# Using expired pharmaceutical Clotrimazole as a corrosion inhibitor for stainless steel in acidic media

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## Abstract

In this work, the effect of expired/unused Clotrimazole drug (ECD) on the corrosion tendency of stainless steel 316 (SS316) in acidic media (0.1 M HCl) at temperatures ranging from 298 to 328 K has been studied. The potentiodynamic polarization (PDP) technique was used to investigate the corrosion inhibition efficiency (*IE*%) of ECD adsorption on SS316 at various concentrations. Atomic Force Microscopy (AFM) technique was used to examine the surface morphology of corroded SS316 with and without inhibition of the acidic solution by ECD. Fourier Transform infrared spectroscopy (FTIR) was used to confirm the ECD adsorption on the surface of SS316. The results demonstrated that the inhibition efficiency rose as the ECD concentration increased, while it decreased as the temperature increased. The inhibition performance reached 99% with 100 ppm at 298 K. The corroded SS316 surface was studied by AFM to confirm the adsorption of ECD on the metal surface. Corrosion current densities at various temperatures were utilized to estimate the apparent activation energy ($E_a$), activation enthalpy ($\Delta H^*$), and activation entropy ($\Delta S^*$). The apparent activation energy increased upon addition of the inhibitor from 19.99 kJ·mol$^{-1}$ to 70.39 kJ·mol$^{-1}$ at 100 ppm of ECD, indicating its effectiveness in inhibiting the corrosive media. The $\Delta H^*$ values were positive and increased upon inhibition of the corrosive media by ECD.

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## 1. Introduction

Stainless steels are commonly employed in the pharmaceutical industry owing to their exceptional corrosion resistance and favorable mechanical properties. These properties are considered crucial since manufactured pharmaceuticals need to adhere to strict standards for purity and quality. Proper selection of a stainless steel grade or protective measures can prevent corrosion issues that may negatively impact the overall production process [1]. Type 304 is an excellent general-purpose alloy for pharmaceutical applications where pitting corrosion is not an issue [2]. Type 316 stainless steel is comparable to type 304, except that it contains 2 to 4% more nickel (Ni), 2% less chromium (Cr), and 2 to 3% molybdenum (Mo) [3].

In the pharmaceutical industry, distinct phases may be distinguished, namely the processing of raw materials, medication manufacture, and product packaging. In certain cases, the production of pharmaceuticals requires the use of equipment that is subjected to various external factors, including high levels of chloride ions, materials containing high amounts of protein, and exposure to organic acids [4, 5]. There are several factors that can contribute to the corrosion of stainless steel in pharmaceutical reactors. These factors include the type of substance being processed, the cleaning method used, the temperature at which the reactor operates, the pH level of the environment, the presence of chlorides, sulfates, or other ions, and the level of microbiological activity [1]. In pharmaceutical reactors, the corrosion processes of stainless steel might include crevice, pitting and/or generalized corrosion as well as cracking corrosion [1, 6, 7].

One method employed to decrease metal corrosion in different acidic media was the use of organic inhibitors [8, 9]. The most effective organic inhibitors for active materials like iron, zinc, magnesium, and copper were compounds containing heteroatoms such as nitrogen (N), oxygen (O), and sulfur (S) [10–13].

A variety of organic compounds have been extensively studied as corrosion inhibitors. However, the majority of these organic inhibitors are both expensive and pose risks to human health, and the harmful nature of these inhibitors limits their practical use. Traditional corrosion inhibitors often have detrimental effects on the environment, highlighting the need for environmentally friendly alternatives [14–16]. Several drugs, such as Ibuprofen, Metformin, Ciprofloxacin, Paracetamol, Aspirin, and various others, have been examined for their potential as corrosion inhibitors for different types of metals [17–20]. Using expired or unused drugs as corrosion inhibitors can be a way of recycling them and reducing their environmental footprint [14, 17, 19]. Clotrimazole [21–23] has been identified as an effective inhibitor in decreasing the corrosion of zinc, aluminum and carbon steel metal surfaces. These pharmaceutical materials are not used as corrosion inhibitors for stainless steel 316, especially on the surface of the stainless steel used in pharmaceutical reactors. The current study introduces a technique for utilizing expired or unused pharmaceutical Clotrimazole drug (ECD) as a corrosion inhibitor for metals in various media.

## 2. Experimental Work

### *2.1. Stainless steel specimens*

The stainless steel used in this study was provided by the pharmaceutical reactor (Middle East Laboratories Co. Ltd., Baghdad, Iraq). It is typically composed of 16–18% Cr, 10–14% Ni, 2–3% Mo and a minor amount of carbon. Prior to its usage, the stainless-steel alloys (type 316) (SS316) were cut into a circular shape (from the old reactor vessel made by stainless steel 316) with dimensions of 25 mm diameter and 0.5 mm thickness. Subsequently, the stainless steel was polished using silica paper of varying grades, starting from the roughest (600 mesh grit) to the finest (2000 mesh grit). Following the polishing process, the

stainless steel underwent a double rinse with tap water and distilled water, followed by ethanol and acetone. Finally, it was dried using a heat gun.

### *2.2. Corrosion test*

Electrochemical tests were conducted with a potentiostat to determine linear polarization (Tafel) slopes and open circuit potential (OCP), and the data were collected using Mlab200 software. The electrochemical cell was composed of three electrodes: a platinum rod counter electrode, an Ag/AgCl reference electrode, and an SS316 working electrode.

### *2.3. Corrosive media and inhibitors*

The ECD (active ingredient) was provided by Middle East Laboratories Co. Ltd., Baghdad, Iraq. It is colorless, odorless and solid crystal with melting point ~147°C and molecular weight ~344.84 $g \cdot mol^{-1}$. The chemical structure of the ECD is depicted in Figure 1. Anodic and cathodic polarization studies of SS316 were executed under potentiostatic conditions in a 0.1 M hydrochloric acid solution and at temperatures ranging from 298–328 K. The electrochemical tests were carried out in the presence and absence of different concentrations of ECD (25, 50 and 100) ppm as a Clotrimazole drug (corrosion inhibitor).

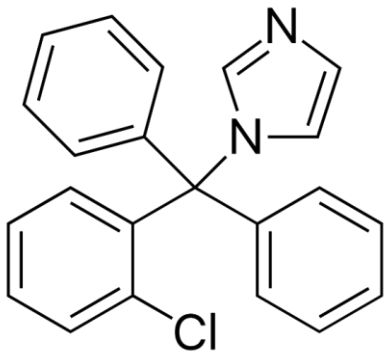


**Figure 1.** Structure of Clotrimazole.

### *2.4. Surface morphology studies*

AFM was employed to analyze the surface morphology of SS316 before and after corrosion, both in the corrosive media in the presence and absence of ECD inhibitor. The CoreAFM model was used for AFM.

### *2.5. Fourier-transform infrared spectroscopy (FT-IR) analysis*

The Shimadzu FTIR-8400 Spectrometer was utilized to analyze the IR spectra within the 4000–400 $cm^{-1}$ IR range. This was done in order to gain a deeper understanding of the corrosion inhibition mechanism and to compare the pure ECD with the adsorption of Clotrimazole on the surface of SS316.

## 3. Results and Discussion

### *3.1. Linear polarization studies*

Figure 2 illustrates the cathodic and anodic polarization Tafel curves for the dissolution of SS316 in 0.1 M HCl with varying concentrations of ECD (25, 50, and 100 ppm) at a temperature range of 298–328 K. The presence of ECD affected both cathodic and anodic Tafel slopes, resulting in a shift towards lower corrosion current ($i_{corr}$) values. This shift indicates the mixed nature of the inhibitors after inhibiting the corrosive media solution (0.1 M HCl) [24]. The anodic curve shape indicates the potential for a passive film to form on the surface of SS316.

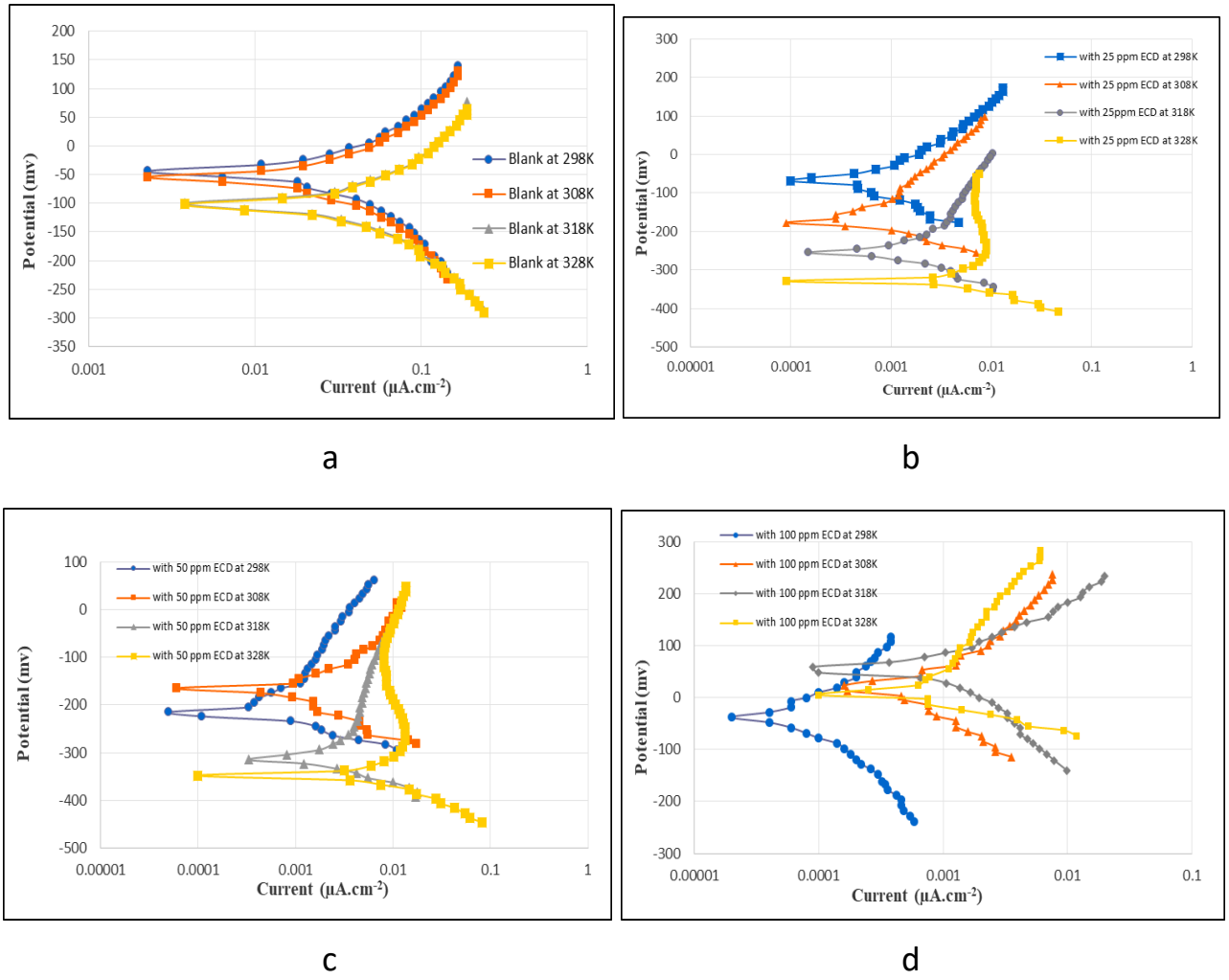


**Figure 2.** Tafel Polarization curves for: a) 0.1 M HCl without ECD, b) 0.1 M HCl with 25 ppm ECD, c) 0.1 M HCl with 50 ppm ECD and d) 0.1 M HCl with 100 ppm ECD.

Upon careful examination of Table 1, it becomes evident that the rise in temperature from 298 to 328 K leads to an increase in $i_{corr}$. Conversely, when the corrosive media is inhibited by ECD, the $i_{corr}$ values exhibit a decrease across the entire temperature range.

The inhibition efficiency (*IE*%) for the inhibitor under study is determined using Equation (1):

$$IE\% = \frac{(i_{corr})_{un} - (i_{corr})_{i}}{(i_{corr})_{un}} \cdot 100 \quad (1)$$

where $(i_{corr})_{un}$ and $(i_{corr})_{i}$ are the uninhibited and inhibited corrosion current densities, respectively.

Upon analyzing the results from the HCl solution with inhibitor (Table 1) and comparing them to the data from the uninhibited acidic solution, a notable decrease in $i_{corr}$ values can be observed. This decrease persists as the concentration of ECD increases, leading to an increase in *IE*%. This suggests that the ECD molecule is adsorbed onto the metal surface, forming a non-conductive layer that protects the SS316 from dissolution in the corrosive media.

**Table 1.** The obtained parameters from liner polarization for SS316 in 0.1 M HCl in the presence and absence of different ECD concentrations at various temperatures.

| **ECD ppm** | ***T* K** | ***E*corr mV** | ***i*corr μA·cm⁻²** | ***IE* %** | ***R*p Ω·cm²** |
|---|---|---|---|---|---|
| Blank | 298 | –44.3 | 16.03 | – | – |
| | 308 | –62.0 | 27.33 | – | – |
| | 318 | –99.5 | 31.08 | – | – |
| | 328 | –112.8 | 34.53 | – | – |
| 25 ppm | 298 | –67.4 | 0.35 | 97.82 | 65494.1 |
| | 308 | –175.7 | 0.56 | 97.95 | 43470.9 |
| | 318 | –257.0 | 1.26 | 95.95 | 22800.2 |
| | 328 | –330.5 | 4.89 | 85.84 | 5582.4 |
| 50 ppm | 298 | –215.6 | 0.44 | 97.26 | 41327.2 |
| | 308 | –164.8 | 0.626 | 97.71 | 26829.5 |
| | 318 | –316.2 | 1.12 | 96.40 | 13573.4 |
| | 328 | –347.3 | 3.66 | 89.40 | 4747.6 |
| 100 ppm | 298 | –39.7 | 0.12 | 99.25 | 216600 |
| | 308 | +17.5 | 0.374 | 98.63 | 64748.8 |
| | 318 | +49.5 | 0.621 | 98.00 | 36840.5 |
| | 328 | +8.4 | 0.916 | 97.35 | 17710.1 |

### *3.2. Thermodynamic activation studies*

The relation between temperature and corrosion rate ($i_{corr}$) is presented by the Arrhenius equation, Equation (2) [25]

$$\log i_{corr} = \log A - \frac{E_a^*}{2.303RT} \quad (2)$$

where $E_a^*$ is the apparent activation energy, $R$ is the universal constant of gases (8.314 J·K$^1$·mol$^{-1}$), $T$ is the temperature in Kelvin (K), and $A$ is the Arrhenius factor. The value of $E_a^*$ was estimated from the slope of a linear plot ($\log i_{corr}$ *vs.* $1/T$) [$E_a^*$=–Slope×2.303$R$], Figure (3).

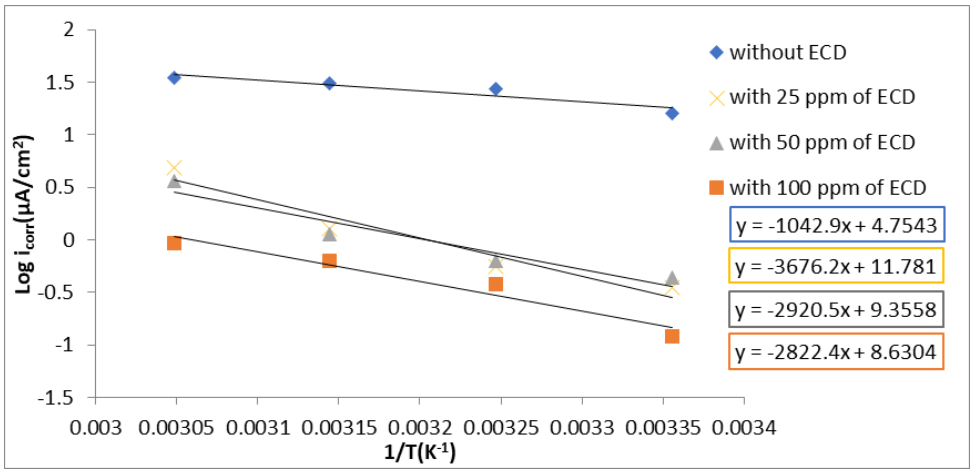


**Figure 3.** Arrhenius plot of the corrosion rate for SS316 in 0.1 M HCl in the presence of different concentrations of ECD inhibitor.

The apparent activation energy ($E_a^*$) calculated using Equation (2) and included in Table (2) shows that the $E_a^*$ values for SS316 in 0.1 M HCl with ECD are higher compared to the uninhibited solution. The $E_a^*$ data (Table 2) consistently decrease as the Clotrimazole concentration increases, suggesting a chemisorption nature of interaction between the inhibitor and the SS316 surface.

**Table 2.** Kinetic and thermodynamic parameters of SS316 in 0.1 M HCl in the presence and absence of Clotrimazole.

| Conc. of ECD | $\Delta H^*$ kJ·mol$^{-1}$ | $-\Delta S^*$ J·mol$^{-1}$·K$^{-1}$ | $E_a^*$ kJ·mol$^{-1}$ | $A$ Molecules·cm$^{-2}$·s$^{-1}$ |
|---|---|---|---|---|
| None | 17.37 | 162.62 | 19.99 | 3.42E+28 |
| 25 ppm | 67.79 | 28.08 | 70.39 | 3.63E+35 |
| 50 ppm | 53.32 | 74.51 | 55.92 | 1.37E+33 |
| 100 ppm | 51.44 | 88.40 | 54.04 | 2.57E+32 |

The estimation of thermodynamic parameters, including adsorption entropy ($\Delta H^*$) and adsorption enthalpy ($\Delta S^*$), was conducted using equation (3) [22] derived from the transition state equation,

$$\log \frac{i_{corr}}{T} = \log \frac{R}{Nh} + \frac{\Delta S^*}{2.303R} - \frac{\Delta H^*}{2.303RT} \quad (3)$$

As shown in Figure 4 and Table 2, the $\Delta H^*$ and $\Delta S^*$ values were obtained using the slope $\left(\frac{\Delta H^*}{2.303R}\right)$ and intercept $\left(\log \frac{R}{Nh} + \frac{\Delta S^*}{2.303R}\right)$ of the linear plots, respectively. The $\Delta H^*$ values were positive and increased after inhibiting the corrosive media by ECD, which suggests that dissolution of SS316 becomes more difficult than SS316 in 0.1 M HCl without inhibitor [26]. The $E_a^*$ and $\Delta H^*$ values decreased with an increase in the concentration of inhibitor in 0.1 M HCl. The rise in the adsorption entropy values when an ECD inhibitor is present, as opposed to the uninhibited acid solution, indicates that the activation complex in the rate-determining step involves association rather than dissociation. This suggests that disorder decreases as one moves from reactants to activated complexes [27].

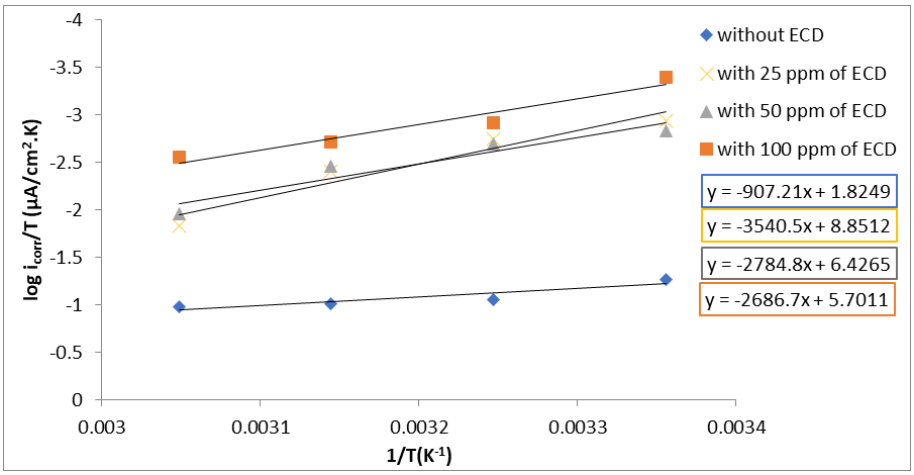


**Figure 4.** Transition-state plot of the corrosion rate for SS316 in 0.1 M HCl in the presence of different concentrations of ECD inhibitor.

### *3.3. AFM analysis*

One of the useful techniques to study surface morphology and investigate the effect of inhibitors used in corrosion protection is AFM, with contact mode. Figure 5a shows the 2D and 3D images of polished SS316, and Figures 5b and 5c show the 2D and 3D images of corroded and inhibited SS316 in 0.1 M HCl, respectively. The images depict the surface roughness of SS316 when immersed in 0.1 M HCl, which is significantly high at 26.03 nm, in comparison to the polished SS316 surface roughness of 2.423 nm. However, when the acidic corrosive media was inhibited by 100 ppm ECD, the surface roughness was smoothed to 9.829 nm. To further analyze the surface, the distribution of particles on the SS316 surface

was examined, as shown in Figure 6a and b. It was observed that the coverage increased from 30.95% to 39.78% while the number of particles decreased from 167 to 123 after inhibition with 100 ppm ECD, which indicates the formation of a thin layer on the steel surface.

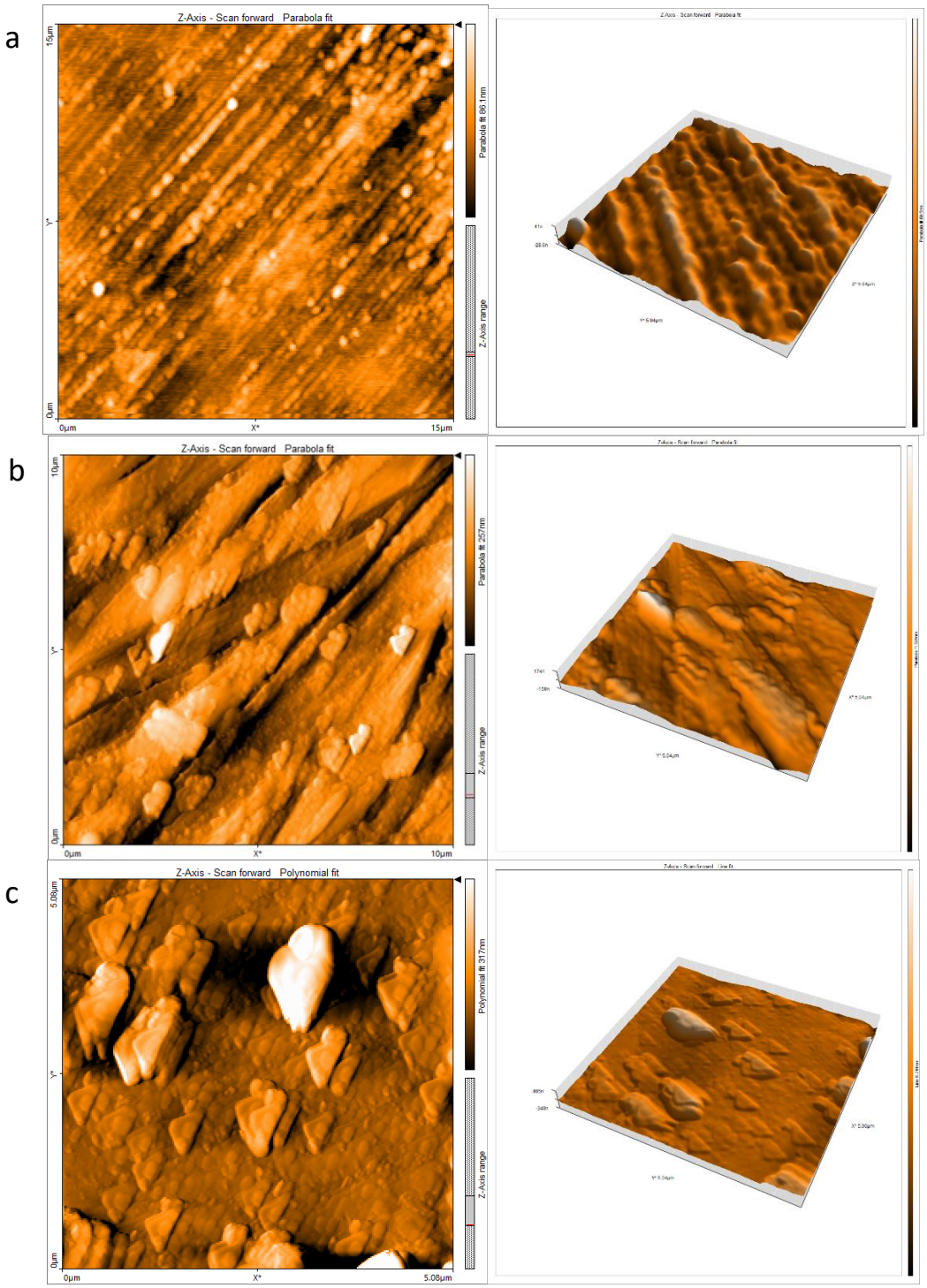


**Figure 5.** AFM images of the surface of (a) Polished SS316, (b) SS316 immersed in 0.1 M HCl, and (c) SS316 immersed in 0.1 M HCl with 100 ppm ECD inhibitor.

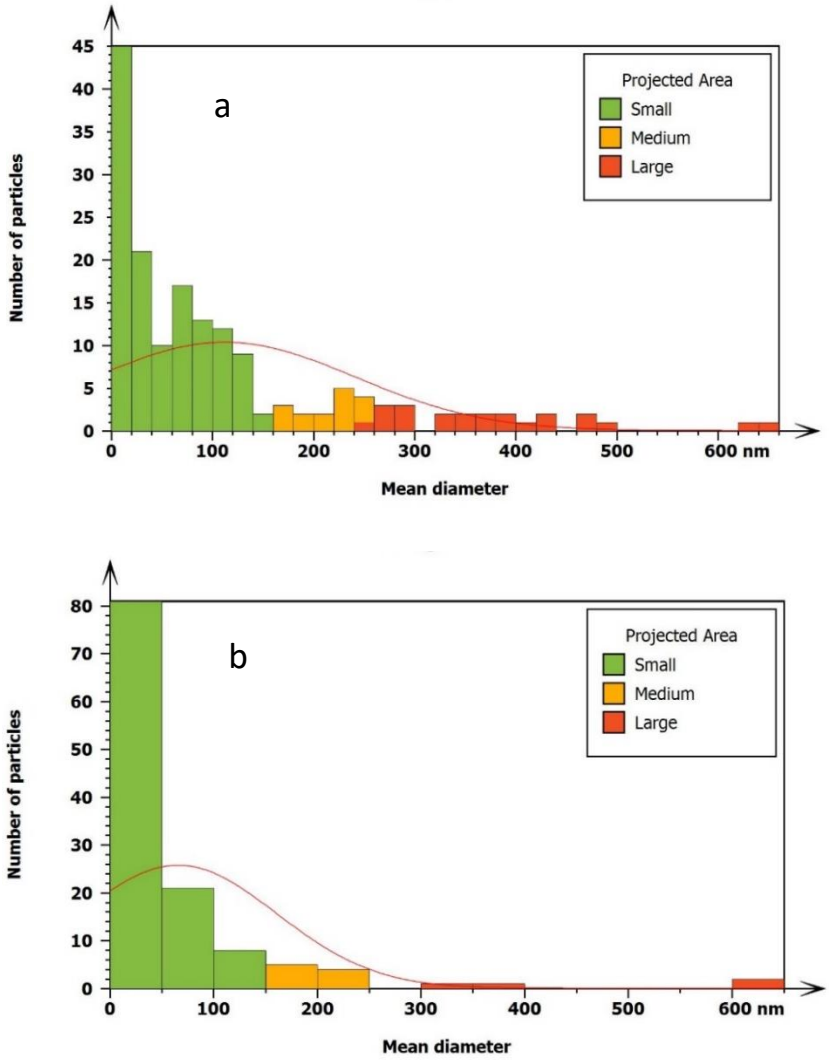


**Figure 6.** Particle analysis for (a) SS316 immersed in 0.1 M HCl, and (b) SS316 immersed in 0.1 M HCl with 100 ppm ECD inhibitor.

### *3.4. FTIR studies*

Many researchers used FTIR spectrometer to estimate and identify the functional groups present in Clotrimazole and compared the findings with a spectrum of Clotrimazole adsorbed on the surface of SS316 to understand the interaction between the metal and inhibitor, which resulted in inhibition. Figure (7a) shows the FTIR spectrum of pure Clotrimazole. One peak was appeared at 3062.75 $cm^{-1}$ [28], which was assigned to the stretching vibration of the C–H aromatic. In addition to appear C=N stretching of Clotrimazole which was assigned at 1639.38 $cm^{-1}$ band [29]. Also the absorption at 1589.23 $cm^{-1}$ could be the stretching of C=C group, the stretching of C–N at 1209.28 $cm^{-1}$, aromatic C–H bending at 761 $cm^{-1}$ [30] and stretching of C–Cl at 748 $cm^{-1}$ were founded.

Figure (7b) shows the FTIR spectrum of the inhibitor adsorbed on SS316 after being immersed in 0.1 HCl solution inhibited by 100 ppm of Clotrimazole. It was noticed that the stretching of C–H aromatic was disappeared. While C=N stretch frequency shifted from

1639.38 $cm^{-1}$ to 1633.58 $cm^{-1}$, also the peak that was assigned to C=C stretch did not appear in the spectrum of thin film on SS316. Besides these, C–N stretch was disappeared and C–H bending almost disappears, furthermore, disappeared the stretch of C–Cl at 748 $cm^{-1}$. The results above indicate that the functional groups found (C=N, C=C, and C–Cl) included N, aligning with the standard structure of inhibitors.

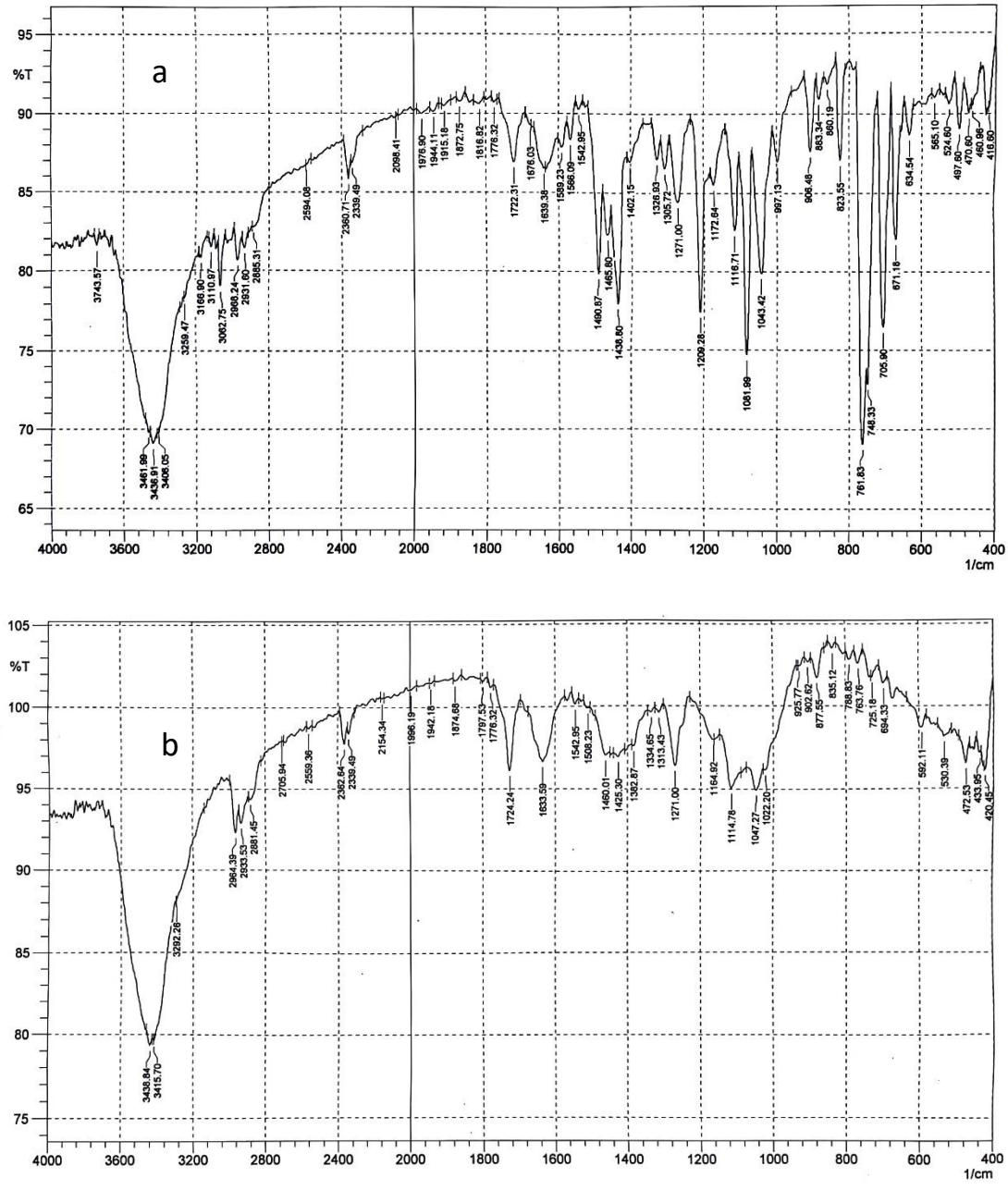


**Figure 7.** FTIR spectrum of a) Pure ECD b) Corrosion production of SS316 in the presence of 100 ppm ECD.

## Conclusions

The inhibition of SS316 corrosion in acidic media can be effectively achieved by using the ECD. The inhibition efficiency was found to be as high as 99.25% at a concentration of 100 ppm at temperature 298 K, and this is considered room temperature. Interestingly, the apparent activation energy increased after the addition of the inhibitor, indicating its effectiveness in inhibiting the corrosive media. Furthermore, it was observed that the activation energy decreased with an increase in the concentration of the inhibitor. The thermodynamic parameters suggested that the inhibition mechanism involved physisorption. Additionally, the surface roughness of SS316 decreased when Clotrimazole was added, resulting in a smoother and freer surface. This was confirmed by AFM, which showed a decrease in the adsorption of Clotrimazole on the surface.

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