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Metronidazole and 2-Methylimidazole as Corrosion Inhibitors in Microbiologically Influenced Corrosion

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Abstract

Microbial corrosion behavior of mild steel was studied by exposing mild steel coupons in *Barr's* medium inoculated with sulfate-reducing bacteria (*Desulfovibrio desulphuricans*). During the investigation, a considerable loss in weight and deterioration of microstructure of mild steel coupons surface was observed. Coupons were further exposed to culture media containing different concentrations of metronidazole (MNZ) and 2- methylimidazole (MIZ) inhibitors. The corrosion behavior of mild steel was measured by weight loss, electrochemical studies, and scanning electron microscopy (SEM). Polarization studies indicated the mixed-type behavior of these inhibitors. MNZ and MIZ exhibited 82.23 and 78.30 % inhibition efficiencies, respectively, as revealed by polarization measurements. The results show that the inhibition efficiencies increased with inhibitor concentration. The surface analysis was performed by SEM.

Keywords: Mild steel; Microbiologically influenced corrosion; Inhibitors; SEM.

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1. Introduction

Metal deterioration remains a key problem to various industries despite constant dedicated attention to corrosion prevention through research and innovation. Mild steel is a widely used alloy due to its favorable physical properties, including outstanding mechanical strength, low cost, and availability [1]. Extensive use of mild steel and its susceptibility to corrosion have heightened research focus on its protection against corrosion [2]. Surroundings that witness growth and accumulation of biomaterials, such as sewage treatment plants, reverse osmosis membrane, and underground pipes, may encourage microbiologically influenced corrosion (MIC) [3,4]. The colonization of metals and alloys of industrial machinery is often caused by the microbial consortium; well known among them is sulfate-reducing bacteria (SRB) [5,6]. The occurrence of MIC or bio-corrosion results from metabolites and the formation of biofilms that can seriously speed up the corrosion process [5]. Consequently, metal wearing due to a corrosive environment weakens its mechanical strength and eventually results in mechanical failure. In some

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countries, leakage of products such as gas or oil has become a criminal offense and can be charged with heavy fines or jail terms. In industries, inhibitors have been the most important method to minimize metal corrosion in acidic and biotic environments [7-15]. According to wang and co-workers [16], choosing an efficient inhibitor for metal corrosion depends on the availability of electronegative functional groups, pi-electrons, and the presence of heteroatoms such as S, P, N, and O in the structure of the organic compound. These sites are found to be excellent adsorption centers [16,17]. Hence, this study presents the inhibitive effects of metronidazole (MNZ) and 2-methyl imidazole (MIZ) on corrosion of mild steel in SRB media.

The study used gravimetric analysis, an electrochemical technique such as open circuit potential, Potentiodynamic polarization, and surface analytical techniques such as scanning electron microscope (SEM) studies.

2. Experimental

2.1. *Inhibitors, reagents, and bacterium*

The two corrosion inhibitors, metronidazole (MNZ) and 2-methyl imidazole (MIZ), were obtained from Merck (India). Ethanol was obtained from Loba Chemie (India).
The bacteria used in the present study were obtained from the National Collection of Industrial Micro-organisms (NCIM), Biochemical Science Division, National Chemical Laboratory, Pune – 411088, Maharashtra. The bacteria used in the present study were *Desulphovibrio desulphuricans* (SRB). The composition of the culture medium is given in Table 1. The structures of MNZ and MIZ are given in Fig. 1.

Table 1**.** The composition of the culture medium is given below.

Name of the organism	NCIM No.	Medium used
Desulphovibrio Desulphuricans (SRB)	2047	*Barr's* medium (sulfate reducing bacteria), K_2HPO_4 0.05g, NH_4Cl 0.19, $CaSO_4$ 0.29, Sodium Lactate 0.79, $MgSO_4.7H_2O$ 0.29, Ferrous Ammonium Sulphate 0.05g, Distilled Water 100 cm^3 (medium is sterilized for three consecutive days at 121^oC for 20 min and the final pH is adjusted to 7.0-7.5).

Metronidazole (MNZ) 2- Methylimidazole (MIZ)

Fig. 1. Structures of metronidazole (MNZ) and 2-methylimidazole (MIZ).

2.2. *Sample preparation*

Mild steel coupons having composition (C - 0.16 %, Si - 0.10 %, Mn - 0.40 %, P - 0.013 %, S - 0.02 % and remaining as iron) were used as working electrode in the present investigation. For weight loss experiments, rectangular-shaped coupons (1 cm × 3 cm) were sheared from mild steel sheets, and flag-shaped specimens with a 1 cm^2 working area were used for electrochemical experiments. The surface of specimens was prepared by sequential polishing with the next higher grade emery papers. During the mild steel surface polishing, the emery paper was impregnated with a dilute solution of paraffin wax in kerosene oil. All specimens were washed with triple distilled water and degreased with 95 % ethyl alcohol. Specimens were dried and stored over silica gel in vacuum desiccators.

2.3. *Immersion test*

Specimens were weighed on an electronic balance (Shimadzu Type BL220H, least count 0.001 g) before and after immersion tests. Specimens were removed from the test solution, and then corrosion products were removed from the surface with the help of a brush. Generally, duplicate experiments were performed in each case, and the mean value of the weight loss was recorded.

2.4. *Electrochemical measurements*

The electrochemical measurement system, DC 105, containing software of D.C. corrosion techniques from M/S Gamry Instruments Inc., (No. 23-25), Louis Drive, Warminster, PA-18974, USA, has been used for performing corrosion potential and polarization experiments. The electrochemical studies were performed in a three electrodes Pyrex glass vessel with mild steel coupons as working electrode, saturated calomel electrode as reference electrode, and spectroscopic grade graphite rod as the counter electrode. About 50 mL of the corrosive medium was used for electrochemical measurements, and it was carried out at room temperature. Electrochemical measurements were carried out in *Barr's* medium inoculated with *Desulphovibrio desulphuricans* (SRB)with and without different concentrations of MNZ and MIZ. The change in open circuit potential of mild steel in the absence and presence of inhibitors was measured after 10 days exposure in *Barr's* medium inoculated with SRB for a period of 1 h with a sample period of one data per second. Then the same sample was used for potentiodynamic polarization (P.D.) experiments. Different electrochemical results obtained from potentiodynamic polarization are reported. For electrochemical polarization studies (corrosion potential and potentiodynamic polarization) flag-shaped specimens with sufficiently long tails were cut from the mild steel sheet. These samples were polished as described earlier. One side with a working area of 1 cm^2 was exposed to a corrosive medium, and the other side was used to provide electrical contact. The rest of the surface was coated with enamel lacquer, including side edges. The test specimen was connected to the working electrode holder through the tip of the tail.

2.5. *SEM analysis*

SEM was used to analyze the surface film formed on a mild steel coupon. The surface of mild steel specimen exposed to *Barr's* medium inoculated with SRB was analyzed after the 10 days incubation period. The surface morphology of mild steel sample after ten days immersion in *Barr's* medium inoculated with SRB at room temperature in the absence and presence of MNZ and MIZ inhibitors was studied by scanning electron microscopy (SEM). An SEM microscope (JEOL, model JSM-5600) with a beam voltage of 15 kV was used to visualize the morphology of the biofilm.

3. Results and Discussion

3.1. *Weight loss measurement*

Mild steel coupons were exposed to the SRB environment without and with different MNZ and MIZ inhibitors concentrations. These coupons were retrieved after 10 days of exposure. After removing corrosion products, they were weighed to study how much SRB promotes steel corrosion and the influence of MNZ and MIZ in mitigating the SRB effect on the steel. The results of weight loss and corrosion inhibition efficiency are presented in Table 2. The result shows that both MNZ and MIZ reduced the weight loss of mild steel in the SRB medium. The highest weight loss recorded for mild steel in the pure SRB medium was a bacterial attack on the steel. Microbial activities accelerate corrosion reaction rates [18-20]. The extent of steel degradation was lowered in the presence of the studied inhibitors as they have biocidal activity [21,22]. Both MNZ and MIZ were found to inhibit the MIC of mild steel in the SRB medium significantly.
Inhibitor efficiency was calculated according to the following equation,

$$\%\,E = \frac{W_0 - W}{W_0} \times 100 \tag{1}$$

where W and W_0 are weight loss of mild steel in the presence and absence of inhibitors, respectively.

Table 2. The weight loss data was obtained for mild steel in *Barr's* medium inoculated with *Desulphovibrio desulphuricans* (SRB) containing different MIZ and MNZ inhibitors concentrations at 298 K.

Inhibitor	Conc. (ppm)	Weight loss (mg)	Surface coverage (θ)	% E
Blank	0.00	168	-------	--------
	100	90	0.4642	46.42
Metronidazole (MNZ)	300	51	0.6964	69.64
	500	35	0.7916	79.16

Inhibitor	Conc. (ppm)	Weight loss (mg)	Surface coverage (θ)	% E
	100	70	0.5833	58.33
2-Methylimidazole (MIZ)	300	51	0.6964	69.64
	500	42	0.7500	75.00

4. Electrochemical Measurements

4.1. *Open circuit potential measurement*

The potential developed on the mild steel electrode relative to the potential of the reference electrode is termed as open circuit potential. The stabilization of OCP is essential before performing electrochemical measurements. In the presence of various concentrations of inhibitors, the corrosion potential of mild steel shifts more towards positive value, and enablement of mild steel is observed. The influence of various concentrations (100, 300, and 500 ppm) of MNZ and MIZ inhibitors on the open circuit potential of mild steel in *Barr's* medium is shown in Figs. 2 and 3. Inhibitors used in this have biocidal activity [21,22]. It is obvious from the Fig. that it exhibits good inhibition performance at 100 ppm and above. The inhibition efficiency was found to increase with inhibitor concentration [23,24].

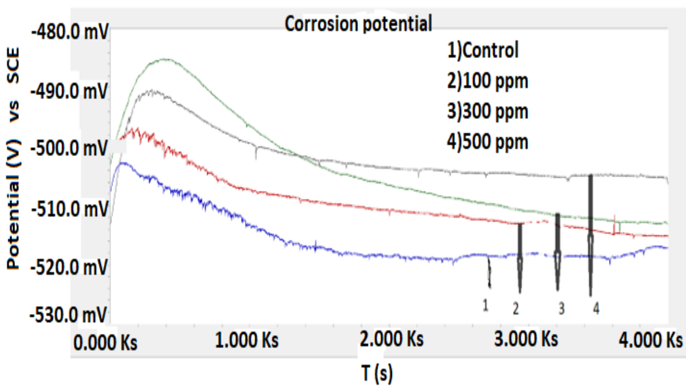

Fig. 2. Open circuit potential of mild steel without and with different concentrations of metronidazole (MNZ) in *Barr's* medium inoculated with SRB.

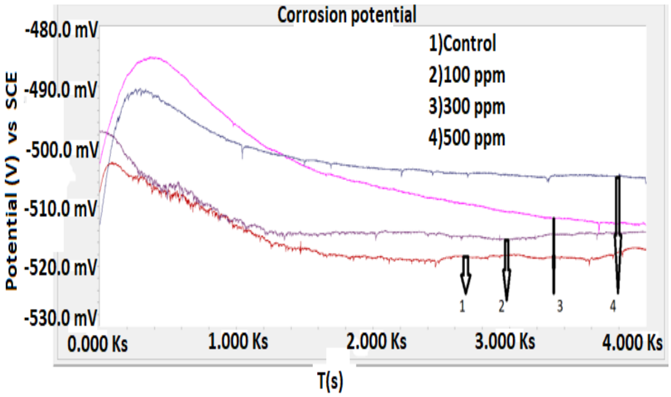

Fig. 3. Open circuit potential of mild steel without and with different concentrations of 2-methylimidazole (MIZ) in *Barr's* medium inoculated with SRB.

4.2. *Potentiodynamic polarization study*

The electrochemical corrosion kinetic parameters such as anodic and cathodic Tafel slopes (β_a and β_c), corrosion potential (E_{corr}), corrosion current density(i_{corr}), and inhibition efficiency (η %) in Table 3 shows anodic and cathodic Tafel slopes (β_a and β_c) with no definite trend. However, there is a remarkable reduction of β_a and β_c values at maximum inhibitor concentration for both studied inhibitors. It is clear that an increase in the inhibitor concentration led to a decrease in corrosion current density (i_{corr}), increasing inhibition efficiency. The E_{corr} values in the presence of different concentrations of the inhibitors are more negative compared to that of the reference medium.

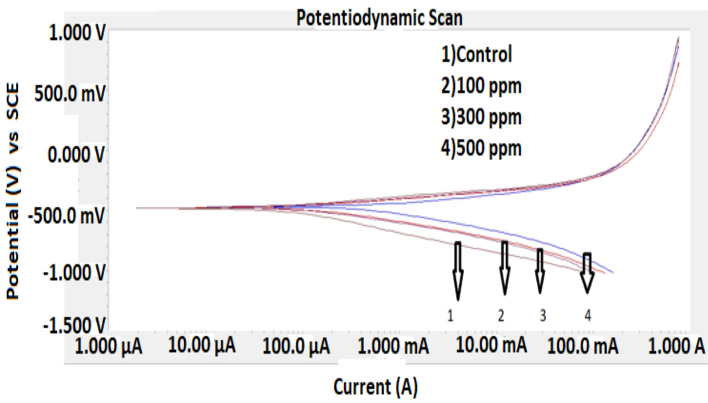

Fig. 4. Potentiodynamic polarization curves for mild steel without and with different concentrations of MNZ in *Barr's* medium inoculated with SRB.

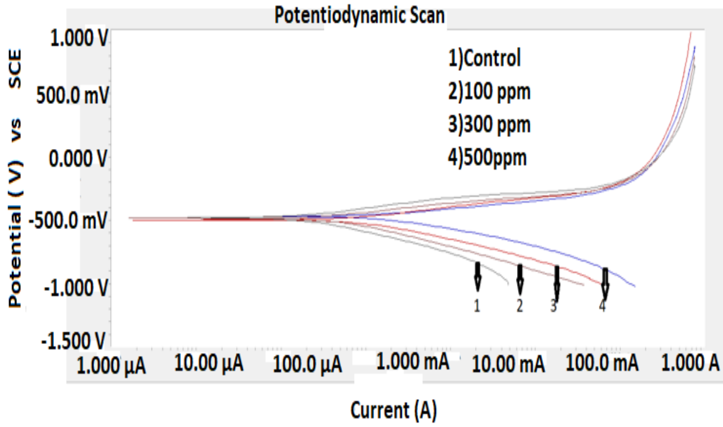

Fig. 5. Potentiodynamic polarization curves for mild steel without and with different concentrations of MIZ in *Barr's* medium inoculated with SRB.

Moreover, the maximum displacement in E_{corr} with reference to the E_{corr} of the uninhibited solution is 50 (mV). This finding suggests that the investigated inhibitors behaved as mixed-type inhibitors [25-30]. At 500 ppm, MNZ and MIZ exhibited 83.23% and 78.30% inhibition efficiencies, respectively. Therefore, as compared to MIZ, MNZ is found to be a good corrosion inhibitor. Results of electrochemical studies revealed the excellent inhibition efficiency of these molecules, which follows the order MNZ > MIZ. The inhibition efficiency (η %) was obtained from the i_{corr} using the equation:

$$\eta\% = 100\,(1 - \frac{i_{corr}}{i^{o}_{corr}}) \tag{2}$$

where i°_{corr} and i_{corr} are corrosion densities for the blank and inhibitor-containing *Barr's* media inoculated with SRB, respectively.

Table 3. Tafel parameters for mild steel without and with different concentrations of MNZ and MIZ in *Barr's* medium inoculated with SRB.

Concentration of inhibitors (ppm)	$-E_{corr}$ (mV)	Icorr (µA/cm^2)	βa (V/dec)	βc (V/dec)	η%
Barr's medium inoculated with SRB	-442	510	84.60 e^{-3}	153.4 e^{-3}	-------
Metronidazole (MNZ)					
100	-452.0	280.32	62.20 e^{-3}	126.8 e^{-3}	45.00
300	-466.0	180.40	64.40 e^{-3}	144.5 e^{-3}	64.62
500	-494.0	85.50	70.60 e^{-3}	166.5 e^{-3}	83.23
2- methyl imidazole (MIZ)					
100	-486.0	190.20	66.13 e^{-3}	124.4 e^{-3}	62.70
300	-488.0	133.50	78.34 e^{-3}	124.1 e^{-3}	73.82
500	-487.0	110.65	76.11 e^{-3}	133.6 e^{-3}	78.30

5. Surface Studies

5.1. *SEM analysis*

A micrograph of the mild steel surface after immersion in *Barr's* medium inoculated with SRB without inhibitor is shown in Fig. 6A, which appears with biofilm formation on its surface. Figs. 6B and 6C show significant improvement in surface morphology of mild steel in *Barr's* medium inoculated with SRB containing 500 ppm of MNZ and MIZ inhibitors, respectively. At the conclusion of the test, the visual inspection of the steel coupons exposed to the biotic system shows dense, thick, and black products covering the surface. In the presence of SRB, the surface film observed visually includes both biofilm and corrosion products. The surface of the coupons with SRB, which contains both corrosion products and the biofilm, suffered from severe corrosion. The addition of inhibitors in bacterial solution successfully reduced the extent of corrosion [31].

The results obtained from weight loss and electrochemical measurements supported SEM analysis.

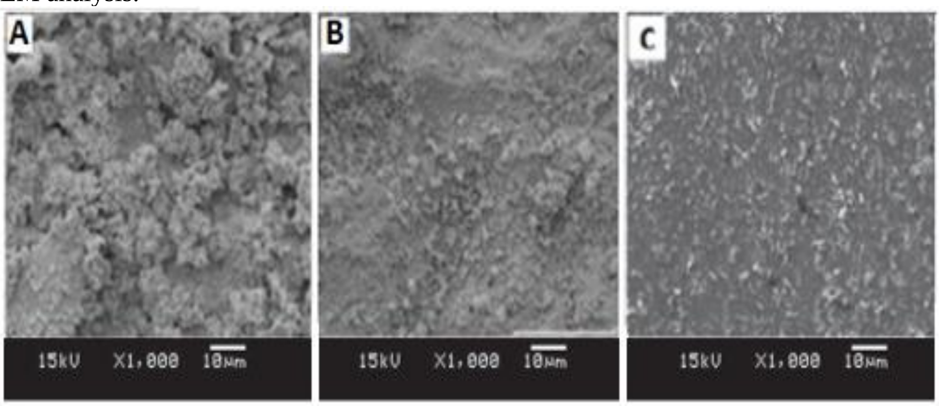

Fig. 6. SEM images of mild steel surface recovered from (A) *Barr's* medium inoculated with SRB (B) 500 ppm of MNZ (C) 500 ppm of MIZ.

6. Conclusion

Experimental studies were carried out on metronidazole (MNZ), and 2- methylimidazole (MIZ) as corrosion inhibitors for mild steel in *Barr's* medium inoculated with *Desulfovibrio desulphuricans* (SRB), and the following conclusions were derived from studies:

i) The inhibition efficiency of these inhibitors increased with an increase in inhibitor concentration.
ii) Results of electrochemical studies revealed the excellent inhibition efficiency of these molecules, which follows the order MNZ > MIZ.
iii) These molecules behaved as mixed-type inhibitors by decreasing both anodic and cathodic reactions.

iv) The result obtained by gravimetric analysis agrees with the result obtained by electrochemical studies and SEM.

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