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Corrosion Inhibition of Mild Steel by Benzotriazole in 1M and 2M Sulfuric Acid Solution

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ABSTRACT: Mild steel is widely used in many industries under different environmental condition due to its low cost, good tensile strength and easy availability. The mild steel material will be corroded in acid media especially in concentrated mineral acid is often a very worrying problem for some industrial facilities. A variety of inorganic compounds like chromates, molybdates and phosphates and organic compounds like nitrogen, sulphur and oxygen are being used as corrosion inhibitors for mild steel. Corrosion inhibitor of steel is studied with some of the organic compounds. These compounds can be adsorbed onto the surface of metals, block the surface-active areas and thus reduce corrosion. The inhibitor leads a formation of a film by oxide protection of the base metal. In this work, the behavior of Benzotriazole solution as corrosion inhibitor for mild steel at different concentration is investigated in sulphuric acid medium at 48 and 72 hours time interval by weight loss method. This inhibitor is also tested with other corrosion measurement techniques like potentiodynamic polarization, electrochemical impedance spectroscopy. From these studies we observe that the Benzotriazole can be used as a good inhibitor for preventing mild steel material.

Keywords: Corrosion, Electrochemistry, Weight loss, Mild Steel, Benzotriazole

I. INTRODUCTION

Corrosion can be defined as the deterioration of a material due to a reaction with its environment. It is the gradual degradation of materials by chemical or electrochemical reaction with the environment. Corrosion is a process, which converts a refined metal to a more chemically-stable form, such as its oxide, hydroxide, or sulfide. Corrosion is an electrochemical Process includes oxidation (anodic reaction) and reduction (cathodic reaction) [1]. Various Factors affecting the corrosion rates are:effects of Corrosion Concentration, effect of Temperature, effect of oxygen, and some metallurgical aspects.Inhibitors form films in several ways like the inhibitor is chemically adsorbed (chemisorption) on the surface of the metal and forms a protective thin film with inhibitor effect or by combination between inhibitor ions and metallic surface [2,3]; some inhibitors retard corrosion by adsorption to form a thin, invisible film only a few molecules thick. Others form bulky precipitates that coat the metal and protect it from attack.The inhibitor causes the metal to corrode in such a way that a combination of adsorption and corrosion product forms a passive layer [4]. The inhibitor reacts with a potential corrosive component present in aqueous media and the product is a complex.The effectiveness of a corrosion inhibitor depends on fluid composition, quantity of water, and flow regime.Benzotriazole (BTA) serves as a corrosion inhibitor in the atmosphere and underwater [5].

Benzotriazole is fairly water-soluble, not readily degradable and has a limited sorption tendency. Benzotriazole is a heterocyclic compound containing three nitrogen atoms, with the chemical formula $C_6H_5N_3$. Benzotriazole and its derivatives are good corrosion inhibitors for many metals and alloys in various aggressive corrosive media. Benzotriazole is an effective corrosion inhibitor for mild steel and its alloys by preventing un-desirable surface reactions. It has been used satisfactorily as a specific corrosion inhibitor for mild steel in acidic solution. Three azoles viz. benzotriazole (BTA), benzimidazole (BIA) and imidazole (IA) were also investigated as corrosion inhibitors for mild steel in alkaline mine water. Interest for BTA in the corrosion inhibition of ferrous metals increased with the finding of synergistic effects in mixtures with other substances. These effects have been demonstrated for the corrosion inhibition of mild steel in mixtures of BTA with molybdate and sodium sebacat. Similar conclusions have been reported for cast iron using benzoate or amines plus BTA. In order to inhibit mild steel from corrosion in H_2SO_4 solution, 1,2,3-benzotriazole (BTA) has been investigated as corrosion inhibitor. 1,2,3, benzotriazole (BTA) is sparingly soluble triazole which forms turbidity in water [6]. According to Subramanyam and Mayanna it form two resonating structures in aqueous solution and shows that azoles as corrosion inhibitors for mild steel in alkaline mine waters and reported that the adsorbed inhibitors or their complexes reinforce the protection of mild steel afforded by iron oxide layer.

Louadi investigated the inhibition mechanism of BF4 for the corrosion of mild steel in 1.0 M HCl using weight loss method and electrochemical measurements [7]. Performance of water soluble chitin (WSC) and its synergistic inhibition were studied with potassium iodide (KI) in 1 M HCl [8]. Amini studied the corrosion inhibition of benzotriazole in 0.5 M sulfuric acid solution on the mild steel specimens with two amounts of surface roughness. [9].

The corrosion behavior of Mild Steel in 1 M and 2M H_2SO_4 solution in the absence and presence of BTA with concentration of 0.2 mM, 0.8 mM, 1 mM is investigated by Weight loss measurement and potentiodynamic polarization measurement [10]. In this study, we evaluate the performance of the Benzotriazole as a corrosion inhibitor on mild steel in sulfuric acid medium. Inhibition characteristics like corrosion current, polarization resistance, corrosion rate and inhibition efficiency are determined. The effect of inhibitor and sulfuric acid concentration on corrosion rate of mild steel were evaluated [11]. The rest of the paper is organised as follows: section 2 presents various techniques and methods used during the study in the laboratory and the material used for experimental purpose. It also covers general experimental procedure. Section 3 shows results of various corrosion measurement experiments that were carried out. Corrosion rate calculations are done in this part and results are compared with different corrosion measurement methods. Section 4 summarises our contribution on the basis of obtained results and its analysis.

II. MATERIAL AND METHODS

For corrosion studies, we followed different steps like sample preparation and cleaning, solution preparation, and different measurement methods. Following sections describes these steps.

A. Specimen Preparation

Preparation of test specimens for corrosion inhibition studies and its characterization needs special attention depending on the instrument used for the studies. In electrochemical measurements, care should be taken.The specimens were first mounted in cold resin to expose only a constant area throughout the experiments followed by specimen surface preparation.For electrochemical experiments, specimen preparation was performed according to ASTM G1 standard [12]. All the specimens were abraded by the sandpapers with 50, 100, 400, 600, 1000 and 1200 grit size followed by ultrasonic cleaning in trichloroethylene ($CHCl{=}CCl_2$). Specimens of mild steel with dimensions of $0.3\times2\times1$ cm^3 were used for weight loss measurement experiments.

B. Preparation of Corrosion Media

In our experiments1M and 2M H_2SO_4 solution prepared on a determinate basis [13]. To prepare a 1M solution, 53.26 ml of concentrated sulfuric acid (98% w/w) taken in a graduated measuring cylinder was slowly added to 500 ml of water in a 1 L beaker. Rinse the cylinder into the beaker with water. Mix the acid-water mixture, allow it to cool, and transfer to a 1-L volumetric flask. Dilute to the mark with water, mix well, and store in a tightly closed glass container.To prepare a 2M solution, the same process isrepeated with a measure 106.52 ml of concentrated sulfuric acid.

C. Preparation of Corrosion Inhibitor

0.2, 0.8 and 1mM benzotriazole were prepared by dissolving 0.2 g, 0.8 g and 1.0 g of the substance in 100 ml of 1M and 2M sulfuric acid.

D. Weight Loss Measurements

The experiments were carried out using mild steelspecimens. The steel coupons of size 2.0 cm×1.0 cm×0.3 cm were polished, dried and weighted and then suspended in a 100-cm^3 aerated solution of 1M and 2M H_2SO_4without and with different concentrationsof Benzotriazole for an exposure period of 48 and 72 hours. After the designated exposure period to the test solution, the specimens were rinsed with distilled water, washed with acetone to remove a film possibly formed due to the inhibitor, dried between two tissue papers, and weighted again [14]. Weight loss measurements were made in triplicate. Corrosion rate and inhibition efficiency is to be calculated as follows:

$$CR\ (mmy) = 87.6 * W/DAT$$

Where W, D, A and T are weight loss (in mg), density of mild steel (7.86 g/cc), area of the specimen in cm square and exposure time in hours respectively.

$$IE\ \% = [(Wo - Wi)/Wo]\ x\ 100$$

Where W_O and W_i are the values of the weight loss (in g) of mild steel in the absence and presence of inhibitor respectively.

E. Corrosion Studies by Tafel Plot

In our experiments, we have used Potentiostat/Galvanostat (Model Autolab 302) with maximum output current of ± 2 amperes and potential range of ±10 volts with frequency response analyzer. Tafel plot is used to measure the corrosion current i_{corr}. The slope of the straight line fit to the Tafel data is called a Tafel constant (β). Anodic Tafel constant β_A is determined from a fit of the anodic linear region and a cathodic Tafel constant β_C from a fit of the cathodic linear region [15]. A Tafel plot can produce corrosion current directly or it can be used to calculate the Tafel constants, β_A and β_C. The Tafel constants can then be used with the R_P value to calculate corrosion current. A single Tafel plot consist of both the anodic and cathodic Tafel regions, the two straight lines should intersect at E_{corr}. Once i_{corr} has been determined, below equation can be used to calculate the corrosion rate [16].

$$Corrosion\ Rate = 0.13\ Icorr\ (E.W.)/d$$

Where E.W. is equivalent weight of the corroding species in gram, d is density of the corroding species in g/cc and $I_{corr}$is the Corrosion current density in µA/cm^2

$$Efficiency = \frac{i^o_{corr} - i_{corr}}{i^o_{corr}}$$

where i^o_{corr} and i_{corr} are the corrosion current density values without and with the corrosion inhibitor, respectively.

III. RESULT AND DISCUSSION

A. Weight Loss Measurement Studies

Effect of Time. The weight loss of the mild steel specimens in 1 M H_2SO_4 without and in the presence of various concentrations of BTA is determined after 48 and 72 hours of immersion at room temperature. Corrosion rate and inhibition efficiency calculated from weight loss data are shown in table 1.

Table 1: Corrosion behaviour of Mild Steel in 1M and 2M H_2SO_4 solution with varying concentration of Benzotriazole by Weight Loss Measurement.

Time in hours	Inhibitor Conc. (mM)	Corrosion Rate (mm/y)		Inhibition Efficiency (%)	
		1M H_2SO_4	2M H_2SO_4	1M H_2SO_4	2M H_2SO_4
48	Blank	8.787	11.181	--	--
	0.2	2.521	3.9881	71.30	64.33
	0.8	2.453	2.9970	72.07	73.19
	1	1.682	2.4056	80.85	78.48
72	Blank	9.886	10.517	--	--
	0.2	1.750	2.8745	82.29	72.66
	0.8	1.702	2.1339	82.78	79.71
	1	1.542	2.0406	84.39	80.59

Corrosion rate of mild steel decreases with increase in inhibitor concentration reaching a lowest corrosion rate of 1.54 mm/year whereas the corresponding inhibition efficiency reaches a maximum value 84.3% at 1mM of BTA concentration in 1M sulfuric acid. The variation of corrosion rate with concentration of inhibitor for 1M and 2M sulfuric acid for 48 hours of immersion time is shown in Fig. 1.

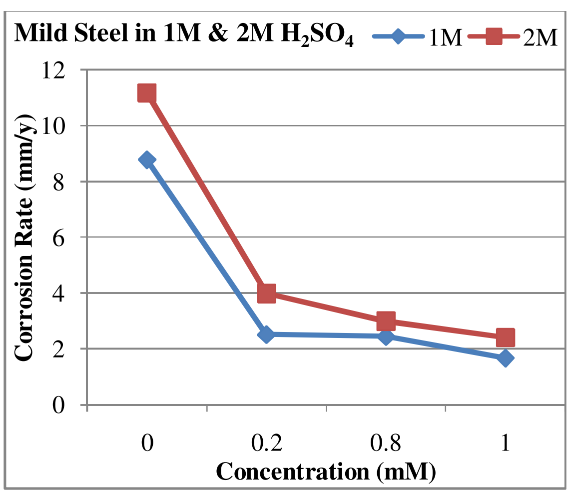


Fig. 1. Corrosion rate of Mild Steel in 1M and 2M H_2SO_4 solution with increasing concentration of Benzotriazole by Weight loss method.

For a particular inhibitor concentration, it is observed that the corrosion rate decreases with increase in immersion hours which may be due to decrease in sulfuric acid concentration or a formation of compact protection layer on the surface of the specimen with time. At 1mM inhibitor concentration, large variations are not observed in the corrosion rate between 48 and 72 hours. Experiments are repeated with same weight percent of inhibitor concentration tested earlier for 2M sulphuric acid and the results are shown in table 1. The lowest corrosion rate observed is 2.04 mm/year at an inhibitor concentration of 1mM for 72 hours immersion. It is very clear that the variation in corrosion rate gradually reaches a minimum value for 1 mM inhibitor concentration for different immersion hours. For our electrochemical experiments, only these two concentrations of sulfuric acid as corrosion medium with Benzotriazole inhibitor limited to a maximum concentration of 1 mM are studied.

Effect of Temperature. The thermodynamic studies of the corrosion of mild steel in 1M H_2SO_4 medium using Benzotriazole is carried out using weight loss techniques. For this purpose the specimen were immersed for 2 hour in 1M H_2SO_4 solution at 30°, 40° and 50° to assess the effect of temperature [17]. The experiments are performed with inhibitor concentration of 0.2, 0.5 and 1mM. From the table 2 it is observed that the corrosion rate of the mild steel increases with the increase in temperature. The inhibition efficiency increased with the increasing concentration but decreased with increase in temperature. The maximum efficiency is found to be 79.93 % at 30°C with 1mM of inhibitor concentration.

Table 2: Corrosion behaviour of Mild Steel in 1M H_2SO_4 solution with varying temperature by Weight Loss Measurement.

	Inhibitor Concentration (mM)	Corrosion Rate (mm/y)	Inhibition Efficiency (%)
30^0C	Blank	28.19928	--
	0.2	6.33045	77.55
	0.5	5.85087	79.25
	1	5.659039	79.93
40^0C	Blank	30.50126	--
	0.2	7.96102	73.89
	0.5	7.001861	77.04
	1	6.714114	77.98
50^0C	Blank	34.24198	--
	0.2	18.12811	47.05
	0.5	17.07303	50.14
	1	17.0208	52.66

It is clear that the corrosion rate is increased from the temperature range of 30°C to 50° C and decreased with the increasing concentration from 0.2 to 1 mM.

B. Potentiodynamic Polarization

Polarization curves of mild steel in 1M and 2M H_2SO_4 in the absence and in the presence of different concentrations of BTA is given in figure 2 to figure 4. Table 3 provides the results of mild steel in 1 M and 2M H_2SO_4.

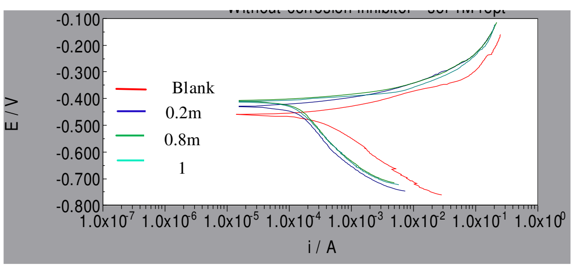


Fig. 2. Tafel Plot for Mild Steel with Blank, 0.2, 0.8 and 1 mM of Inhibitor in 1M H_2SO_4 Solution.

From the table it is clear that the values of the corrosion current I_{corr} and corrosion rate decreases with the increasing concentration while the efficiency increases. In 1M H_2SO_4 solution the corrosion rate in 1 mM inhibitor concentration, decreases up to 0.58 mm/y as compared to the 3.343 mm/y of the inhibitor free solution. The inhibition efficiency of BTA for the corrosion of mild steel is calculated by using corrosion current and found increasing up to 82.2% with the increasing concentration.

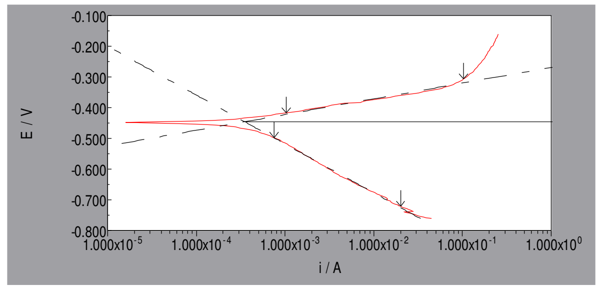


Fig. 3. Tafel Plot for Mild Steel without inhibitor in 2M H_2SO_4 Solution.

As compared to 2M solution, 1M solution shows better efficiency and corrosion rate. However, BTA influences the anodic reactions with increasing potential. This result indicates that BTA exhibits both cathodic and anodic inhibition effects. This suggests a mixed-type control. Thus BTA mainly acts as a mixed-type inhibitor in 1M and 2M H_2SO_4.

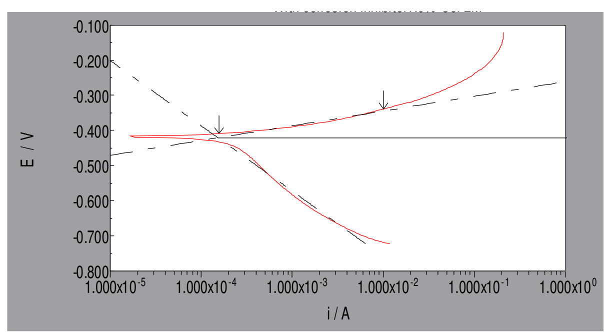


Fig. 4. Tafel Plot for Mild Steel with 1 mM of Inhibitor in 2M H_2SO_4 Solution.

Table 3: Corrosion behaviour of Mild Steel in 1M H_2SO_4 and 2M H_2SO_4 solution with different concentration of Benzotriazole as an Inhibitor by Potentiodynamic polarization.

	Inhibitor Concentration (mM)	Icorr (μA/cm)	βc (V/dec)	βa (V/dec)	- Ecorr (mV)	Corrosion Rate (mm/y)	Inhibition Efficiency (%)
1 M H_2SO_4	Blank	284	0.159	0.06	466	3.343	--
	0.2	122	0.188	0.036	438	1.429	57.04
	0.8	96	0.21	0.031	412	1.12	66.19
	1	50.4	0.212	0.015	391	0.5854	82.25
2 M H_2SO_4	Blank	336	0.159	0.51	445	3.65	--
	0.2	172	0.192	0.042	450	2.027	48.80
	0.8	155	0.245	0.024	393	1.82	53.86
	1	95.1	0.255	0.023	408	1.1	71.69

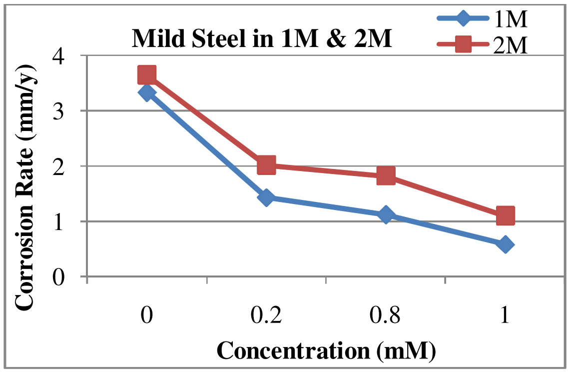
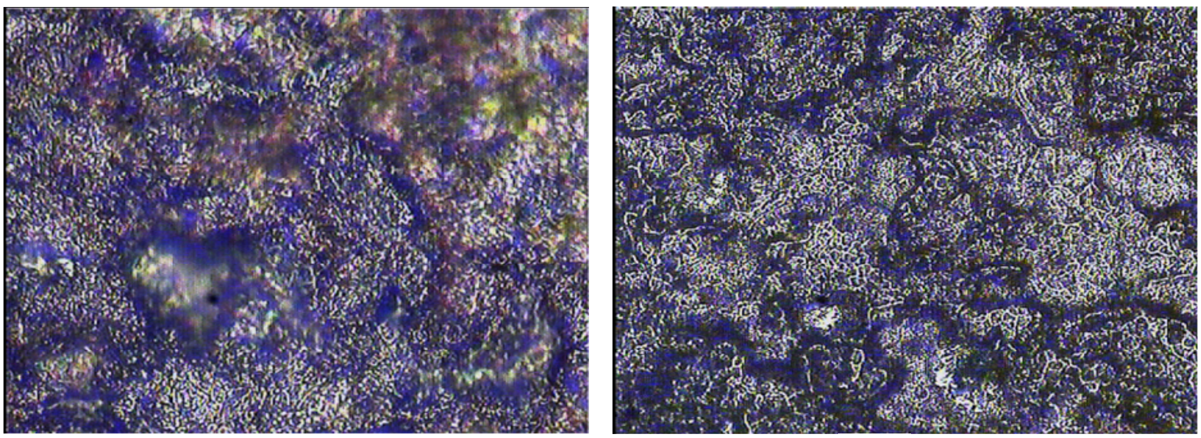


Fig. 5. Corrosion rate of Mild Steel in 1M and 2M H_2SO_4 solution with increasing concentration of Benzotriazole by Potentiodynamic polarization.

C. Surface Analysis

For monitoring the surface morphological changes, optical Microscopes are used. For this purpose, finely polished mild steel plates are immersed in H_2SO_4 solution in the presence and absence of BTA inhibitor. Then the specimens were cleaned and dried in air and used for the analysis [18]. We used metallurgical microscope for the surface analysis.The image shows that the inhibition is due to the formation of a film on the metal surface via adsorption process. Photograph presented in figure 6 is without inhibitor and figure 6 is with inhibitor.



(a) (b)

Fig. 6. Metallurgical microscope imageof Mild steel surface after immersion (a) in 2M H_2SO_4 without inhibitor (b) in 2M H_2SO_4 with 0.8 mM inhibitor.

IV. CONCLUSION AND FUTURE SCOPE

In this work we evaluated the performance of Benzotriazole as a corrosion inhibitor to control the rate of corrosion. This compound has been investigated as corrosion inhibitor to prevent mild steel from corrosion in Sulphuric acid medium at different concentration. Behavior of the samples is analyzed by weight loss method, potentiodynamic polarization. For mild steel potentiodynamic polarization shows a consistent decrease in the corrosion rate up to 0.58 mm/y with the increasing concentration in 1M solution. Similarly the results obtained by the different experimental methods showed good agreement with each other. Benzotriazole was found to be an effective inhibitor for mild steel in the acidic medium giving inhibition efficiency up to 84.3% in 1M H_2SO_4 by weight loss method.

The following results can be drawn from this study:

- The corrosion rate of Mild steel was found to decrease with the increasing concentration of BTA.
- The inhibition efficiency of BTA on Mild steel increases with increasing concentration of BTA and immersion time whereas decreased with increase in temperature.
- The corrosion inhibition behavior of Benzotriazole is greater in 1M H_2SO_4 when compared to 2M H_2SO_4 solution. More studies have to be carried out to identify the reasons.
- Triazole derivatives can be used as corrosion inhibitors for mild steel in H_2SO_4.

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