ABSTRACT
Corrosion inhibition of mild steel in 0.5M H₂SO₄ by the total alkaloids and tannins extracted from Jatropha curcas stem bark was investigated using gravimetric method at 303K. The results showed that it contains 1.66% alkaloids and 1.53% tannins, these phytocompounds were found to inhibit corrosion process of mild steel in the test solutions and the inhibition efficiency depends on the concentration of alkaloids and tannins as well as the exposure time. The adsorption of both alkaloids and tannins on the mild steel was found to obey the Temkin and Langmuir adsorption isotherms and this suggested that the inhibitor molecules have been spontaneously adsorbed onto the surface of mild steel through a physical adsorption mechanism. The inhibition efficiency is markedly higher in addition of alkaloid extracts when compared with that of tannins extracts. Corrosion inhibition is attributed to the spontaneous physical adsorption of the plant constituents on the surface of the mild steel. Keywords: Alkaloids, Inhibition, Mild steel, Tannins

INTRODUCTION
Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment, the corrosion of iron or iron-based alloys with formation of corrosion products consisting largely of hydrous ferric oxide (Winston and Herbat, 2008). Mild steel is an alloy of iron containing small amounts of carbon 0.1-0.25%, strong and tough (Collins, 1998). Beside carbon, there are many elements that form part of steel alloy such as chromium, manganese, tungsten and vanadium. When steel is exposed to an industrial atmosphere, reacts to form the reaction product rust of approximate composition Fe₂O₃·H₂O (Loto, 2011). Corrosion is one of the major problems that must be confronted for the safety of our environment and for economic reasons. It occurs in various mechanical, metallurgical, biochemical and medical engineering appliances and more specifically in the design of a much more varied number of mechanical parts which equally vary in size, functionality and useful lifespan (Thompson et al., 2007). Several efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors is one of them (Ashassi-sorkhabi et al., 2008). In line with the emerging concept of ‘Green Chemistry’ and the related principles of ‘Less hazardous synthesis,’ therefore, the use of green inhibitors for the control of corrosion of metals (Loto, 2011) and alloys which are in contact with aggressive environment is an accepted and growing practice (Taylor and Raja, 2007; Khalid and Amin, 2009). Plant is one of the great chemical factories which can supply us with the chemicals required to inhibit the corrosion process, since most naturally occurring substances are safe and can be extracted by simple and cheap procedures (Taylor and Raja, 2007). An inhibitor is a chemical substance that, when added in small concentration to an environment, it effectively decreases corrosion rate (Winston and Herbat, 2008). The mechanism of action of inhibitors involve formation of a thin film passivation layer on the surface of the material that hinders access of the corrosive substances to the metal surface, thereby inhibiting either the oxidation or reduction part of the redox corrosion system or scavenging the dissolved oxygen. In acid medium, nitrogen-base materials and their derivatives, sulphur-containing compounds, aldehydes, thioaldehydes, acetylenic compounds, and various alkaloids, for example, papaverine, strychnine, quinine, and nicotine are used as inhibitors. In neutral media, benzoate, nitrite, chromate, and phosphate act as good inhibitors (Malik et al., 2011; Ebenso, 2004). Some investigations have in recent times been made into the corrosion inhibiting properties of natural products of plant origin and have been found to generally exhibit good inhibition efficiencies (Okafor and Ebenso, 2007). The yield of these natural products as well as the corrosion inhibition abilities of the plant extracts vary widely depending on the part of the plant and its location.
**MATERIALS AND METHODS**

**Collection and Identification of Sample**

Sample of stem bark of *Jatropha curcas* plant was collected from Afaka area of the Nigerian Defence Academy, Kaduna, Nigeria. Identified and authenticated by Mr Yahaya Abdullahi of Botany section, Department of Biological Sciences, Nigerian Defence Academy, Kaduna, Nigeria. The voucher specimen was deposited in the Herbarium. Mild steel was collected from Panteka market, Kaduna, Nigeria.

**Sample Preparation**

The stem bark of *Jatropha curcas* plant was carefully removed and oven dried at 40 °C for 2 hours and left for 2 days to air dry (Loto, 2011). The dried sample was pulverized using a wood mill machine. The pulverized sample was weighed and preserved for hot continuous extraction.

Phytochemical analysis of the extract of stem bark of *Jatropha curcas* plant was carried out according to the method reported by (Eddy and Ebenso, 2008).

**Total Alkaloids Extraction**

Total alkaloids extracts was extracted from the stem bark of *Jatropha curcas* according to method described by Garba and Okeniyi (2012).

**Total Tannins Extraction**

Total Tanninexstracts was extracted from the stem bark of *Jatropha curcas* according to method reported by Faten, et al (2014).

**Preparation of Mid Steel Sample**

The nominal percent of mild steel used in this study is Carbon (0.19), silicon (0.25), Mn (0.64), S (0.05), P (0.06), Ni (0.09), Cr (0.08), Mo (0.02), and Cu (0.27), the rest been Fe. The bar was cut into various rectangular pieces of coupons with dimensions 4 x 2 x 0.65 cm. The test specimen was washed using a wire brush; polished with silicon carbide abrasive paper of 240, 320 and 400 grits; polished to 1micron and thoroughly cleaned and rinsed in ultrasonic cleaner, dried and kept in desiccators for further use (Loto, 2011).

**Preparation of test media with the extracts**

The alkaloids and tannins extracts of the plant was used in the preparation of the test solutions by dissolving 0.1, 0.2, 0.3, 0.4 and 0.5 g of the alkaid and tannins extracts differently in 1 L of 0.5 M H$_2$SO$_4$. This correspond to the concentrations of 0.1, 0.2, 0.3, 0.4 and 0.5 g/L, while the blank medium without extract is made up of only 1 L of 0.5 M of H$_2$SO$_4$ (Loto, 2011).

**Weight Loss Experiment**

Previously weighed test specimens of mild steels were totally immersed in each of the test media contained in a 250 cm$^3$ beaker for 25 days. The beaker was inserted into a water bath maintained at a temperature of 303 K. Experiment was performed with acid test media in which some had the solution extract added. Test specimen were taken out of the test media every 5 days, washed with distilled water, rinsed with methanol, air dried and re weighted. The difference in the weight before the experiment and after the experiment were used as to determine the weight loss (Loto, 2011).

**RESULTS AND DISCUSSION**

The results obtained from phytochemical screening and extraction shows the presence of alkaloids and tannins with the percentage yields of the total alkaloids and Tannins extracted from the stem bark of *Jatropha curcas* to be 1.66% and 1.53% respectively. Inhibition of total alkaloids and Tannins extracted from *Jatropha curcas* showed that inhibition rates increases with increase in concentration in the H$_2$SO$_4$ medium. Plot of weight loss versus time of exposure and calculated corrosion rate against time of exposure were used as the percentage inhibitor efficiency. Figures 1 and 2 below shows the variation of weight loss with time of exposure for the corrosion of mild steel in 0.5 M H$_2$SO$_4$ acid containing various concentrations of alkaloids and Tannins extract of *J. curcas* at 303 K. It can be seen that weight loss of mild steel increases with increase in the period of contact but decreases with increase in concentration of alkaloids extracts indicating that the rate of corrosion of mild steel increases as the period of contact increases and that alkaloids extract inhibited the corrosion of mild steel in H$_2$SO$_4$ medium.
At the 25th day, the weight loss of the mild steel increased to 2.8g which is very close to that of the sample without extract i.e 3.2g (figure 1). Similar trend was observed in all media of the experiments, thus the height in chart is corresponding to increase in weight loss with increase in period of contacts.

For the tannins extract, in (figure 2) similar trends was observed except that values of weight loss were relatively lower than those obtained when alkaloids extracts were used at various concentrations. Figure 2 revealed that the corrosion rate increase with increase in the period of contact but decreases with increase in the concentration of tannins extract of the plant indicating that the rate of corrosion of mild steel in H$_2$SO$_4$ increases with increase in the period of contact but decreases with increase in the concentration of Tannins extract.

Values of corrosion rates of mild steel and inhibition efficiencies of plants extract of \textit{J. curcas} at 303K are recorded in Table 1. The percentage inhibitor efficiency was calculated as at 25th days of the experiment from the relationship:

\[
\% \text{IE (Percentage Inhibition Efficiency)} = \frac{1 - W_L}{W_O} \cdot 100
\]

Where $W_O$ and $W_L$ = corrosion rate in the absence and presence of inhibitor predetermined concentration respectively.

Corrosion rates (CR) for the mild steel in different concentrations of H$_2$SO$_4$ was determined using equation below:

\[
CR (gh^{-1}cm^{-2}) = \frac{W}{A}\text{eqt 2}
\]
Where \( W \) = weight loss (g), \( A \) = area of specimen (cm) and \( t \) = period of immersion (h)

The adsorption of the Alkaloid and Tannins is through functional groups which the inhibitors interact with the metal surface. Their structural backbone contains additional functional groups that enhance the electronic bonding strength of the interacting group on the metal surface. Electron donating substituent increase inhibition by increasing the electron density of the anchoring group (COOH group); on the other hand, electron-withdrawing, substituent’s decrease inhibition by decreasing the electron density. This result is in agreement with the findings reported on the use of \textit{Jatropha curcas} whole extracts for corrosion inhibition of brass in 1 M HCl (Deepa, 2011), and also in agreement with the finding reported on alkaloid extract from \textit{Palicourea guianensis} plant as corrosion inhibitor for C\textsubscript{38} steel (Lebe \textit{et al}., 2013).

### Table 1: Alkaloids and Tannins Extracts of \textit{Jatropha curcas} corrosion inhibition efficiency in H\textsubscript{2}SO\textsubscript{4} medium at the 25\textsuperscript{th} day

<table>
<thead>
<tr>
<th>Extracts</th>
<th>Concentration (g/L)</th>
<th>Corrosion Rate (gh\textsuperscript{-1}cm\textsuperscript{-2})\textsuperscript{10\textsuperscript{-4}}</th>
<th>Inhibition Efficiency (%)</th>
<th>Surface coverage ( \Theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaloids</td>
<td>0.1</td>
<td>5.01</td>
<td>13</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>3.32</td>
<td>27</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>3.13</td>
<td>40</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>2.91</td>
<td>50</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1.66</td>
<td>70</td>
<td>0.70</td>
</tr>
<tr>
<td>Tannins</td>
<td>0.1</td>
<td>5.83</td>
<td>7</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>5.01</td>
<td>20</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>2.50</td>
<td>40</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>0.4</td>
<td>2.31</td>
<td>60</td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1.88</td>
<td>67</td>
<td>0.60</td>
</tr>
</tbody>
</table>

The Temkin and Langmuir adsorption isotherm equation were used to deduced the adsorption characteristics of the inhibitors.

- **Temkin adsorption isotherm equation**
  
  \[ \exp(-2a\Theta) = K \Theta \]

- **Langmuir adsorption isotherm equation**
  
  \[ \frac{\Theta}{1 - \Theta} = \frac{K}{C} \]

where \( \Theta \) = degree of coverage, \( a \) = an interaction parameter, taking into account the attraction \( a>0 \) or repulsion \( a<0 \) between the adsorbed species, \( C \) = concentration of the inhibitor in the electrolyte, and \( K \) = equilibrium constant of the adsorption process.

From Fig 3-4, the straight line plot is linear with a correlation coefficient; \( R^2 \) about 0.98, indicates that the adsorption of both alkaloids and tannins on the mild steel obey both Langmuir and Temkin adsorption isotherms and this suggested that the inhibitor molecules have been spontaneously adsorbed onto the surface of mild steel through a physical adsorption mechanism. The result indicates that Temkin and Langmuir adsorption isotherms are valid for various extract concentrations of \textit{J. curcas} plant.
Fig 3a: Temkin adsorption isotherm for Alkaloids extracted from *Jatropha curcas* on mild steel in H$_2$SO$_4$ medium at 303K

\[ y = 0.784x + 0.883 \]

\[ R^2 = 0.967 \]

Fig 3b: Langmuir adsorption isotherm for Alkaloids extracted from *Jatropha curcas* on mild steel in H$_2$SO$_4$ medium at 303K

\[ y = 0.732x + 0.909 \]

\[ R^2 = 0.961 \]

Fig 4a: Temkin adsorption isotherm for Tannins extracted from *Jatropha curcas* on mild steel in H$_2$SO$_4$ medium at 303K

\[ y = 0.742x + 0.836 \]

\[ R^2 = 0.992 \]
CONCLUSION
The gravimetric method was found to have proved the inhibitive nature of the alkaloids and tannins extracts on the corrosion of mild steel in H₂SO₄. The plant extracts were found to obey Temkin and Langmuir adsorption isotherms from the fit of experimental data. Comparison of the results with Temkin and Langmuir adsorption isotherm indicates that the extracted secondary metabolites forms strong protective film on the surface of mild steel to conform with physical adsorption mechanisms. Use of the plant as a corrosion inhibitor will be of great socio-economic importance, therefore some direction for further research on this area may include Phytocompounds such as phenols, phenolic acid be investigated as they are reported to have great inhibitor properties. Studies on the plants should be expanded to cover additional media and other metals.

REFERENCES


