Research Article

INVESTIGATING THE CORROSION INHIBITION EFFICIENCY OF SURGICAL CARBON STEEL INSTRUMENTS USED IN MEDICAL FIELD

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ABSTRACT

The corrosion inhibition efficiency of Triton X 100 in controlling surgical carbon steel instrument corrosion in well water has been analysed by weight loss method. Mechanistic aspects of corrosion inhibition efficiency have been studied by Polarization and AC impedance measurements. The formulation consisting of 200 ppm of Triton X 100 and 50 ppm of Zn^{2+} provides 84 % corrosion inhibition efficiency. A synergistic effect exists between the surfactant Triton X 100 and Zn^{2+} . Polarization study confirms that Triton X 100 - Zn^{2+} system functions as a mixed type of inhibitor. AC impedance spectra shows that a protective film is formed on the carbon steel surface. Cyclic voltammetry data confirms the stability of the protective film in presence of 3.5% NaCl solution. FTIR spectra reveals that the protective film consists of Triton X 100- Fe^{2+} complex and $Zn(OH)_2$. SEM, EDX, data indicate the possibility of formation of protective layer on the metal surface. FTIR spectra confirms the formation of protective film on the metal surface. AFM study reveals the surface morphology and gives the information of the thickness of the protective film. Contact angle measurement confirms the hydrophobic nature of the protective film formed on the carbon steel surface.

Keywords: Carbon steel, Triton X 100, AFM, Contact angle measurement, FTIR, SEM, EDX, Hydrophobicity.

INTRODUCTION

Surgical instrument corrosion is the serious problem in many healthcare facilities. Many metals are used in the manufacturing of surgical instruments¹. Among them carbon steel is used in the manufacturing of both dental and medical instruments. Carbon steel blades are also used for surgical purpose. There are many problems arising due to corrosion of surgical instruments for example, a hemostat may not open because of corrosion in the box area, scissors and scalpels could become dull, and instruments could break during surgery as a result of severe corrosion. Corrosion can result in a shortened instrument life, which results in increased cost. The major problem is the formation of rust on the surgical instrument after the sterilization process. Corrosion inhibitors can reduce, control or prevent reactions among a metal and its surroundings when added to the medium in small quantities. Surfactants are used as corrosion inhibitors to minimize the corrosion of carbon steel surface by adsorbing on the metal surface.

The present work is undertaken, to evaluate the inhibition efficiency of Triton X 100 to prevent the corrosion of carbon steel, to analyze the protective film on carbon steel by FTIR spectra, to understand the mechanistic aspects of corrosion inhibition by potentiodynamic polarization studies and AC impedance spectra, to study the stability of the protective film formed on the metal surface by cyclic voltammetry measurement, to study the hydrophobic nature of the Triton X 100 by contact angle measurements, to propose a suitable mechanism for corrosion inhibition².

MATERIALS AND METHODS

Preparation of the carbon steel specimens

The carbon steel specimens were chosen from the same sheet of the following composition:

Elements	C	Mn	P	Si	S	Cr	Ni	Mo	Fe
COMPOSITION	0.1	0.4	0.06	0.022	0.026	0.0020	0.018	0.012	Rest

Carbon steel specimens of the dimensions 1.0 cm x 4.0 cm x 0.2 cm were polished to mirror finish, washed with double distilled water, degreased with trichloroethylene, dried and were used for the weight loss and surface examination studies. The carbon steel specimens were stored in a desiccators and used for all investigations. Carbon steel rod encapsulated in Teflon with an exposed cross section of a 1 cm² diameter was used as the working electrode in potentiodynamic polarization studies. The

surface of working electrode was polished to mirror finish and degreased with trichloroethylene.

Preparation of stock solutions Triton X 100

1 g of Triton X 100 was dissolved in double distilled water and then made up to 100 ml in a standard measuring flask. 1 ml of this

solution was diluted to 100 ml which yields 100 ppm of Triton X 100.

Zinc sulphate solution

4.4 g of zinc sulphate was dissolved in double distilled water and made up to 1 litre. 2.5 ml of this solution was diluted to give 100 ml of 25 ppm and 5 ml of this solution was diluted to give 100 ml of 50 ppm of Zn^{2+} ion concentration.

Sodium chloride solution

3.5 g of sodium chloride was dissolved in double distilled water and then made up to 100 ml in a standard measuring flask.

Preparation of environments

Triton X 100 surfactant solution of various concentrations such as 50, 100, 150, 200 and 250 ppm are prepared and 25, 50 ppm of Zn^{2+} ion concentrations are maintained.

Weight loss method

Determination of surface of the specimens

The length, breadth and thickness of carbon steel specimens, the radius of the hole was determined with the help of vernier calipers of high precision and the surface areas of the specimens were calculated.

Weighing the specimens before and after corrosion

Weighing of the carbon steel specimens before and after corrosion were carried out using a digital balance, Shimadzu AY 62 model.

Determination of corrosion rate

The weighed specimens in triplicate were suspended by means of plastic hooks in 100 ml beakers containing 100 ml of well water containing various concentrations of the inhibitor in the absence and presence of Zn^{2+} for one day. After one day immersion, the specimens were taken out, washed with distilled water, running water, dried and weighed. From the change in weight of the specimens, corrosion rates were calculated using the following equation 1.

$$\text{Corrosion rate} = \frac{\text{Loss in weight (mg)}}{\text{Surface area of the specimen (dm}^2\text{) x Period of immersion (days)}} \quad (1)$$

The corrosion rate is expressed in mdd units [mdd = mgm/(dm²) (day)]

Corrosion inhibition efficiency (IE) was then calculated using the equation 2.

$$IE = 100 [1 - (W_2 / W_1)] \% \quad (2)$$

Where,

W_1 = Corrosion rate in the absence of inhibitor

W_2 = Corrosion rate in the presence of inhibitor

Synergism Parameters (S_I)

The synergism parameters (S_I) were calculated using the following equation 3 given by Aramaki and Hackerman.

$$S_I = \frac{1 - \theta_{1+2}}{1 - \theta'_{1+2}} \quad (3)$$

Where,

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

θ'_{1+2} = combined inhibition efficiency of substance 1 and substance 2.

Surface Examination Studies

Potentiodynamic polarization study

The polarization measurements were carried out using CHI 660A electrochemical workstation model. A three-electrode cell assembly was used. The working electrode (WE) used was a rectangular specimen of carbon steel with one face of the electrode of 1 cm² area exposed and the rest being shielded with red lacquer. A rectangular platinum foil was used as the counter (CE) electrode. The area of the counter electrode was much larger when compared to the area of the WE. This can exert a uniform potential field on the WE and minimize the polarization effect on the CE. The reference electrode (RE) used was saturated calomel electrode (SCE). The RE was placed close to the WE to minimize iR contribution. A time interval of about 5 to 10 min was given for the WE to attain a steady state open circuit potential. The results such as inhibition efficiency, Tafel slopes, E_{corr} and I_{corr} values were calculated.

AC impedance measurement

AC Impedance measurements were carried out using CHI 660A Electrochemical work station model as that used for polarization measurements. A time interval of 5-10 minutes was given for the system to attain a steady state open circuit potential. Then over this steady state potential, an AC potential of 10 mV was superimposed. The AC frequency was varied from 100 MHz to 100 KHz. The real part (Z') and the imaginary part (Z'') of the cell impedance were measured in ohms for various frequencies. The values of the charge transfer resistance (R_t) and the double layer capacitance (C_{dl}) were calculated by using equations 4 and 5.

$$R_t = (R_t + R_s) - R_s \quad (4)$$

Where,

R_s = Solution Resistance

$$C_{dl} = \frac{1}{2\pi \times R_t \times f_{max}} \quad (5)$$

Where,

f_{max} = maximum frequency

Cyclic voltammetry

Cyclic voltammograms were recorded using Versa STAT MC electrochemical system. A three-electrode cell assembly was used for recording. Carbon steel was the working electrode and the exposed surface area was 1 cm². The reference electrode was saturated calomel electrode (SCE). A rectangular platinum foil was the counter electrode. The cyclic voltammetry curves were recorded in the scan range of -2.3 to -2.3V (SCE) with a scan rate of 20 mV S⁻¹.

Surface analysis by FTIR spectroscopy

After one day immersion, the specimens were taken out of the solutions and dried. The film formed on the surface was scratched carefully and it was thoroughly mixed so as to make it uniform throughout. FTIR spectrum of the powder (KBr pellet) was recorded using Perkin-Elmer 1600 FTIR spectrometer.

Scanning electron microscopic studies (SEM)

The carbon steel immersed in blank solution and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology. The surface morphology measurements of carbon steel were examined using JEOL MODEL 6390 computer controlled scanning electron microscope.

Energy dispersive analysis of X-rays (EDX)

The elemental analysis of the carbon steel surface at the same condition was carried out using an energy dispersive X-ray analyzer (EDX) unit attached to the SEM machine.

Contact Angle measurements

The contact angle measurements for the carbon steel surface were recorded using a VCA Optima instrument equipped with a CCD camera for imaging. The double distilled water under fixed conditions with a drop volume of 5 mL was used to determine the contact angle. VCA Optima XC software provided with instruments was used for fitting the drop shapes to find the contact angle of water on the carbon steel surface. The contact angle measurement was repeated three times for each carbon steel surface, and the average values with standard deviations ± 2 degree are reported.

Atomic force microscopy characterization (AFM)

Atomic Force Microscopy (AFM) is a new technique which allows metal surface to be imaged at higher resolutions and

accuracies than ever before. The carbon steel specimen immersed in blank and in the inhibitor system for one day. The carbon steel specimens were removed, rinsed with double distilled water, dried, and subjected to the surface examination. Veeco Innova model was used to observe the carbon steel surface in tapping mode, using cantilever with linear tips. The scanning area in the images was $50\ \mu\text{m} \times 50\ \mu\text{m}$ and the scan rate was 0.6Hz S^{-1} . A two dimensional, and a three dimensional topography of metal surface films gave various roughness parameters of the film.

RESULTS AND DISCUSSION

Synergistic effect of Triton X 100 and Zn^{2+}

Analysis of the results of weight loss method

Corrosion rates (CR) of carbon steel^{3,4,5} immersed in well water in the absence and presence of inhibitor (Triton X 100) are given in Tables 1 to 3. The inhibition efficiencies (IE) are also given in these Tables. The inhibition efficiencies of the Triton X 100- Zn^{2+} systems as a function of concentrations of Triton X 100 are shown in Figure 1.

It is observed from Table 1 that Triton X 100 shows some inhibition efficiencies. 200 ppm of Triton X 100 has 32% inhibition efficiency, as the concentration of Triton X 100 increases, the inhibition efficiency increases. This is due to the fact that as the concentration of Triton X 100 increases, the protective film (probably Fe^{2+} -Triton X 100 complex) formed on the metal surface. At concentrations ≥ 250 ppm of Triton X 100, the protection efficiency decreases. It may be due to the fact that these molecules aggregate together to form micelles. They are not uniformly adsorbed on the metal surface. Hence corrosion inhibition efficiency decreases.

Table 1 Corrosion rates (CR) in milligram per decimeter per day (mdd) of carbon steel immersed in well water in the presence and absence of Triton X 100- Zn^{2+} system at various concentrations and the inhibition efficiencies (IE) obtained by weight loss method

Inhibitor system: Triton X 100- Zn^{2+} (0 ppm)

Immersion period: One day

Triton X 100 (200 ppm)	Zn^{2+} (50 ppm)	CR (mdd)	IE%
0	0	18.18	-
50	0	16.18	12
100	0	14.72	19
150	0	13.45	21
200	0	11.27	32
250	0	13.09	27

Influence of Zn^{2+} on the inhibition efficiencies of Triton X 100

The influence of Zn^{2+} on the inhibition efficiencies of Triton X 100 is given in Table 2 and Table 3. It is observed that as the concentration of Triton X 100 increases the IE increases. Similarly for a given concentration of Triton X 100, IE increases as the concentration of Zn^{2+} increases. At concentrations ≥ 250 ppm of Triton X 100, the inhibition efficiency decreases. It may be due to the fact that these molecules aggregate together to form micelles. They are not uniformly adsorbed on the metal surface. Hence corrosion inhibition efficiently decreases. It is also observed that a synergistic effect exists between Triton X 100 and Zn^{2+} . For example, 50 ppm of Zn^{2+} has 10 % IE; 200 ppm of Triton X 100 has 32% IE. Interestingly their combination has a high IE, namely 84 %.

In the presence of Zn^{2+} more amount of Triton X 100 is transported towards the metal surface. On the metal surface Fe^{2+} -Triton X 100 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 $\text{Zn}(\text{OH})_2$ on the cathodic sites of the metal surface. Thus the anodic and cathodic reactions are controlled effectively. This accounts for the synergistic effect existing between Zn^{2+} and Triton X 100.

$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$ (Anodic reaction)

$\text{Fe}^{2+} + \text{Zn}^{2+}$ -Triton X 100 complex $\rightarrow \text{Fe}^{2+}$ -Triton X 100 complex + Zn^{2+}

$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ (Cathodic reaction)

$\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn}(\text{OH})_2 \downarrow$

Table 2 Corrosion rates (CR) in milligram per decimeter per day (mdd) of carbon steel immersed in well water in the presence and absence of Triton X 100-Zn²⁺ system at various concentrations and the inhibition efficiencies (IE) obtained by weight loss method

Inhibitor system: Triton X 100-Zn²⁺ (25 ppm)

Immersion period: One day

Triton X 100(ppm)	Zn ²⁺ (ppm)	CR (mdd)	IE%
0	0	18.18	-
0	25	16.91	7
50	25	9.45	48
100	25	8.73	52
150	25	7.99	56
200	25	6.18	66
250	25	8.36	54

Table 3 Corrosion rates (CR) in milligram per decimeter per day (mdd) of carbon steel immersed in well water in the presence and absence of Triton X 100-Zn²⁺ system at various concentrations and the inhibition efficiencies (IE) obtained by weight loss method

Inhibitor system: Triton X 100-Zn²⁺ (50 ppm)

Immersion period: One day

Triton X 100 (200 ppm)	Zn ²⁺ (50 ppm)	CR (mdd)	IE%
0	0	18.18	-
0	50	16.36	10
50	50	5.82	68
100	50	4.36	76
150	50	3.64	80
200	50	2.91	84
250	50	3.99	78

Figure 1 Corrosion rates (CR) of carbon steel immersed in various test solutions

Synergism parameter (S_I)

Synergism parameter (S_I) have been used to know the synergism effect existing between two inhibitors^{6,7,8}. The synergism parameter (S_I) can be calculated using the following equation (3) given by Aramaki and Hackerman.

$$\text{Synergism parameter (S}_I\text{)} = \frac{1-\theta_{1+2}}{1-\theta_1-\theta_2} \quad (3)$$

Where,

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

θ₁= Surface coverage by Triton X 100

θ₂= Surface coverage by Zn²⁺

1-θ₁₊₂= Surface coverage by both Triton X 100 and Zn²⁺

Where,

$$\text{Surface coverage } (\theta) = \frac{\text{IE}\%}{100}$$

The synergism parameters of Triton X 100 -Zn²⁺ system are given in Tables 4 and 5. 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 there is no synergistic effect exists and it is observed that the S_I value is found to be greater than one, indicating synergistic effect existing between Triton X 100-Zn²⁺ of concentrations 25 ppm and 50 ppm with various concentrations of Triton X 100. S_I value is higher for the system containing 200 ppm of Triton X 100 and 50 ppm of Zn²⁺ than for the system containing 200 ppm of Triton X 100 and 25 ppm of Zn²⁺ indicating that there is more transport of Triton X 100. Thus, the enhancement of the inhibition efficiency caused by the addition of 50 ppm of Zn²⁺ ions to Triton X 100 is due to the synergistic effect.

Table 4 Synergism parameters for Triton X 100-Zn²⁺ system, when carbon steel immersed in well water
Inhibitor system: Triton X 100-Zn²⁺ (25 ppm) Immersion period: One day

Triton X 100(ppm)	Surface coverage θ_1	Surface coverage θ_2	Combined Surface coverage θ'_{1+2}	Synergism parameters S_1
50	0.12	0.07	0.48	1.56
100	0.19	0.07	0.52	1.54
150	0.21	0.07	0.56	1.64
200	0.32	0.07	0.66	1.79
250	0.27	0.07	0.54	1.43

Table 5 Synergism parameters for Triton X 100-Zn²⁺ system, when carbon steel immersed in well water
Inhibitor system: Triton X 100-Zn²⁺ (50 ppm) Immersion period: One day

Triton X 100(ppm)	Surface coverage θ_1	Surface coverage θ_2	Combined Surface coverage θ'_{1+2}	Synergism parameters S_1
50	0.12	0.10	0.68	2.44
100	0.19	0.10	0.76	2.96
150	0.21	0.10	0.80	3.45
200	0.32	0.10	0.84	3.62
250	0.27	0.10	0.78	2.86

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^{9,10,11}. If a protective film is formed on the metal surface, the linear polarization resistance value (LPR) increases and 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 Figures 2(a) and 2(b). The corrosion parameters are given in Table 6. When carbon steel was immersed in well water the corrosion potential was -828mV Vs SCE. When Triton X 100 (200 ppm) and Zn²⁺ (50 ppm) were added to the above system the corrosion potential shifted to the noble side -824mV Vs SCE. This shows that the corrosion potential difference is very small therefore behaving like mixed type inhibitor which controls both anodic and cathodic reaction to an equal extent. This suggests 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 Triton X 100 (200 ppm)-Zn²⁺ (50 ppm) obtained from potentiodynamic polarization study

System	E_{Corr} mV Vs SCE	b_c mV/ decade	b_a mV/ decade	I_{Corr} A/cm ²	LPR ohmcm ²
Well water	-828	0.165	0.164	8.915×10^{-7}	35319.7
Well water + Triton X 100 (200ppm) + Zn ²⁺ (50ppm)	-824	0.161	0.161	8.231×10^{-7}	37276.5

Figure 2 Polarization curves of carbon steel immersed in various test solutions
(a) Well water (blank)
(b) Well water containing 200 ppm of Triton X 100 and 50 ppm of Zn²⁺

Analysis of AC impedance spectra

AC impedance spectra (electro chemical impedance spectra) have been used to confirm the formation of protective on the metal surface^{12,13,14}. If a protective film is formed on the metal surface, charge transfer resistance (R_t) increases; double layer capacitance value (C_{dl}) decreases and the impedance $\log (Z/\text{ohm})$ value increases. The AC impedance spectra of carbon steel immersed in well water in the absence and presence of inhibitors Triton X 100 (200 ppm) and Zn^{2+} (50 ppm) are shown in Figures 3 (a,b) (Nyquist plots) and Figures 4 (a, b) and Figures 5(a,b) (Bode

plots). The AC impedance parameters namely charge transfer resistance (R_t) and double layer capacitance (C_{dl}) derived from Bode plots are also given in Table 7.

It is observed that when the inhibitors Triton X 100 (200 ppm) and Zn^{2+} (50 ppm) are added, the charge transfer resistance (R_t) increases from $1011.4 \Omega\text{cm}^2$ to $1127.0 \Omega\text{cm}^2$. The C_{dl} values decreases from $4.9823 \times 10^{-5} \text{ F/cm}^2$ to $4.4154 \times 10^{-5} \text{ F/cm}^2$. The impedance value [$\log (Z/\text{ohm})$] increases from 3.16 to 3.19. These results lead to the conclusion that a protective film is formed on the metal surface.

Table 7 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		Bode plot Impedance value $\log(Z/\text{ohm})$
	R_t ohmcm^2	C_{dl} F/cm^2	
Well water	1011.4	4.9823×10^{-5}	3.16
Well water +Triton X 100(200ppm) + Zn^{2+} (50 ppm)	1127.0	4.4154×10^{-5}	3.19

Figure 3 AC impedance spectra of carbon steel immersed in various test solution (Nyquist plot)

(a) Well water (blank)
(b) Well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+}

Figure 4 AC impedance spectra of carbon steel immersed in various test solution (Impedance Bode plot)

Figure 5 AC impedance spectra of carbon steel immersed in various test solution (Phase Bode plot)

(a) Well water (blank)
(b) Well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+}

Cyclic voltammetry

Cyclic voltammetry is a type of potentiodynamic electrochemical measurement. It is generally used to study the electrochemical properties of an analyte solution^{15,16,17}.

The cyclic voltammogram of polished carbon steel immersed in 3.5% NaCl solution

The cyclic voltammogram recorded for the number of one cycle for the polished carbon steel immersed in 3.5% NaCl is shown in Figure 6(a). It is observed that during anodic sweep a peak appeared at -425 mV which is called as metal dissolution peak. When the anodic polarization of carbon steel reaches a certain critical potential, a peak appeared at -100mV is corresponding to the pitting potential (E_{pit}), that is the pitting potential for polished carbon steel surface is appeared at more negative side due to corrosion. Because it does not have protective film on the metal surface.

Whereas, cathodic sweep shows two cathodic peaks; one peak appeared at -420mV corresponding to the reduction of corrosion product and another peak appeared at -1.10V which is known as reduction of iron oxide product and the reduced corrosion current density occurs at $-1.0 \times 10^{-3} \text{ A}$. When the metal dissolves, $\text{Fe}(\text{OH})_2$ and/or FeO film is formed on the metal surface. As the result of high polarizability of the Chloride ions, the Cl^- ions are adsorbed on the metal surface than that of OH^- ions. The adsorbed Chloride ions penetrates the oxide film at the flaws and defects in the oxide film. When the penetrated Cl^- ions reaches the metal surface they promote local corrosion.

Cyclic voltammogram for polished carbon steel surface immersed in well water for one day

The Cyclic voltammogram recorded for the number of one cycle for the polished carbon steel, immersed in well water for one day. A film was found on the metal surface. The metal surface containing this protective film was immersed in 3.5% NaCl solution is shown in Figure 6(b). It is observed that during anodic sweep, the metal dissolution peak does not appear. The film is stable because electrons are not released on the metal surface.

When the anodic polarization of carbon steel reaches a certain critical potential, a peak appeared at 150mV which is corresponding to the pitting potential. This shows that when carbon steel is immersed in well water, a protective film is formed on the metal surface due to the presence of various anions and cations present in the well water. When this electrode containing this protective film is immersed in 3.5% NaCl and when cyclic voltammogram is recorded the protective film is not broken; it seems to be stable hence, the potential is shifted to the anodic side (+150mV). The protective film may consist of stable iron, iron oxide film and other iron compounds.

During the cathodic sweep reduction of pitting corrosion product peak is shifted to -500mV indicating that pitting corrosion takes place. The peak due to reduction of iron oxide is shifted from -1.10V to -1.30V; that is towards more negative side and its current density is $-1.30 \times 10^{-3} \text{ A}$ indicating that the film is unstable that is unreactive.

Cyclic Voltammogram for polished carbon steel surface in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+} for one day

The Cyclic Voltammogram recorded for the number of one cycle of polished carbon steel, immersed in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+} for one day. A film was

found on the metal surface. The metal surface containing this protective film was immersed in 3.5% NaCl solution is shown in Figure 6(c). It is observed that during anodic sweep, dissolution of metal does not take place and a passive state is observed. Electrons are not transferred from the metal surface and a passive region is observed. In the passive region the corrosion resistance increases due to the formation of thin surface film. The passive film becomes stable and corrosion rate falls to very low value and hence protects the metal against further oxidation. Pitting potential (E_{pit}) peak appears at 250mV that is shifted to more positive side due to the formation of stable Fe-inhibitor complex formed on the metal surface.

During cathodic sweep, the peak due to the reduction of pitting corrosion product is absent, this reveals that pitting corrosion does not take place under the given experimental conditions. The peak due to the reduction of iron oxide peak to iron is shifted from -1.10V to -1.40V that is more negative side and its current density is shifted from $-1.0 \times 10^{-3} \text{ A}$ to $-1.10 \times 10^{-3} \text{ A}$. This confirms the formation of stable and compact protective film of self-assembling monolayer of Fe-inhibitor complex and there is also a possibility of deposition of zinc-inhibitor complex on the metal surface and hence it can withstand the attack of chloride ion present in 3.5% NaCl.

Figure 6 Cyclic voltammogram of
(a) Polished carbon steel immersed in 3.5% NaCl solution
(b) Polished carbon steel surface immersed in well water for one day
(c) Polished carbon steel surface in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+} for one day

Analysis of FTIR spectra

FTIR spectra have been used to analysis the protective film formed on the metal surface^{18,19}. The FTIR spectrum (KBr) of pure Triton X 100 is shown in Figure 7(a). The FTIR spectrum of the film formed on the metal surface after immersion in the solution containing well water, 200 ppm of Triton X 100 and 50 ppm Zn^{2+} is shown in Figure 7(b). The peak at 3410.2 cm^{-1} is due to OH^- stretching. The $\text{C}=\text{O}$ stretching frequency has Shifted from 1609.17 to 1627.4 cm^{-1} . This observation suggest that Triton X 100 has coordinated with Fe^{2+} on metal surface through oxygen atom of resulting in the formation of Fe^{2+} -Triton X 100 complex on the anodic sites of the metal surface. The peak at 687 cm^{-1} corresponds to Zn-O stretching. This confirms that $\text{Zn}(\text{OH})_2$ is formed on the cathodic sites of the metal surface. The spectrum exhibits a strong C-O-C band at 1113.5 cm^{-1} is shifted to 1300 cm^{-1} . The CH_2 band is shifted from 1354.55 cm^{-1} to 1450 cm^{-1} . The C-C band is shifted from 1609.17 cm^{-1} to 1630 cm^{-1} . The band at 1458.6 corresponding to benzene ring is shifted to 1460 cm^{-1} . The C-H band at 837.63 cm^{-1} suggests disubstituted benzene is shifted to 800 cm^{-1} . Thus the FTIR spectral study leads to the conclusion that the protective film consist of Fe^{2+} -Triton X 100 and $\text{Zn}(\text{OH})_2$.

Figure 7 FTIR Spectra of
(a) Pure Triton X 100

(b) Film formed on metal surface after immersion in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+}

SEM analysis of metal surface

SEM provides a pictorial representation of the surface²⁰. To understand the nature of the surface film in the absence and the presence of inhibitors and the extent of corrosion of carbon steel, the SEM micrographs of the surface are examined.

The SEM images of different magnification (X1000) of carbon steel specimen and carbon steel specimen immersed in well water for one day in the absence and presence of inhibitor system are shown in Figure 8 as images (a, b and c) respectively.

The SEM micrographs of polished carbon steel surface (control) in Figure 8(a) illustrate the smooth surface of the metal indicating that there is absence of any corrosion products formed on the metal surface.

The image 8(b) denote the SEM micrographs of carbon steel surface immersed in well water which show the type of rough surface characteristic of the uniform corrosion of the metal surface in well water, indicating in an inhibitor free solution, the surface is highly corroded.

Figure 8 SEM micrographs of

(a) Carbon steel; Magnification X1000 (control)

(b) Carbon steel immersed in well water; Magnification X1000

(c) Carbon steel immersed in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+} ; Magnification X1000

The image 8(c) confirm that in the presence of 200 ppm Triton X 100 and 50 ppm of Zn^{2+} mixture in well water, the rate of corrosion is suppressed, as can be seen from the decrease in corroded areas. This is as a result of the formation of insoluble Triton X 100- Zn^{2+} inhibitor complex on the surface of the metal. These results support all of the electrochemical and weight loss measurements.

Energy dispersive X-ray analysis (EDX)

Energy Dispersive Analysis of X-rays is the most powerful method to find out the formation of protective film on the metal surface^{21,22}.

The EDX spectrum of polished carbon steel surface (Control)

The EDX spectrum of polished carbon steel surface is shown in Figure 9(a). The atomic percentage of various elements of the polished carbon steel is given below. It is observed that the carbon steel surface contains mainly Fe (58.6%), carbon (11.6%) and small concentration of oxygen (1.48%).

The EDX spectrum of polished carbon steel surface immersed in well water (Blank)

The EDX spectrum of carbon steel surface immersed in well water is shown in Figure 9(b). The atomic percentage of various elements of the carbon steel is given below. It is observed from the table that the atomic percentage of Fe increases to 89.73% and the carbon percentage decreases to 8.74%. The atomic percentage of oxygen increases to 34.68% indicating that there is $Fe(OH)_2$ (or) FeO film formed on the metal surface which enhances the local corrosion of carbon steel surface.

The energy dispersive spectrum of polished carbon steel surface immersed in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+} (Inhibitor system)

The energy dispersive spectrum of polished carbon steel surface immersed in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+} is shown in Figure 9(c). It is observed that in the presence of inhibitor system, the atomic weight percentages of Fe, oxygen and carbon decreases to 6.76%, 29.45% and 7.89%

respectively, indicating that there is a passive film formed on the metal surface. The corrosion resistance increases due to the formation of stable Fe-inhibitor complex on the metal surface. There is also a possibility of deposition of Zn^{2+} -inhibitor complex on the metal surface and the atomic percentage of Zn is 43.96%. The passive film formed on the metal surface becomes stable and corrosion rate falls to very low value and hence protects the metal against further oxidation.

Figure 9 EDX spectra of
(a) Polished metal
(b) Carbon steel immersed in well water
(c) Carbon steel immersed well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+}

Table 8: Contact angle measurement for polished metal and metal surface after immersion in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+}

S.No.	Contact angle value for polished metal	Contact angle value for metal surface after immersion in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+}
1.	66°	81.1°

Figure 10 Contact angle measurement for
(a) Polished metal
(b) Metal surface after immersion in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+}

Contact angle measurements

When Self-assembling nano films are formed on metal surface, the surface becomes hydrophobic hence it becomes water repellent. Water molecules cannot sit on the metal surface this is very similar to lotus effect (water droplets rolling on lotus leaves) so corrosion is prevented. As the hydrophobicity increases corrosion inhibition nature also increases.

Contact angles of water droplets formed on various metal surfaces²³ are given in the following Table 8. It is observed that for water droplet on polished carbon steel surface the contact angle is 66°. In the case of metal surface immersed in the corrosion medium (well water) the contact angle increases to 81.1°. It is interest in note that in the presence of inhibitor, the contact angle increases by 15.1°. Thus, it is evident that in presence of corrosion inhibitor (Triton X 100), because of formation of Self-assembling nano films contact angle increases; hydrophobicity increases and hence corrosion inhibition increases shown in Figures 10 (a) and 10(b).

Formation of monolayers can be confirmed by analysis of the position of aliphatic –CH stretching frequencies appear at 2940.0 cm^{-1} and 2878.0 cm^{-1} (Figure 9 (a, b)).

In the presence of inhibitor Triton X 100 monolayers are formed on the metal surface by chemical deposition method. In this case the aliphatic –CH stretching frequencies appear at 2936.0 cm^{-1} and 2870.0 cm^{-1} . That is the shift is not very much. Hence it is concluded that the aliphatic –CH groups are free. This confirms the formation of monolayers on the metal surface.

Atomic force microscopy characterization

Atomic force microscopy is a powerful technique for gathering roughness statistics from a variety of surfaces^{24,25}. AFM is becoming an accepted method of roughness investigation. The two dimensional (2D), three dimensional (3D) of the AFM morphologies, AFM cross-sectional profile of surface for polished carbon steel surface, carbon steel surface immersed in well water and carbon steel surface immersed in well water containing the formulation consisting of 200 ppm of Triton X 100 and 50 ppm of Zn^{2+} are shown in Figures 11(a, b, c) and 12(a, b, c) respectively.

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

AFM image analysis was performed to get 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 calculated 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). Table 10 is a summary of the average roughness (R_q), RMS roughness (R_a) and maximum peak-to-valley height (P-V)

values for carbon steel surface immersed in different environments.

The AFM images of carbon steel immersed in well water in the absence and presence of Zn^{2+} are shown in Figures 11(a, b, c) and 12(a, b, c). The values of (R_q), (R_a) and (P-V) height for the polished carbon steel surface (Control) are 20.75 nm, 16.49 nm, and 107.26 nm, respectively. The small roughness observed on the polished carbon steel surface is due to atmospheric corrosion. Figures 11(b) and 12(b) display the corroded metal surface with few pits in the absence of the inhibitor immersed in well water. The (R_q), (R_a), (P-V) height values for the carbon steel surface are 118.65 nm, 84.37 nm and 631.13 nm respectively. These data suggests that carbon steel surface immersed in well water has a better surface roughness than the polished metal surface, which

shows that the unprotected carbon steel surface is rougher and was caused by the corrosion of the carbon steel in the well water environment. Figures 11 (c) and 12(c) display the steel surface after immersion in well water containing Triton X 100 (200 ppm) and Zn^{2+} (50 ppm). The (R_q), (R_a), (P-V) height values for the carbon steel surface are 81.62 nm, 61.79 nm, and 393.71 nm respectively. The (R_q), (R_a), (P-V) height values are considerably less in the inhibited environment compared to the uninhibited environment. These parameters prove that there is a formation of a protective film consisting of self-assembling mono layers of Triton X 100 and the surface is smoother. The smoothness of the surface is due to the development of self-assembling mono layer of Fe^{2+} -Triton X 100 complex and $\text{Zn}(\text{OH})_2$ on the metal surface, thereby inhibiting the corrosion of carbon steel.

Figure 11 Two dimensional AFM images of the surface of
(a) Polished carbon steel (control)
(b) Carbon steel immersed in well water (blank)

(c) Carbon steel immersed in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+}

Figure 12 Three dimensional AFM images of the surface of
(a) Polished carbon steel (control)
(b) Carbon steel immersed in well water (blank)

(c) Carbon steel immersed in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+}

Table 10 AFM data for carbon steel surface immersed in inhibited and uninhibited environment for Triton X 100- Zn^{2+} system

Sample	RMS Roughness (R_q) (nm)	Average Roughness (R_a) (nm)	Maximum Peak-to-valley height (nm)
Polished carbon steel	20.75	16.49	107.26
Carbon steel immersed in well water (blank)	118.65	85.37	631.13
Carbon steel immersed in well water containing 200 ppm of Triton X 100 and 50 ppm of Zn^{2+}	81.62	61.79	393.71

Mechanism of corrosion inhibition

The following corrosion inhibition mechanism was derived from the above results.

- When the solution containing well water, 50 ppm Zn^{2+} and 200 ppm of Triton X 100 is prepared, there is formulation of Zn^{2+} -Triton X 100 complex in solution.
- When carbon steel is immersed in this solution, the Zn^{2+} -Triton X 100 complex diffuses from the bulk of the solution towards metal surface.
- Zn^{2+} -Triton X 100 complex diffuses from the bulk solution to the surface of the metal and is converted into a Fe^{2+} -Triton X 100 complex, which is more stable than Zn^{2+} -Triton X 100.

- On the metal surface Zn^{2+} -Triton X 100 complex is converted into Fe^{2+} -Triton X 100 on the anodic sites, Zn^{2+} is released.
 Zn^{2+} -Triton X 100 + Fe^{2+} → Fe^{2+} -Triton X 100 + Zn^{2+}
- The released Zn^{2+} combines with OH^- to form $\text{Zn}(\text{OH})_2$ on the cathodic sites.
 $\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn}(\text{OH})_2 \downarrow$
- Thus the protective film consists of Fe^{2+} -Triton X 100 complex and $\text{Zn}(\text{OH})_2 \downarrow$
- The EDX analysis SEM micrographs and AFM images confirm the formation of protective layer on the metal surface.

CONCLUSION

The results of this study showed that Triton X 100 surfactant have greater corrosion inhibition efficiency on carbon steel surface which is used in the manufacturing of surgical instruments. The protective film formed on the carbon steel surface is very stable even in the presence of 3.5% NaCl solution which is confirmed by cyclic voltammetry studies.

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