

## **Evaluation of Trimethoprim Drug as a Green Corrosion Inhibitor for Mild Steel in 1.0 M Sulfuric Acid**

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### **Abstract**

The mitigation of mild steel corrosion in 1.0 M H<sub>2</sub>SO<sub>4</sub> solution by trimethoprim drug as a green and commercially available inhibitor was studied at room temperature using weight loss, open circuit potential, and potentiodynamic polarization techniques. The results showed that the investigated compound's inhibition efficiency depended on the concentration and nature of the inhibitor. The inhibition efficiency was found to increase with the concentration of the inhibitor. The polarization result indicated that the compound behaved as mix type inhibitor. The inhibition is assumed to occur via physical adsorption of inhibitor on the metal surface, which obeyed Langmuir adsorption isotherm. The scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX) results confirmed the formation of a protective layer on the mild steel surface.

*Keywords:* Trimethoprim; Mild steel; Acid corrosion.

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### **1. Introduction**

Mild steel has found wide industrial applications due to its excellent mechanical properties and low cost. The study of corrosion of iron and its alloys is of great importance due to economic, safety, and conservation [1-3]. Sulfuric acid solutions are widely used for chemical cleaning, descaling, pickling, and oil well acidizing, leading to electrochemical corrosion. Among the various methods available, the use of inhibitors is one of the most economical and effective methods in protecting metal from corrosion attacks in acidic media [4-12]. Organic compounds containing a heteroatom such as nitrogen, sulfur, phosphorous, oxygen, etc., and aromatic ring, heterocyclic ring, double bond, and triple bond in their structure serve as good corrosion inhibitors of metals with great effectiveness, especially in the aggressive acidic environment [13-18]. However, most of these inhibitors are poisonous, costly, and cause harm to the environment. So, it is required to find cheap, non-poisonous compounds that have a small negative impact on the environment. Several research studies reveal that drugs can fulfill all these criteria.

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Different types of drugs, such as tinidazole, metronidazole, dapson, penicillin, etc., can be used as effective corrosion inhibitors to mitigate corrosion of mild steel in acid media [19-24].

The present work comprises the inhibition property of pharmaceutically active compound trimethoprim towards corrosion of mild steel in 1.0 M H<sub>2</sub>SO<sub>4</sub> solution. The corrosion mechanism of mild steel has been studied using weight loss, open circuit potential, potentiodynamic polarization, and Surface analytical techniques.

## 2. Experimental

### 2.1. Materials and methods

#### 2.1.1. Mild Steel

A commercial grade of mild steel sheets were purchased from the market and sheered into the dye in 3 cm × 1 cm × 0.1 cm dimensions, then polished with a series of SiC grit papers of grade 400 to 2000 to obtain scratchless and mirror-finished specimen surface. Then washed with soap, rinsed with bi-distilled water, degreased with acetone, and finally dried in desiccators for immediate use for corrosion study.

#### 2.1.2. Test solution

1.0 M sulfuric acid solution was prepared by diluting 98 % sulfuric acid (analytical grade) in bi-distilled water. The concentration range of 10 to 500 ppm solution of trimethoprim in 1.0 M sulfuric acid was prepared.

#### 3.1.3. inhibitor

The inhibitor is an antibiotic drug procured commercially and was selected as a corrosion inhibitor, and its molecular structure is shown in Fig. 1.

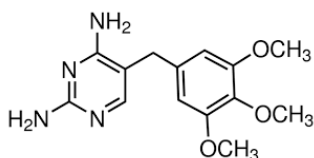


Fig. 1. Molecular structure of trimethoprim molecule.

### 2.2. Weight loss measurements

Weight loss measurements were carried out in test tubes containing 10 mL test solutions with and without inhibitor solution ranging from 10 to 500 ppm. The immersion time was 24 h at 26 ± 1 °C, the coupons were withdrawn from test tubes, rinsed with double

distilled water, washed with acetone, dried, and weighed. The average value of weight loss was noted.

### **2.3. Open circuit potential (OCP) and polarization measurement**

The electrochemical measurement system, DC 105, containing software of DC corrosion techniques from M/S Gamry Instrument, was used for OCP and potentiodynamic polarization experimental studies. Above mentioned polished and cleaned mild steel coupons were coated with enamel lacquer, leaving a 1 cm<sup>2</sup> working area on one side and a small portion at the tip to provide electrical contact. Finally, the coupons were dried into the desiccators for immediate use. Saturated calomel electrode and graphite rod were used as reference and counter electrodes. The working surface area of the mild steel electrode and the remaining two electrodes were sufficiently immersed into the Pyrex glass vessel containing about 50 mL of corrosive medium solution and connected to the Gamry instrument. The potential was swept between -0.5 and 0.5 V at the scan rate of 5 mV/s. The open circuit potential was carried out for 2 h to obtain a steady horizontal curve, and then potentiodynamic polarization was run. The variation in potential and polarization of mild steel with respect to with and without inhibitor was measured against saturated calomel electrode.

### **2.4. Scanning electron microscopy and electron dispersive X-Ray analysis**

The composition and surface morphology of corrosion product on mild steel samples after 24 h of immersion in 1.0 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of an inhibitor was studied using a scanning electron microscope coupled with EDX (Hitachi S-3400 N with thermoran EDS analyzer). The accelerating voltages for the SEM picture were 10.0 KV and 15.0 KV.

## **3. Results and Discussion**

### **3.1. Weight loss measurements**

The effect of different trimethoprim concentrations on mild steel corrosion in 1.0 M H<sub>2</sub>SO<sub>4</sub> was studied by weight loss measurement at 303 K after immersion for 24 h. Inhibition efficiencies (%IE) were calculated according to the following equation.

$$\%IE = \frac{W_0 - W_{\text{corr}}}{W_0} \times 100 \quad (1)$$

$W_{\text{corr}}$  and  $W_0$  are the corrosion rates of steel with and without inhibitor, respectively.

Table 1. Weight loss data for inhibition of corrosion of mild steel exposed to 1.0 M H<sub>2</sub>SO<sub>4</sub> with different concentrations of trimethoprim.

Inhibitor	Concentration (ppm)	Weight loss (mg)	Corrosion rate (mg cm <sup>-2</sup> h <sup>-1</sup> )	surface coverage (θ)	(% E)
1 M H <sub>2</sub> SO <sub>4</sub>	0.00	194	26.944	-	-
	10	115	15.972	0.4072	40.72
	100	90	12.500	0.5360	53.60
Trimethoprim	200	62	8.611	0.6804	68.04
	300	39	5.416	0.7990	79.90
	400	34	4.722	0.8247	82.47
	500	14	1.944	0.9278	92.78

The corrosion rate (CR) was calculated from the following equation:

$$CR = \Delta W / At \quad (2)$$

Where  $CR$  is corrosion rate (mg cm<sup>2</sup> h<sup>-1</sup>),  $\Delta W$  is the weight loss (mg),  $A$  is surface area (m<sup>2</sup>), and  $t$  is immersion time in h. The data shows that the corrosion efficiency of inhibitors increases with increasing inhibitor concentration. The potentiodynamic data confirms the main gravimetric results [25,26].

### 3.2. Langmuir adsorption isotherm

Adsorption isotherms are often used to demonstrate the adsorbent performance on the substrate, which describes the relationship between surface coverage,  $\theta$ , and bulk concentration. It is observed that the surface coverage values,  $\theta$  (defined as  $\theta = \% IE/100$ ), increase with increasing inhibitor concentrations as a result of more adsorption of inhibitor molecules on the surface of mild steel takes place. The adsorption behavior of trimethoprim obeys Langmuir's adsorption isotherm as it gives a straight line with a regression coefficient value ( $R^2=0.973$ ) when the graph of  $C/\theta$  is plotted against  $C$ , as shown in Fig 2. The protective layer of inhibitor on the mild steel combines both physisorption and chemisorptions [27,28].

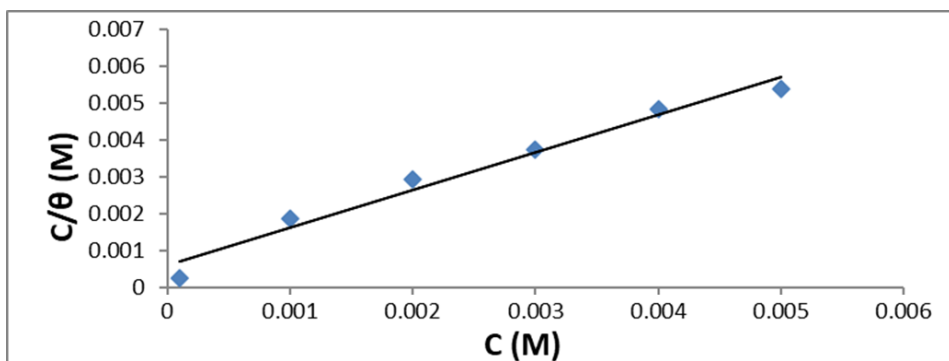


Fig. 2. Langmuir adsorption isotherm plot for the adsorption of trimethoprim on mild steel surface in 1.0 M H<sub>2</sub>SO<sub>4</sub> solution.

### 3.3. Open circuit potential measurement (OCP)

The electrochemical behavior of mild steel in 1.0 M H<sub>2</sub>SO<sub>4</sub> was studied based on the change in corrosion potential (E<sub>corr.</sub>) with time. The change in the open circuit potential of mild steel in the absence and presence of various concentrations of inhibitor in 1.0 M H<sub>2</sub>SO<sub>4</sub> is shown in Fig. 3. The change in OCP of mild steel in the absence and presence of inhibitor was measured for the period of two h with a sample period of one data per second. The potential attains a steady state after exposure of approximately 30 minutes.

The steady-state potential is an equilibrium state at which I<sub>ox</sub> is equal to I<sub>red</sub>. It has been observed that the OCP of mild steel from the moment of immersion in 1.0 M H<sub>2</sub>SO<sub>4</sub> tends towards a more negative value in the absence of an inhibitor. This shows the corrosiveness of the medium, which is due to the breakdown of pre-immersion, the air-formed oxide film on the metal surface. In various concentrations of inhibitors, the steady-state potential of mild steel shifts more towards a positive value. This is due to inhibitor adsorption on the metal surface resulting in the passivation of metal [29].

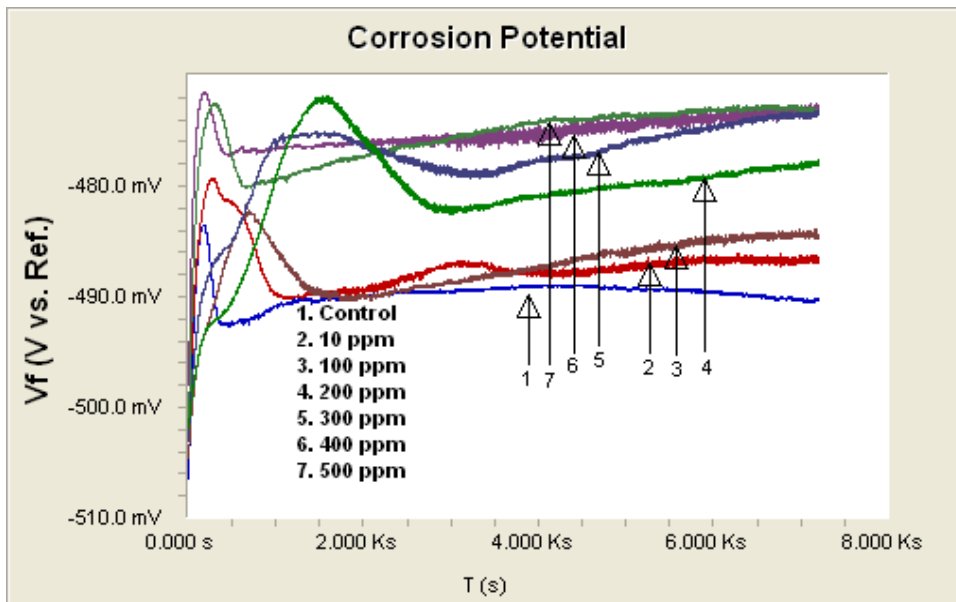


Fig. 3. Open circuit potential of mild steel in 1.0 M H<sub>2</sub>SO<sub>4</sub> without and with different concentrations of trimethoprim.

### 3.4. Potentiodynamic polarization measurement

The anodic and cathodic behavior of mild steel in 1.0 M H<sub>2</sub>SO<sub>4</sub> containing different concentrations of trimethoprim is given in Fig. 4. There is a reduction in current density and shift of corrosion potential towards a more positive value with the increasing concentration of inhibitor. The aim of this investigation was to determine the influence of trimethoprim on the electrochemical behavior of mild steel in 1.0 M H<sub>2</sub>SO<sub>4</sub>. The values of

electrochemical parameters like corrosion potential ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ), cathodic and anodic Tafel slopes, corrosion rate and % IE of inhibition efficiency, etc., determined from this experiment are summarized in Table 2. The corrosion inhibition efficiency was calculated by using the following equation:

$$\%E = \left(1 - \frac{i_{corr}}{i_{corr}^0}\right) \times 100 \quad (3)$$

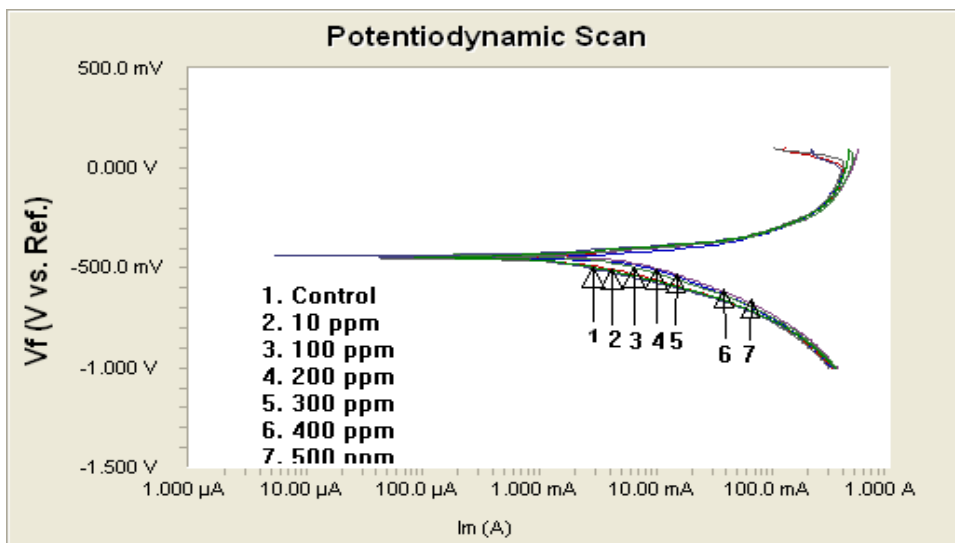


Fig. 4. Potentiodynamic polarization of mild steel in 1.0 M  $H_2SO_4$  with and without different concentrations of trimethoprim.

Where  $i_{corr}^0$  and  $i_{corr}$  are the corrosion current densities in the absence and presence of inhibitor in the solution, respectively. The inhibition efficiency increases with an increase in the concentration of the inhibitor. The maximum inhibition efficiency is 93.11 % at 500 ppm for trimethoprim. It can also be observed that the hydrogen liberation and mild steel dissolution are reduced in the presence of an inhibitor, suggesting that the studied compound acted as a mixed-type inhibitor [30].

Table 2. Electrochemical parameters of mild steel in 1.0 M  $H_2SO_4$  with and without different concentrations of trimethoprim.

Conc. (ppm)	$\beta_a$ (V/dec.)	$\beta_c$ (V/dec.)	$i_{corr}$ $(\mu A \cdot cm^{-2})$	$E_{corr}$ (mV)	(% E)
1.0 M $H_2SO_4$	73.6e-3	130.7	1090	-509.0	-
Trimethoprim					
10	49.0e-3	162.5e-3	630.0	-472.0	42.20
100	45.8e-3	147.7e-3	490.0	-478.0	55.04
200	46.5e-3	135.3e-3	384.0	-485.0	64.77
300	43.6e-3	130.3e-3	285.0	-483.0	73.85
400	42.1e-3	127.7e-3	171.0	-484.0	84.31
500	35.1e-3	100.2 e-3	75.10	-480.0	93.11

### 3.5. Scanning electron microscopic (SEM) analysis

The results obtained from the chemical method and electrochemical measurements were further supported by SEM and EDX analysis. SEM micrographs obtained from mild steel surface after specimens' immersion in 1.0 M H<sub>2</sub>SO<sub>4</sub> for 24 h. in the absence and presence of 500 ppm trimethoprim are shown in Fig. 5.

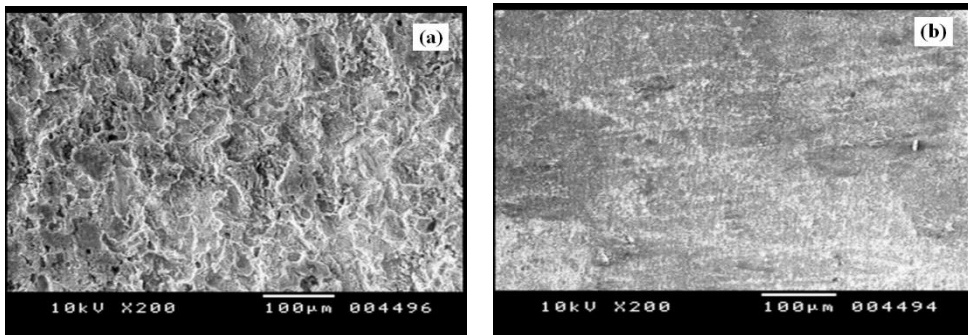
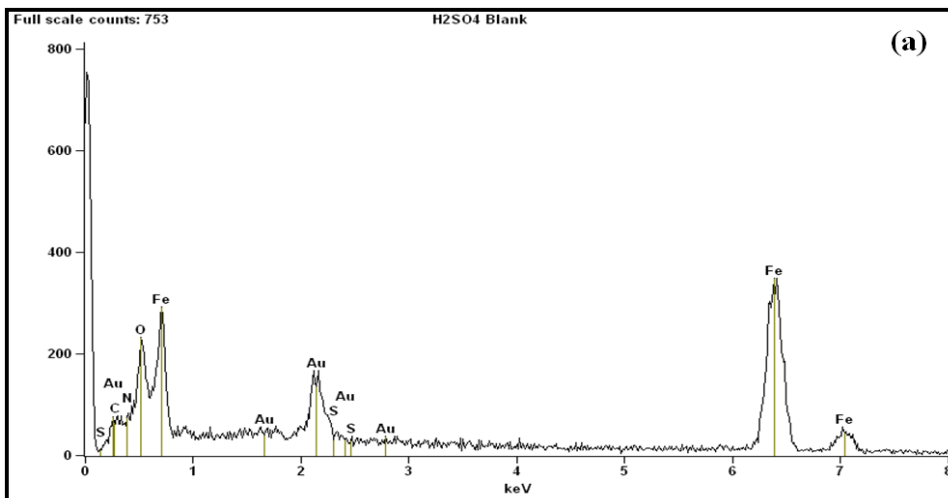


Fig. 5. SEM of mild steel: a) after immersion of 1 M H<sub>2</sub>SO<sub>4</sub> without inhibitor. b) After immersion in 1 M sulfuric acid with 500 ppm of inhibitor.

Fig. 5(a) represents an SEM micrograph of a mild steel surface immersed in 1.0 M H<sub>2</sub>SO<sub>4</sub> without an inhibitor which appears to be highly corroded and damaged due to a free acid attack. Fig. 5(b) shows an SEM micrograph of the mild steel surface after immersion in 1.0 M H<sub>2</sub>SO<sub>4</sub> containing 500 ppm trimethoprim. It could be observed that the extent of damage to a mild steel surface is very less, the rate of corrosion was reduced considerably in the presence of inhibitor, it revealed that there was a good protective film adsorbed on the metal surface, which acted as a barrier and was responsible for the inhibition of corrosion [31].



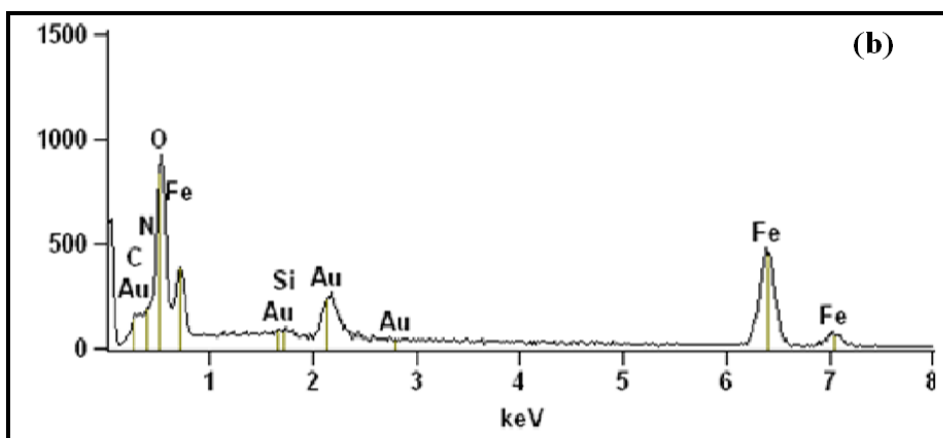


Fig. 6. EDX of mild steel samples (a) after immersion in 1.0 M  $\text{H}_2\text{SO}_4$  solution without inhibitor, (b) after immersion in 1.0 M  $\text{H}_2\text{SO}_4$  solution in the presence of 500 ppm trimethoprim.

### 3.6. Energy dispersive X-ray spectroscopy (EDX) analysis

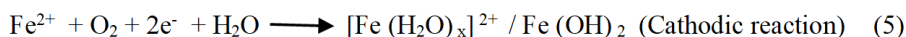
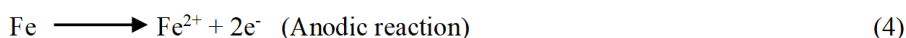
Fig. 6 shows two EDX spectra recorded for mild steel samples exposed to 1.0 M  $\text{H}_2\text{SO}_4$  in the absence and presence of 500 ppm trimethoprim. In an inhibitor-containing solution, the EDX spectra (Fig. 6b) show a signal for the existence of N, and in addition intensity of C and O signals are enhanced appreciably. The appearance of the N signal and enhancement of C and O signals are due to the adsorption of N, C, and O atom of trimethoprim. EDX data shows that carbonaceous organic molecule containing N-atom has formed a protective covering. The high-intensity nitrogen signal and high intensity of C and O signals are not observed in EDX spectra (Fig. 6a) of mild steel surface exposed to 1 M  $\text{H}_2\text{SO}_4$  without inhibitor. Fig. 6b also shows that Fe peaks are considerably suppressed in the samples containing trimethoprim. This suppression of the Fe line is due to inhibitor film on the surface of mild steel. The result from EDX also confirms gravimetric and polarization measurement, which suggests that corrosion inhibition is due to the formation of the protective surface film resulting in retardation of hydrogen evolution reaction [32].

## 4. Mechanism of Inhibition

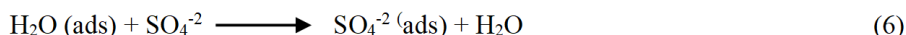
The inhibition efficiency of trimethoprim in sulfuric acid may be attributed to adsorption (chemisorptions and physisorption) of the molecule onto the surface of mild steel. The compound act as a mixed-type inhibitor. In acidic media, the compound is protonated to form a cation-like structure and gets adsorbed on cathodic sites reducing the evolution of hydrogen gas, thus protecting the cathode and inhibiting the dissolution of metal. The adsorption on the anodic site may be attributed to the transfer of lone pair of electrons on N and O atoms,  $\pi$  electrons of the double bond, and aromatic structure to the vacant d



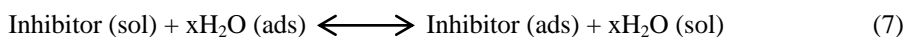
orbital of iron. This shows it is a mixed-type inhibitor. The adsorption phenomenon is also determined by nature, composition and surface condition of metal, electrolytic solution, temperature, exposure period, and also the different interacting forces between metal and organic molecule. [33-35]



In presence of  $\text{SO}_4^{2-}$  ions, following rapid reaction proceeds on the metal surface



The substitution of water molecules with  $\text{SO}_4^{2-}$  ions leads to the probability of the formation of adsorbed ion pairs and neutral molecules formed by the adsorbed  $\text{SO}_4^{2-}$  ions and trimethoprim ion. Trimethoprim molecule provides an abundance of  $\pi$  electrons and unshared electron pair on the nitrogen and oxygen atom, which can interact with the vacant 'd' orbital of Fe to form a coordinate covalent bond resulting in the formation of a complex film on the mild steel surface. This blocks the surface by adsorption and film formation and also decreases the effective area of attack by sulfate ion resulting in increased inhibition efficiency. Adsorption can also occur via electrostatic interaction between negatively charged surfaces, providing a specifically adsorbed anion on Fe and a positive charge of the inhibitor. The presence of four nitrogen atoms, three oxygen atoms, and  $\pi$ -electrons of benzene in the structure of trimethoprim has maximum contribution towards inhibition efficiency and consequently facilitates adsorption phenomenon on steel surface, thus protecting a steel surface from aggressive sulfate ions. The affinity of these molecules towards the adsorption of the mild steel surface is more than that of  $\text{H}_2\text{O}$  and sulfate ions. The strength and stability of the bond depend upon Pearson's Hard and Soft Acid and Base Principle [36].



A single inhibitor displaces many water molecules and sulfate ions and forms a complex with the metal and adsorbed uniformly over the entire metal surface. The complex formed is stabilized on the surface, assumed nonporous and insoluble in the medium, whereas the inhibitor is chemically inert and doesn't decompose during service conditions. It is inferred that trimethoprim inhibits corrosion. The complex film acts as a barrier and effectively protects the mild steel surface from the aggressive nature of sulfate ions [37].

## 6. Conclusion

Corrosion inhibition of mild steel in 1.0 M  $\text{H}_2\text{SO}_4$  solution using trimethoprim as an inhibitor was studied using gravimetric, polarization, SEM, and EDX techniques. The main conclusions are,

Trimethoprim acted as an excellent inhibitor for mild steel in 1.0 M  $\text{H}_2\text{SO}_4$  solution.

The inhibitor efficiency increases with the concentration of the inhibitor to attain near 93 % for the inhibitor at 500 ppm.

The adsorption of trimethoprim on mild steel surface obeyed Langmuir adsorption isotherm.

SEM and EDX examination of mild steel surface showed that protective surface film is formed on the metal surface, which inhibits metal dissolution in H<sub>2</sub>SO<sub>4</sub> and retards hydrogen evolution.

Trimethoprim acts as a mixed-type inhibitor.

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