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# Electrochemical and Surface Investigation of the Use of Expired Linezolid as an Anti-corrosive Material for Mild Steel in 1 M HCl

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**ABSTRACT**

The aim of this study is to investigate the corrosion inhibition efficiency of expired Linezolid (LIN) on mild steel (MS) in 1 M HCl at 303 K using experimental techniques such as electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PDP), and Scanning Electron Microscopy (SEM). Results show that the LIN is a good inhibitor and inhibition efficiency (IE %) reach 90.2% for EIS and 93.2% for PDP at an optimum concentration of 2.5 mM. EIS measurements revealed a charge transfer-controlled corrosion mechanism and the formation of a thick double layer on the steel surface. Polarization curves show that the addition of inhibitors to the corrosive media dramatically changed the anodic Tafel constants (βa) and cathodic Tafel constants (βc), indicating a mixed type nature. Scanning electron microscopy analyses affirmed the formation of a protective film on mild steel surfaces.

***Keywords*:** Linezolid, mild steel, potentiodynamic polarization, inhibition efficiency, mixed-type inhibitor, SEM.

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## 1. INTRODUCTION

The corrosion of metals is a common occurrence during metal processing, transportation, and storage. The corrosion products formed on degrading metal surfaces have become deadly contaminants in pharmaceutical, dye, and packaged goods industries and, in the long run, jeopardize the health of the consumers of these product [1]. Preventing corrosion using conventional methods typically involves using hazardous substances, raising worries about their impact on both the environment and human health [2-4]. Alternative ways to prevent corrosion have been explored by researchers to address these challenges, which are both effective and environmentally friendly, and one of the most effective technical methods is by using non-toxic organic corrosion inhibitors [5–7]. Several studies on corrosion inhibition have been performed, including synthetic (organic and non-organic) inhibitors [8-10] and natural products inhibitors [11, 12]. Generally, organic substances form a protective barrier at the metal/environment interface to limit corrosion [13-15].

The applicability of pharmaceutical compounds as eco-friendly corrosion inhibitors for metals in acidic medium has been recognized for a long time. The choice of some drugs used as corrosion inhibitors is based on the following: (a) drugs are reportedly environmentally friendly and important in biological reactions, (b) drug molecules contain oxygen, nitrogen, and sulphur as active centers, and (c) drugs can be easily produced and purified [16, 17]. One of the studies on the use of expired drugs as corrosion inhibitor was carried out by Hameed in 2011, where expired ranitidine was used as corrosion inhibitor for aluminium in hydrochloric acid environment [18]. The inhibition action of these drugs was attributed to blocking the surface via formation of insoluble complexes on the metal surface.

Linezolid is a synthetic antibiotic belonging to a new class of antimicrobials called the oxazolidinones. It works by stopping the growth of bacteria. Linezolid disrupts bacterial growth by inhibiting the initiation process of protein synthesis, a mechanism of action that is unique to this class of drugs. The purpose of this research is to investigate the inhibition properties of expired Linezolid (LIN) drug on the dissolution of mild steel in 1 M HCl using electrochemical methods and Scanning electron microscopy analyses. The chemical structure of Linezolid is shown in Fig. 1.

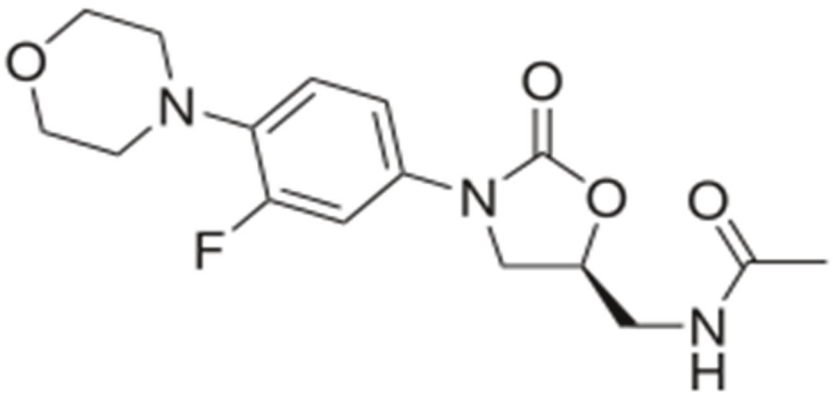



**Figure 1.** Chemical structure of LIN; molar mass = 337.351 g·mol$^{-1}$, formula = $C_{16}H_{20}FN_3O_4$

## 2. MATERIALS AND METHODS

### 2.1. Materials and Electrolyte Preparation

Mild steel (MS) specimens with the following composition (weight %): 0.370 C, 0.230 Si, 0.680 Mn, 0.016 S, 0.077 Cr, 0.011 Ti, 0.059 Ni, 0.009 Co, 0.160 Cu, and balance Fe were used in this investigation. The steel was mechanically cut to coupons of dimension, 2 cm x 4 cm. The steel samples were abraded using silicon carbide (SiC) abrasive paper with grit sizes ranging from 180 to 1200. The samples were then polished, rinsed with distilled water, allowed to air dry at room temperature, and stored under vacuum in a desiccator. The test solution (1 M HCl) was prepared using analytical grade 37% HCl and bi-distilled water. The inhibitor (expired Linezolid) concentration range is between 1.0 mM and 2.5 mM. All solutions were made with bi-distilled water.

### 2.2. Electrochemical Measurements

To measure the corrosion open circuit potential, all electrochemical measurements, including electrochemical impedance spectra and potentiometric polarization curves, were made using a standard three-electrode system, with saturated calomel electrode (SCE) as a reference electrode, platinum gauze as an auxiliary electrode, mild steel electrode as a working electrode, and all potentials referenced to the saturated calomel electrode. All experiments were carried out at a constant temperature of 303 K. Before the start of each electrochemical investigation, for a 30 minute period, the MS electrode (exposing a surface area of 0.20 $cm^2$) was submerged in the electrolytes to provide a constant open circuit potential (OCP). EIS measurements were carried out by applying an AC signal with an amplitude of 10 mV, covering a frequency range from 100 kHz to 10 mHz. Potentiodynamic polarization tests were performed from −250 to +250 mV, cathodic to anodic potential against the OCP at a scan rate of 1 $mV \cdot s^{-1}$. Each experiment was repeated three times to ensure data reproducibility.

### 2.3. Surface Investigation

Scanning electron microscopy (SEM) on a JEOL 5300 microscope with a 5 kV was employed to examine the MS in the absence and presence of the expired Linezolid inhibitor. Pre-treated mild steel specimens were immersed for 6 h in 1 M HCl solution with and without 2.5 mM LIN. The specimens were then removed and cleaned with double distilled water, dried in warm air and submitted for SEM analysis.

## 3. RESULTS AND DISCUSSION

### 3.1. Potentiodynamic Polarization Technique

Potentiodynamic polarization curves were recorded for mild steel in the aggressive acid environmrnt in the absence and presence of various concentrations of LIN to gain insight into the corrosion kinetics of the anodic oxidative metallic dissolution and cathodic reductive hydrogen evolution. Figure 1 shows the PDP curves without and with different concentrations of the inhibitor in 1 M HCl solution at a temperature of 303 K. The linear Tafel segments of the anodic and cathodic polarization curves were extrapolated to the corrosion potential $E_{corr}$ to obtain electrochemical kinetic parameters including the corrosion current density ($i_{corr}$), anodic (βa) and cathodic (βc) Tafel slopes.

The percentage inhibition efficiency was calculated by using the equation:

$$\%IE_{PDP} = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \quad (1)$$

where $i^0_{corr}$ and $i_{corr}$ are the corrosion current densities in the absence and presence of the LIN, respectively.

The values of polarization parameters are as represented in Table 1. Figure 1 and Table 1 show that both the rate of cathodic and anodic reactions are reduced as the concentrations of inhibitor increased by reducing the $i_{corr}$ on both sides of the polarization curves [19, 20]. The values of cathodic Tafel lines, βc, as shown in Table 1 reveal a slight change with increasing inhibitor concentration, indicating the influence of the LIN on the kinetics of hydrogen evolution. This may probably be due to a diffusion or barrier effect. The values of the slopes of the anodic Tafel lines, βa, was noticeably changed which proposes the role of inhibitor molecules adsorption on the active anodic sites on the iron dissolution mechanism. It is evident from the results (Table 1) that the maximum shift in the $E_{corr}$ in presence of the inhibitor relative to the blank acid is 14.9 mV observed at 0.5 and 2.5 mM of LIN. An inhibitor can be classified as a cathodic or anodic inhibitor only if the displacement in $E_{corr}$ is greater than 85 mV; otherwise, it is a mixed-type inhibitor [21–24]. The slight shift in $E_{corr}$ in the present study implies that the studied inhibitor is a mixed-type inhibitor.

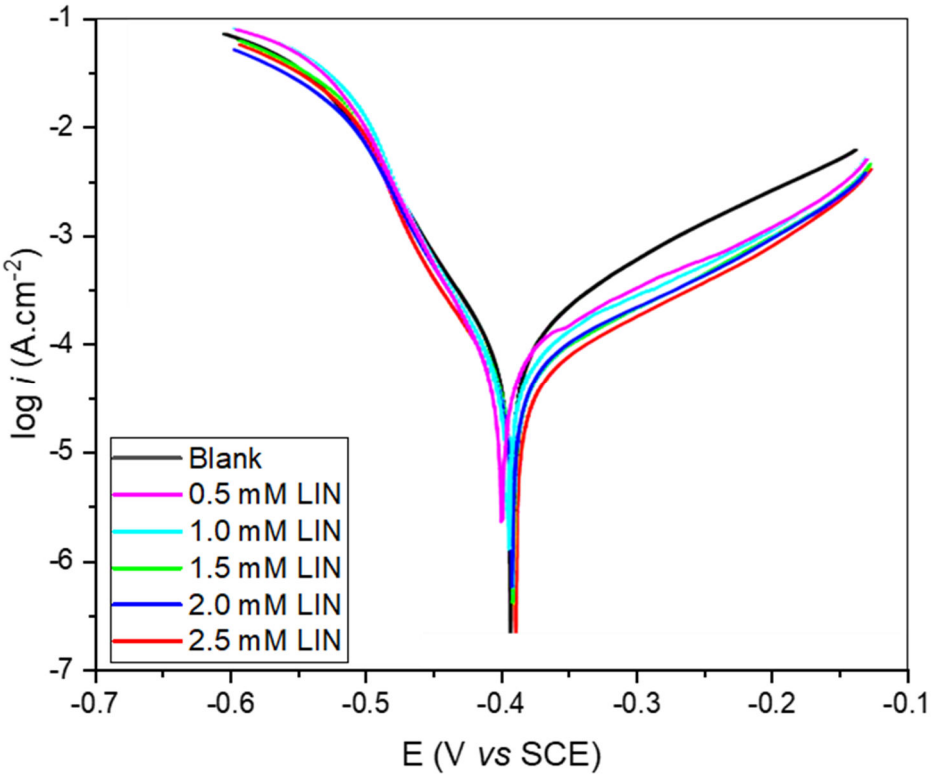



**Figure 1.** PDP curves for mild steel corrosion in 1 M HCl solution in the absence and presence of different concentrations of LIN.

**Table 1.** Polarization parameters for mild steel in 1 M HCl without and with different concentrations of LIN at 303 K.

| Conc. (mM) | $E_{corr}$ (mV/SCE) | $i_{corr}$ (μA cm$^{-2}$) | $\beta_a$ (mV dec$^{-1}$) | $-\beta_c$ (mV dec$^{-1}$) | $IE_{PDP}$ (%) |
|---|---|---|---|---|---|
| Blank | -395.3 | 805.1 | 185.2 | 161.8 | - |
| 0.5 | -403.8 | 306.9 | 103.6 | 96.4 | 61.9 |
| 1.0 | -394.1 | 218.4 | 82.5 | 80.5 | 73.4 |
| 1.5 | -390.6 | 102.1 | 78.6 | 76.5 | 87.3 |
| 2.0 | 391.0 | 86.9 | 75.0 | 73.2 | 89.2 |
| 2.5 | 388.9 | 54.5 | 71.8 | 69.3 | 93.2 |

### 3.2. Electrochemical Impedance Spectroscopy (EIS)

The inhibition process of expired LIN was also investigated by the EIS. The impedance measurements presented in the Nyquist format for mild steel immersed in 1 M HCl with and without inhibitor are shown in Figure 2 and the data were fitted to an equivalent circuit, as illustrated in Fig. 3. The the outcomes are detailed in Table 2, providing information on solution resistance ($R_s$), charge-transfer resistance ($R_{ct}$), and capacitance of the double layer ($C_{dl}$). Additionally, the percentage inhibition efficiency ($\%IE_{EIS}$), derived from EIS data in terms of inhibited ($R_{ct}^{in}$) and uninhibited ($R_{ct}^{un}$) charge transfer resistance, is calculated using Eq. (2) [25, 26].

$$\%IE_{EIS} = \frac{R_{ct}^{in} - R_{ct}^{un}}{R_{ct}^{in}} \times 100 \qquad (2)$$

There are insignificant changes in the appearance of Nyquist plots of the uninhibited and inhibited MS, as shown in Fig. 2, indicating that the mechanism of corrosion was not altered in the presence of LIN [27-29]. Table 2 demonstrates that $R_s$ values were quite low as compared to the $R_{ct}$ values, which demonstrated that the corrosion mechanism was primarily regulated by the transfer of electrons between the MS and the defensive layer and the resistance of the specimen to oxidation during the application of an external potential. It is easy to notice that Nyquist curves present a single capacitive loop over at frequency range from 10 mHz to 100 kHz, which is usually related to charge transfer phenomenon [30-32]. The capacitive plots are semicircles (imperfect circle), this is accredited to frequency spreading as a consequence of inhomogeneous behavior of electrode surface [33-36]. Meanwhile, the size of these loops increases with the rise of LIN concentration, which signifies that LIN was adsorbed on the mild steel surface, and the area exposed to the corrosive 1 M HCl solution was reduced. From the data presented in Table 2, it is clear that introduction of LIN lead to an increase in the $R_{ct}$ values at all concentrations in 1 M HCl, which validated that the inhibitor's adsorption layer had greater corrosion resistance. In addition, the reduction in $C_{dl}$ value was seen because of the enhancement in the width of the double layer or drop in the local dielectric constant as a result of inhibitor adsorption on the MS surface. This is steady with the Helmholtz model, as shown by the subsequent equation [37,38]:

$$C_{dl} = \frac{\varepsilon\varepsilon_0}{\delta} S \qquad (3)$$

where the protective layer's dielectric constant and the permittivity of free space (8.854 x $10^{-14}$ F $cm^{-1}$) is denoted by $\varepsilon$ and $\varepsilon_0$, $\delta$ denotes the protective layer's width, and $S$ represents the electrode's surface area. Table 4 also demonstrates that the n values are higher in the presence of LIN compared to the blank, indicating that the presence of a the inhibitor reduces surface inhomogeneity. This phenomenon is shown by the formation of a protective film on the surface of the steel. However, due to the adsorption of LIN molecules, n values change as inhibitor concentration increases. This suggests that LIN molecules interact with steel morphology, gradually replacing $H_2O$ molecules at the steel/solution interface with LIN compounds. These results confirm the good inhibition effect of LIN on mild steel in acidic solution.

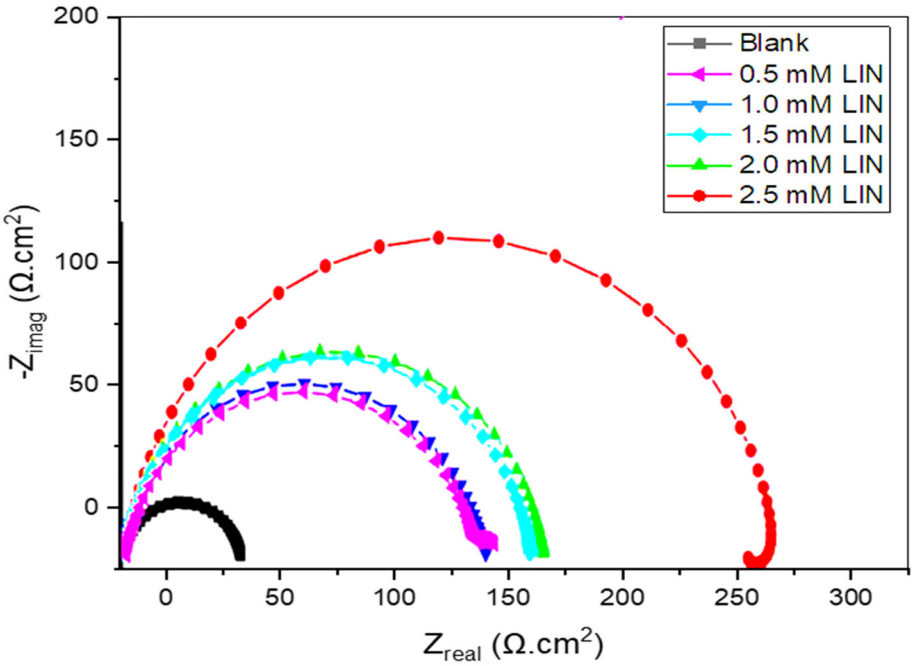
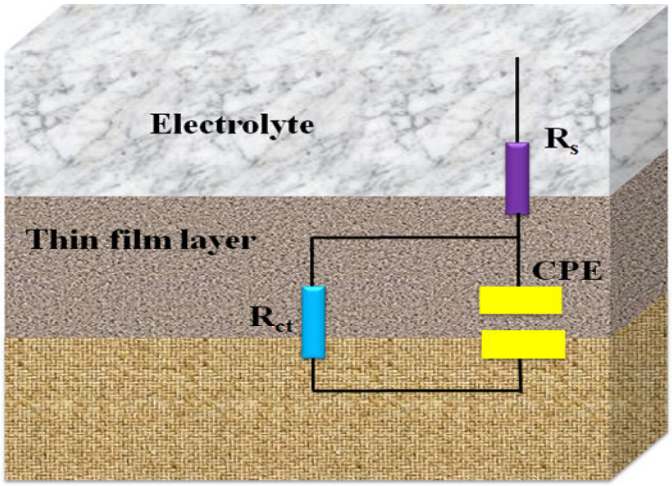



**Figure 2.** Nyquist plots for the MS at 303 K and 1 M HCl without and with different LIN concentrations.




$R_s$ = solution resistance
$R_{ct}$ = charge transfer resistance
CPE = Constant phase element

**Figure 3**. Equivalent circuit used in modeling impedance results.

**Table 2.** EIS parameters obtained for mild steel in 1 M HCl without and with different LIN concentrations at 303 K

| Conc. (mM) | $R_s$ (Ω cm$^2$) | $R_{ct}$ (Ω cm$^2$) | $C_{dl}$ (μF cm$^{-2}$) | $n$ | $IE_{EIS}$ (%) |
|---|---|---|---|---|---|
| Blank | 2.84 | 30.6 | 163.2 | 0.879 | - |
| 0.5 | 2.07 | 92.8 | 105.2 | 0.921 | 67.0 |
| 1.0 | 2.43 | 123.0 | 67.0 | 0.935 | 75.1 |
| 1.5 | 2.25 | 186.9 | 38.1 | 0.958 | 83.6 |
| 2.0 | 2.53 | 225.4 | 15.6 | 0.974 | 86.4 |
| 2.5 | 2.14 | 312.5 | 5.9 | 0.983 | 90.2 |

### 3.3. Surface Morphological Analysis

The surface microstructure of the mild steel without and with 2.5 mM LIN for 6 h was evaluated by SEM, and the obtained micrographs are presented in Figure 4. As seen in Fig. 4a, the SEM image revealed surface damage owing to the aggressive attack of 1 M HCl solution that caused the formation of flakes of corrosion products [39, 40]. However, the surface roughness reduced significantly after the introduction of LIN to the acid environments. This decrease is ascribed to the inhibitor film's creation, which acts as a barrier to prevent corrosion and lessens the sample's surface roughness and damage.

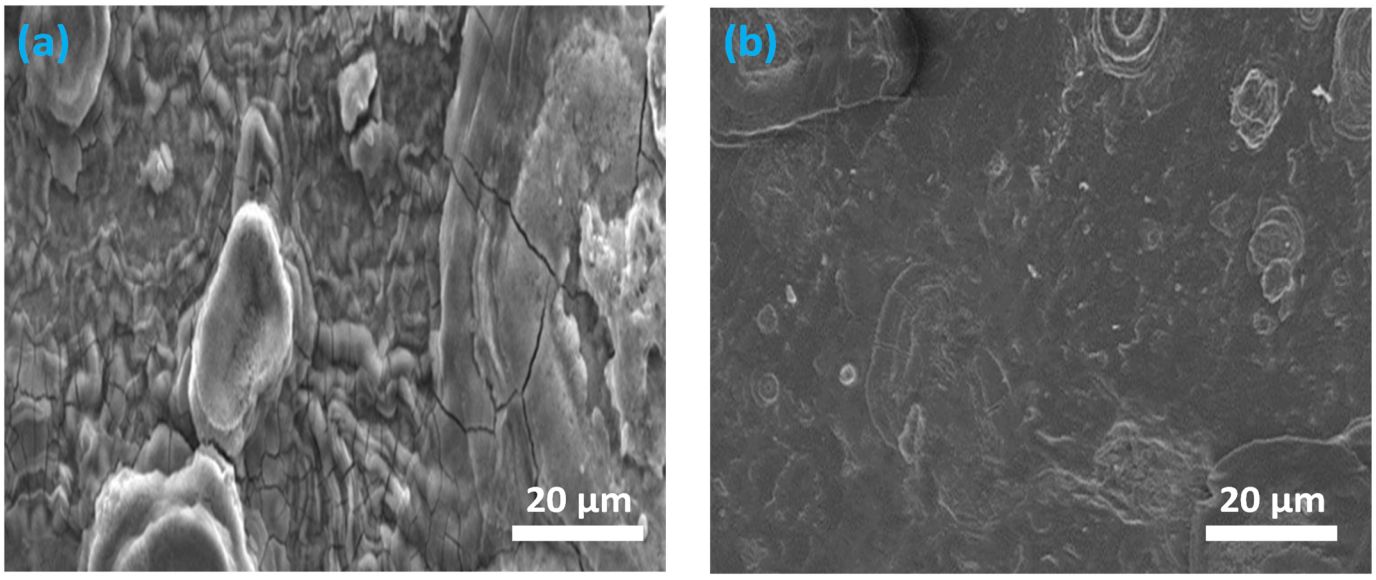



**Figure 4.** Scanning electron micrographs of a mild steel surface immersed for 6 h in (a) blank 1 M HCl and (b) presence of 2.5 mM LIN.

## 4. CONCLUSIONS

Electrochemical techniques demonstrated that expired Linezolid (LIN) acted as a good corrosion inhibitor for mild steel in 1 M HCl, and the inhibition increased as the concentration of LIN increased. Potentiodynamic polarization study suggested that LIN is a mixed-type corrosion inhibitor for mild steel in 1 M HCl, affecting both the anodic metal dissolution reaction and the cathodic hydrogen evolution reaction. EIS results showed that the $R_{ct}$ values increased and the $C_{dl}$ values decreased with rise in the concentration of the inhibitor, indicating that LIN protects the mild steel from corrosion by the formation of a protective film at the metal surface. The surface microstructure evaluated by SEM revealed that the surface morphology in the presence of LIN was pretty smooth, and the cavities were clearly closed compared to the morphology in the blank solution, due to the protective effect of LIN.

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