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Fungal Corrosion of Mild Steel and the Application of Aframomum melegueta Biomass Extract as Natural Source of Inhibition

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Abstract
Studies on fungal influenced corrosion of mild steel (MS) in the presence of *Acremonium kiliense* and *Aspergillius fumigatus* and their inhibition by seed extracts of *Aframomum melegueta* were carried out using gravimetric and potentiodynamic polarization techniques. The results revealed that the metal reacted differently to the impact of fungi. The influence depends on the capacity of fungi to develop on the metal surface and produce metabolites stimulating changes in polarization resistance and destruct the surfaces. *A. fumigatus* proved to be the most active destructor of mild steel with cumulative corrosion rate (∑CR) of 7.85±0.91mpy and corrosion current density (I_{corr}) of 279.4μA/cm^2. The gravimetric analysis further revealed that the corrosion rate and weight loss of the metals increased with time. The anticorrosion studies at 25mg/mL concentration showed that the inhibitor exhibited a mixed-type inhibition, inhibiting both the cathodic and anodic sites. *A. melegueta* was more effective against *A. kiliense* (85%IE).
Keywords: Corrosion, Fungi, Inhibition, Plant extract, Polarization, Mild steel

1. Introduction

A very large variety of microorganisms can enhance the corrosion rate of metals through their metabolic processes. The physiological activity of fungi and the abundance of their metabolites allow them to attach to metals: aluminum, iron, copper, zinc and poly-aniline-modified nickel (Juzeliunas *et al.* 2006). According to Svidirenok *et al.* (1994), metal surface is a convenient basis for fungal mycelia to attach. Acid produced by fungi are damaging to metals (Little and Ray 2001). These include formic, citric and acetic acids.

When fungi grow on metal surfaces, they not only can consume the nitrate and sulfur accumulated on the eroded poles (such as iron) but also the hydrogen, oxygen and other gaseous products formed on the metals hence depolarizing the metals and enhancing corrosion (Obuekwe 1981). Therefore microbial corrosion processes at metal surfaces are associated with microorganisms or the products of their metabolic activities [5 (Beech *et al.* 1999)]. These microbial metabolic products can affect cathodic and/ or anodic reactions thereby altering the electrochemistry at the metal solution interface (Hector and Liz 2005).

MIC has been linked with most of the internal corrosion problems in oil transportation pipelines, storage tanks and drainage systems including the growth of microorganisms on industrial systems and materials resulting in fouling and corrosion problems with serious attendant economic consequences (Maiara *et al.* 2011). Corrosion of oil field equipments, piping and industrial system materials can lead to potentially hazardous system malfunctions as well as costly damage and repair cost (Akpabio *et al.* 2011). Fungi can affect metals and structural parts of buildings thereby accelerating the corrosion rates and deterioration of such materials and these may lead to problems even in buildings less than five years old (Muthukumar *et al.* 2003).

Fungi and their functional capacity are important ecological factors of the environment, which often determine the duration of the effective use of metal and their ware (Lugauskas *et al.* 2008). Fungi find their way unto metal surface under the action of adhesion forces and they start to function even at the lowest moisture (Lugauskas *et al.* 2009). In such a manner they form chemical bound with the metal. However, not all fungi can survive on metal surface. Most of them die from stress, unfavourable conditions on the metal surface, such as alternating moisture, temperature, physical, chemical and technical parameters (Juzelinas *et al.* 2007). Only fungi that are able to incorporate the metal as a link into their activity chain connecting them with the environment and whose functioning helps minimize the tension between the metal and their vital needs can survive (Lugauskas *et al.* 2009).

Fungi have been implicated in the corrosion of many metals and their alloy used in fabrication and construction of buildings. Fungal influenced corrosion (FIC) has been reported for some metals and aluminum alloys exposed to hydrocarbon fuels during transport or storage (Videla (1989). De Mele *et al.* (1979) reported that corrosivity increased with contact time due to accumulation of metabolites under fungal colonies attached to metal surfaces. De Meybaum and de Schiapparelli (1980) demonstrated that the metabolic products of fungi enhanced aqueous phase aggressiveness even after the life cycle of *Cladosporium* sp was completed. Rosales (1985) also demonstrated metal ion binding by fungi mycelia, resulting in metal ion concentration cells on aluminium surfaces.

However, the methods employed to prevent biocorrosion act by inhibiting the growth or metabolic activity of microorganisms and changing the environment in which the corrosion process occurs in order to avoid the adaptation of these organisms (Maiara *et al.* 2003). These methods tend to reduce or eliminate metal exposure to the action of biocorrosion, either by direct elimination of microorganisms or reduce the effect of their metabolites on the metal (Videla 2003).The use of inhibitors or biocides is one of the best ways to prevent metal and alloy from corrosion. Several inhibitors in use are toxic to human and the environment. There are serious efforts to develop new inhibitors of plant origin for metals subjected to various environmental conditions. Plant represents an interesting source of compounds currently being explored for use in metal corrosion protection including the inhibition of microbial growth and biofilm formation. This is because inhibitors of plant origin are biodegradable, non toxic, environmentally friendly and cheap.

In this study, the inhibiting effect of cold water extracts of *Aframomum melegueta* on the fungal influenced corrosion of mild steel including evaluation of the phytochemical constituents of the extract was investigated. The antifungal activities of the extract on the corrosion associated *Acremonium kiliense* and *Aspergillius fumigatus* was assessed using gravimetric and electrochemical techniques. Antifungal screening to determine the growth inhibition of the extract against the fungi was by agar well diffusion method.

2. Materials and methods

2.1Material Preparation:

Metal coupons: Corrosion experiments were performed on mild steel with weight percentage composition of Carbon (C) -0.30, Silicon (Si) – 0.30, Manganese (Mn) – 0.30, Phosphorus (P) – 0.045, Sulfur (S) – 0.050, Chromium (Cr) – 0.064, Copper (Cu) – 0.040, Titanium (Ti) – 0.04 and the balance Fe. The coupons were first polished with silicon carbide abrasive paper (from grade no. 400 to 1000). The coupons were then cleaned with distilled water, dried in acetone and weighed with electronic weighing balance (Nicolet Model 37500). Weighed coupons were stored in moisture-free desiccators prior to use.

2.2 Plant extracts

The dried plant seeds were washed with sterile distilled water. The seeds were then pulverized with a blender. The stock solution was prepared using standard procedure outlined by Hussian *et al.* (2011). Hundred grams (100g) of the powdered seed was soaked in 500mL of 95% ethanol (ET), methanol (MT), cold water (CW) and hot water (HW) for 48 hrs to allow for maximum extraction of components. The filtrates were then evaporated to eliminate the solvents using a rotary evaporator. The residue (crude extracts) were then stored in sterile reagent bottles at 21 C until analysis. The amount of plant material extracted was quantified by comparing the weight of the dried residue with the initial weight of the dried plant material before extraction. From the individual stock inhibitor test solutions were prepared in the desired concentration range by diluting with distilled water. Quantitative and qualitative phytochemical screening of the extract was done using standard laboratory procedures (Oguzie *et al.* 2013).

2.3 Fungal isolates

One gram (1g) of corroded metal samples was serially diluted into 9mL of sterile distilled water in sterile 20mL test tube. About 0.1mL of dilutions 10^{-5} to 10^{-7} was plated in triplicate on potato dextrose agar PDA (Oxoid) plates, supplemented with antibiotics streptomycin (5µg/mL). Each morphological discrete fungal colony was then sub-cultured and purified by repeated streaking on PDA plates. Pure cultures were then preserved on PDA slants in Bijou bottles and stored at 4 C in a refrigerator for further studies. Each fungal isolate was characterized and identified based on their morphological characteristics and microscopic analysis using taxonomic guides and standard procedures as outlined by Hussian *et al.* (2011).

2.4 Antifungal screening

2.4.1 Preparation of inoculums

The inoculums used the work were prepared according to the method outlined by Mayuri *et al.* (2015). Three well-isolated colonies of each fungus were selected from agar culture. The top of each colony was touched with a loop and the growth was transferred into a tube containing 5 mL PDA broth medium. The broth culture is incubated at 27ºC for 5-7 days until it achieves turbidity after which colonies were counted and average counts recorded and used for the calculation of colony forming units per milliliter (CFU/mL).

The antifungal activities of the extracts were tested by agar well diffusion method Mayuri *et al.* (2015) against the three fungi at 50 mg/ mL and 100 mg/ mL concentrations for each. A loop full of the standardized fungal suspension was evenly spread on the agar surface. Using a sterile cork borer of 4 mm in size, each plate was punched and 0.1 mL of the extract poured in the bore. Blank hole filled with sterile distilled water was used as control. Each sample was prepared in triplicate. The plates were allowed to stand for 30 minutes and then incubated at 27^0C for 7 days. The radius of the zone of inhibition was measured from the edge of the hole to the

edge of the zone and recorded as percentage mycelia inhibition.

2.5 Gravimetric Experiments

2.5.1 Corrosion test

The corrosion test was conducted by using the procedure outlined by Lugauskas *et al.* (2009). The coupons were first prepared following the procedure earlier described. The metal coupons were placed in Petri dishes filled with malt extract poor in nutritive materials and supplied with streptomycin (5µg/mL). The medium with the metal coupons was then inoculated with 0.4 mL suspension (containing $1x10^8$ CFU/mL) of fungi isolated from corroded metals. Two controls were also provided, in control one K1, metal was exposed to common conditions (room temperature and humidity) and not contaminated with fungi. In control two K2, metal was placed on malt extract medium but not inoculated with fungi. Medium with metals was incubated at 27 C. The entire experiments were uniformly prepared in triplicates, labeled accordingly and inserted on the same day for each fungi isolated. The experiment was observed for a period of 60 days at 10 days intervals.

2.5.2 Corrosion inhibition test

The experiment is set up as above but in this case, the medium with the metal coupons were treated with the *A. melegueta* extract (25mg/mL conc.) and then inoculated with *Aspergillus fumigatus* and *Acremonium kiliense* isolated from corroded mild steel pipe. For the control C1, metal was exposed to common conditions (room temperature and humidity) and not contaminated with fungi. Medium with metals was incubated at 27 C. The entire experiments were uniformly prepared, labeled accordingly and inserted on the same day. The experiment was observed for a period of 60days.

To determine weight loss with respect to time, the coupons were retrieved after 10 days intervals progressively, scrubbed with bristle brush, washed with distilled water, dried and weighed. The weight loss was taken to be the difference between the weight of coupons at a given time (day) and its initial weight. All tests were in triplicate and the data showed good reproducibility.

Weight loss (W_L) = W_i - W_f (1)

Where W_i = Initial weight

W_f = Final weight

$$\mathbf{CR} = \frac{k\Delta M}{A\rho t} \quad (2)$$

A= Exposed surface area =2(LW+LH+HW) cm^2

Where L= length of the coupon

W= width of the coupon

H= height of the coupon or thickness

k = corrosion rate constant (143,700 mpy)

ρ =density of metal coupon (g/cm^3)

ΔM= weight loss of coupon (g)

t = time (days)

2.5.3Inhibition efficiency

The inhibition efficiency IE (%) was quantified by comparing the corrosion rate of mild steel specimen without inhibitor ($CR_{uninhibited}$) and in the presence of inhibitor ($CR_{inhibited}$).

$$IE\ \% = \left(\frac{CR_{uninhibited} - CR_{inhibited}}{CR_{uninhibited}}\right) x100 \quad (3)$$

2.5.4 Electrochemical measurement

The potentiodynamic polarization test was carried out in a standard three-electrode glass cell of 500 ml capacity using Electrochemical System workstation (PAR 263). A graphite rod served as counter electrode and, a saturated calomel electrode (SCE) was used as reference electrodes. A mild steel specimen of 1 cm^2 dimension were used as working electrode. Electrochemical measurements were carried out at 30±1°C, using standard procedures as outlined by Oguzie *et al.* (2013), in aerated solutions at the end of 1800s of immersion, which allowed the open circuit potential (OCP) values to attain steady state. The potentiodynamic polarization (PDP) experiments were then conducted at a scan rate of 0.333 mV/s. The potential range employed was -250 mV to + 300 mV versus corrosion potential. Powersuite software was used in analyzing the polarization data.

3. Results

3.1 Phytochemical analysis

Table 1 shows the results of the phytochemical screening and the percentage amounts of key phytochemical constituents present in *A. melegueta* seed extract. They include saponins, alkaloids, tannins, flavonoids and

phenol.

Table 1 Qualitative and quantitative phytochemical constituents of *A.melegueta* seed extracts.

Parameters	***Aframonium melegueta***	
Alkoloids	+++	5.17±0.29
Tannins	++	0.41±0.11
Saponins	+	1.23±0.03
Phenols	++	36.68 ±1.5
Flavonoids	++	2.04±0.05
Terpenes	++	-
Cardiac glycoside	+++	58.58±1.10
Steroids	+++	-

3.1.2 Antifungal activity of the extract

The results of the fungicidal activity of the extract of *Aframomum melegueta* against *A.fumigatus* and *Acremonium kiliense* are shown in Table 2. The highest growth inhibitory activity was obtained from the stock solution of the cold water extract. Table 2 also shows the summary of the minimum inhibitory concentration (MIC) of the extracts. The MIC closely followed the same trend as the growth inhibition effect of the extracts with only the cold water extract exhibiting significant inhibition of the mycelia growth of *A.fumigatus* and *A. kiliense* at the 25mg/mL concentration.

Table 2 Antifungal activity of the seed extract of *Aframomum melegueta* against *Aapergillius fumigatus* and *Acremonium kiliense*

Plant Extract	Solvent	Percentage mycelia inhibition at different concentrations					
		Acremonium kiliens			***Aspergillius fumigatus***		
		50%	25%	12.5%	50%	25%	12.5%
A. melegueta	CW	10.5	9.5	-	10.5	9.5	-
A. melegueta	HW	11.0	-	-	9.5	-	-
A. melegueta	ET	-	-	-	8.0	-	
A. melegueta	MT	-	-	-	11.0	-	-

Legend: CW=Cold water, HW=Hot water, ET=Ethanol and MT=Methanol

3.2 Corrosion results

The gravimetric results of the influence of *A. kiliense* and *A. fumigatus* on the corrosion behavior of mild steel after 60days exposure are shown in figures 1 and 2. The results showed that the growth and attachment of *A. kiliense* and *A. fumigatus* on mild steel significantly influenced their corrosion progressively over the period as was evident in the increase in weight loss (ΔW) corrosion rate (CR). The CR of mild steel increased from 0.05mpy in 10days to 3.0mpy in 60days. Similarly, there was also increase in weight loss (ΔW) form 0.01g in 10days to 0.09g in 60days.

3.3 Corrosion inhibition results

The inhibitive effects of cold water CW extract of *A. melegueta* seeds on the corrosion behavior of mild steel in the presence of *Aspergillius fumigatus* and *Acremonium kiliense* were studied using gravimetric technique. Figure 3, 4, and 5 shows the weight loss and corrosion rates of mild steel in the presence of the inhibitor and the fungi. The plots show that *A. melegueta* extract effectively retarded mild steel corrosion at the concentration studied. Furthermore, the weight loss and corrosion rate was found to increase with exposure time. Table 3 shows the inhibiting effects of extracts of *A.melegueta* on the corrosion behavior of mild steel in the presence of *A.kiliense* and *Aspergillius fumigatus*. For example, there were significant variations ($p < 0.05$) on the cumulative corrosion rate (∑CR) 0.98±0.10 mpy obtained in the presence of the inhibitor *A. melegueta* when compared with ∑CR results obtained 6.51±0.19 mpy when metals were exposed to *Acremonium kiliense* in the absence of inhibitor. The result also showed significant variations ($p < 0.05$) in the ∑CR 0.79±0.07mpy obtained in presence of *A.melegueta*, compared with ∑CR (7.85±0.91mpy) obtained from the influence of *A. fumigatus* in the absence of the inhibitor.

3.4Percentage inhibition efficiency (IE %)

The result of the efficiency of the extract on the corrosion of mild steel is shown in Table 4 and Figure 6. The

results confirm that *A. melegueta* was more effective (87%) against *Aspergillius fumigatus* than *Acremonium kiliense* (40%).

3.5 Electrochemical corrosion measurement

The results of the potentiodynamic polarization test and the corresponding polarization data for the corrosion behavior of mild steel in the presence of *A. kiliense* and *A. fumigatus* and the effects of the extracts of *A. melegueta* on the kinetics of the anodic and cathodic partial reactions of the corrosion processes are presented in Table 5. *A. fumigatus* gave the highest corrosion current density (I_{corr}) of 279.4μA/cm^2 followed by *A. kiliense* with 223μA/cm^2 respectively.

Figure 6 and 7 show typical potentiodynamic polarization curves for mild steel in the presence of fungi. The mild steel is seen to exhibit active dissolution with no clear transition to passivation within the studied potential range in the presence of all the fungi but especially in the presence of *A. fumigatus*. The plots also showed that the anodic and cathodic reactions (without inhibitors) follow Tafel's law and the related anodic (i_a) and cathodic (i_c) current densities.

Figure 7 shows typical potentiodynamic polarization curves for mild steel in the presence of fungi and inhibitors. The polarization curve show that the adsorption of *A.meleguta* on the mild steel surface inhibits both anodic and cathodic reactions reducing, corrosion current density (I_{corr}) from 223.0 to 113μA/cm^2 in the presence of *A.melegueta*.

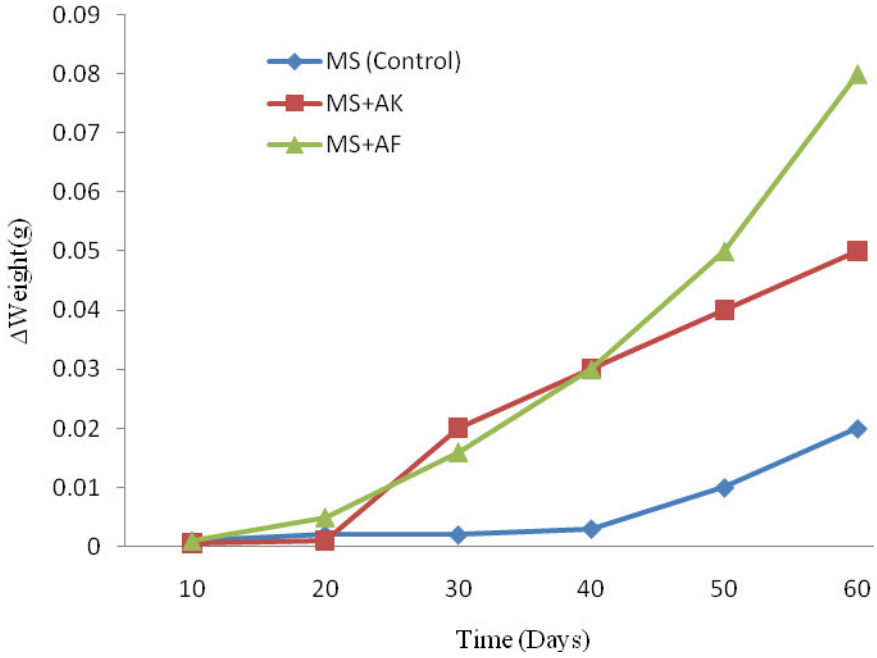

Figure 1 Weight loss of mild steel in the presence of *Aspergillius fumigatus and Acremonium kiliense*

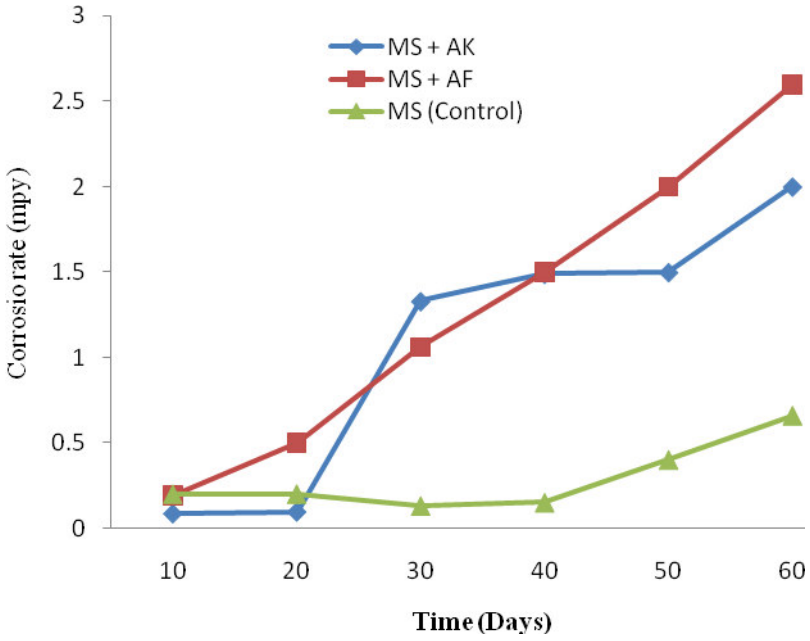

Figure2: Corrosion rate of mild steel in the presence of *Acremonium kiliense* and *Aspergillius fumigatus*

Table 3 Cumulative corrosion rate and weight loss of *A. kiliense A. fumigatus* influenced corrosion in the presence and absence of inhibitors after 60days.

Parameters	**Cumulative corrosion rate and weight loss (∑CR and ∑ΔW)**			
	Acremonium kiliense		***Aspergilluius fumigatus***	
	MS	+AM	MS	+AM
∑CR	6.51±0.19	0.98±0.10	7.85±0.91	0.79±0.07
∑ΔW	0.14±0.02	0.02±0.00	0.18±0.03	0.07±0.00

Legend: MS=Mild steel, AL= Aluminium AM=*Afrmomnium melegueta*, PG= *Piper guineense*, ∑CR= cumulative corrosion rate and ∑ΔW=cumulative weight loss

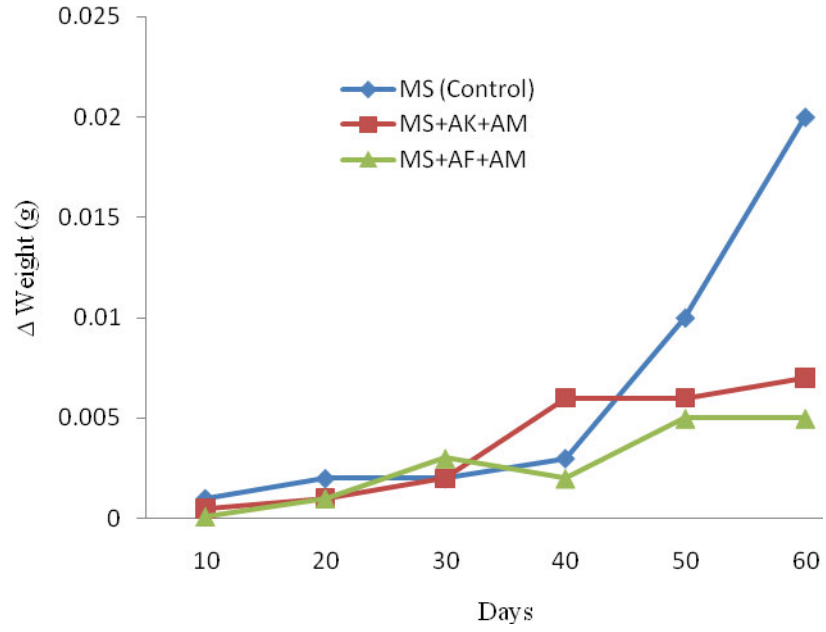

Figure 3: Inhibitive effects of *A. melegueta* on the corrosion of mild steel
Legend: MS=Mild steel, AK=*Acremonium kiliense*, AF= *Aspergillius fumigatus*, AM=*Aframomum melegueta*

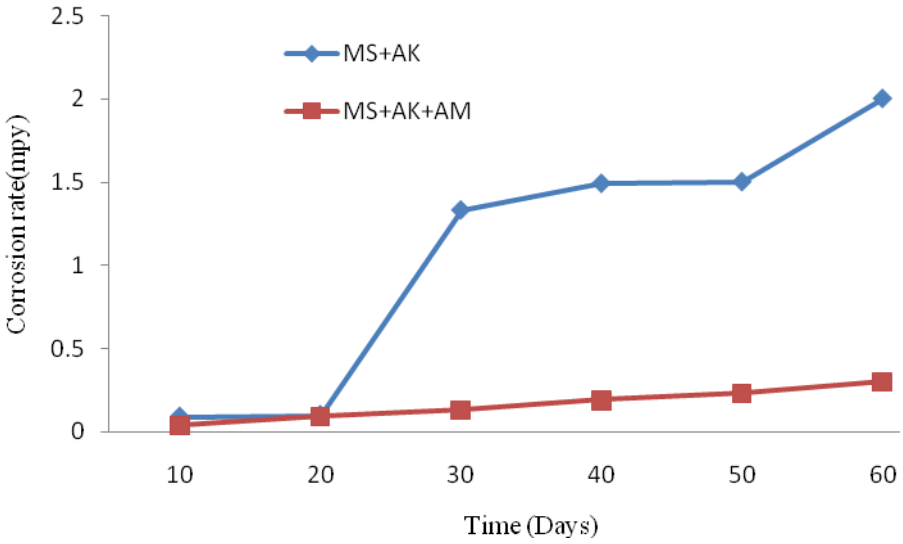

Figure4: Corrosion rate of *A. kiliense* influenced corrosion of mild steel in the presence and absence of inhibitors *A. melegueta.*
Legend: MS=Mild steel, AK= *A. kiliense* and AM= *A. melegueta.*

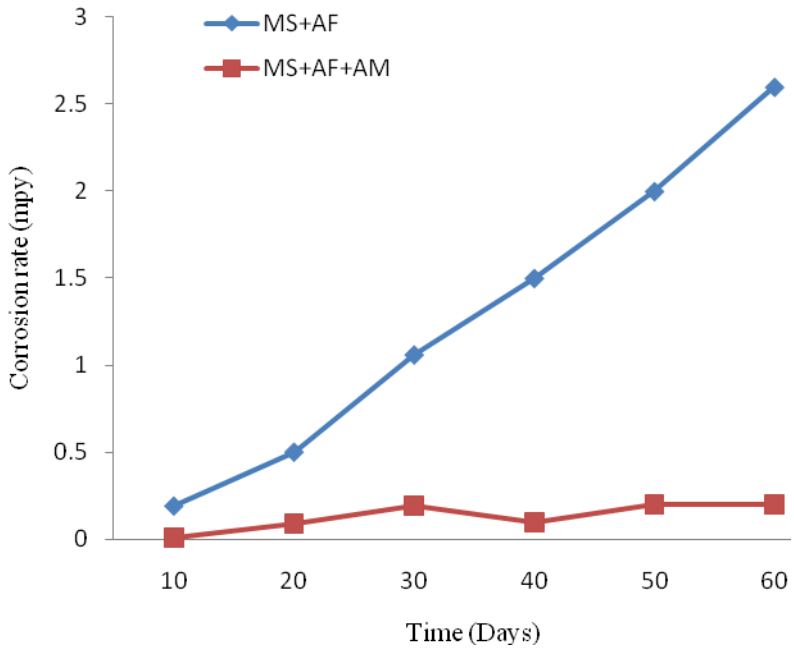

Figure 5: Corrosion rate of *A. fumigatus* influenced corrosion of mild steel in the presence and absence of inhibitor *A. melegueta*.
Legend: MS=Mild steel, AF= *A. fumigatus* and AM= *A. melegueta.*

Table 4: Inhibition efficiency of the extracts on the corrosion of mild steel and aluminium in the presence and absence of *A.kiliense* and *A. fumigatus* after 60 days.

	Inhibition efficiency IE%
Fungi+ Inhibitor	Mild Steel
Acremmnium kiliense + *Aframomum melegueta*	40
Aspergillius fumigatus + *Aframomum melegueta*	85

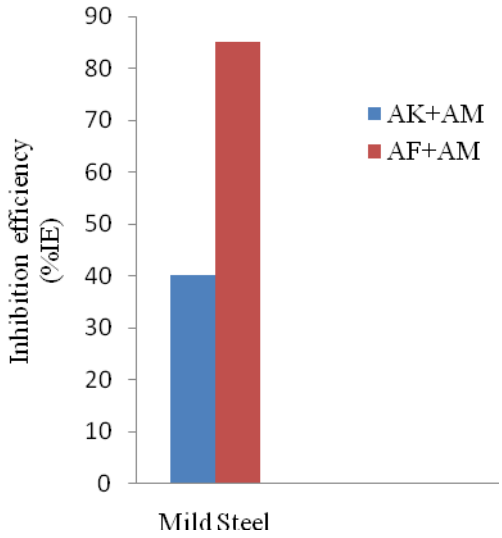

Figure 6: Inhibition efficiency of *A.melegueta* in the presence of *A. kiliense* and *A. fumigatus*
Legend: MS=Mild steel, AK= *A. kiliense,* AM = *A.melegueta* and AF=*A. fumigatus*

3.5.1Electrochemical data

Potentiodynamic polarization studies were carried to ascertain the effects of the fungi on the corrosion behavior of the metals, the influence of the fungi on the anodic and cathodic reactions processes and the influence of the extract on the kinetics of anodic and cathodic partial reactions of the corrosion processes. The electrochemical parameters including the corrosion current density (I_{corr}) and corrosion potential (E_{corr}) in the presence of the inhibitor can be observed from Tafel plot (Figure 6, 7 and 8).

Table 5 Polarization data for mild steel in the presence and absence of fungi and the inhibitors.

Fungi		**I_{corr} ($\mu A/cm^2$)**	**E_{corr} mV Vs SEC**	**β_a**	**β_c**
Acremonium kiliense	MS1	223.0	−417.3	122.7	100.6
Aspergillius fumigatus	MS2	279.4	−485.4	115.1	75.1
Control	MS4	187.9	−491.8	105.3	69.2
Aframomum melegueta	MS5	113.0	−548.2	104.2	71.4

Legend: MS1 =Mild Steel with *Acremonium kiliense*
MS2 = Mild Steel *Aspergillus fumigatus*
MS4 = CONTROL
MS5 = Mild Steel + *A. kiliense* with INHIBITOR *Aframomum melegueta.*

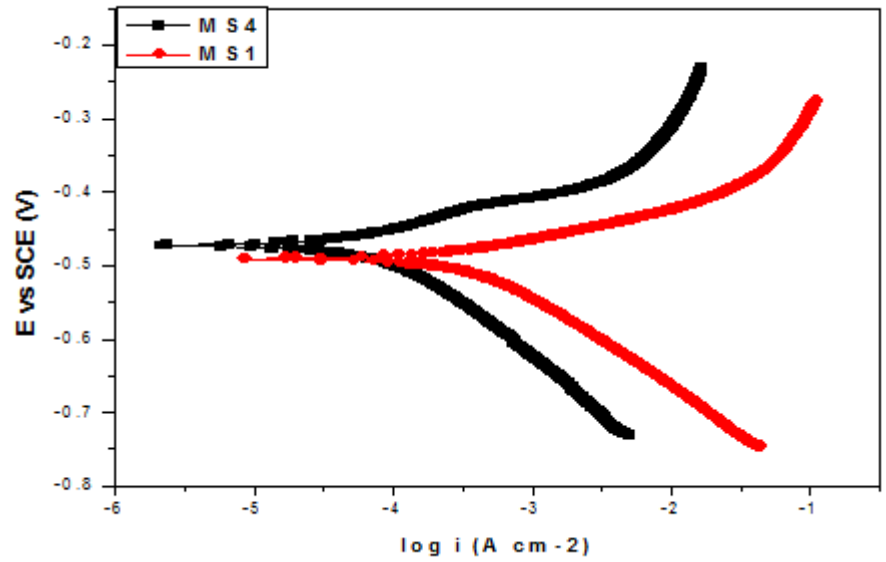

Figure 6: Potentiodynamic polarization curves of mild steel in the presence of *A. kiliense*

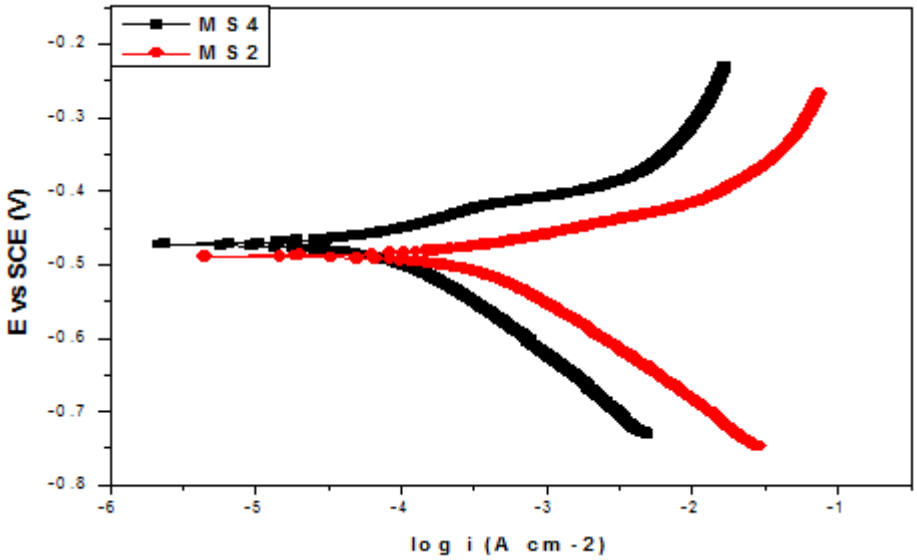

Figure 7: Potentiodynamic polarization curves of mild steel in the presence of *A. fumigatus*

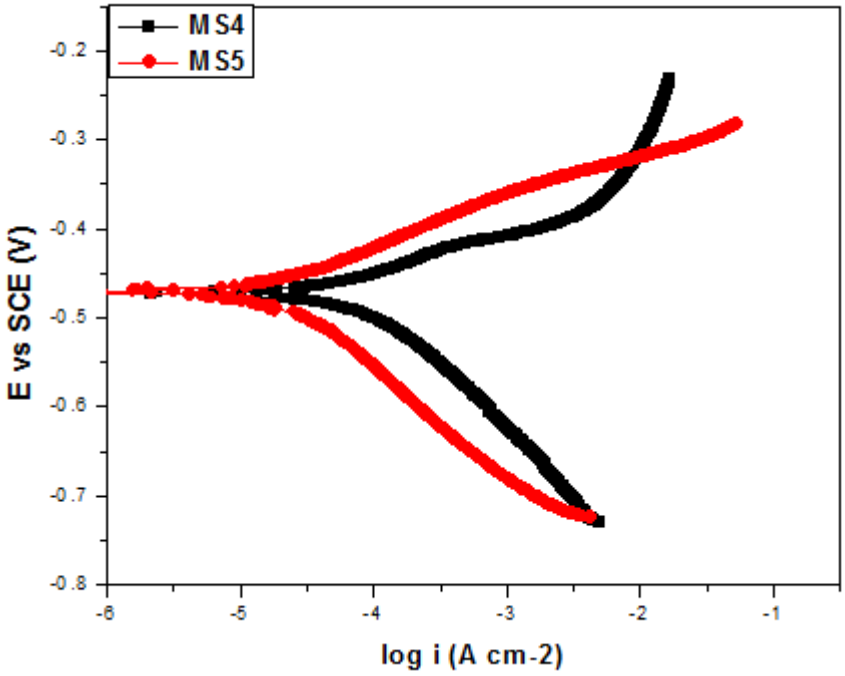

Figure 8: Potentiodynamic polarization curve for mild steel in the presence of *A. kiliense* and inhibitor *Aframomum melegueta.*

4. Discussion

The results of the phytochemical screening and percentage amount of key phytochemical constituents of *A. melegueta* revealed the presence of alkaloids, tannins, saponins, phenols, and flavonoids. This is in line with the findings of Okoye and Ebeledike (2013). Similarly the phytochemical screening of *A. melegueta* conducted by Echo *et al.* (2012) showed that the seeds of the plant contained alkaloids, flavonoids, tannin, saponin, steroids, terpenes, phenols and cardiac glycosides. Oguzie *et al.* (2013) observed that saponin extracts act on the microbial cells as detergents and as quaternary ammonium salts, dissolving lipids and thus causing the loss of cellular contents. They also noted that the tannin moieties, with their protein-binding abilities, could interact with basic constituents of proteins present in cell walls, cell membranes and cytoplasm with resultant inhibition of key metabolic functions of the cells. The above effects could have contributed to the observed fungal growth inhibition.

Echo *et al*. (2012) also observed that these phytochemicals exhibit a wide range of biological effects as a consequence of their antioxidant properties. Okoye and Ebeledike (2013) observed that flavoids possess antioxidant activity and equally anti-inflammatory. Kubmarawa *et al.* (2007) reported the importance of alkaloids, saponins and tannins in various antibiotics used in treating common pathogenic strains. Doss *et al.* (2009) reported that tannins extracted from the plant *Solanum trilobatum* Linn and assayed against the bacteria *Staphylococcus aureus*, *Streptococcus pyrogens*, *Salmonella typhi*, *Pseudomonas aeruginosa*, *Proteus vulgaris* and *Escherichia coli* using agar diffusion method exhibited antibacterial activities against the microorganisms. Kredy (2010) also evaluated the antimicrobial activities of sapronin extract from *Zizihus spina* and found it to be active against *E. coli, Proteus mirabilis* and *Streptococcus pneumonia*. Also alkaloids have been shown to be effective against most bacteria and fungi (Cushine and Lamb 2005).

The result of the exposure of these fungi to mild steel for 60 days and their capacity to adapt, grow and destruct the metal surface were studied. The results of the influence of *A. kiliense* and *A. fumigatus* on the corrosion behavior of mild steel after 60 days exposure are shown in Figure 1 and 2. The results showed that the growth and attachment of these fungi on mild steel significantly influenced their corrosion rate over the period as evident from the increase in corrosion rates and weight loss. For example, the corrosion rate of mild steel exposed to *A. kiliense* and *A. fumigatus* increased from 0.09mpy to 2.0mpy, 0.19mpy to 2.6mpy respectively between 10 to 60 days of exposure. Similarly, there was also corresponding increase in weight loss (ΔW) observed for all the fungi with time. It could also be seen that corrosion rate increased with increase in time. This observation is typical of a metal that demonstrates passivity effects. Similar observations have been reported (Agarry and Salam 2016). Videla (2002) reported that corrosivity increased with contact time due to accumulation of metabolites under fungal colonies attached to metal surfaces.

Results of the gravimetric analysis, showed that *A. fumigatus* was more corrosive with the cumulative

corrosion rate ∑CR and ΔW of 7.85±0.9 and 0.18±0.03 followed by *A. kiliense* 6.51±0.79 and 0.14±0.02 respectively. Bento *et al*. (2005) reported the corrosive activities on mild steel ASTM 283-93-C used as storage tank for urban diesel. They observed that *A.fumigatus* gave the greatest value for steel weight loss. The authors also observed that solid phase micro extraction (SPME) showed that the main acid present in the phase after 60 days incubation with *A. fumigatus* was propionic acid.

A substantial shift of E_{corr} towards noble values occurred throughout the period of exposure of the mild steel (Table 5) to fungi. The shift to positive potential observed (–417.3mV/SCEfor *A.keliense*,–485.4mV/SCE for *A. fumigatus* and –490.2) correlates with the growth of fungi on the mild steel when compared with –491.8 mV/SEC obtained in the absence of fungi. Similar observation was reported by (Faisal *et al.* 2013). The potential shift clearly supports the findings that activities and growth of fungi species enhanced the redox quality of the medium and accelerated the metal dissolution. The positive shifts in E_{corr} also lead to ennoblement which is an indicator for potential corrosion. Ennoblement in microbiologically influenced corrosion (MIC) has been acknowledged by different investigators as probably the most notable phenomenon in MIC studies (Faisal *et al.* 2013; Little *et al*.2001 and Hussian *et al.* 2011). It has been attributed to the microbial colonization and biofilm formation which collectively result in organometallic catalysis and acidification of the metal surface which promotes pitting corrosion as was observed on the mild steel in the presence of fungi

The results of inhibition of the plant extracts on the corrosion behavior of mild steel in the presence of fungi showed that the extracts extensively inhibited both the growth of fungi and corrosion processes. This is evident from the gravimetric data on the corrosion rate and weight loss observed. For example, the ∑CR of 0.79±0.07 mpy and 0.98±0.10 mpy was recorded when *A. melegueta* extract was applied compared to the ∑CR of 7.85±0.91mpy and 6.51±0.19 mpy observed in the presence of *A. fumigatus* and *A. kiliens* respectively after 60days without the extract. The weight loss analysis also followed the same trend. Oguzie *et al.* (2012) studied the anticorrosion effects of the ethanol extract of *Capsicum frutescens* on the low carbon in acidic media using gravimetric, impedence and polarization techniques. They observed that *C. frutescens* effectively inhibited both corrosion and growth of sulfate reducing bacteria (SRB) due to the action of the phytochemical constituents present therein which included alkaloids, tannins and saponins (which are also present in *A. melegueta*). It is therefore possible that the inhibition of the corrosion and fungal growth observed might have been as a result of the presence of these phytochemicals in the seed extracts. The authors also stated that saponin possesses fungicidal activities against *A. fumigatus* species. Although the detailed mechanism of the fungicidal actions of *A. melegueta* were not extensively investigated, actions of the observed growth inhibition abilities could be attributed to lipids dissolving ability of saponin moieties (Oguzie *et al.* 2012; Imo *et al.* 2018) which results in loss of cellular content as well as the protein binding abilities of tannins which facilitates interferes with key metabolic functions of the cells.

The values of the CR in the absence ($CR_{uninhibited}$) and presence of inhibitor ($CR_{inhibited}$) were used to estimate the inhibition efficiency from gravimetric data. *A.melegueta* was more effective *A. fumigatus* (85%) and against *A. kiliense* (40%). Singh *et al.* (2012) reported that *Andrographis paniculata*, *Strychnous nuxvomica* and *Moringa oleifera* plant extracts showed inhibition efficiency above 98%. The authors used weight loss methods to determine the inhibition efficiency of the inhibitors. Rajam *et al.* (2013) also investigated the inhibition efficiency of an aqueous extract of garlic on the corrosion of carbon steel in well water by weight loss method.

Potentiodynamic polarization studies were carried to ascertain the effects of the fungi on the corrosion behavior of the metals, the influence of the fungi on the anodic and cathodic reactions processes and the influence of the extracts on the kinetics of anodic and cathodic partial reactions of the corrosion processes. From the electrochemical corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic Tafel slope (β_a) and cathodic Tael slope (β_c) in Table 5, it can be observed that the corrosion (I_{corr}) increased in the presence of all the fungi when compared with the readings in the absence of fungi, indicating an increase in corrosion reaction. This suggests that the presence of the fungi and their metabolites might have induced an increase in corrosion rates of mild steel thus showing slight electrochemical activities on the mild steel. Qing *et al.* (2007) pointed out that metabolic by-products and biofilm formation accelerated pitting and corrosion rate of AZ1B magnesium alloy in artificial seawater. Juzeliunas *et al.* (2007) observed that the overgrowth of metallic surfaces with fungus mycelia was closely related to electrochemical processes. It is also possible that since corrosion is an electrochemical process, the increase in corrosion rate observed could have been due to fungal growth on the metals. Mansfield and Little (1990) used potentiodynamic polarization technique to examine the overall corrosion behavior of a corrosion system. The authors observed that increase in corrosion current (I_{corr}) density was due to the influence of microorganisms on the rate of the anodic and cathodic reactions. In this study, it can be seen from the results that the rate of metal dissolution or oxidation is proportional to the corrosion current (I_{corr}). This is in line with the findings of Videla (2000) who stated that corrosion rate is proportional to corrosion current density.

5. Conclusions

As microorganisms like fungi adhere to metal surfaces by means of their physiological activities, they are able to change electrochemical conditions on the metal in the most corrosion relevant way. This study shows that *A. melegueta* seed extract inhibited the fungal influenced corrosion of mild steel caused by *A. fumigatus* and *A. kiliense*. The potentiodynamic polarization measurement further showed that the mechanism of corrosion inhibition process proceeded via mixed –type mechanism. The results obtained are consistent with our hypothesis that the phytochemical constituents of *A. melegueta* seed extract can be used as inhibitors against the fungal influenced corrosion of metals.

Conflict of interest

The authors declare that there is no conflict of interest.

6. References

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