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Protection of Mild Steel against Corrosion using Extract of *Cajanus cajan* Leaves Corrosion Inhibitor in Simulated Seawater Environment

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ABSTRACT

There is a new direction in research towards the use of plant as corrosion inhibitors for metals and alloys. Thus, the corrosion inhibition of mild steel in 3.5% sodium chloride (NaCl) solution by Cajanus cajan leaves extract was studied using weight loss technique. The corrosion rates of the studied samples were found to decrease with increase in concentration of the inhibitor. The inhibition efficiency also increased with increase in the extract concentration and decreased with increase in temperature. Thermodynamic parameters show that the inhibition is through adsorption of plant extract onto the metal surface and it obeys Langmuir adsorption isotherm and occurs spontaneously. The activation energy as well as other thermodynamic parameters for the inhibition process were calculated and these thermodynamic parameters show strong interaction between inhibitor and mild steel surface.

1. INTRODUCTION

Plants are viewed as an incredibly rich source of chemical compounds that can be extracted by simple methods with low cost and are biodegradable (Awe *et al*., 2015). Presently, there is an increasing awareness of protecting metals from corrosion which can lead to a great loss in both lives and equipment in industries. Various works have been carried out on plant extracts as effective corrosion inhibitors of mild steel in acidic/alkaline media and have been reported, and these include: Helen *et al*., 2014 (*Aquilaria crassna)*, Adejo *et al.,* 2013 (*Portulaca oleracea)*, Punita *et al*., 2014 (*Tagetes erecta*), Abiola and James, 2010 (*Aloe vera)*, Eddy and Odoemelam, 2009 (*Aloe vera*), Satapathy *et al*., 2009 (*Justicia gendarussa)*, Okafor *et al.*, 2008 (*Phyllanthus)*. It was found that the inhibition performance of plant extract is normally ascribed to the presence of complex organic species such as tannins, alkaloids and nitrogen bases, carbohydrates, amino acids and proteins as well as hydrolysis products. These organic compounds contain polar functions with nitrogen, sulphur and oxygen atoms as well as conjugated double bonds or aromatic rings in their molecular structures, which are the major adsorption centers (Avwiri and Igho, 2003).

In the past, the use of chemical inhibitors has been limited because of their environmental hazard and regulations regarding its uses. Plant extracts are generally acceptable today and readily available, cheap, in addition to being a renewable source for a wide range of corrosion inhibitors (Howida *et al.,* 2014).

Cajanus cajan (Pigean pea) is one of the most common tropical and subtropical legumes cultivated for its edible seeds. Pigean pea is fast growing, hardy, widely adaptable, and drought resistant. The fruit of C*ajanus cajan* is a flat, straight, pubescent pod, 5-9 cm long and 12-13 mm wide. Pigean pea is used as a contour hedge in erosion control (Varshney *et al*., 2012).

The aim of the present work is to determine the potential of *Cajanus cajan* leaves extract as corrosion inhibitor of mild steel in simulated seawater environment.

2. MATERIALS AND METHODS

2.1. Materials Preparation

The composition of the steel used for this research is presented in Table 1. The steel was mechanically cut in to 1 cm x 2.5 cm x 0.05 cm coupons. These were polished with various grades of emery paper 600, 800, 1000 and 1200), degreased in absolute ethanol, dried in acetone and stored in a desiccator before use as described elsewhere (Varshney *et al*., 2012).

Cajanus cajan leaves were collected from Okene market in Kogi State, Nigeria, washed and dried. It was later pulverized with mortar and 100 g out of it was soaked in distilled water (1000 ml) and refluxed for 12 hours. The aqueous solution was filtered and concentrated to 100 ml. This concentrated solution was used to prepare solutions of different concentrations by dilution method. To obtain the mass of plant extract, it was dried at 100 ^{o}C under vacuum in the vaporizer. From the weight of the vacuum dried liquid, plant extract was found to contain 50 mg/ ml of plant compounds.

Table 1: Composition of mild steel

Element	Fe	C	Si	Mn	P	Cr	Ni
Composition (%)	99.59	0.076	0.026	0.192	0.012	0.050	0.050

2.2. Phytochemical Screening

The phytochemical screening of the plant was carried out at Chemistry Department of the University of Nigeria, Nsukka. using standard procedure (Obot and Obi-Egbedi, 2009; Lakshman, 2012).

2.3. Corrosion Studies

The corrosion studies were carried out at the following temperatures: 303 K, 313 K, 323 K and 333 K for an exposure period of 24 hours in the absence and presence of various amounts of inhibitors. After the elapsed time, the specimen was taken out, washed, dried and reweighed accurately. All the experiments were performed in triplicate and average values were recorded. The differences in the initial and final weights were recorded as weight loss. The corrosion rates (CR) was calculated from the weight loss using Equation 1, while the inhibition efficiency (IE%) and surface coverage (ϴ) were calculated using Equations 2 and 3 as follows:

$$CR = \frac{87.6\, w}{AtD} \quad (1)$$

Where *w* is the corrosion weight loss of mild steel (mg), *A* is the area of the coupon, *t* is the exposure time (h) and *D* is the density of mild steel (g /ml)

$$\text{IE\%} = \left(1 - \frac{\text{W1}}{\text{W}}\right) \times 100\ \% \quad (2)$$

Where, W_1 and Ware the weight loss value in presence and absence of inhibitor.

$$\theta = 1 - \frac{W1}{W} \quad (3)$$

2.4. Thermodynamic Studies

Thermodynamic parameters play an important role in studying the inhibitive mechanism. The standard adsorption free energy (ΔG^o_{ads}) was obtained according to (Lebrini *et al.*, 2010)

$$\Delta\text{Gads} = -\text{RT} \ln (55.5\ \text{K}) \quad (4)$$

Where R is the molar gas constant, T is the temperature in Kelvin, 55.5 is the molar concentration of water, K is the adsorption equilibrium constant representing the degree of adsorption

$$K_{ads} = \theta/(1 - \theta)\ C \quad (5)$$

2.5. Isotherm Studies

In acidic solution, the adsorption of the inhibitor molecules is governed by the quasi-substitution process between the adsorbed water molecules on the metal surface and the inhibitor in the aqueous phase. The reaction can be represented as follows (Yadav et al., 2010).

$$\text{Inhibitor (sol)} + x\ \text{H 2 O (ads)} \leftrightarrow \text{Inhibitor (ads)} + x\ \text{H 2 O (sol)} \quad (6)$$

Here, *x* represents the number of water molecules replaced by one inhibitor molecule. To obtain the isotherm, a linear function of different values of θ and inhibitor concentration (C_{inh}) is plot- ted. Isotherms such as Langmuir, Temkin, Frumkin, and Freundlich were normally used to check adsorption characteristics. Frumkin adsorption isotherm is represented by the expression:

$$\text{Log}\left(\frac{\theta}{1-\theta}\right) = 2.303\ \text{Log K} + 2\alpha\theta \quad (7)$$

K = adsorption equilibrium constant, α = the lateral interaction term describing the molecular interaction in the adsorbed layer. α is A parameter which indicates the attractive behavior of the surface of the metal (Eddy and Odiongenyi, 2010).

The effectiveness of an inhibitor can be ascribed to the adsorption of molecules of the inhibitors through their polar function on the metal surface. The adsorption behavior of *Cajanus cajan* leaves extract was investigated and the test revealed that adsorption of leaves extract on the surface of the mild steel is constant with Langmuir adsorption isotherms. Langmuir adsorption model can be represented as follows

$$\frac{c}{\theta} = \frac{1}{K} + c \quad (8)$$

Where c is the inhibitor concentration and K is the adsorption equilibrium constant representing the degree of adsorption. θ is the degree of surface coverage (Singh *et al*., 2010).

3. RESULTS AND DISCUSSION

3.1. Phytochemical Screening of *Cajanus cajan Leaves*

The phytochemical screening of extract of *Cajanus cajan leaves* is presented in Table 2. Result obtained shows that tannins, saponins, flavonoids, steroids, phenols and alkaloids are present in the extract of *Cajanus cajan*.

Table 2: Qualitative phytochemical analysis of *Cajanus cajan*

Compound	Level
Alkaloid	++
Phenol	+++
Tannins	++
Saponins	+
Flavonoids	+++
Steroids	++

+++ = very high, ++ = high, + = low

3.2. Corrosion Studies

3.2.1. Effect of inhibitor concentration on corrosion rate

The variation of corrosion rate with immersion time at different temperatures is shown in Figure 1 and it was observed that the corrosion rate of the mild steel decreased with addition of inhibitor. At 30 °C, the corrosion rate for the control was 0.5604 mg/cm^{2}hr but this value was reduced to 0.0656 mg/cm^{2}hr at 250 mg/l inhibitor concentration. Similar trend was observed at 60 °C. This may be due to the increased protection offered by the inhibitor as concentration increases, thereby preventing the breakdown of the passive films leading to an increase in the corrosion resistance of the mild steel compared with the uninhibited samples (Obot and Obi-Egbedi, 2009). The least corrosion rate was obtained at 30 °C and at 250 mg/l. However, as the temperature increased to 60 °C, the corrosion rate increase. This could be that there is desorption of inhibitor from the surface of the mild steel or break down of protective film formed earlier due to increase in temperature thereby exposing it to the aggressive medium (Adejo et al., 2013).

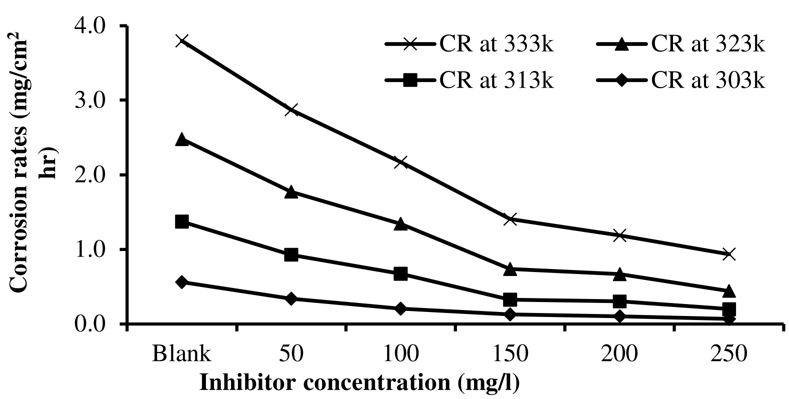

Figure 1: Corrosion rate of mild steel in 3.5 wt.% NaCl solution in the absence and presence of *Cajanus cajan* leaves extract at various temperatures

3.2.2. Effect of inhibitor concentration on inhibitor efficiency

In Figure 2 the variation of inhibitor efficiency with inhibitor concentration is shown. The inhibition efficiency increased with increase in the concentration of *Cajanus cajan* leaves extract. At a temperature of 30 ^{o}C, maximum inhibition efficiency of 88.29 % was obtained at 250 mg/l inhibitor concentration. The reduction in inhibition efficiency at 60 ^{o}C to about 62.58% can be attributed to the acceleration of the breakdown of the passive film at higher temperature. Consequently, the increase of the inhibitor efficiency was ascribed to the increase in surface. (Umoren and Ebenso, 2008).

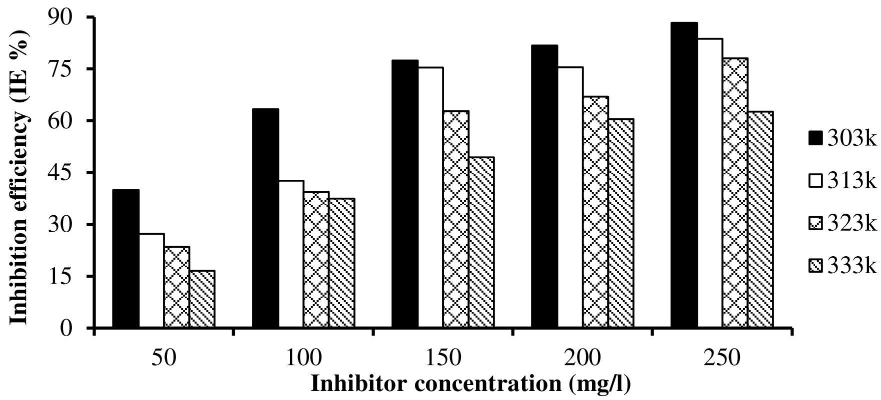

Figure 2: Inhibition efficiency of mild steel in 3.5 wt.% NaCl solution in the absence and presence of *Cajanus cajan* leaves extract at various temperatures

3.3. Thermodynamic Studies

To evaluate the stability of adsorbed layer/film of inhibitor on mild steel surface and activation parameters of the corrosion process in the medium, weight loss measurements were carried out in the absence and presence of *Cajanus cajan* leaves extract at optimum concentration and over the exposure time using the Arrhenius equation as shown in Equations (9) and (10) (Lakshman, 2012).

$$\log CR = \log A - Ea/2.303RT \quad (9)$$

$$\log\left(\frac{CR}{T}\right) = \{\log\left(R/NA\,h\right) + \Delta Sa/2.303R\} - \Delta Ha/2.303RT \quad (10)$$

Where CR is the corrosion rate of the metal, A is the Arrhenius or pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the temperature of the system. N_A is the Avogadro's constant, ΔSa is the entropy of activation and ΔHa is the enthalpy of activation. From Equation 10, plot of log CR versus reciprocal of absolute temperature, 1/T is as presented in Figure 3, which gives a straight line with slope equal to $-\frac{Ea}{2.303R}$, from which the activation energy for the corrosion process was calculated.

From Equation (10), plot of $LogCR/T$ versus reciprocal of absolute temperature, $1/T$, as shown in Figure 4 gives a straight line with slope equal to - $\frac{\Delta Ha}{2.303R}$ and intercept of $\left[Log\frac{R}{NAh} + \frac{\Delta Sa}{2.303R}\right]$, from which the enthalpy and entropy for the corrosion process was calculated. Values of Ea, ΔSa, and ΔHa are presented in Table 3. The data shows that the activation energy of the corrosion in mild steel in simulated seawater in the presence of extract is higher than that in absence of the extract, indicating that the extracts of *Cajanus cajan* leaves extract retarded the corrosion of the alloy in the studied medium. The increase in the apparent activation energy for mild steel dissolution in inhibited solution may be interpreted as physical adsorption (Lebrini *et al*., 2010). However, increasing the solution temperature weakens the inhibition effect by enhancing the counter process of desorption. That is why the inhibition efficiency values decreased with increase in temperature.

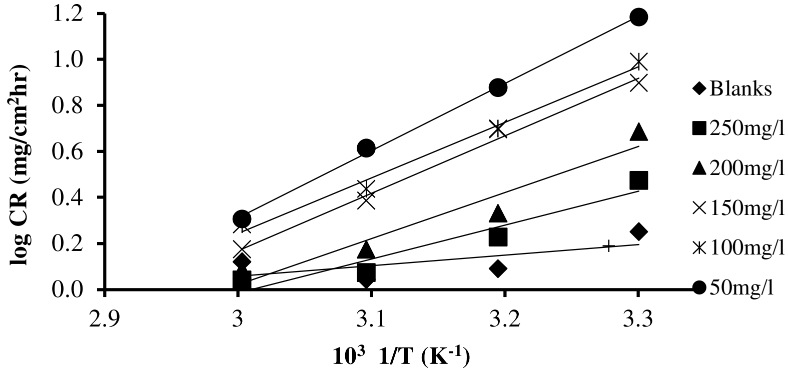

Figure 3: Arrhenius plots of log CR vs 1/T for the mild steel corrosion in the absence and presence of C*ajanus cajan* leaves extract

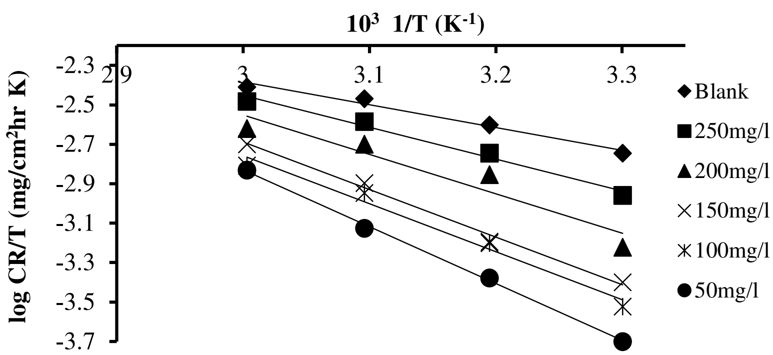

Figure 4: Arrhenius plots of log CR/T vs 1/T for the mild steel corrosion in the absence and presence of C*ajanus cajan* leaves extract

Table 3: Activation parameters for the mild steel corrosion in the absence and presence of *Cajanus cajan* leaves extract

Inhibitor conc. (mg/l)	Ea (kJ/mol)	ΔHa (kJ/mol)	ΔSa (kJ/mol/K)
Blank	22.44	22.13	-238.12
50	55.85	55.23	-147.33
100	53.80	46.58	-171.91
150	47.82	46.24	-171.62
200	38.27	38.21	-193.09
250	28.26	30.84	-213.29

3.4. Adsorption Isotherm

Calculated values of the free energy are presented in Tables 4. Generally, values of ΔG^o_{ads} around -20 kJ / mol or lower are consistent with the electrostatic interaction between the charge molecules and the charged metal (physisorption).Those around -40 kJ /mol or higher involve charge sharing or charge transfer from organic molecule to the metal surface to form a coordinate type of bond (chemisorption) (Obot*et al*., 2011). From the result obtained, the values were found to be negative, physisorption, and a suggestion that the adsorption of *Cajanus cajan* leaves extract onto the mild steel surface is a spontaneous process and adsorbed layer is stable (Hui *et al*., 2013). The plot of log c / Θ versus log c as shown in Figure 5 gave linear plots indicating that Langmuir adsorption isotherm is applicable to the adsorption of *Cajanus cajan* leaves extract on the surface of the mild steel.

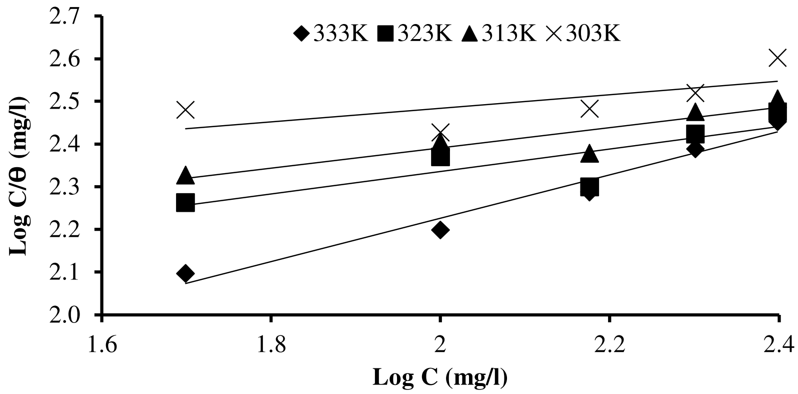

Figure 5: Langmuir plots of log C/Θ vs log C for the mild steel corrosion in the absence and presence of *Cajanus cajan* leaves extract

Table 4: Langmuir adsorption isotherm parameter

Temperature (K)	R^2	ΔG_{ads} (kJ/mol)
303	0.454	- 12.06
313	0.817	- 12.14
323	0.693	- 12.38
333	0.966	- 11.64

4. CONCLUSION

Cajanus cajan leaves extract showed inhibitive effect on corrosion of mild steel in simulated seawater environment. Inhibition efficiency was found to increase with an increase in inhibitor concentration for the extract. The adsorption of *Cajanus cajan* extract on the surface of the mild steel obeyed Langmuir adsorption isotherm. The extract proved to be better corrosion inhibitor having provided higher inhibition efficiency.

5. ACKNOWLEDGEMENT

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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