Inhibitive Effect by *Ricinus communis* on the HCl/H₃PO₄ Acid Corrosion of Aluminium Alloy

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The assessment of *Ricinus communis* as corrosion inhibitor for aluminium alloy in 2M HCl and H₃PO₄ acid solution using gravimetric and potentiodynamic polarization techniques was investigated at 298K. The results revealed that *Ricinus communis* oil in 2M HCl and H₃PO₄-aluminium environment decreased the corrosion rate at various concentrations considered. Inhibitor efficiency (IE) as high as 75.75% at 20%v/v *Ricinus communis* addition and 82.35%/100%v/v *Ricinus communis* addition using gravimetric method were demonstrated in HCl and H₃PO₄ solution respectively. The IE from the potentiodynamic polarization method in both conditions was significantly enhanced. The scanning electron microscope (SEM) surface morphology of as-corroded uninhibited condition showed severe damage and pits formation than as-corroded inhibited conditions. The additions of *Ricinus communis* as corrosion inhibitor in each solution indicate higher potential value, IE and polarization resistance with decreased in current density. The methods for the corrosion assessment of the aluminium were in agreement and a mixed-type corrosion exist which obeyed Langmuir adsorption isotherms.

1. INTRODUCTION

Aluminium and its alloys have been identified as an important and useful engineering material. It is attracted by its various unique properties; such as appearance, strength-to-weight ratio, and excellent thermal and workability properties [1-10]. However, the alloy still exhibit insufficient and poor performance in service condition that required high hardness, wear and aggressive corrosion environment [7,11]. Hence, methods for enhancing these limitations become necessary. Corrosion of this alloy has been subject of interest among researchers because of the aforementioned importance. Although, over the years, various methods that ranges from alloying, heat treatment and nano-particle

enhancement have been put forward to address these limitations [12-15]. Equally, corrosion resistance of aluminium and its alloys using inhibitors have also been investigated in majority of environments [1,5,8-10,16-18]. However, some synthetic corrosion inhibitors have been reported as non-eco-friendly [19,20]. In view of this, search for a potential eco-friendly and non-toxic corrosion inhibitors have been subject of interest among researchers recently. The use of plant extract and natural oils; otherwise known as green corrosion inhibitors has been recognized as an effective corrosion inhibitor due to their availability, non-toxic nature and renewable source of materials for wide range of corrosion control [10,21]. In the present study, the influence of Castor oil (*Ricinus communis)* as corrosion inhibitors for aluminium alloy in 2M HCl and H_3PO_4 solution have been investigated using gravimetric and potentiodynamic polarization techniques.

2. EXPERIMENTAL PROCEDURES

2.1 Materials and sample preparation

Aluminium alloy specimen of dimension 20 x 20 x 3 mm with chemical composition shown in Table 1 was used as coupons for the corrosion study in *Ricinus communis*-2M hydrochloric acid (HCl) and *Ricinus communis*-2M phosphoric acid (H_3PO_4) solution.

Table 1. Chemical composition of aluminium alloy used

Element	Al	Si	Mn	Mg	Sr	Bi	Ca	Na	Fe	Ti	P, Cr, Zr,Cu,Zn	B,Ni,Ag, Co
%	99.01	0.157	0.025	0.5	0.0001	0.0024	0.0012	0.001	0.281	0.0046	0.01	0.004
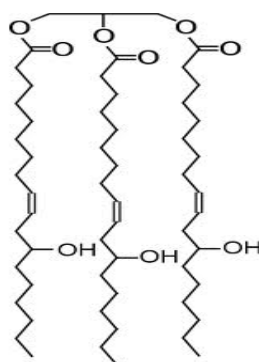
Figure 1. Molecular structure of *Ricinus communis* natural oil

Initially, the coupons were mechanically polished with emery papers down to 600. The samples were degreased in ethanol, dried, weighed and stored in a desiccator. The initial weight of each sample

was taken and recorded. In each of hydrochloric and phosphoric acid, 2M concentration was prepared fresh as required for each experiment. The natural castor oil (*Ricinus communis)* used was obtained from Technology Innovation Agency, Chemical Station, Ga-Rankuwa, TUT, Pretoria with molecular structure shown in Figure 1. The corrosion studies were conducted at 298K.

2.2 Gravimetric measurement

The corrosion measurement by gravimetric analysis was carried out on the previous weighed samples with and without inhibitor at 298K. The volume of the solution was 100 mL with and without the addition of *Ricinus communis* inhibitor. The *Ricinus communis* inhibitor concentration was varied from 20, 50 and 100%v/v in 100 ml of 2M HCl and H_3PO_4 acidic solutions. For each sample, using gravimetric method, the samples were washed, dried and weight taken at interval of 12, 24 and 36 h of exposure time. The corrosion rate, degree of surface coverage and inhibitor efficiency were calculated for the inhibitor concentrations at 298K.

2.3 Electrochemical measurement

The potentiodynamic polarization and linear polarization resistance was used to characterize the corrosion rate of the aluminium in *Ricinus communis* -acidic media. In the electrochemical test, a glass corrosion cell kit with a platinum counter electrode, a saturated Ag/Ag reference electrode and aluminium sample as working electrode were used. The working electrode samples were positioned at the glass corrosion cell kit, leaving 1 cm^2 surfaces in contact with the solution. Polarization test were carried out in two different solution consisting of 2M HCl and H_3PO_4 solution at room temperature using a potentiostat. The polarization curves were determined by stepping the potential at a scan rate of 0.003V/sec. The polarization curves were plotted using Autolab data acquisition system (Autolab model: AuT71791 and PGSTAT 30), and both the corrosion rate and potential were estimated by the Tafel extrapolation method.

2.4 Surface morphology

The surface morphology of as-corroded uninhibited and inhibited aluminium sample were examined with scanning electron microscopy equipped with energy dispersive spectroscopy to analyze the elements in the surface (Model: Joel 6100).

3. RESULTS AND DISCUSSION

3.1 Results

The results from the gravimetric corrosion study for aluminium in 2M HCl and H_3PO_4 can be found in Table 2, Figures 2 and 3. Tables 3 and 4 indicate the electrochemical corrosion data obtained

for aluminium-2M HCl and H$_3$PO$_4$/*Ricinus communis* interface. Figures 4 and 5 show the linear polarization curves for aluminium-2M HCl and H$_3$PO$_4$/*Ricinus communis* environment respectively. In Figure 6, the open circuit potential (OCP) curve can be found for aluminium in H$_3$PO$_4$ solution/*Ricinus communis*. While the surface morphology of as-corroded uninhibited/inhibited aluminium in 2M HCl and H$_3$PO$_4$/*Ricinus communis* are presented in Figures 7-10. In Figures 11 and 12, the percentage inhibitor efficiency (% IE) for *Ricinus communis* were demonstrated using different methods of corrosion evaluation. Figure 13 depicted the adsorption isotherms for the two environments considered in this work.

3.2 Discussion

3.2.1 Gravimetric measurement

Two environmental service conditions consisting of 2M HCl and H$_3$PO$_4$ solutions were simulated separately for corrosion behavior of aluminium-*Ricinus communis* using different inhibitor concentrations at 298K. From the results, corrosion rate (CR) of aluminium in each environment decreased with addition of *Ricinus communis* natural oil for exposure time of 12, 24 and 36 h (Tables 2, Figures 2 and 3) in both environmental conditions. In 2M HCl-*Ricinus communis* interface, at various exposure times, corrosion rate decreased, with less percentage inhibitor efficiency (% IE) at higher exposure time in the gravimetric study.

Table 2. Corrosion rate (CR), Inhibition efficiency and surface coverage (θ) for aluminium in 2M HCl and H$_3$PO$_4$ solution without and with varying concentration of *Ricinus communis* at 298K

Exposure time (h)	Concentration of inhibitor (%v/v)	CR x 10^{-3} (mm/day) For 2M HCl	CR x 10^{-3} (mm/day) For 2M H$_3$PO$_4$	Surface coverage (θ) for H$_3$PO$_4$	Inhibition Efficiency (%) for H$_3$PO$_4$
12	0	4.62	3.65	-	-
	20	1.12	1.79	0.2352	23.52
	50	1.21	1.07	0.7058	70.58
	100	1.25	0.645	0.8235	82.35
24	0	9.57	3.87	-	-
	20	2.71	2.79	0.2777	27.77
	50	4.81	2.47	0.3611	36.11
	100	5.84	1.18	0.6944	69.44
36	0	8.99	4.58	-	-
	20	1.67	3.72	0.1875	18.75
	50	4.64	3.44	0.2500	25.00
	100	6.42	1.43	0.6875	68.75

Specifically, Figure 2 shows a decreased in corrosion rate with concentration of inhibitor for all the immersion time at 298K. For this condition, 20%v/v of inhibitor addition has the highest corrosion resistance for 12 h exposure time. Equally in 2M H$_3$PO$_4$-*Ricinus communis* interface, similar trends

were demonstrated with a progressive decrease in corrosion rate along addition of inhibitor for all the exposure time (Figure 3). In the 2M HCl-*Ricinus communis* condition, highest IE was found to be 75.75% at the lowest inhibitor addition of 20%v/v for 12 h exposure time. While for 2M H$_3$PO$_4$-*Ricinus communis* condition, higher IE was calculated to be 82.35% at 100%v/v *Ricinus communis* addition for exposure time of 12 h,. While at 100%v/v inhibitor additions for 24 and 36 h exposure time, corrosion rate/IE were found to be 0.00118/69.44% and 0.00143/68.75% respectively. However, corrosion resistance of aluminium in H$_3$PO$_4$- *Ricinus communis* is lower than that in HCl-*Ricinus communis*. This occurrences have been attributed to the formation of thin oxides as evidenced in the EDS (Figures 7-9) adheres to the metal surface which interfere with the reaction sites, thus impede the formation of pits and their growths. Similar results have been reported [4,22].
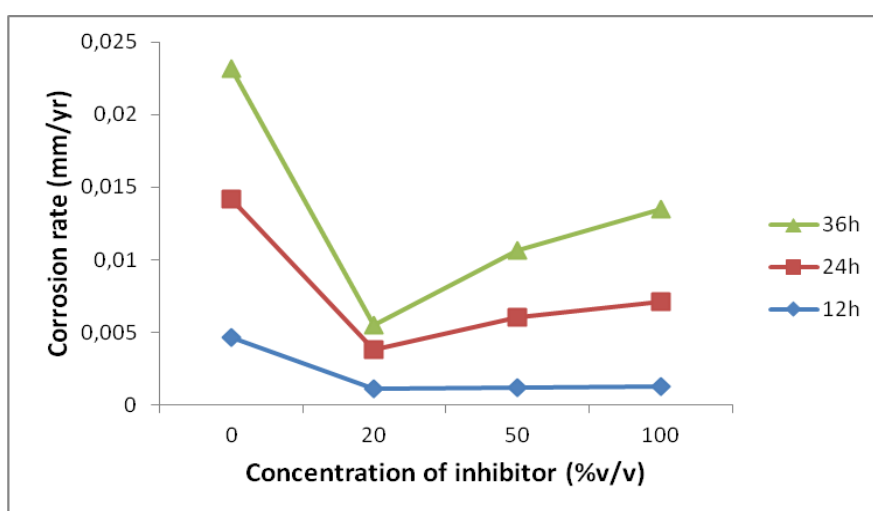
Figure 2. Variation of corrosion rate with concentration of inhibitor for aluminium in 2M HCl without and with varying concentration of *Ricinus communis* at 298K
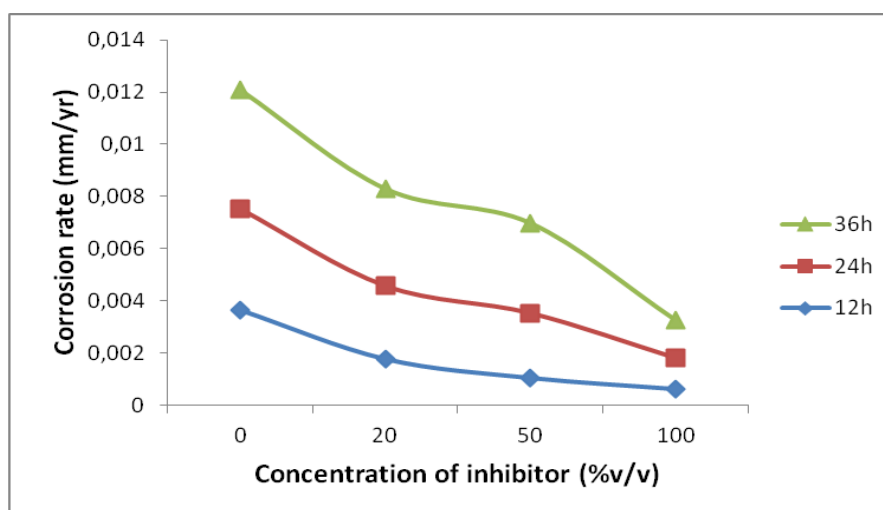
Figure 3. Variation of corrosion rate with concentration of inhibitor for aluminium in 2M H$_3$PO$_4$ without and with varying concentration of *Ricinus communis* at 298K

*3.2 2 Potentiodynamic polarization*

In the potentiodynamic polarization for HCl and H_3PO_4/*Ricinus communis* environments (Tables 3 and 4), different measurement consisting of potentiodynamic polarization-corrosion rate (PP-CR), potentiodynamic polarization-corrosion density (PP-I_{corr}), and linear polarization resistance (LPR) were used as criteria for evaluation of corrosion resistance of aluminium in each environments. Figures 4 and 5 indicate the polarization curves for 2M HCl and H_3PO_4-*Ricinus communis* at 298K. Generally, each studied environments demonstrated a decreased corrosion rate and current density with addition of *Ricinus communis* inhibitor at all concentrations. While the corrosion potential (E_{corr}) and polarization resistance (R_p) increases with inhibitor concentrations. This agreed with previous reports [6,9]. The inhibited aluminium in HCl showed that corrosion rate decreased from 0.0009374 mm/yr to 0.0000002455, 0.0000008237 and 0.000001359 mm/yr at 20, 50, and 100%v/v *Ricinus communis*. While in H_3PO_4 environment, corrosion rate decreased from 66.883 mm/yr to 3.454, 0.003555, and 0.001281 mm/yr at 20, 50, and 100%v/v *Ricinus communis* respectively. The result from the OCP for H_3PO_4-*Ricinus communis* (Figure 6) demonstrated that corrosion potentials decreased with open circuit time and the trends became linear due to the passive film formation with 50%v/v *Ricinus communis* indicating higher potentials. This equally agrees with the result from the linear polarization for H_3PO_4-*Ricinus communis* condition. At this point, the metals can be said to be protected. Although this is not permanent since the thin film can be damaged, thereby creating an active-passive/passive-active stages. It is worthy to note that corrosion resistance of aluminium-H_3PO_4-*Ricinus communis* interface is much higher than that of HCl-*Ricinus communis* interface with IE of 99.99% obtained at 50 and 100%v/v *Ricinus communis* addition for PP and 82.35% at 12 h for GM (aluminium-H_3PO_4-*Ricinus communis* interface). The occurrence of higher corrosion resistance can be confirmed from the SEM surface morphology (Figure 8), which shows that there was less surface damage in the uninhibited aluminium-H_3PO_4 solution as compared with uninhibited aluminium-HCl interface (Figure 7). This occurrences have been attributed to the formation of thin oxides as evidenced in the EDS (Figures 7-9) adheres to the metal surface which interfere with the reaction sites, thus impede the formation of pits and their growths. However, with respect to the anodic and cathodic change in each environment, the mixed-type corrosion inhibition was evidenced by both environments.

Table 3. The electrochemical parameters of aluminium in 2M HCl-*Ricinus communis* environment at 298K

S/N	C (%v/v)	I_{corr} (A/cm^2)	b_a (v/dec)	LPR R_p (Ωcm^2)	$-E_{corr}$ (V)	CR (mm/yr)
1	0	9.399E-1	0.0150	0.3658	0.8172	9.374E-4
2	20	1.613E-3	0.6543	8.7412	0.5776	2.455E-7
3	50	5.467E-3	2.1121	89.833	0.6670	8.237E-7
4	100	8.927E-3	0.2229	10.475	0.7516	1.359E-6

Table 4. The electrochemical parameters of aluminium in 2M H_3PO_4-*Ricinus communis* environment at 298K

S/N	C (% v/v)	I_{corr} (A/cm^2)	b_a (v/dec)	LPR R_p (Ωcm^2)	-E_{corr} (V)	CR (mm/yr)
1	0	3.8503E-3	0.2418	29.448E+0	0.7848	66.883E+0
2	20	1.9032E-4	1.2120	1388.4E+0	0.1396	3.454E+0
3	50	1.9592E-5	0.1197	1.6622E+4	0.6650	3.555E-3
4	100	7.0613E-5	0.0392	2.0272E+3	0.6923	1.281E-3
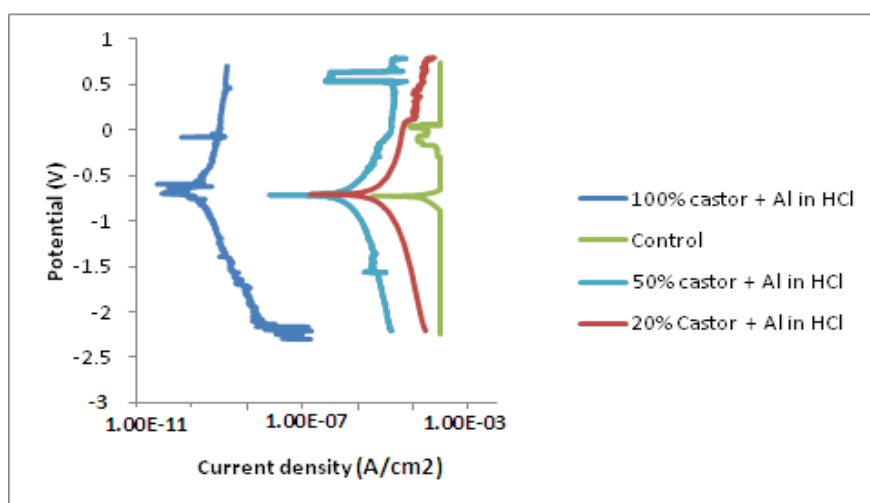
Figure 4. Linear polarization for aluminium in HCl solution/*Ricinus communis*
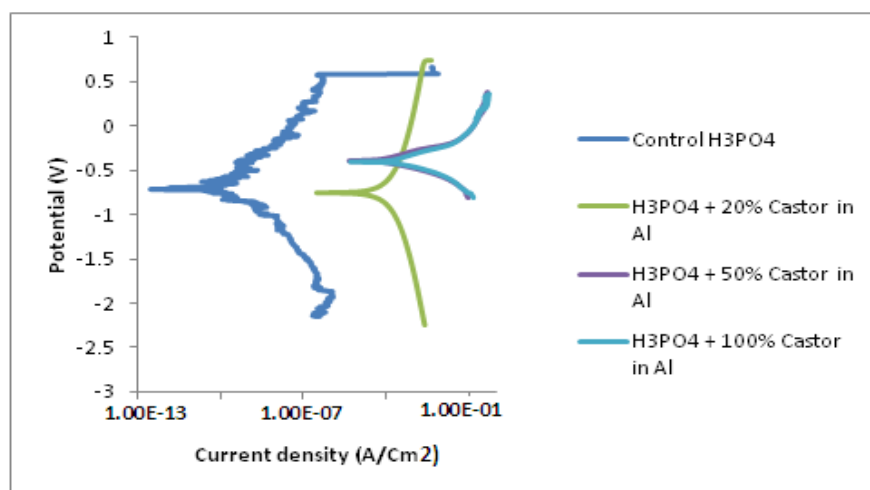
Figure 5. Linear polarization for aluminium in H_3PO_4 solution/*Ricinus communis*
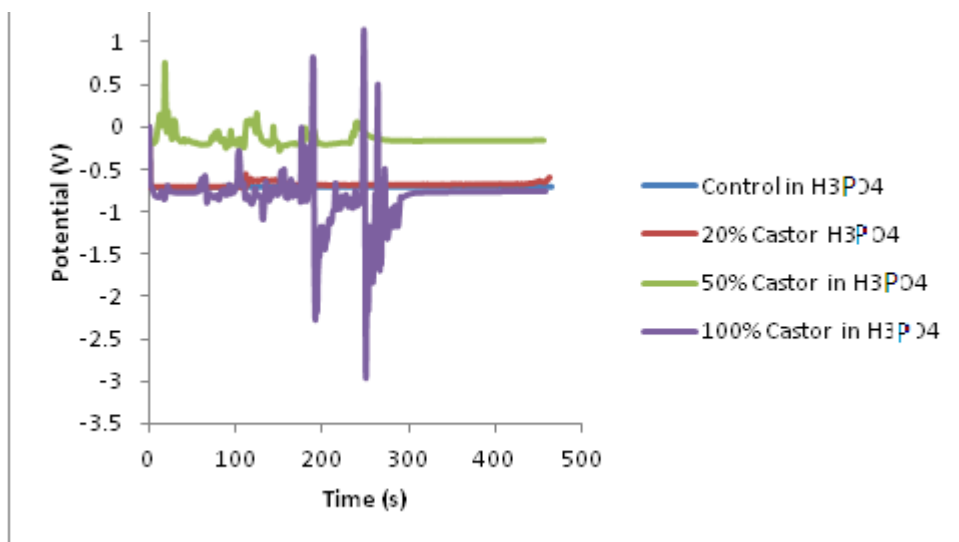
**Figure 6.** OCP for aluminium in H$_3$PO$_4$ solution/*Ricinus communis*

3.2.3 Scanning electron microscope-Energy dispersive spectroscopy (SEM-EDS)

The surface morphology of uninhibited aluminium-HCl interface in Figure 7 indicates severe pits, cracks and selective dissolution of intermetallic at the surface as compared with Figures 9 and 10. Equally in the uninhibited aluminium-H$_3$PO$_4$ interface after 12 h exposure time, similar but less surface deterioration (Figure 8) exists. In Figures 9 and 10, effect of 36 h exposure time were assessed on the aluminium surface in the inhibited conditions, which showed that even at higher exposure time of 36 h for HCl-50%v/v *Ricinus communis* (Figure 8) and H$_3$PO$_4$- 50%v/v *Ricinus communis* (Figure 9), indicate less surface degradation and pit formation as compared with exposure time of 12 h for the Figures 7 and 8. This shows that the natural *Ricinus communis* oil was able to exhibit protection for the aluminium within the experimental conditions considered.
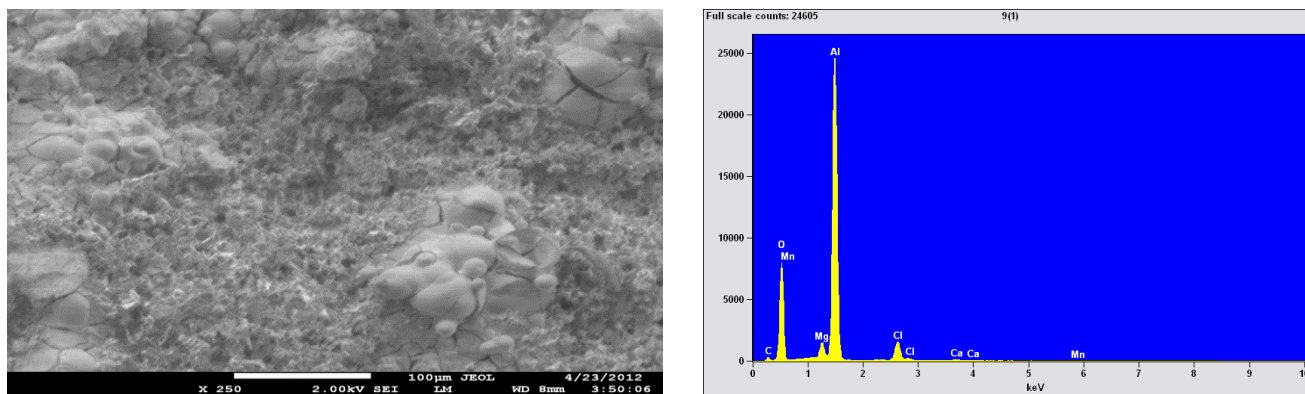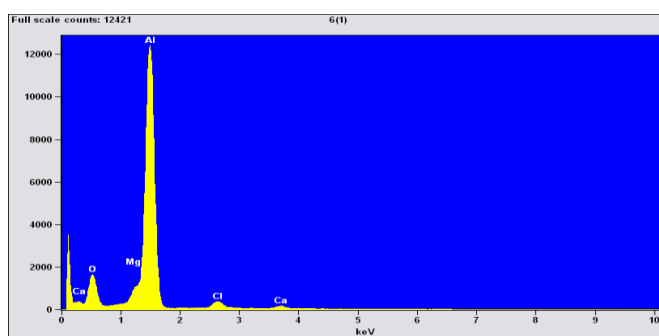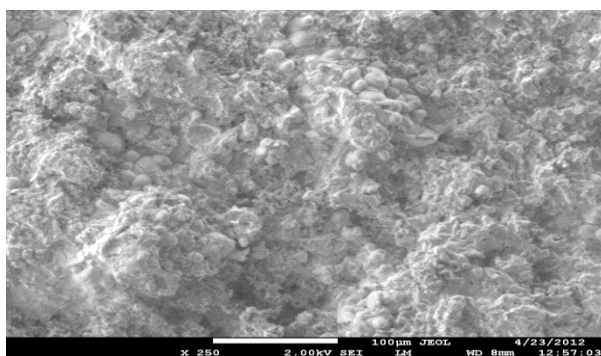

Figure 7. SEM micrograph of aluminium in uninhibited 2M HCl solution after 12 h exposure time with the EDS
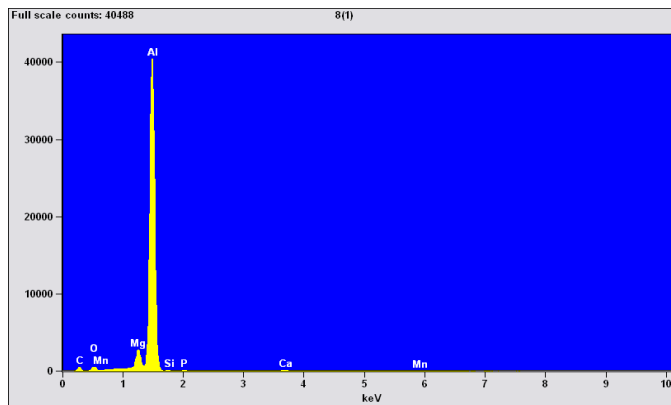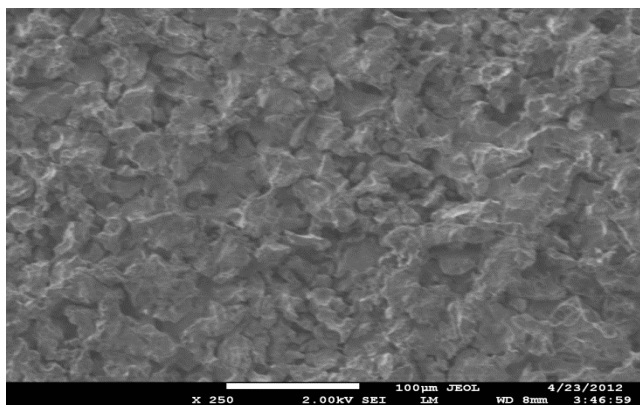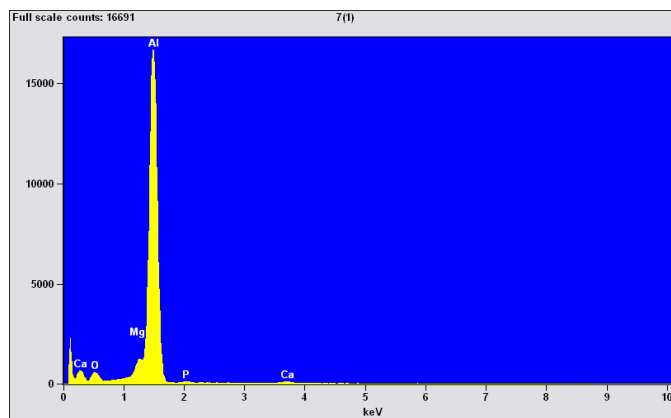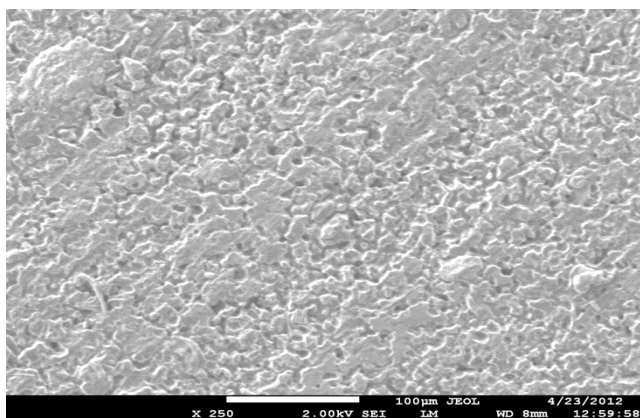
Figure 8. SEM micrograph of aluminium in uninhibited 2M H_3PO_4 solution after 12 h exposure time with the EDS

Figure 9. SEM micrograph of aluminium in 50%v/v *Ricinus communis*-2M HCl solution after 36 h exposure time with the EDS


Figure 10. SEM micrograph of aluminium in 50%v/v *Ricinus communis*-2M H_3PO_4 solution after 36 h exposure time with the EDS

3.2.4 Inhibitor efficiency and adsorption behavior

The computed percentage inhibitor efficiency (% IE) of the aluminium-*Ricinus communis* in each HCl and H_3PO_4 solution were done using the equation reported [10]. The variation in the % IE using gravimetric (GM), potentiodynamic polarization-corrosion rate (PP-CR), potentiodynamic

polarization-corrosion density (PP-I_{corr}), and linear polarization resistance (LPR) are presented in Figures 11 and 12 for 2M HCl and H_3PO_4/ *Ricinus communis.* The results show that addition of *Ricinus communis* increased the IE with an increase in the inhibitor concentrations. This may be attributed to the fact that, as the *Ricinus communis* addition increases, the surface area covered by this inhibitor increased hence higher IE was achieved. *Ricinus communis* oil can be said to exhibit a mixed-type corrosion inhibition because of the simultaneous change in the anodic and cathodic region during the electrochemical evaluation of the two conditions.
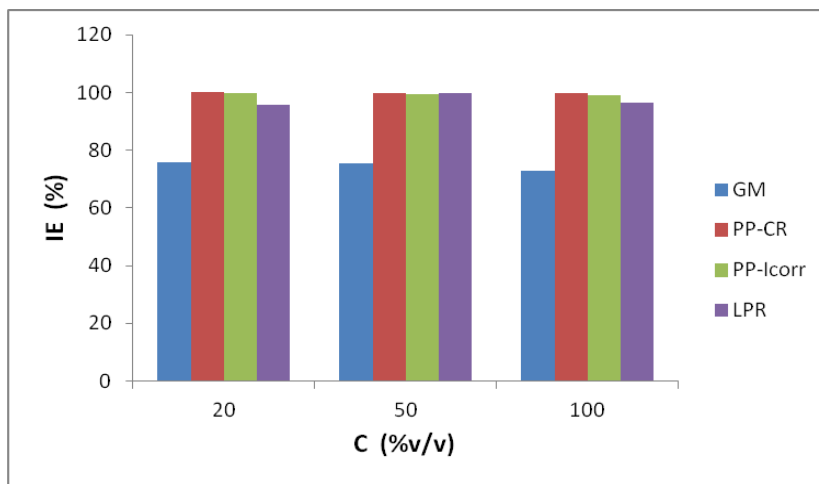
Figure 11. Comparative chart of inhibitor efficiency (IE) for aluminium-2M HCl solution/ *Ricinus communis* concentration obtained by gravimetric at (GM; 12 h), potentiodynamic polarization-corrosion rate (PP-CR), potentiodynamic polarization-corrosion current (PP-Icorr) and linear polarization resistance (LPR)
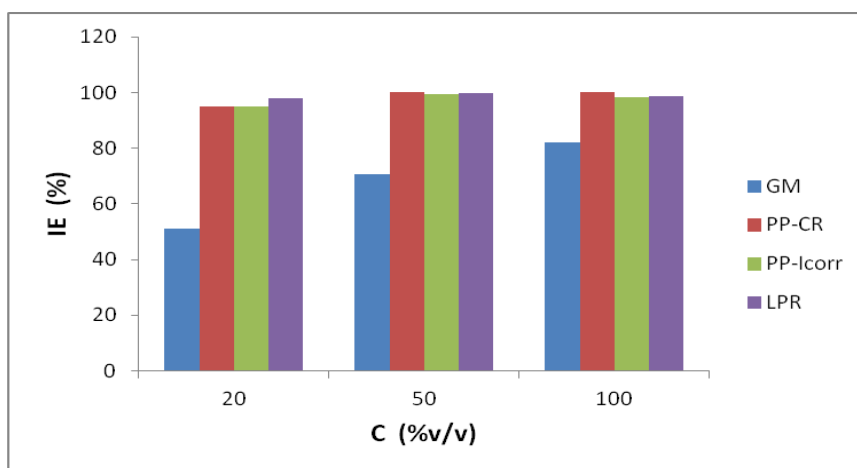
Figure 12. Comparative chart of inhibitor efficiency (IE) for aluminium-2M H_3PO_4 solution/ *Ricinus communis* concentration obtained by gravimetric at (GM; 12 h), potentiodynamic polarization-corrosion rate (PP-CR), potentiodynamic polarization-corrosion current (PP-Icorr) and linear polarization resistance (LPR)
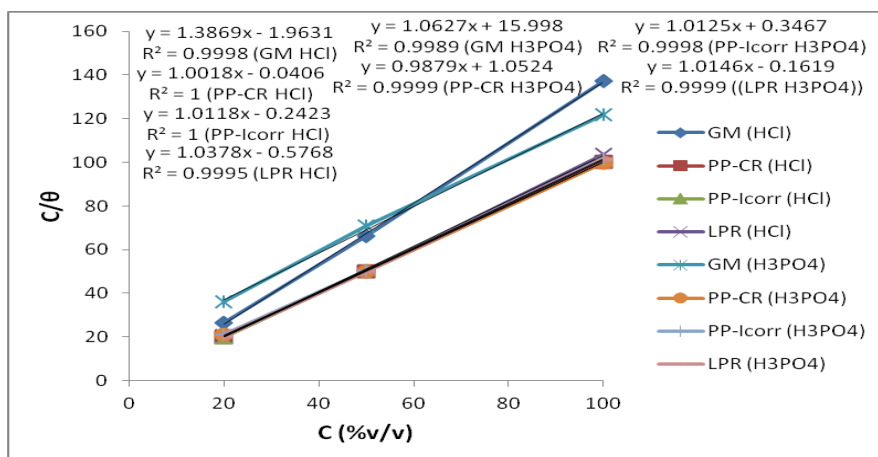
Figure 13. Langmuir isotherm for the adsorption of *Ricinus communis* compounds on the aluminium surface in 2M HCl and H₃PO₄ solution obtained by gravimetric and potentiodynamic polarization methods at 298K

The trend observed in this study is not uncommon and have been previously reported [6,10]. Equally, there seems to be agreement with GM and potentiodynamic polarization techniques for 2M HCl and H₃PO₄-*Ricinus communis/*aluminium conditions, with that in 2M HCl- *Ricinus communis* higher. The adsorption mechanism has been shown with a relationship between C/θ against C that indicated linearity at 298K in each environment (Figure 13). Since the correction factors (R^2) were evidenced to be approximately/or equal to unity: HCl- GM (0.9998), PP-Icorr/PP-CR (1), LPR (0.9995) and H₃PO₄- GM (0.9989), PP-Icorr (0.9998), PP-CR/LPR ((0.9999) the adsorption behavior is assumed to have followed Langmuir adsorption isotherms.

4. CONCLUSIONS

1. *Ricinus communis* have been demonstrated to be an effective corrosion inhibitor for HCl and H₃PO₄ environments at 25°C
2. The corrosion resistance and inhibitor efficiency of aluminium increased with addition of *Ricinus communis* as inhibitor. IE as high as *99*.99% in H₃PO₄-*Ricinus communis* condition was observed.
3. Surface morphology of uninhibited aluminium sample shows severe pits and cracks
4. That the mixed-type corrosion inhibition exist and Langmuir adsorption isotherms were proposed for the aluminium alloy in the two environments considered.
5. These occurrences have been attributed to the formation of thin oxides which adhered to the metal surface and interfered with the reaction sites, thus served as a barrier to the formation of pits and their growths.

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