



## The corrosion inhibition of mild steel in acidic media by benzotriazole compound

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### ABSTRACT

Benzotriazole has been prepared as a corrosion inhibitor to control the rate of corrosion. This compound has been investigated as corrosion inhibitor at room temperature for preventing mild steel corrosion in Sulphuric acid medium at different concentration at two hour time interval by weight loss method. The result showed that the corrosion inhibition efficiency of these compounds was found to vary with Sulphuric acid concentration. Also, it was found that the corrosion inhibition behavior of Benzotriazole is greater in 1M H<sub>2</sub>SO<sub>4</sub> when compared to 2M H<sub>2</sub>SO<sub>4</sub> at two hour time interval. So Benzotriazole can be used as a good inhibitor for preventing mild steel material for many construction purpose.

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### Introduction

Mild steel find its application in many industries due to its easy availability, ease of fabrication, low cost and good tensile strength, besides various other desirable properties [1-6]. Inorganic compounds like chromates, phosphates, molybdates etc., and a variety of organic compounds containing heteroatom like nitrogen, sulphur and oxygen are being used as corrosion inhibitors for mild steel [7-10]. 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. Several researchers devoted their attention to develop more effective and non-toxic inhibitors to reduce both acid attack and protection aspects [11-13].

The use of organic compounds based corrosion inhibitors against metal dissolution is often associated with chemical and / or physical adsorption, involving a variation in the charge of adsorbed substance and a transfer of charge from one phase to other. Special attention was paid to the effect of electron donating on the atom, electron withdrawing atom or groups responsible for adsorption mainly depends on steric factors, aromaticity, the structural properties of the organic compounds studied such as the presence of  $\pi$ - electrons and heteroatoms, which induce greater adsorption of the inhibitor molecules onto the surface of mild steel [14-16]. Therefore, the aim of this paper is to investigate, the organic compound benzotriazole is used as corrosion inhibitor to prevent mild steel on 1M H<sub>2</sub>SO<sub>4</sub> and 2M H<sub>2</sub>SO<sub>4</sub> solution in the absence and presence of the inhibitor at two hour at ( $\pm 30^\circ$  C) temperature.

### Experimental

#### Sample Preparation

According to ASTM method as reported already [17], cold rolled mild steel strips were cut into pieces of 5 cm  $\times$  1 cm

having the following composition (in percentage) % C-0.017, Si-0.007, Mn-0.196, S-0.014, P-0.009, Ni-0.013, Mo-0.015, Cr-0.043 and Fe- 99.686 was used. The samples were polished, drilled a hole at one end and numbered by punching. During the study the samples were polished with various grades of SiC abrasive papers (from grits 120 to 1200) and degreased using Acetone.

#### Solutions:

All the solutions were prepared using NICE brand AR grade chemicals in double distilled water and bubbling purified by nitrogen gas for 30 minutes to carry out de-aeration of the electrolytes. 1M H<sub>2</sub>SO<sub>4</sub> and 2M H<sub>2</sub>SO<sub>4</sub> solution was prepared by double distilled water. The corrosion inhibitor solution of Benzotriazole was prepared by dissolving 1% Benzotriazole solution have been prepared as a test solution. From this various milli molar concentration of inhibitor solutions has been prepared.

#### Corrosion Studies

##### Weight loss measurement:

The weight of specimen were noted and then immersed in test solution containing various concentrations of inhibitors at room temperature. After the duration of two hour in 1M H<sub>2</sub>SO<sub>4</sub> and 2M H<sub>2</sub>SO<sub>4</sub>, the specimens were removed from test solutions, dried and finally weighed.

##### Scanning Electron Microscope (SEM analysis):

The mild steel specimens were immersed in the blank (1M H<sub>2</sub>SO<sub>4</sub> and 2M H<sub>2</sub>SO<sub>4</sub>) containing the inhibitor Benzotriazole for 2 h after which they were taken out, washed with distilled water and then the specimens was observed under Scanning Electron Microscope (SEM- HITACHI S3000H, Japan).

##### FT-IR Studies:

The corrosion products formed on the steel surface during

polarization was removed by scrapping and was used for recording FT-IR spectra. This study reveals the possibility of the adsorption of the inhibitor on the metal surface.

The Fourier transform infrared (FT-IR) spectra of the scraped films were recorded using a (Perkin Elmer-1400) FT-IR spectrophotometer.

**Result and Discussion**

**Weight loss method**

The corrosion behaviour of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> and 2M H<sub>2</sub>SO<sub>4</sub> with Benzotriazole was given in Figure 1, which was studied by weight loss method at two hour at (± 30° C) temperatures. From the graph, it was observed that the weight loss of mild steel in the acid decreases with increasing concentration of additives.

Which suggesting that the additives are corrosion inhibitor for mild steel in 1M H<sub>2</sub>SO<sub>4</sub> and 2M H<sub>2</sub>SO<sub>4</sub>. From the data of weight loss method, the corrosion rate (CR) was calculated using the equation:

$$CR = (87.6 \times W) / (D \times A \times T) \text{ ----- (1)}$$

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

Similarly, Inhibition efficiency was calculated using the equation,

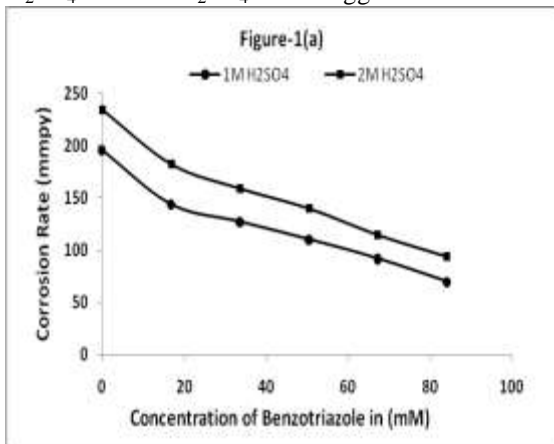
$$IE \% = [(W_o - W_i) / W_o] \times 100 \text{ ----- (2)}$$

Where W<sub>o</sub> and W<sub>i</sub> are the values of the weight loss (in g) of mild steel in the absence and presence of inhibitor respectively. The values of corrosion rate and inhibition efficiency in absence and presence of difference concentration of inhibitor used in 1M H<sub>2</sub>SO<sub>4</sub> and 2M H<sub>2</sub>SO<sub>4</sub> solution at (± 30° C) temperature for two hour were given in Table 1.

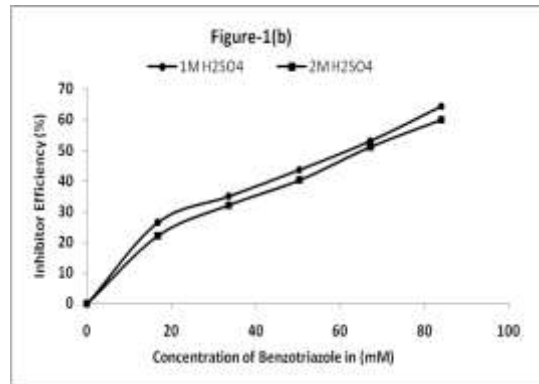
From Table 1, it was clear that the corrosion rate was decreased with increasing concentration of inhibitor and inhibition efficiency increased with increasing the concentration of the inhibitor.

In addition, the maximum corrosion inhibition efficiency of Benzotriazole was 64.29 % at 1M H<sub>2</sub>SO<sub>4</sub> and 59.91 % at 2M H<sub>2</sub>SO<sub>4</sub> respectively at 84.03 (mM) solution of inhibitor in one hour at room temperature.

And also, it was concluded that the inhibitor was best inhibitor in mild steel corrosion in 1M H<sub>2</sub>SO<sub>4</sub> and 2M H<sub>2</sub>SO<sub>4</sub>. But when comparing with acids the inhibitor efficiency was best in 1M H<sub>2</sub>SO<sub>4</sub> than 2M H<sub>2</sub>SO<sub>4</sub> due to aggressiveness of an acid.



**Figure 1: (a) Comparison of corrosion rate (CR) with concentration of Benzotriazole (in mM) in 1M H<sub>2</sub>SO<sub>4</sub> and 2M H<sub>2</sub>SO<sub>4</sub> solution at two hour at (± 30° C) temperature**



**(b) Comparison of inhibition efficiency (IE) with concentration of Benzotriazole (in mM) in 2N HCl and 2N H<sub>2</sub>SO<sub>4</sub> solution at two hour at (± 30° C) temperature.**

**Adsorption Isotherm:**

Basic information on the interaction between the inhibitor and the mild steel surface can be proved by the adsorption isotherm and in general, inhibitors can function either by physical (electrostatic) adsorption or chemisorption with the metal. To obtain more information about the interaction between the inhibitor molecules and the metal surface, different adsorption isotherms were tested. The fractional surface coverage  $\theta$  at different concentrations of inhibitors 1M H<sub>2</sub>SO<sub>4</sub> and 2M H<sub>2</sub>SO<sub>4</sub> solutions were determined from the weight loss measurements data [18] using the formula,

$$\theta = \frac{W_o - W_i}{W_o} \text{ ----- (3)}$$

where, W<sub>o</sub> and W<sub>i</sub> are the values of corrosion current density of uninhibited and inhibited specimens, respectively.

$$Kc = \frac{\theta}{1 - \theta} \text{ ----- (4)}$$

Where, c is the concentration of the inhibitor,  $\theta$  is the fractional surface coverage. The Langmuir isotherm, Eq. (4), which is based on the assumption that all adsorption sites are equivalent and that molecular binding, occurs independently from the fact whether the nearby sites are occupied or not, was verified for all the studied inhibitors. The adsorption equilibrium constant K is related to the free energy of adsorption  $\Delta G_{ads}$  as,

$$K = \frac{1}{C_{solvent}} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \text{ ----- (5)}$$

Where, C<sub>solvent</sub> represents the molar concentration of the solvent, which in the case of water is 55.5 mol dm<sup>-3</sup>, R is the gas constant and T is the thermodynamic temperature in K. The Langmuir isotherm, Eq. (6), can be rearranged to obtain the following expression,

$$\frac{c}{\theta} = \frac{1}{K} + c \text{ ----- (6)}$$

so that a linear-relationship can be obtained on plotting c/ $\theta$  as a function of c, with a slope of unity. The thermodynamic parameters K and  $\Delta G_{ads}$  for the adsorption of the studied inhibitors on mild steel is obtained by Langmuir's adsorption isotherm are plotted in Figure 2 and the obtained values are given in Table 2. It was found that the linear correlation coefficients clearly prove that the adsorption of the Benzotriazole from 1M H<sub>2</sub>SO<sub>4</sub> and 2M H<sub>2</sub>SO<sub>4</sub> acid solutions on the mild steel corrosion obeys the Langmuir adsorption

isotherm. The negative values of  $\Delta G_{ads}^0$  for the addition of inhibitors indicates that the process of adsorption of studied inhibitors are spontaneous in nature [19]. The free energy of adsorption of ( $\Delta G_{ads}$ ), in 1M  $H_2SO_4$  was found to be  $-6.853 \text{ kJmol}^{-1}$  while for 2M  $H_2SO_4$  it was found to be  $-5.688 \text{ kJmol}^{-1}$  respectively.

It is well known that the values of  $\Delta G_{ads}$  in the order of  $-20 \text{ kJ mol}^{-1}$  or lower indicate a physisorption while those about  $-40 \text{ kJ mol}^{-1}$  or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond [20].

The calculated adsorption values for all the studied inhibitor show that the adsorption is of physical in nature, and there is no chemisorption between the inhibitor molecule and the metal surface. This indicates that the adsorption of Benzotriazole at 2 h takes place through electrostatic interaction between the inhibitor molecule and the metal surface. Hence it indicates that the interaction between the inhibitor molecule and metal surface is physisorption.

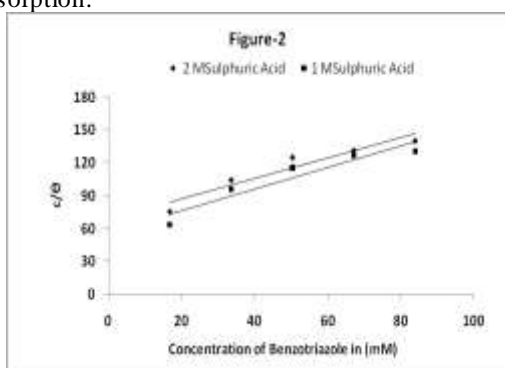


Figure 2- Langmuir isotherm for adsorption of Benzotriazole on mild steel surface studied at various acid media (2M)

#### SEM Analysis:

The polished specimen (MS) and the test specimens were immersed in the blank (1M  $H_2SO_4$  and 2M  $H_2SO_4$ ) and in the inhibitor Benzotriazole for 2 h, then the specimens were observed under Scanning Electron Microscope (SEM). The specimens are shown in the Figure 3 & 4 shows polished specimen which was kept in the blank solution of 1M  $H_2SO_4$  and 2M  $H_2SO_4$ , which is associated with polishing scratches. Figure 5 & 6 shows specimen which was kept in the 84.03 mM concentration of inhibitor solution with 1M  $H_2SO_4$  and 2M  $H_2SO_4$  depends upon the concentration of the inhibitor solution suggesting that the presence of adsorbed layer of the inhibitor on mild steel surface which impedes corrosion rate of metal appreciably.

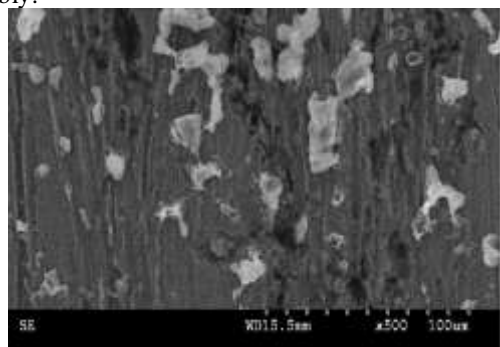


Figure 3-SEM images obtained for the mild steel surfaces immersed for 2 h in 1M  $H_2SO_4$  (blank acid solution)

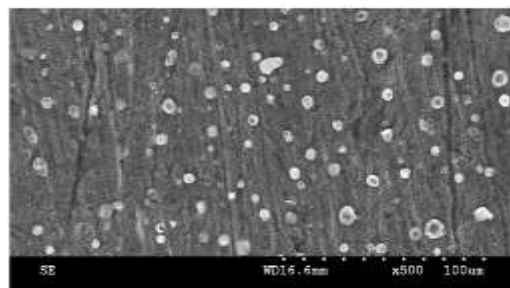


Figure 4- SEM images obtained for the mild steel surfaces immersed for 2 h in 2M  $H_2SO_4$  (blank acid solution)

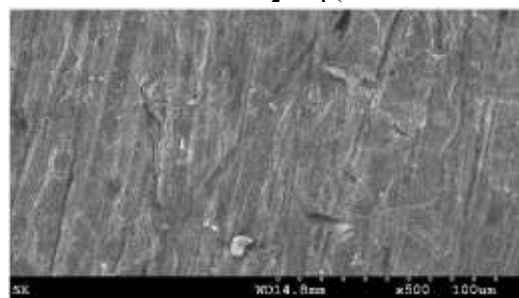


Figure 5- SEM images obtained for the mild steel surfaces immersed for 2 h in 1M  $H_2SO_4$  with 84.03 mM inhibitor solution

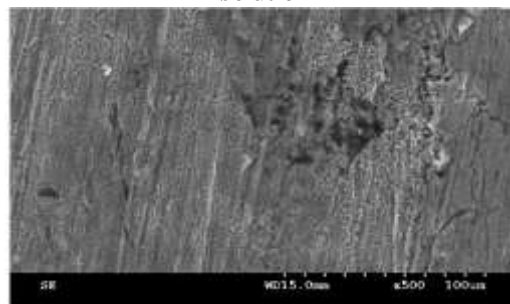
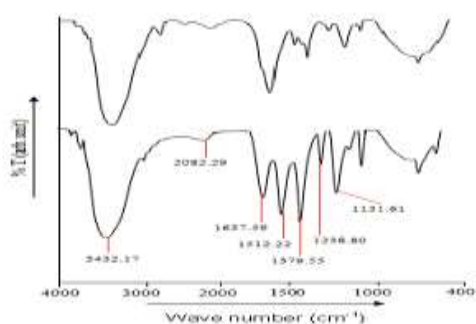


Figure 6- SEM images obtained for the mild steel surfaces immersed for 2 h in 2M  $H_2SO_4$  with 84.03 mM inhibitor solution

#### FT-IR Studies

It is well established that FT-IR spectrophotometer is a powerful tool that can be used to identify the type of bonding particularly functional group(s) present in organic compounds. Since extracts contained organic compounds and these organic compounds were adsorbed on the metal surface providing protection against corrosion. So, FT-IR analyses of metal surface can be useful for predicting whether organic inhibitors are adsorbed or not adsorbed on the metal surface [21]. Therefore, FTIR spectra were used to support the fact that corrosion inhibition of mild steel in acid medium is due to the adsorption of inhibitor molecules on the mild steel surface as well as providing new bonding information on the steel surface after immersion in inhibited HCl solution. Figure 7.1(a) shows the IR spectrum of the Benzotriazole. In this spectrum the peak appeared at  $3432 \text{ cm}^{-1}$  corresponds to amide N-H stretching, the band appeared at around  $1379 \text{ cm}^{-1}$  to  $1637 \text{ cm}^{-1}$  corresponds to C-C stretching, the band appeared at around  $1238 \text{ cm}^{-1}$  to  $1131 \text{ cm}^{-1}$  corresponds to C-N stretching bonding nature. Figure 7.1 (b) is similar to Figure 7.1 (a) which indicates the corrosion products contains Benzotriazole. Therefore from the spectra it is revealed that the inhibition is due to the adsorption of corresponding organic molecule. Moreover the spectrum shows there is no any coordinate type of metal inhibitor bond.



**Figure 7.1 IR spectrum of the corrosion product showing adsorption in the presence of aqueous extract of Benzotriazole**

### Conclusions

- Benzotriazole was found to be effective inhibitor in the acidic medium giving upto 64.29 in 1M H<sub>2</sub>SO<sub>4</sub> and 59.91 in 2M H<sub>2</sub>SO<sub>4</sub>.
- The inhibition efficiency increased with increase in concentration of inhibitors for 16.80 mM to 84.03 mM at two hour at ( $\pm 30^\circ\text{C}$ ) temperature.
- From the comparative studies of weight loss method, it was concluded that the inhibitor efficiency is better in 1M H<sub>2</sub>SO<sub>4</sub> than 2M H<sub>2</sub>SO<sub>4</sub> due to aggressive nature of an acid.
- The adsorption of the compound investigated follows the Langmuir isotherm and the FT-IR results also reveal the adsorption of inhibitor molecule on the metal surface and blocking the active sites.

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**Table 1: Corrosion inhibition behaviour of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> and 2M H<sub>2</sub>SO<sub>4</sub> solution in absence and presence of Benzotriazole is studied by weight loss measurement**

Corrosion Inhibitors	Conc. of inhibitor (mM)	Corrosion Rate		INHIBITOR EFFICIENCY	
		(mm/y)		1M H <sub>2</sub> SO <sub>4</sub>	2M H <sub>2</sub> SO <sub>4</sub>
		1M H <sub>2</sub> SO <sub>4</sub>	2M H <sub>2</sub> SO <sub>4</sub>	1M H <sub>2</sub> SO <sub>4</sub>	2M H <sub>2</sub> SO <sub>4</sub>
Benzotriazole	Blank	195.7068	233.8229	---	---
	16.80	143.8824	181.9884	26.48	22.16
	33.61	127.2763	158.7053	34.96	32.12
	50.42	110.3358	139.6473	43.62	40.27
	67.22	91.9465	114.3480	53.01	51.09
	84.03	69.8793	93.7297	64.29	59.91

**Table 2: Thermodynamic parameters for the adsorption of Benzotriazole in various acids (2M) on the mild steel**

Name of the Acid	Concentration in (mM)	Surface coverage ( $\theta$ )	$\Delta G_{ads}$ KJ/mol <sup>-1</sup>	$K_x$ ( $10^{-2} M^{-1}$ )
1M H <sub>2</sub> SO <sub>4</sub>	84.03	0.6429	-6.853	1.79
2 M H <sub>2</sub> SO <sub>4</sub>	84.03	0.5991	-5.688	1.79