Effect of Chlorhexidine on Corrosion of Mild Steel in 1M Sulfuric Acid Solution

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Abstract: Corrosion inhibition effect of Chlorhexidine in 1M sulfuric acid with concentration range from 10 -500 ppm have been investigated on mild steel substrate by weight Loss, Open Circuit Potential and Potentiodynamic Polarization techniques. Shifting of Open Circuit Potential curves towards the positive direction with increasing the inhibitor concentrations, indicates the adsorption of inhibitor molecules on the surface of mild steel, consequently this lead to the corrosion mitigation. Chlorhexidine shows its best inhibition performance with 500 ppm solution. The result obtained by Potentiodynamic Polarization method is in good agreement with the weight Loss method. From the polarization parameters it is revealed that inhibitor is of mixed type of inhibitor. The surface analysis has been done by Scanning Electron Microscopy. This inhibitor obeys the Langmuir's adsorption isotherm phenomenon.

Keywords: Corrosion, Inhibitor, Mild Steel, Adsorption, Sulfuric Acid.

Introduction

The process of corrosion cannot be completely prevented but can be minimize the rate of corrosion and this is the ultimate goal of the corrosion study [1]. The Phenomenon of corrosion mainly of iron and its alloys remains a measure concern in various kind of industries around the world. Iron has wide commercial applications such as in cooling water, oil and gas industries, refineries, containers, in building and bridges construction etc. Despite of much more advancement in this field, there are serious consequences due to the corrosion mainly the economics loss [2]. Sulfuric acid is used for cleaning, descaling, acid pickling of mild steel. It is also used in petrochemical refineries and oil wells, etc. In spite of highly efficient and durable inhibition capacity of inhibitors that can protect iron and low carbon steel materials in aggressive environments such as sulfuric acid is yet to be well realize [3].
There are several techniques to control the corrosion of metal like coating on metal surface, physical vapors deposition, chemical vapors deposition, plasma spraying, sol-gel process, electrochemical deposition and use of inhibitors in a small quantity etc. [4,5]. Since corrosion is an electrochemical process, the rate of corrosion can be controlled to a great extent by selection of a proper corrosion inhibitors. [6]

The corrosion inhibitors in acid media, especially for the material like Mild Steel (MS) have widely used in oil and gas industries. Mostly the organic inhibitors are employed as acid inhibitors [7-9]. Organic inhibitors adsorb on the metal surface in acidic medium and thus are responsible for corrosion mitigation of a metal [10-16]. Adsorption depends mainly on the charge and nature of the metal surface, electronic characteristic of inhibitor molecules, adsorption of solvent and other ionic species, temperature of corrosion reaction and electrochemical potential at the solution-interface. The important aspect of inhibition normally considered by the corrosion scientists is a relation between the molecular structure and corrosion inhibition efficiency. Such aspects were studied by many authors [17-21]. Adsorption of inhibitor on the metal surface involves two types of interactions- One is Physiosorption which is weak, unidirectional electrostatic force of attraction between inhibiting organic ions or dipoles and the electrical charged surface of a metal. Another is the Chemisorption; which occurs when directed forces governs the interaction between the adsorbate and adsorbent. The chemisorption may takes place in presence of organic compounds containing heteroatoms like- N, O, S or P possesses loan pair of electrons [22, 23] which are donated to the vacant d-orbitals of iron to form coordinate bond on a metal surface. The chemisorption may also take placed by interaction between delocalized π-electrons of aromatic rings and vacant d-orbitals in iron.

The aim of present investigation is to explain the possible mechanism of inhibition and better inhibition performance of the Chlorhexidine molecules on the mild steel surface in 1M sulfuric acid medium by applying conventional weight loss method and modern Potentiodynamic polarization technique. The surface analysis has been performed by the Scanning Electron Miscroscopy (SEM) technique.

Material

Specimen Preparation: Chemical composition of Mild steel is as in Table 1.

Sample	Elements	Si	Mn	S	P	C	Fe
Mild Steel	Content Wt %	0.47	0.08	0.04	0.041	0.16	Balance

Table 1: Chemical composition of Mild steel

The MS-specimens used for Weight loss technique, Electrochemical technique (Open Circuit potential & Potentiodynamic polarization) and for SEM-technique is purchased from MS Flange Manufacturer, Mazgaon, Mumbai. The content of MS is already tested as per above mentioned configuratin, in Table 1. The MS-specimens for weight loss technique study was mechanically cut into the dye of size 3cm x 1cm x 0.01 cm dimensions, then polished with a series of Si-C grit papers of grade 400, 500, 600, 800, 1000, 1200, 1600 and 2000 so as to obtain a scratchless mirror- finish surface. Specimens washed with soap, rinsed with bi-distilled water degreased with acetone and finally dried in desiccators for immediate use. For electrochemical measurement by Open Circuit Potential (OCP) and Potentiodynamic Polarization, 1cm^2 surface area of above abraded specimen is exposed as a working electrode and rest of area including faces are coated with enamel lacquer, only by leaving some tip portion of specimen open to holding clamp to attach to the Potentiostat through connecting wire.

Test solution preparation: 1M sulfuric acid solutions were prepared by dilution of 98% sulfuric acid (analytical grade) in bi-distilled water. The concentration range of 10-500 ppm solution of Chlorhexidine in 1M sulfuric acid were prepared and 1M sulfuric acid solution in absence of inhibitor treated as a control solution.

Methods

1) Weight loss method: This is the conventional method which has its own importance to study the corrosion mechanism of metal. Above mentioned abraded MS-specimen weighed and each specimen embedded in a test tube containing 10 cm^3 of test solution of 1M sulfuric acid solution without and with different concentrations of (10-500 ppm) inhibitor solution for 24 h at 28C^0. Then specimen removed from test tubes washed with distilled water and then with acetone. The specimens dried and weighed accurately. Each test solution was performed in triplicate.

2) Electrochemical Method: Electrochemical experiments were performed in a three electrodes Pyrex glass vessel with a mild steel polished coupons as mentioned earlier used as a working electrode. A saturated calomel electrode used as a reference electrode and graphite rod as a counter electrode. Electrochemical Measurement System, DC 105 from Gamry Instruments Inc., (No. 23-25) 734, Louis Drive, Warminster, PA-18974, USA was used for OCP and Potentiodynamic Polarization study. Before the polarization study, three electrodes partially immersed in a cell containing 50 ml. 1M sulfuric acid solutions without and with inhibitor for 2 hours to obtained steady open circuit potentials. Then the same solution without shaking used for polarization experiments. The potential was swept between -500 to 500 mV at the scan rate 5mV/sec. The different electrochemical parameters obtained by the help of inbuilt Tafel calculations in the software are reported in Table-4.

Scanning Electron Microscopic (SEM) Analysis: The surface morphology of the mild steel with and without 500 ppm inhibitor after 24 h immersion in 1M sulfuric acid was studied by SEM. The accelerating potential was 10 KV.

Results and Discussion

Weight loss method: The weight loss data of mild steel in 1M sulfuric acid with and without inhibitor were obtained as in Table 2. It is found that with rise in concentration of inhibitor, Chlorhexidine, the weight loss of mild steel decreases. This indicates the increase in corrosion Inhibition Efficiency (IE). At the highest concentration of 500 ppm inhibitor solution, it has highest inhibition efficiency of about 78 %. This result indicated that Chlorhexidine is a very good corrosion inhibitor in 1M Sulfuric acid media. Percentage Inhibition Efficiency (IE %) of Mild steel with different concentrations of inhibitor calculated by formula-

$$IE\ \% = [W_o - W]/W_o \times 100$$

Where, W and W_o are the weight loss of mild steel in the presence and absence of inhibitor, respectively.

Inhibitor	Conc. (ppm)	Weight Loss (mg)	Surface coverage (θ)	Inhibition Efficiency (IE %)
Blank	-	284	-	-
Chlorhexidine	10	235	0.17	17
	100	184	0.34	34
	200	133	0.53	53
	300	122	0.57	57
	400	79	0.72	72
	500	62	0.78	78

Table 2: Weight loss data for inhibition of corrosion of mild steel exposed to sulfuric acid with different concentration of Chlorhexidine.

Concentration. (C)	logC	θ	(1-θ)	θ/(1-θ)	log θ/(1-θ)
0.000010	-5.0000	0.17	0.83	0.2048	-0.6886
0.000100	-4.0000	0.34	0.66	0.5151	-0.2881
0.000200	-3.6989	0.53	0.47	0.1276	-0.8941
0.000300	-3.5228	0.57	0.43	1.3255	0.1223
0.000400	-3.3979	0.72	0.28	2.5714	0.4101
0.000500	-3.3010	0.78	0.22	3.5454	0.5496

Table 3: Adsorption parameters Chlorhexidine

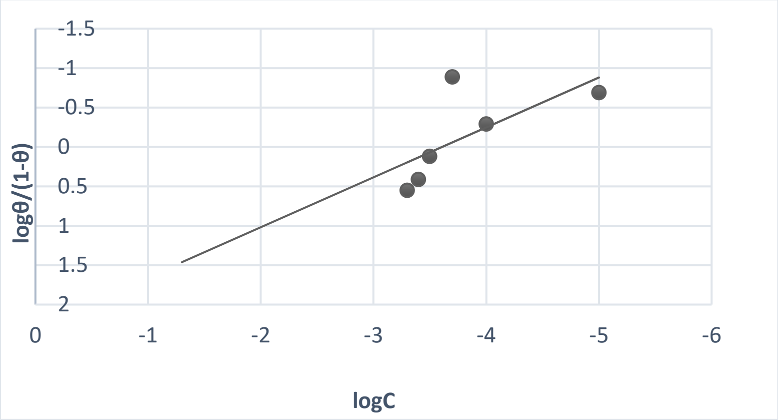


Fig. 1: Adsorption isotherm of Chlorhexidine

Electrochemical method

Opencircuit potential: The potential of mild steel in absence and in presence of inhibitor with different concentrations in 1M sulfuric acid is depicted in Fig.2. It is revealed that all the potential curves obtained achieved steady states after nearly 30 min. It is shown that the potential is continuously increases as per the concentration of inhibitor. Thus, it is concluded that the rate of corrosion reaction decreases as the concentration of inhibitor increases. The inhibitor molecules adsorbed on the surface of iron in mild steel and form a protective film which mitigates the corrosion rate. At the 500 ppm of solution Chlorhexidine shows its best inhibition performance. Chlorhexidine solution in different concentrations in 1M sulfuric acid tested for corrosion mitigation in mild steel by using Polarization technique. The various electrochemical kinetic parameters such as Corrosion potential (Ecorr), Corrosion current density (Icorr), Anodic Tafel slope (β_a) and Cathodic Tafel slope (β_c) obtained by inbuilt software Tafel calculations by extrapolating straight lines through Anodic and Cathodic polarization curves respectively as shown in Fig.3 and Table 4.

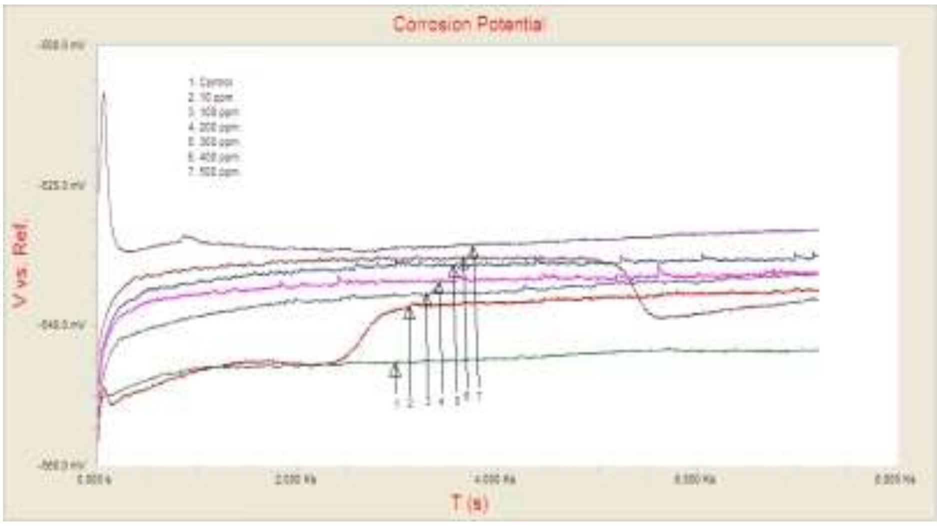


Fig. 2: Opencircuit potential of mild steel with different concentrations of Chlorhexidine in 1M sulfuric acid solution.

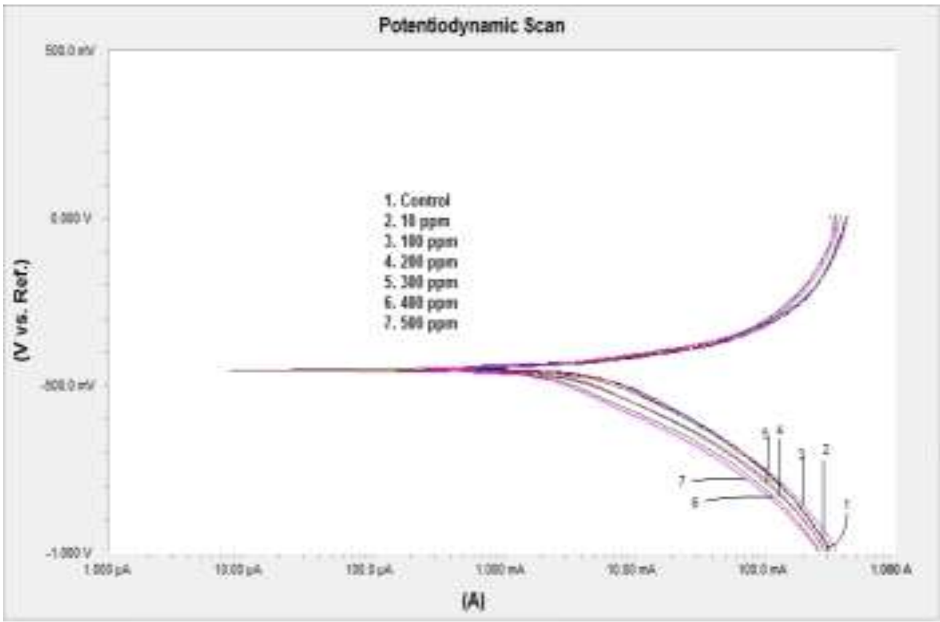


Fig. 3: Potentiodynamic polarization of mild steel with different concentrations of Chlorhexidine in 1M sulfuric acid.

Conc. **(ppm)**	**β_a** **(V/dec.)** **e^{-3}**	**β_c** **(V/dec.)** **e^{-3}**		**I_{corr}** **(μA.cm^2)**	**E_{corr}** **(mV)**	**Corr.Rate** **(mpy)**	**%IE**
Control	145.0	302.6		8980	-446	4.103	-
	Chlorhexidine						
10	108.6	274.2		7460	-449	3.411	16.93
100	106.4	242.4		6050	-450	2.765	32.63
200	96.0	234.9		4250	-452	1.940	52.67
300	77.40	193.9		3160	-453	1.446	58.20
400	77.40	207.2		2600	-454	1.187	71.05
500	63.60	197.3		2060	-453	0.942	77.70

Table 4: Potentiodynamic polarization parameters with different concentrations of Chlorhexidine in 1M sulfuric acid solution.

It is revealed that the corrosion efficiency increases as per the inhibitor concentration. Chlorhexidine shows its best performance at 500 ppm solution. It is also observed that both Anodic and Cathodic current density decreases from 10 to 500 ppm inhibitor solution hence this can be concluded that this is mixed- type of inhibitor, since they affect both the metal ionization and the hydrogen evolution reactions [24]. However, their cathodic action is more pronounced as shown by the higher values of β_c. The decrease in current density represents the decrease in rate of corrosion of the metal. These parameters suggest that the geometrically blocking in the cathodic site of the metal surface is caused by the adsorption of inhibitor molecules. It is observed that addition of inhibitor of various concentrations, the cathodic current density decreases. Generally, the anodic domain the inhibition mode by organic compounds depends upon the electrode potential[25]. It is seemed that corrosion potential values do not sufficiently changed. This result indicates that Chlorhexidine act preferentially as a cathodic inhibitor [26]. Fig. 3 shows that the cathodic curves from 300 to500 ppm inhibitor solution are parallel to each other, which indicate that hydrogen evolution reaction in activation is controlled. The lowest cathodic current density at 300 ppm solution indicate more blocking at the hydrogen evolution site.

Scanning Electron Microscopic Analysis

The SEM analysis of bare polished mild steel, with and without inhibitor in 1M sulfuric acid by immersion period of 24 h was taken. It is seen that mild steel in aggressive solution was very rough with ridges and furrows on the surface as compared to bare one whereas it was least rough with 500 ppm inhibitor solution as shown in fig. 4. This shows a clear picture of corrosion inhibition of mild steel by Chlorhexidine.

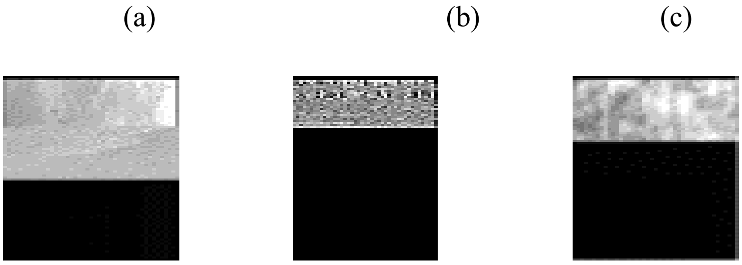
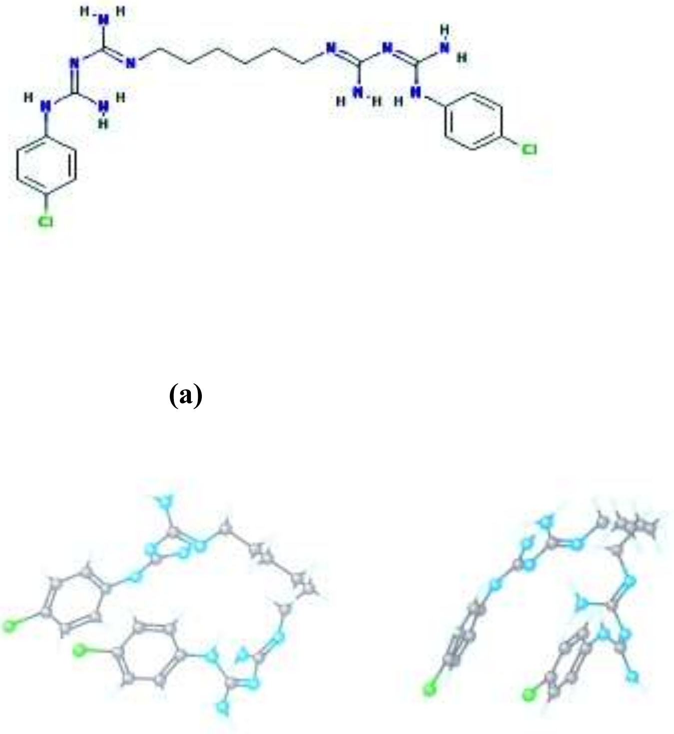


Fig. 4: SEM of Mild Steel: a) Polished and without inhibitor. b) After immersion 1M sulfuric acid without inhibitor. c) After immersion in 1M sulfuric acid with 500 ppm of Chlorhexidine solution.

Mechanism of corrosion inhibition

The first stage of corrosion inhibition mechanism on the inhibitor in the aggressive acid media (1M sulfuric acid solution) is based on its adsorption capability on the metal surface. The process of adsorption of inhibitors are depends on the structure of inhibitor molecule, steric factor, electrolyte and not only on the nature of the metal, but also on the actual exposed area of the working electrode says Mild Steel. The organic aromatic compounds containing heteroatoms like N, S and O are very good corrosion inhibitors[27]. The Chlorhexidine as an inhibitor containing several N-atoms in its molecular structure (Fig. 5) are easily protonated in acid solution [28]. The mild steel surfaces alredy become negatively charged due to the adsorption of sulphate ions from the sulfuric acid solution by displacing water molecules on the surface. This influenced the physiosorption of positively charged protonated chlorhexidine molecules on the negatively charged metal surface by the electrostatic force of attraction and forming a barrier compact film of Chlorhrexidine on the metal MS-surface. When the metal surface attained zero charge with respect to the potential of zero charge, the chemisorption takes placed through the planar π-orbitals of the inhibitor molecule with vacant d-orbitals of iron [29]. The structure Chlorhrexidine moleculeis as shown in Fig. 3, which has NH_2 groups, favors formation of coordination bonds through its filled p-orbitals with the vacant d-orbitals of iron of MS. The alkyl group shift their electron density towards the iminic nitrogen by mesomeric effect also allows an efficient interaction towards metal surface. This effect is also pronounced in chlorine towards the benzene consequently; the filled p-orbitals of nitrogen and π-delocalized electrons in the benzene with vacant d-orbitals of iron are responsible for the chemisorption.

Thus the compact and uniform layer of inhibitor molecules formed on the surface of mild steel by both, physiosorption and chemisorption are responsible for the corrosion mitigation of mild steel in 1M sulfuric acid. The inhibition effect increases as per the concentration of inhibitor and thus 500 ppm solution of inhibitor,Chlorhrexidine exhibits its best performance.



(a)

(b) (c)

Fig. 5: a) Structural diagram of chlorhexidine molecule. b) side view c) front view geometry of Chlorhexidine molecule.

Conclusion

The corrosion mitigation of mild steel with different concentrations of chlorhexidine in 1M sulfuric acid solution studied by Weight loss, OCP and Potentiodynamic polarization techniques, the result obtained by those techniques is in good agreement among them. It revealed that the inhibition efficiency increases as per the concentration of inhibitor. Thus the 500 ppm solution of inhibitor shows its best performance of about 78 % inhibition. The SEM of mild steel with 500 ppm solution of Chlorhexidine is smooth as compared to the absence of inhibitor and thus obey Langmuir's adsorption isotherm which obtained a straight line. The Chlorhexidine is of a mixed type of inhibitor, but predominantly cathodic, since the cathodic polarization is more. The cathodic curves at the concentrations from 200-500 ppm are parallel, it seems that the adsorption of inhibitor molecules at the cathodic sights shows without change in hydrogen evolution mechanism. The physiosorption and chemisorption of inhibitor molecules gives the formation of uniform thin film of inhibitor, Chlorhexidine on the mild steel surface which mitigate the rate of corrosion and gives good protection to the Mild steel surface.

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