Original Article

Potentiodynamic polarization studies of Cefadroxil and Dicloxacillin drugs on the corrosion susceptibility of aluminium AA6063 in 0.5 M nitric acid

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Abstract

The inhibition effectiveness of Cefadroxil (C) and Dicloxacillin (D) drugs on aluminium in 0.5 M nitric acid solution have been holistically studied using potentiodynamic polarization techniques, weight loss measurements, computational studies and structural characterization. The structural characterizations were carried with the aid of scanning electron microscope equipped with energy dispersive spectrometer (SEM/EDS), optical microscope (OPM) and XRD. Potentiodynamic polarization test revealed the corrosion protective nature and adsorbing ability of Cefadroxil and Dicloxacillin drugs on aluminium (Al). The mixed inhibitive characteristics of Cefadroxil and Dicloxacillin drugs were confirmed through the Tafel plot, which further established their predominant effect on the anodic reaction as a result of $E_{corr}$ value shift to more positive sides. The combined effect of Cefadroxil and Dicloxacillin drugs reduced the exchange in current density and corrosion rate drastically from $484 \mu A/cm^2$ to $199 \mu A/cm^2$ and $0.4502 mm/year$ to $0.2152 mm/year$ respectively. $44.4\%$ increase in microhardness was achieved and Inhibition efficiency of $58.9\%$ was accomplished.

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1. Introduction

Multi-industrial application and relevance of aluminium have necessitated the studies of its behaviour in a corrosive environment [1–4]. Research has shown that aluminium is the second most used metal for manufacturing and production in the world [5], exhibiting relatively good corrosion resistance compared to iron in different aggressive environment as a result of its ability to form a thin oxide film upon exposure [6,7]. Aluminium alloys are commonly employed in a marine environment where lighter density and superior mechanical...
attributes are needed [8]. Marine corrosion takes place amidst parts of machine and piping that are exposed to contaminated water which might be acidic, alkaline or saline in nature. Susceptibility of components can be continuous or sporadic. Ships, pipelines, marine structures, are prevalent instances of systems that encounter marine degradation [9]. In recent years, wider usage of aluminium and its alloy in acidic and sodium chloride solution have exposed their vulnerability to attack by localized corrosion [10-14]. Hence, protection of aluminium from corrosion is imminent.

One of the recent corrosion protection measures involves doping metals with inhibitive drugs. Organic and inorganic compounds have provided protection against the corrosion of metal; however, some of them are poisonous, extremely expensive and difficult to synthesis from natural sources [15-18]. These reasons have evoked the attraction for inhibitive drugs in recent time, making it one of the most shot out methods through which metals are protected against corrosion [19-23]. Apart from the eco-friendly nature of inhibitive drugs, they are also been found to be cost effective, highly efficient and easy to synthesis [24,25]. The protective efficiency of drug inhibitors is a function of their absorbability on the surface of metals, thereby forming thin film of protective layer against attack by corrosive species in the environment [26]. Although, a lot of drugs, including the expired ones have infinitesimally provide corrosion resistance to metals in an aggressive environment [27,28]. In view of this, inhibitive capability of Cefadroxil and Dicloxacillin drugs on aluminium alloy was examined in 0.5 M nitric acid solution via potentiodynamic polarization techniques, mass loss measurements, computational studies and microstructural characterization.

2. Experimental procedures

2.1. Sample preparation

The chemical composition of type AA-6063 aluminium alloy obtained commercially from the aluminium rolling mill in Kempton Park, South Africa was analyzed in Table 1. Rectangular aluminium specimens were mechanically cut to size of (15 × 15 × 2) mm was used for the studies. The surfaces of the specimens were mechanically polished with different grades (400, 600 and 1200 μm) of emery papers, rinsed quickly with distilled water and allowed to dry naturally. 1 g of Cefadroxil and 1 g of Dicloxacillin sodium monohydrate white powders were obtained from Sigma-Aldrich in South Africa. They were prepared in volume concentrations 1.5 ml per 100 ml of 0.5 M HNO₃ acid. Cefadroxil and Dicloxacillin were diluted with distilled water to 10 ml concentrated solution. The molecular formula of Cefadroxil is C₁₆H₁₇N₃O₅S and its molar mass is 363.39 g/mol. Molecular mass and molar mass of Dicloxacillin are C₁₉H₁₆Cl₂N₂NaO₅S·H₂O and 510.32 g/mol respectively. Molecular structure of Cefadroxil and Dicloxacillin are shown in Fig. 1.

![Molecular structure of Cefadroxil and Dicloxacillin](image)

**Fig. 1 – Molecular structure of Cefadroxil** [29] and **Dicloxacillin** [30] respectively.

### Table 1 – Chemical composition of aluminium alloy used (%w).

<table>
<thead>
<tr>
<th>Fe</th>
<th>Mn</th>
<th>Cu</th>
<th>Si</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.42</td>
<td>0.027</td>
<td>0.11</td>
<td>0.20</td>
<td>Balance</td>
</tr>
</tbody>
</table>

2.2. Microstructural test of inhibited samples

The surface adhesion and texture of the of the inhibitor on the aluminium alloy were characterized using energy dispersive spectroscopy (EDS) attached to scanning electron microscope (SEM), OPM and XRD.

2.3. Microhardness testing

Vickers microhardness measurements were carried out on the inhibited and uninhibited specimens using an Emco test durascan microhardness tester equipped with Ecos workflow ultra-modern software. This can be obtained from Eq. (1). The indenting load of 100 g was applied during a testing period of 15 s, after which it was removed. The samples surface was indented randomly at five different positions and the average was recorded.

$$HV = 1.854 \left( \frac{F}{d^2} \right)$$  

(1)

F, load in kgf, and d, mean of two diagonal in mm.
2.4. **Linear polarization resistance**

The corrosive environment of 0.5 M HNO₃ was simulated in a beaker. Aluminium alloy coupon acting as the working electrode was welded to wire and mounted on resin. Graphite rod was used as the counter electrode immersed in solution and silver chloride electrode (SCE) acting as reference electrode was placed on sample surface. Autolab PGSTAT 101 Metrohm potentiostat/galvanostat with NOVA software of version 2.1.2 was used with linear polarization (LR) resistance and the current was set to 10 mA (max) and 10 nA (min). LSV staircase parameter start potential of −1.5 V, step potential 0.001 m/s and stop potential of 1.5 V set for 60 min. This was repeated for about five times for the aluminium in 0.5 M HNO₃ simulated solution without inhibitors and with 1.5 ml Cefadroxil, 1.5 ml Dicloxacillin, 1.5 ml Cefadroxil + 1.5 ml Dicloxacillin inhibitors so as to check for reproducibility. Applied potential vs. current density were plotted and on extrapolation of linear portion, the corrosion potential and corrosion current were obtained. In anodic and cathodic plot, the slope of the linear portion gives Tafel constants ‘bₐ’ and ‘bₖ’ respectively. According to

![Optical micrographs of Al alloy with (a) 1.5 Cefadroxil, (b) 1.5 Dicloxacillin and (c) 1.5 Cefadroxil + 1.5 Dicloxacillin inhibitor after potentiodynamic experiment.](image)
Stern–Geary equation, shown in Eq. (2), the steps of the linear polarization plot are substituted to get corrosion current.

\[ I_{corr} = \frac{(b_a \times b_c)}{2.303(b_a + b_c) \times R_p} \]  

(2)

where PR is the polarization resistance.

Inhibition efficiencies (IE) were calculated using Eq. (3)

\[ \text{IE}(\%) = \frac{(j_{corr} - j_{corr})}{j_{corr}} \times 100 \]  

(3)

\( j_{corr} \), corrosion current without inhibitor and \( j_{corr} \), corrosion current with inhibitor.

2.5. Weight loss experiment

Aluminium coupon samples of dimension (15 × 15 × 2) mm were prepared, drilled at one end and polished with abrasive paper, rinsed with distilled water and allowed to dry. The pre-cleaned and weighed samples were suspended in beakers using glass hooks and rods containing the test solutions of different concentrations of 0.1; 0.3; 0.5 and 1.0 ml. Tests were conducted under total immersion conditions in 25 ml of the solution. Immersion time was varied from 1 to 21 days (504 h). The samples were retrieved from test solutions after every 72 h, appropriately cleaned, dried and reweighed. The weight loss was taken to be the difference between the weight of the samples at a given time and its initial weight.

The corrosion rate (R) values are obtained by using Eq. (4)

\[ R = \frac{87.6W}{DAT} \]  

(4)

where W is the weight loss in milligrams, D, the density in g/cm², A, the area in cm², and T, is the time of exposure in hours.

The %IE was calculated from the relationship:

\[ \% \text{IE} \text{ inhibition efficiency} = \frac{(W_1 - W_2)}{W_1} \]  

(5)

where \( W_1 \) and \( W_2 \) are the weight loss in the absence and presence of inhibitors. The %IE was calculated for all the inhibitors every 72 h during the course of the experiment, while the surface coverage is calculated from the relationship:

\[ \theta = \left[ 1 - \frac{W_1}{W_2} \right] \]  

(6)

\( \theta \) is the amount of substance adsorbed per gram (or kg).

3. Results and discussion

3.1. Surface morphology and structural analysis of the inhibited samples

The optical micrographs in Fig. 2 affirmed the uniform dispersion of inhibitive drug particles synergistically embedded on the surface of aluminium alloy. Particles embedded on the alloy surface promote increase number of nucleation site thereby preventing crystal growth which eventually resulted in small-sized grains [31]. The refined microstructure could be attributed to the natural ability of Cefadroxil and Dicloxacillin drugs to adhere uniformly to metal surfaces. It is worthy of note that the uniform distribution and small micro link around major lattice generates adorable and compatible grains in the structure. Fig. 2a revealed that the surface of 1.5 Cefadroxil inhibited Al alloy appeared the smoothest exhibiting the finest morphology while 1.5 Dicloxacillin inhibited Al alloy in Fig. 2b is the roughest with the coarsest morphology.

The optical micrograph in Fig. 3 indicates different magnification of 1.5 Cefadroxil + 1.5 Dicloxacillin inhibited sample after weight loss experiment. Regular shaped, uniformly dispersed, darker and shiny particles of the inhibitive drugs were observed to have adsorbed on the surface of the metal. The darkened nature of the inhibited surface could be attributed to longer period of time Al alloy spent in the corrosive medium compared to the time spent during the potentiodynamic experiment.

SEM/EDS micrographs of Al samples after corrosion test and weight loss experiment are shown in Fig. 4a and b respectively. SEM images of the samples shows that the pitting evolution at the interface was not visible after the corrosion and weight loss experiment. Good surface topography and morphological were observed due to the inability

Fig. 3 – Optical micrographs of Al alloy with 1.5 Cefadroxil + 1.5 Dicloxacillin inhibitor after weight loss experiment.
of corrosive ion to ingress the inhibited surface. Although
the surface of the sample used for the weight loss experi-
ment as shown in Fig. 4b was observed to be rougher, but
the metal surface was better covered than that Fig. 4a. The
natural adsorbing effect of the inhibitors minimizes the
redox chemical reactions that would have caused the dis-
charge of valence electrons by the nitride ion and diffusion
of $\text{Al}^{3+}$ cations in the nitride solution. The SEM images in

Fig. 4 – SEM/EDS micrographs of Al alloy with 1.5 Cefadroxil + 1.5 Dicloxacillin inhibitor after (a) corrosion test and (b) weight loss experiment.

Fig. 5 – XRD of Al alloy with 1.5 Cefadroxil + 1.5 Dicloxacillin after (a) weight loss, (b) potentiodynamic experiment.
accordance with the work of author in reference [32] reveal mild scars on the surface indicating the adsorption characteristics of the inhibitive drugs on the aluminium interface, through physico-chemical reaction. It is significant to note that the EDS image in Fig. 4a and b confirms the presence of Cefadroxil and Dicloxacillin, establishing the natural adhesive ability and dispersive strength [33] of the antibiotic inhibitive drugs.

Fig. 5 shows the intermediate dispatched inhibiting phases observed from XRD patterns for the Cefadroxil and Dicloxacillin inhibited aluminium alloy. From the pattern, visible build-up phases of strong intermetallic precipitate leads to fine grain structure. Generation of intermetallic phases of Cefadroxil and Dicloxacillin present was ascertained by the intensities and degrees of diffractive angle patterns. The main peaks found are Al and Al-C-D at 2θ Braga angle intensity of = (37.5°, 43.5°, 64.3°, 77.5°, 81.5°) for the XRD in Fig. 5a. Fig. 5b has 2θ Braga angle intensity of = (37.5°, 44.1°, 64.3°, 77.5°, 81.5°) which is similar to the values in Fig. 5a. In comparison with literature studies, the height of any peak is considered an indication of quantity of phase deposit [34]. From observation, the inhibitive effect of Cefadroxil and Dicloxacillin result in new orientation of the metal particle precipitate contributing to the strong character and adsorbing tendency of individual inhibitor. It should be noted that the presence of Cefadroxil and Dicloxacillin drug inhibitors led to the visible interfacial formation depicted by the red like phases on the alloy surface which are more visible in Fig. 5b.

3.2. Linear potentiodynamic polarization

Potentiodynamic data of aluminium in 0.5 M HNO₃ in the absence and presence of Dicloxacillin and Cefadroxil drugs are shown in Table 2. The resulting polarization curves are shown in Fig. 6. The potentiodynamic study revealed that the inhibitors reduced the anodic and cathodic reaction, thereby minimizing the corrosion current density \( j_{corr} \). Although, these inhibitors are mixed-type but predominantly anodic. The anodic inhibitive characteristics of Cefadroxil and Dicloxacillin influenced the shift in the values of corrosion potential \( E_{corr} \) to more positive side relative to the uninhibited samples indicating that the inhibitors affected the anodic reaction more than the cathodic reaction, adsorbing its molecules on the surface of the aluminium and consequentially incapacitating the mobility of the nitride ion \( (\text{N}^{3^-}) \) to the active site to the metal [35,36].

3.3. Inhibition efficiency of Cefadroxil and Dicloxacillin

Fig. 7 shows the inhibition efficiency of the used inhibitors. It can be seen that the synergistic combination of Cefadroxil and Dicloxacillin exhibit the best corrosion inhibition efficiency. However, application of Cefadroxil and Dicloxacillin individually inhibits aluminium by 40.7% and 29.3% respectively. The inhibition efficiency of these drugs is as a result of the interaction and reduction of complex activities on the coverage site [37].

3.4. Influence of Cefadroxil and Dicloxacillin on corrosion rate of aluminium

The values of corrosion rates (CR) represented in Fig. 8 were found to reduce in the presence of the added inhibitors.

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**Table 2 – Polarization data for inhibited and uninhibited aluminium in acid media.**

<table>
<thead>
<tr>
<th>Samples</th>
<th>( E_{corr} ) (V)</th>
<th>( j_{corr} ) (µA/cm²)</th>
<th>( b_a ) (V/dec)</th>
<th>( b_c ) (V/dec)</th>
<th>CR (mm/year)</th>
<th>PR (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>−0.6760</td>
<td>484</td>
<td>0.4251</td>
<td>0.6443</td>
<td>0.4502</td>
<td>230.0</td>
</tr>
<tr>
<td>1.5 Dicloxacillin</td>
<td>−0.2554</td>
<td>342</td>
<td>0.1408</td>
<td>0.1941</td>
<td>0.3710</td>
<td>103.60</td>
</tr>
<tr>
<td>1.5 Cefadroxil</td>
<td>−0.3702</td>
<td>287</td>
<td>0.2648</td>
<td>0.4564</td>
<td>0.2926</td>
<td>253.83</td>
</tr>
<tr>
<td>1.5 Dicloxacillin + 1.5 Cefadroxil</td>
<td>−0.2920</td>
<td>199</td>
<td>0.3479</td>
<td>1.0459</td>
<td>0.2152</td>
<td>570.96</td>
</tr>
</tbody>
</table>

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**Fig. 6 – Cathodic and anodic polarization scans for aluminium substrate with and without inhibitive drugs in 0.5 M HNO₃.**

**Fig. 7 – Inhibitor efficiency of inhibited samples.**

**Fig. 8 – Corrosion rate of the aluminium samples.**
The minimum corrosion rate was found with the 1.5 Cefadroxil + 1.5 Dicloxacillin inhibited sample. The reduction in the rate of corrosion could be as a result of the synergy between the molecules of the two drugs. The synergetic effect of these inhibitive drugs invigorates the binding energy between them, leading to their continuous adsorption on the surface of the metal. Cefadroxil and Dicloxacillin like most antibiotics and their decomposition products possess electron donor groups that can bind naturally occurring metal ions, there by forming complexes with metal ions [38].

3.5. Microhardness behaviour of inhibited and uninhibited samples

The microhardness results obtained for Cefadroxil and Dicloxacillin inhibited and uninhibited samples are represented in Fig. 9. Comparison of the hardness results revealed that 1.5 Cefadroxil + 1.5 Dicloxacillin inhibited aluminium possess 130 kgf/mm², which is the highest value of hardness in the series. This value of hardness depicts 44.4% increase in hardness compared to the uninhibited aluminium with the hardness value of 90 kgf/mm². The individual usage of the drugs notably improved the microhardness of aluminium as shown in Fig. 9. Improvement in microhardness could be attributed to the formation of intermetallic adhesives and synergetic mechanism by the inhibitive drugs on the substrate samples.

3.6. Weight loss measurement

Results obtained from weight loss measurements are shown Fig. 10. It can be seen that introduction of the inhibitive drugs to the corrosive medium was observed to have had notable effect on the rate of weight loss. Combined synergetic effect of Cefadroxil and Dicloxacillin on aluminium alloy impedes the weight loss better than the individual application as shown in Fig. 10. The minimal weight loss is as a result of the ability of Cefadroxil and Dicloxacillin to form strong adhesive layer on the metal surface like some other antibiotic. This result is in good agreement with corrosion characteristics observed by author in references [39,40].

Fig. 9 – Microhardness comparison of uninhibited and inhibited aluminium in linear polarization experiment.

Fig. 10 – Variation of weight loss by the inhibited and uninhibited samples.

4. Conclusions

In summary, this work reported the effect of Cefadroxil and Dicloxacillin inhibitive drugs applied synergistically on the surface of aluminium alloy. It was confirmed that these inhibitors had significant impact on the structural build-up of the base metal resulting to the reduction of current density and corrosion rate. The inhibited samples show uniform growth, flawless crystals and improved inhibition efficiencies. There is no doubt that the formation of intermetallic adhesives and synergetic mechanism by the inhibitive drugs on the metal surface was responsible for the improvement of microhardness.

Conflicts of interest

The authors declare no conflicts of interest.

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