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Research Article

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Moringa Oleifera Seed Oil as Green Corrosion Inhibitor for Ductile Cast Iron in Cassava Fluid

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Abstract
Cassava fluid is acidic and corrodes the ductile cast iron parts from which many machineries used in processing cassava, a staple source of carbohydrates in most West African countries are made. The corrosion behavior of ductile cast iron cassava fluid with Moringa Oleifera seed oil as inhibitor was studied using 0, 0.2, 0.4, 0.6, and 0.8 %v/v concentrations and at two different temperatures of 40°C and 60°C by potentiodynamic polarization (Tafel) technique. Some thermodynamic, Corrosion inhibition and adsorption studies were also addressed. Moringa Oleifera seed oil extract was found to successfully inhibit the corrosion of cast iron in cassava fluid. Moringa Oleifera acted as a mixed type inhibitor. The corrosion inhibition efficiency was found to increase with increase in concentration of the extract but decrease with rise in temperature. The maximum inhibition efficiency of the extract on ductile cast iron corrosion was noted to be about 73%. Adsorption studies showed that Langmuir isotherm describes the manner in which the inhibitor was adsorbed on the metal surface. The adsorption process was found to be spontaneous as all the free energy of adsorption values calculated were negative and ranged from -3.43 kJ/mol to -1.34 kJ/mol, signifying a spontaneous physical adsorption on metal surface. The stereo-micrograph images of the metal surface after immersion in corrosive medium confirmed the protection offered by the Moringa Oleifera extract on the surface of the metal. It was further shown that the corrosion rate was influenced by the combined interactions of temperature of operation and concentration of the inhibitor.

Keywords: Moringa Oleifera, Corrosion Inhibitor, Cast Iron, Adsorption, Inhibition Efficiency, Potentiodynamic Polarization

Introduction
Corrosion of engineering structures and components in service has continued to be a major concern to corrosion experts in the academia and industries. This is primarily due to its deleterious effect on material integrity and mechanical properties resulting in failure in severe cases [1]. Corrosion prevention and control have become a perpetual struggle between man and nature, particularly in view of the modern age technological development and the increasing need and use of metallic material in all facet of technology. This has necessitated the increasing interest in research into the metal environment interface reaction and the means of mitigating the damaging effects of corrosion on metals and alloys [2]. One of the best options adopted to reduce and control the corrosion of metals is the addition of inhibitors due to ease of application and one of the most useful in the industry. This method is growing due to low cost and practice method [3, 4].

Many researches have been carried out to examine compounds that are suitable to mitigate the corrosion of metals in different environments such as Water hyacinth Sida acuta, Jatropha curcas [5-9]. Their inhibition efficiencies and adaptability for commercial use have been very promising and have raised hope for complete replacement of the more expensive and toxic synthetic inhibitors. Nonetheless, there still exists the need for research on other potential plant-based inhibitors especially those with competing applications. This research investigated the corrosion behavior of ductile cast iron in mix of *Moringa Oleifera* seed oil and cassava fluid using potentiodynamic polarization (Tafel) technique in order to extend the usage of such naturally occurring, cheap and environmentally safe substances to mitigate corrosion of metals. Surface morphology was studied by stereo-microscopic investigation.

Experimental procedure
Preparation of the test sample
Ductile cast iron used for the research was obtained from Standard Metallurgical Company Sagamu Ogun State Nigeria. Its chemical composition was determined using Thermo Scientific ARL OES Spectrometer and the results are presented in Table 1.

The ductile cast iron sample was cut into pieces measuring 10 mm × 10 mm, polished using successive grades of silicon carbide papers of grades P60, P120, P600, P1000 and P1200 grit, degreased in ethanol, dried in acetone and stored in desiccator as described by Odusote *et al*., [9].

Table 1: The Chemical Composition of As-received Ductile Cast Iron

Element	C	Si	Mn	Cr	S	Cu	P	Ni	Mo	**Bal**
Composition(%)	3.747	2.249	0.784	0.1165	0.1045	0.0650	0.0419	0.0367	0.0081	Fe

Preparation *Moringa Oleifera* Seed (Mos) Oil

MOS oil preparation involved the collection *Moringa Oleifera* fruit sourced from a farm in Isanlu, Kogi State, Nigeria, followed by drying, which stimulates the opening of the fruits to separate the seed and other impurities. They were then dried in an electric oven to eliminate moisture. Dried *Moringa Oleifera* seeds were milled into paste using thermal Willey mill.

10 gram of the paste was weighed and placed on a filter paper which was folded carefully. The filter paper containing the sample was then inserted into the Soxhlet apparatus. 200 ml of the solvent (hexane) was poured into a 500 ml round bottom flask with the sample. It was heated at 60^{o}C for 6 hours after which the sample was removed and transferred into the air oven to dry at 105^{o}C for 20 minutes. The oil was recovered by solvent evaporation. It was heated at a low temperature until the solvent finally evaporated leaving behind the oil. The phytochemical screening was there by carried out on the extract and inhibition test solutions were prepared from the extract to obtain 0.2, 0.4, 0.6, and 0.8%v/v in 250ml of cassava fluid.

Potentiodynamic Polarization Measurement

It involved polarization of a working electrode and monitoring the current that is produced as a function of time and potential. The test was carried out using three electrode cell assemblies at temperature of room, 40 and 60^{o}C with the Autolab VERSASTAT4 equipped with Versa STUDIO and connected to a thermostated water bath which maintains the preset temperature in the cell. The metal samples were embedded in polyester resins, polished and used as the working electrode, platinum rod was used as the counter electrode and saturated silver/silver chloride electrode as reference electrode. The electrolyte used for the study was 250ml of cassava fluid in the absence and presence of varying concentrations of *Moringa Oleifera* seed oil as inhibitor. The electrochemical measurement was carried out for about 30 minutes according to ASTM standard and reported by Haleem *et al*., (2017) for corrosion to reach a steady state at a scan rate of 0.5 mv/s to determine the current density, corrosion rate and inhibition efficiency [10]. Surface coverage and inhibition efficiency were calculated using equation 1 and 2 respectively. This was also reported according to Alaneme *et al*., [1].

$$(\Theta) = \frac{I_{corr} - I_{corr(i)}}{I_{corr}} \quad (1)$$

Where; I_{corr} and $I_{corr(i)}$ are corrosion current density in the absence and presence of the inhibitor respectively.

$$(\text{IE }\%) = \frac{C.R0 - C.R1}{C.R0} \times 100 \quad (2)$$

Where; $C.R_0$ and $C.R_1$ are corrosion rates in the absence of inhibitor and presence of inhibitor respectively.

Results and Discussion

Phytochemical Screening of (MOS) Oil

Phytochemical screening was carried out on *Moringa Oleifera* seed oil. The result shows the presence of active constituents responsible for corrosion inhibition of most metals. The phytochemicals identified in the *Moringa Oleifera* seed oil are presented in Table 2. This agrees with the findings of Kasolo *et al*. as well as Egereonu and Nduchukwu [11, 12]. Previous results have attributed the inhibitory properties of most green plants to the presence of active agents such as flavonoids, tannins, saponins and alkaloids [1, 13, 14].

Table 2: The Phytochemical Screening of MOS Oil

S/N	Phytochemical Constituent
1	Alkaloids ++
2	Flavonoids ++
3	Glycoside +++
4	Phlobatannins -
5	Tannins ++
6	Terpenoids +
7	Saponin +
8	Steroids +++
9	Oxalate +
10	Pheno +

Potentiodynamic Polarization

Corrosion Behaviour at Room Temperature

Figure 1 shows the Potentiodynamic (Tafel) polarization plot for the ductile iron in the absence and presence of different concentrations of inhibitor at room temperature. The linear section of cathodic and anodic Tafel lines was extrapolated to corrosion potential in order to calculate associated polarization parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), and corrosion rate. The inhibition efficiencies using values of corrosion rate were calculated and computed. The results are presented in Table 3. It is clear from Figure 1 that increasing concentrations of inhibitor caused significant decrease in corrosion current density and increase in inhibition efficiency as the concentrations increased. Further observations revealed that the As-received sample possessed the highest corrosion current density 38.402 A/cm^2 and hence the highest corrosion rate of 0.44561 mmpy compared with values obtained for samples immersed in cassava fluid in the presence of MOS inhibitor.

Table 3: Polarization parameters for ductile iron in cassava fluid in the absence and presence of various concentrations of *Moringa Oleifera* seed oil at room temperature.

Inhibitor Concentration (%v/v)	I_{corr} (A/cm^2)	E_{corr} (mv)	Corrosion Rate (mmpy)	IE (%)
As-received	38.402	-549.713	0.44561	-
0.2	20.740	-541.717	0.24067	45.9
0.4	17.573	-551.737	0.20392	54.2
0.6	16.464	-552.674	0.19105	57.1
0.8	10.384	-543.617	0.12012	73.0

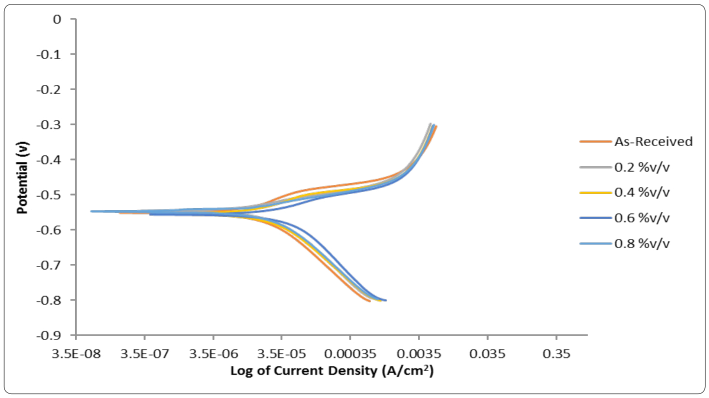

Figure 1: Tafel Polarization Plot of ductile cast iron in cassava fluid at room temperature

It was observed from Figure 1 that the cathodic and anodic polarization curves were shifted toward lower current densities as the inhibitor concentration increases; this is an indication that the inhibitor affected the mechanism of both the cathodic and anodic reactions and therefore behaved as a mixed type inhibitor [15]. It was clearly observed that in the presence of *Moringa Oleifera* seed (MOS) oil, the corrosion resistance increases tremendously which leads to an increase in inhibition efficiency. The highest inhibition efficiency of 73% was obtained at 0.8 %v/v concentration. This means that more inhibitor particles were adsorbed on the surface of the metal thus providing a wider surface coverage [16].

Corrosion Behaviour at 40°C

Figure 2 shows the potentiodynamic polarization curves of corrosion inhibition of the ductile iron in cassava fluid in the absence and presence of different concentrations of *Moringa Oleifera* seed extract at 40°C. It can be observed from Figure 2 that the corrosion current density decreased with increase in the concentration of the extract as there appeared to be a shift towards more negative potential. According to the literature, if the shift in corrosion potential (E_{corr}) value for inhibited system is more than ± 85 mv with respect to uninhibited system then the inhibitor can be regarded as either anodic or cathodic type [17].

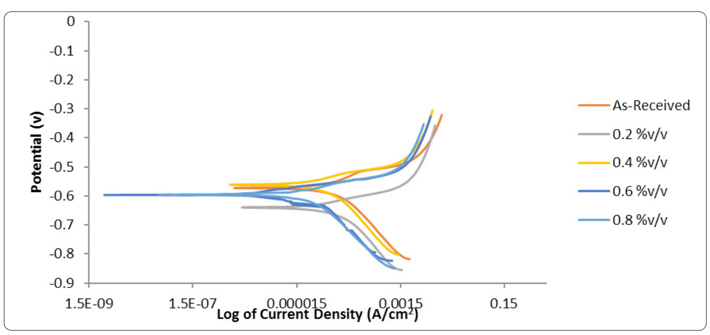

Figure 2: Tafel Polarization Plot of ductile cast iron in cassava fluid at 40°C

It can be seen from Figure 2 that there was no noticeable shift observed in corrosion potential (E_{corr}) values for inhibited system with respect to the uninhibited system therefore the inhibitor acted as mixed mode type of corrosion inhibition. However, the Ecorr values of 0.2 %v/v concentration of inhibitor was slightly shifted in the cathodic direction (up to – 46.8 mv) (Table 4) suggesting a mixed-mode of corrosion inhibition with slightly cathodic effect. The inhibition efficiency was found to decrease with rise in temperature, indicating that lower amounts of inhibitor molecules were adsorbed on the surface of the metal at higher temperature thus providing less surface coverage. This slight decrease of inhibition efficiency with rise in temperature may be associated with weakening of adsorbed inhibitor on the metal surface as reported [17].

Table 4: Polarization parameters for ductile iron in cassava fluid in the absence and presence of various concentrations of *Moringa Oleifera* seed oil at 40°C.

Inhibitor Concentration (%v/v)	I_{corr} (A/cm²)	E_{corr} (mv)	Corrosion Rate (mmpy)	IE (%)
As-received	89.905	-570.767	1.0432	-
0.2	72.788	-617.569	0.8450	18.9
0.4	67.997	-560.930	0.7895	24.3
0.6	47.287	-587.955	0.5487	47.3
0.8	40.999	-593.573	0.4782	54.0

Corrosion Behavior at 60°C

Figure 3 shows the linear polarization Tafel plot for the ductile iron in the absence and presence of different concentrations of inhibitor at 60°C. In the same way, it was observed that As-received possess the highest corrosion current density 216.406 A/cm² and corrosion rates 2.9252 mmpy respectively (Table 5) when compared with the samples immersed in cassava solution in the presence of inhibitor. This implies that as the concentration of inhibitor is increased, there is decrease in current density and corrosion rate respectively which results in an increased inhibition efficiency.

Table 5: Polarization parameters for ductile iron in cassava fluid in the absence and presence of various concentrations of *Moringa Oleifera* seed oil at 60°C.

Inhibitor Concentration (%v/v)	I_{corr} (A/cm²)	E_{corr} (mv)	Corrosion Rate (mmpy)	IE (%)
As-received	216.406	-615.813	2.9252	-
0.2	194.998	-604.08	2.6412	9.7
0.4	178.992	-608.198	2.4268	17
0.6	152.150	-605.438	2.0568	29.7
0.8	142.120	-612.887	1.9214	34.3

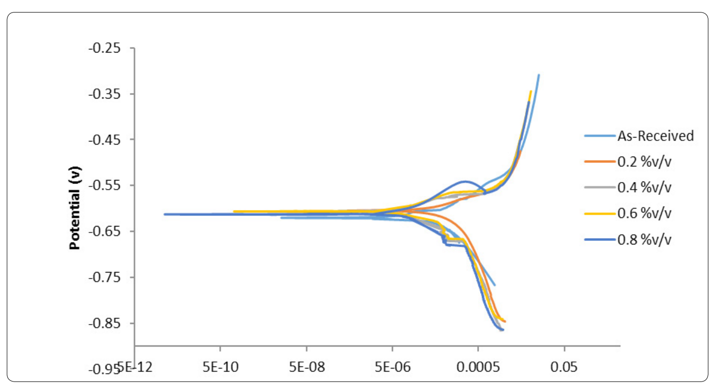

Figure 3: Tafel polarization plot of ductile cast iron in cassava fluid at 60°C

There was significant decrease in the inhibition efficiency with rise in temperature when compared with room temperature and 40°C indicating low inhibitor particles were absorbed on the surface of the metal thus providing a less surface coverage. This significant decrease of inhibition efficiency with rise in temperature may be due to weakening of adsorbed inhibitor on the metal surface [17]. There was higher loss of the material at 60°C both in the absence and presence of the *Moringa Oleifera* seed extract. This agrees with the other studies such as that of Umoren *et al.,* [6].

Surface Investigation

Further investigation of the corrosion inhibition ability of the extract was carried out by means of XTD series stereo-microscope equipped with a pair of wide-field and plane-scope eyepieces of X40 magnification. The micrographs were taken with high resolution camera to ascertain the surface morphology. It is observed from Figure 4(A) that the surface of the uninhibited sample of ductile cast iron was fairly more aggressively damaged due to dissolution in corrosive medium. The resulting micrograph shows evidence of cracks and pits whereas the surface of a ductile cast iron sample which was immersed in cassava fluid in the presence of an the optimum concentration (0.8 %v/v) of *Moringa Oleifera* seed oil extract presented a significantly smoother surface in comparison with uninhibited ductile cast iron surface. The micrograph in Figure 4(B) also features some adsorbed inhibitor film dispersed on the ductile iron surface which indicates that the adsorbed inhibitor molecules present in the extract of *Moringa Oleifera* seed contributed to the inhibition of the corrosion of ductile cast iron in cassava environment.

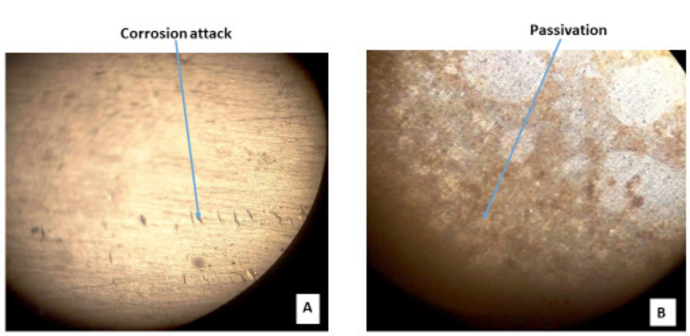

Figure 4: Stereo-micrograph (X40) for (A) Ductile Cast Iron in the absence of Inhibitor (B) Ductile Cast Iron in the presence of Inhibitor

The *Moringa Oleifera* seed extract deposits, the distribution was quite uniform on the metal surface resulting in good corrosion resistance.

Adsorption Studies

Adsorption isotherms are usually used to describe the adsorption process. They provide basic information about the interaction(s) between inhibitor and the metal surface [18]. Attempts were made to fit the surface coverage (Θ) values to various isotherms including Freundlich, Langmuir, Temkin and Frumkin isotherms. The best fit was obtained with the Langmuir isotherm which is represented by the following equation (3).

$$\frac{C}{\Theta} = \frac{1}{K_{ads}} + C \qquad (3)$$

Where; K_{ads} is the adsorption equilibrium constant, C is the inhibitor concentration and Θ is the surface coverage. Straight lines were obtained when we plot $\frac{C}{\Theta}$ against C (Figure 5) which suggested the adsorption of inhibitor on the surface of ductile and grey cast iron follows Langmuir adsorption isotherm.

The adsorption equilibrium constant (K_{ads}) is related to free energy of adsorption (ΔG^{o}_{ads}) and was calculated using equation (4).

$$\Delta G_{ads} = -RT \ln(55.5\, K_{ads}) \qquad (4)$$

Where; R is universal gas constant, T is the absolute temperature, K_{ads} is adsorption equilibrium constant and 55.5 is the concentration of water in solution. The values of K_{ads} and ΔG^{o}_{ads} were calculated and values obtained are presented in Table 6,

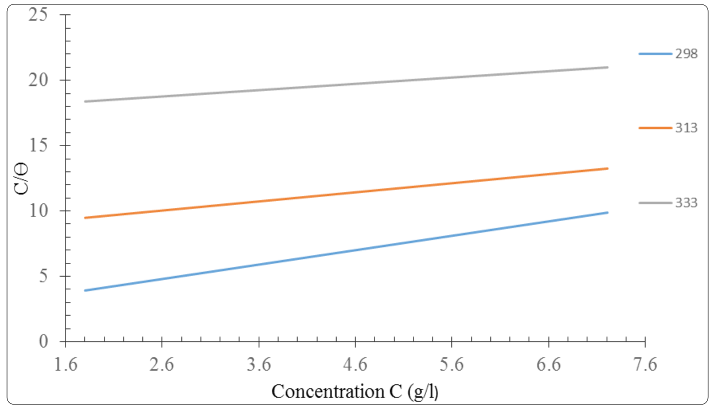

Figure 5: Langmuir adsorption isotherm for Moringa Oleifera Seed Oil on ductile cast iron

The adsorption parameters (K_{ads}) obtained from the plots help to infer the binding power of the inhibitor molecules to the surface of the metal. In this case, K_{ads} was seen to decrease with increasing temperature [19]. This behavior may be because an increase in temperature results in desorption of some initially adsorbed components of the extracts on the metal surface. Such desorption with increasing temperature may infer that the adsorption was entirely physical and little to no bonding occurred initially.

A higher value of K_{ads} means better inhibition efficiency of an inhibitor and strong interaction between the inhibitor molecules and the metal surface [17].

It has been reported that values of ΔG^{o}_{ads} ranging up to -20 kJ mol^{-1} are consistent with electrostatic interaction between charged inhibitor molecules and a charged metal (indicating physical adsorption), while those more negative or cloe to -40 kJ mol^{-1} or higher are associated with the charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond which indicates chemisorption [6]. Therefore, results presented in Table 6 indicate that the values of free energy of adsorption (ΔG^{o}_{ads}) for studied inhibitor has been considered within the range -3.43 kJ mol^{-1} to -1.34 kJ mol^{-1}. The negative value of free energy of adsorption (ΔG^{o}_{ads}) confers spontaneity on the adsorption process and stability on the adsorbed layer on the metal surface. This signifies a spontaneous adsorption of the additives via physisorption mechanism.

Table 6: Langmuir adsorption parameters and change in free energy at different temperatures.

Material	Temperature (K)	Slope	ΔG ads (kJ/mol)	K_{ads} (g/l)
Ductile	298	1.1488	-3.43	0.43
	313	0.4392	-1.91	0.10
	333	0.2829	-1.34	0.05

Conclusions

Based on the results of experimental investigation, the following conclusions were drawn:

1. *Moringa Oleifera* seed Oil greatly inhibits the corrosion rate of ductile cast iron in cassava fluid.
2. The corrosion inhibition efficiency of *Moringa Oleifera* seed Oil increases with increasing concentrations in the cassava fluid but decreases with increase in temperature.
3. Tafel polarization results showed that *Moringa Oleifera* seed Oil acts as a mixed type inhibitor via simple (physical) adsorption of the phytochemicals present in the extract on the cast iron surface in the cassava environment.
4. The adsorption of *Moringa Oleifera* seed Oil on ductile iron surface occurs spontaneously via physisorption mechanism and the adsorption process obeys Langmuir isotherm.
5. Surface investigation reveals that the inhibitor molecules adsorbed on metal surface restricts the diffusion of ions to or from the metal surface.
6. The inhibition efficiency of the *Moringa Oleifera* seed extract and the consequent corrosion rate of the metal are influenced by the interplay between concentration of the oil and the prevailing temperature.

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