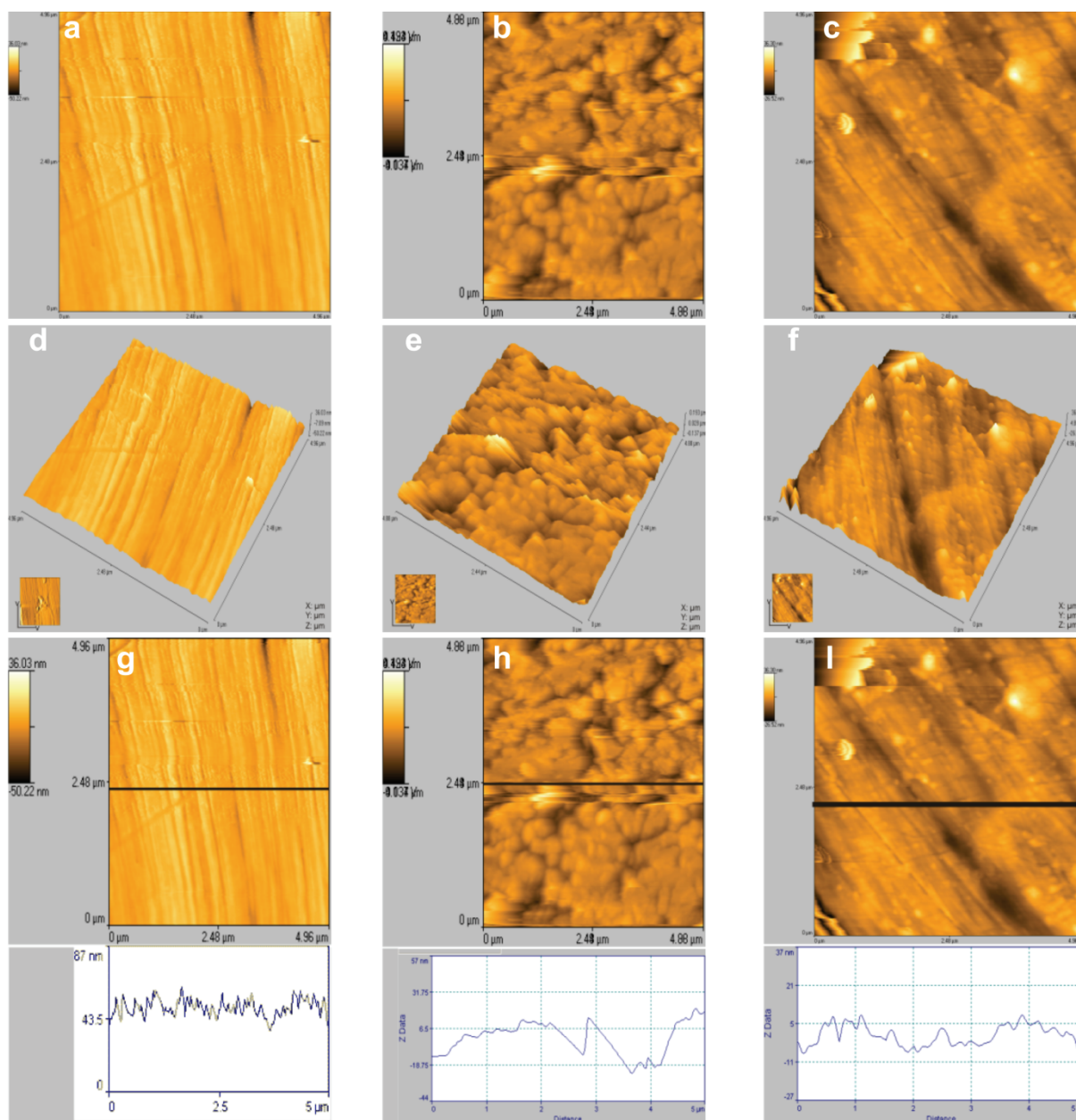
surface of the metal [54]. In the presence of DL-arginine and Zn<sup>2+</sup>, the surface is covered by a thin layer of inhibitors which effectively controls the dissolution of carbon steel.

**Atomic Force Microscopy Characterization**

Atomic force microscopy is a powerful technique for gathering of roughness statistics from a variety of surfaces [57]. AFM has become an accepted method of roughness investigation [58-64].

All atomic force microscopy images were obtained in a VEECO Lab incorporation AFM instrument operating in contact mode in air. The scan size of all the AFM images are 0.5 μm × 0.5 μm areas at a scan rate of 6.835 μm s<sup>-1</sup>.

The two dimensional (2D), three dimensional (3D) AFM morphologies and the AFM cross-sectional profile for polished carbon steel surface (reference sample), carbon steel surface immersed in well water (blank sample) and carbon steel surface immersed in well water containing the formulation of DL-arginine 250 ppm and 5 ppm of Zn<sup>2+</sup> are shown as Figs. 9a, 9d and 9g, Figs. 9b, 9e and 9h and Figs. 9c, 9f and 9i, respectively.



**Figure 9. a), b) c) 2D AFM images; d), e), f) 3D AFM images and g), h), i) Cross sectional profile which are corresponding to as shown lines on 2D AFM images of**

**a), d), g)** Polished carbon steel (Control); **b), e), h)** Carbon steel immersed in well water (blank) and **c), f), i)** Carbon steel immersed in well water containing DL-arginine 250 ppm + Zn<sup>2+</sup> 5 ppm

*Root-mean-square roughness, average roughness and peak-to-valley value*

AFM image analysis was performed to obtain the average roughness,  $R_a$  (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness,  $R_q$  (the average of the measured height deviations taken within the evaluation length and measured from the mean line) and the maximum peak-to-valley (P-V) height values (largest single peak-to-valley height in five adjoining sampling heights) [63].  $R_q$  is much more sensitive than  $R_a$  to large and small height deviations from the mean [64].

Table 6 is the summary of the average roughness ( $R_a$ ), RMS roughness ( $R_q$ ) maximum peak-to-valley height (P-V) value for carbon steel surface immersed in different environments.

**Table 6.** AFM data for carbon steel surface immersed in inhibited and uninhibited environments

| Samples  | $R_q$ / nm | $R_a$ / nm | P-V value, nm |
|--|------------|------------|---------------|
| Polished carbon steel (control)  | 5          | 3          | 50            |
| Carbon steel immersed in well water  | 28         | 21         | 137           |
| Carbon steel immersed in well water DL-arginine (250 ppm) + Zn <sup>2+</sup> (5 ppm) | 6          | 4          | 26            |

The value of  $R_{RMS}$ ,  $R_a$  and P-V height for the polished carbon steel surface (reference sample) are 5 nm, 3 nm and 50 nm respectively, which show a more homogeneous surface, with some places in which the height is lower than the average depth [57]. Figs. 9a, 9d and 9g display the uncorroded metal surface. The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion. The RMS roughness, average roughness and P-V height values for the carbon steel surface immersed in well water are 28 nm, 21 nm and 137 nm respectively. These data suggest that carbon steel surface immersed in well water has a greater surface roughness than the polished metal surface. This shows that the unprotected carbon steel surface is rougher and this is due to the corrosion of the carbon steel in well water. Figs. 9b, 9e and 9h display the corroded metal surface with few pits.

The presence of 250 ppm of DL-arginine and 5 ppm of Zn<sup>2+</sup> in well water reduces the  $R_q$  by a factor of 6 nm from 28 nm and the average roughness is significantly reduced to 4 nm when compared with 21 nm of carbon steel surface immersed in well water. The maximum peak-to-valley height also was reduced to 26 nm from 137 nm. These parameters confirm that the surface appears smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe<sup>2+</sup>- DL-arginine complex and Zn(OH)<sub>2</sub> on the metal surface thereby inhibiting the corrosion of carbon steel.

Also the above parameters observed are somewhat greater than the AFM data of polished metal surface which confirms the formation of the film on the metal surface, which is protective in nature.

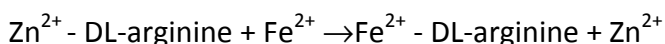
When carbon steel immersed in well water the  $R_q$ ,  $R_a$  and maximum peak-to-valley (P-V) height are very high. In the presence of inhibitor system, these values are very close to those of polished carbon steel. This indicates that the formation of protective film starts even before the starting of corrosion process. Suppose the film is formed on the iron oxide surface then roughness would be greater than the  $R_q$ ,  $R_a$ , maximum peak-to-valley (P-V) height of the carbon steel surface immersed

in well water. But this is not the case. Hence this is concluded that the protective film is formed in the initial stage itself.

### Mechanism of Corrosion inhibition

The results of the weight-loss study show that the formulation consisting of 250 ppm DL-arginine and 5 ppm of Zn<sup>2+</sup> has 98% IE in controlling corrosion of carbon steel in well water. A synergistic effect exists between Zn<sup>2+</sup> and DL-arginine. Polarization study reveals that this formulation functions as anodic 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<sup>2+</sup>- DL-arginine complex and Zn(OH)<sub>2</sub>. In order to explain these facts the following mechanism of corrosion inhibition is proposed [65-71].

- When the solution containing well water, 5 ppm Zn<sup>2+</sup> and 250 ppm of DL-arginine is prepared, there is formulation of Zn<sup>2+</sup> - DL-arginine complex in solution.
- When carbon steel is immersed in this solution, the Zn<sup>2+</sup> - DL-arginine complex diffuses from the bulk of the solution towards metal surface.
- Zn<sup>2+</sup>- DL-arginine complex diffuses from the bulk solution to the surface of the metal and is converted into a Fe<sup>2+</sup>- DL-arginine complex, which is more stable than Zn<sup>2+</sup>- DL-arginine [66].
- On the metal surface Zn<sup>2+</sup> - DL-arginine complex is converted in to Fe<sup>2+</sup> - DL-arginine on the anodic sites. Zn<sup>2+</sup> is released.



- The released Zn<sup>2+</sup> combines with OH<sup>-</sup> to form Zn(OH)<sub>2</sub> on the cathodic sites [65,66].  

$$\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2 \downarrow$$
- Thus the protective film consists of Fe<sup>2+</sup>- DL-arginine complex and Zn(OH)<sub>2</sub>.
- The SEM micrographs and AFM images confirm the formation of protective layer on the metal surface.

### Conclusions

Inhibition of corrosion of carbon steel in well water by arginine-Zn<sup>2+</sup> system has been evaluated by weight-loss method. A synergistic effect exists between arginine and Zn<sup>2+</sup> system. The formulation consisting of 250 ppm of arginine and 5 ppm of Zn<sup>2+</sup> offers good inhibition efficiency of 98%. Polarization study reveals that this formulation functions as an anodic inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. The FTIR spectral study leads to the conclusion that the Fe<sup>2+</sup>- DL-arginine complex formed on anodic sites of the metal surface controls the anodic reaction. Zn(OH)<sub>2</sub> formed on the cathodic sites of the metal surface controls the cathodic reaction. The SEM micrographs and AFM images confirm the formation of the protective layer on the metal surface.

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### References

- [1] A. Baral, R.D. Engelken, *Environ. Sci. Policy* **5** (2002) 121-133
- [2] J.M. Gaidis, *Cement Concrete Comp.* **26** (2004) 181-189.
- [3] E. Stupnisek-Lisac, A. Loncaric Bozic, I. Cafuk, *Corrosion* **54** (1998) 713-720
- [4] A.Y. El-Etre, *Corros. Sci.* **45** (2003) 2485-2495.
- [5] A.Y. El-Etre, *Corros. Sci.* **40** (1998) 1845-1850.

- [6] H. Ashassi-Sorkhabi, M.R. Majidi and K. Seyyedi, *Appl. Surf. Sci.* **225** (2004) 176-185.
- [7] Z. Ghasemi, A. Tizpar, *Appl. Surf. Sci.* **252** (2006) 3667-3672.
- [8] D.Q. Zhang, L.X. Gao, G.D. Zhou, *J. Appl. Electrochem.* **35** (2005) 1081-1085.
- [9] O. Olivares, N.V. Likhanova, B. Gomez, J. Navarrete, M.E. Llanos-Serrano, E. Arce, J.M. Hallen, *Appl. Surf. Sci.* **252** (2006) 2894-2909.
- [10] W.A. Badawy, K.M. Ismail, A.M. Fathi, *Electrochim. Acta* **51** (2006) 4182-4189.
- [11] K.M. Ismail, *Electrochim. Acta* **52** (2007) 7811-7819.
- [12] H. Ashassi-Sorkhabi, Z. Ghasemi, D. Seifzadeh, *Appl. Surf. Sci.* **249** (2005) 408-418.
- [13] E.E. Oguzie, Y. Li, F.H. Wang, *J. Colloid Interf. Sci.* **310** (2007) 90-98.
- [14] A.A. Aksut, A.N. Onal, *B. Electrochem.* **11** (1995) 513-521.
- [15] C.K. Gomma, *B. Electrochem.* **14** (1998) 291-297.
- [16] D.J. Kalota, D.C. Silverman, *Corrosion* **50** (1994) 138-145.
- [17] L.H. Madkour, M.M. Ghoneion, *B. Electrochem.* **13** (1997) 1-7.
- [18] M.S.S. Morad, A.E.A. Hermas, M.S.A. Aal, *J. Chem. Technol. Biot.* **77** (2002) 486-494.
- [19] A.A. El-Shafei, M.N.H. Moussa, A.A. El-Far, *J. Appl. Electrochem.* **27** (1997) 1075-1078.
- [20] A. Fouda, M. El-Semongy, *J. Indian Chem. Soc.* **59** (1982) 89-96.
- [21] A. Aksut, S. Bilgic, *Corros. Sci.* **33** (1992) 379-387.
- [22] G. Gomma, H. Wahdan, *Mater. Chem. Phys.* **39** (1994) 142-148.
- [23] G. Moretti, F. Guidi, *Corros. Sci.* **44** (2002) 1995-2011.
- [24] M. Rylkina, A. Chikanova, L. Trubacheva, S. Reshetnikov, *Prot. Met.* **35** (1999) 23-26
- [25] H. Baba, T. Kodama, *Corros. Sci.* **41** (1980) 1987-2000.
- [26] B.I. Ita, *B. Electrochem.* **21** (2005) 319-323.
- [27] M.A. Pech Canul, P. Bartolo-Perez, *Surf. Coat. Technol.* **184** (2004) 133-140.
- [28] M.A. Pech-Canul, M. Echeverria, *Corr. Eng. Sci. Technol.* **38** (2003) 135-138.
- [29] S.K. Rajappa, T.V. Venkatesha, *Turk. J. Chem.* **27** (2003) 189-196.
- [30] M.A. Pech-Canul, L.P. Chi-Canul, *Corrosion* **55** (1999) 948-956.
- [31] A. Akiyama, N. Nobe, *J. Electrochem. Soc.* **117** (1970) 999-1003.
- [32] G. Wranglen, *An introduction to corrosion and protection of metals*, Chapman & Hall, New York, USA (1985).
- [33] R.J. Holness, G. Williams, D.A. Worsley and H.N. McMurray, *J. Electrochem. Soc.* **152** (2005) B73-B81.
- [34] J. Telegdi, M.M. Shaglouf, A. Shaban, F.H. Karman, I. Betroti, M. Mohai, E. Kalman, *Electrochim. Acta* **46** (2001) 3791-3799.
- [35] J. A. Selvi, S. Rajendran and J. Jeyasundari, *Zastita Materijala* **50 (2)** (2009) 91-98.
- [36] J. Hilden, J. Virtanen, O. Forsen, J. Aromaa, *Electrochim. Acta* **46** (2001) 3859-3866
- [37] J.M. Roque, T. Pandiyan, J. Cruz. E Garcia-Ochoa, *Corros. Sci.* **50** (2008) 614-624.
- [38] O. Benali, L. Larabi, M. Traisnel, L. Gengembre, Y. Harek, *Appl. Surf. Sci.* **253** (2007) 6130-6139.
- [39] H. Amar, T. Braisaz, D. Villemin, B. Moreau, *Mater. Chem. Phys.* **110** (2008) 1-6
- [40] J. A. Selvi, S. Rajendran, V. G. Sri, A. J. Amalraj, B. Narayanasamy, *Port. Electrochim. Acta* **27(1)** (2009) 1-11.
- [41] S. Rajendran, J. Paulraj, P. Rengan, J. Jeyasundari and M. Manivannan, *J. Dent. Oral Hyg.* **1** (2009) 1-8.
- [42] E. Kalman, I. Felhosi, F.H. Karman, et al., *Corrosion and Environmental Degradation*, M. Schutze, Ed., Weinheim: Wiley-VCH, 1 (2000) 471.
- [43] S. Zhang, Z. Tao, W. Li, B. Hou, *Appl. Surf. Sci.* **255** (2009) 6757-6763.
- [44] F. El-Taib Heikal, A.S. Fouda, M.S. Radwan, *Mater. Chem. Phys.* **125** (2011) 26-36.
- [45] S. Rajendran, M. Kalpana Devi, A.P.P. Regis, A. J. Amalraj, J. Jeyasundari and M. Manivannan, *Zastita Materijala* **50** (2009) 131-140.

- [46] R. Kalaivani, B. Narayanasamy, J.A. Selvi, A.J. Amalraj, J. Jeyasundari and S. Rajendran, *Port. Electrochim. Acta* **27** (2009) 177-187.
- [47] J. Sathiyabama, S.Rajendran, J. A. Selvi and J. Jeyasundari, *Open Corrosion J.* **2** (2009) 77-82.
- [48] R.M. Silverstein, G.C. Bassler, T.Moril, *Spectrometric Identification of Organic Compound*, John Wiley and Sons, New York (1981) 95.
- [49] A.D. Cross, *Introduction to practical infrared spectroscopy*, Butterworths, Scientific Publication, London (1990) 73
- [50] K. Nakamoto, *Infrared and Raman spectra of inorganic coordination compound*, Willey Interscience, New York (1986).
- [51] S. Rajendran, B.V. Apparao and N. Palaniswamy, *B. Electrochem.* **12** (1996) 15-19.
- [52] I. Sekine and V. Hirakawa, *Corrosion* **42** (1986) 272-277.
- [53] S. Rajendran, B.V. Apparao and N. Palaniswamy, *8<sup>th</sup> Europ. Symp. Corros. Inhibitors*, Ferrara, Italy, (1995) Proc. Vol 1, p. 465.
- [54] D. Gopi, S. Manimozhi, K. M. Govindaraju, P. Manisankar and S. Rajeswari, *J. Appl. Electrochem.* **37** (2007) 439-449.
- [55] M.A. Amin, S.S. Abd El-Rehim, E.E.F. Ei-Sherbini, R.S. Bayoumi, *Electrochim. Acta* **52** (2007) 3588-3600.
- [56] M.A. Amin, S.S. Abd El-Rehim, H.T.M. Abdel-Fatah, *Corros. Sci.* **51** (2009) 882-894.
- [57] R. Vera, R. Schrebler, P. Cury, R. Del Rio, H. Romero, *J. Appl. Electrochem.* **37** (2007) 519-525.
- [58] Ph. Dumas, B. Butffakhreddine, C. Amra, O. Vatel, E. Andre, R.Galindo and F. Salvan, *Europhys. Lett.* **22** (1993) 717-722.
- [59] J. M. Bennett, J. Jahannir, J.C. Podlesny, T. L. Baiter and D.T. Hobbs, *Appl. Optics* **34** (1995) 213-230.
- [60] A. Duparre, N. Kaiser, H. Truckenbrodi, M Berger and A. Kohler, *Int. Symp. on Optics, Imaging and Instrumentation*, 11-16 Jul 1993., San Diego, CA, Proc. SPIE. 1995 (1993) p. 181-192.
- [61] A. Duparre, N. Kaiser and S. Jakobs, *Annual Symp. on Optical Materials for High Power Lasers*. 27-29 October 1993, Boulder, CO, Proc. SPIE, 2114 (1993) p. 394.
- [62] C. Amra. C. Deumie. D. Torricini. P, Roche, R. Galindo. P. Dumas and F. Salvan, *Int. Symp. on Optical Interference Coatings*. 6-10 June 1994. Grenoble, Proc. SPIE. 2253 (1994) p. 614-630.
- [63] T.R. Thomas, *Rough Surfaces*, Longman, New York, 1982.
- [64] K.J. Stout, P.J. Sullivan and P.A. McKeown, *CIRP Annals-Manuf. Techn.*, **41** (1992) 621.
- [65] D. Gopi, N. Bhuvaneshwaran, S. Rajeswari, *B. Electrochem.* **18** (2002) 29-34.
- [66] D. Gopi, S. Rajeswari, *J. Solid State Electr.* **6** (2002) 194-202.
- [67] D. Gopi, S. Rajeswari, *International Conference on Advances in Surface Science and Engineering (INSURE)*, Chennai, India, 21 – 23 Feb. (2001) Proc. p. 210.
- [68] D. Gopi, S. Rajeswari, *NACE International Conf., Corrosion its Mitigation and Preventive Maintenance*, Mumbai, India, 20-23 Nov. (2000) Proc. Vol 1, p. 435.
- [69] D. Gopi, S. Rajeswari, *Tenth National Congress on Corrosion Control, Conf.*, Madurai, India, 6-8 Sep. (2000) Proc. p. 353.
- [70] A. Veres, G. Reinhard, E. Kalman, *Brit. Corros. J.* **27** (1992) 147-150.
- [71] E. Kalman, *Corrosion Inhibitors*, Published for EFC No.11, Institute of Materials London, UK (1994).

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